

Carbonates in natural and geotechnical settings – chemical sediments as environmental archives

RONNY BOCH*

19 Text-Figures

Österreichische Karte 1:50.000

BMN / UTM

101 Eisenerz / NL 33-02-15 Eisenerz

104 Mürrzuschlag / NL 33-02-12 Mürrzuschlag

105 Neunkirchen / NL 33-02-18 Voralpe

134 Passail / NL 33-02-23 Weiz

Calcium carbonate

Erzberg

Geothermal energy

Karst caves

Environmental monitoring

Clumped isotopes

Contents

Abstract	67
Zusammenfassung	68
Preface	68
Introduction	69
Calcium carbonate – Precipitation and polymorphs	72
Calcium carbonate – Element and isotope fractionation	77
Diverse environmental settings	81
Caves, Speleothems and Climate Reconstruction	83
Uranium-Thorium based speleothem chronologies	83
Speleothem stable oxygen isotope records	86
Multi-proxy approach of climate parameters	88
Environmental Monitoring	90
Periodical sampling and data loggers	92
Monitoring carbonate precipitation dynamics	96
Carbonates from the ‘Erzberg’ Iron Ore Mine (Austria)	98
Growth dynamics of aragonite-calcite veins (“Erzbergite”)	100
Environmental implications on fracture formation and paleoclimate	103
Carbonate Scales forming during Geothermal Energy Production	107
Scaling – unwanted mineral deposits	107
Scaling Forensics – Reconstructing site-specific production conditions	108
Processes determining carbonate scale material characteristics	111
Summary and Outlook	115
Acknowledgements	117
References	118

Abstract

The diverse geoscientific topics of this publication are centered around the carbonate system and in particular on anhydrous and hydrous calcium carbonates and the distinct polymorphs of CaCO₃. A broad range of physicochemical processes from sub-microscopic to regional scale opens the discussion on fundamental and applied research aspects connecting modern geochemistry with geology. The deposition of carbonate minerals in various natural and (geo)technical settings represents a chemical-sedimentary archive capturing site-specific natural and human-made environmental conditions. Different environmental parameters – changing temporally and spatially – can be reconstructed from the evolving mineral deposits. An in-depth process understanding of fluid-solid (e.g. water-rock) interaction is a key to manifold applications. This involves an advanced understanding of carbonate precipitation (growth) dynamics, inorganic or microbially-mediated crystallization mechanisms and the resulting material characteristics and their environmental dependencies. State-of-the-art and mostly high spatial resolution laboratory analytical geochemical and imaging techniques are utilized. This includes computer-controlled micromill and laser ablation based solid material sampling strategies in combination with mass

* RONNY BOCH: Graz University of Technology, Institute of Applied Geosciences, Rechbauerstraße 12, 8010 Graz, Austria. ronny.boch@tugraz.at

spectrometric, electron and X-ray interactive analyses of elemental concentrations and isotopic ratios and fractionation, as well as of variable crystal growth and fabrics. Radiometric uranium-thorium age and rate determination and multiply-substituted isotopologue (clumped isotopes) measurements yielded valuable information. Field-based periodical or on-site and online environmental monitoring mainly of fluid phases applying automated data loggers constitutes an integral part in some of the studies presented.

Applying geochemical approaches and tools to geotechnical settings is focused on unwanted mineral deposits – dominantly carbonate scaling – impairing geothermal energy production from deep aquifers or artificial water channels of different settings. This includes reduced (thermal) water and energy transfers from deep wells, in pipelines and heat exchangers, as well as in tunnel and surface drainages. The concept of 'Scaling Forensics' represents a multi-proxy high-resolution analytical approach of the carbonate scale materials and was developed and applied in order to evaluate and adapt unfavourable site-specific production conditions. Scale depositing geogenic and operational environmental processes determining the scaling progress and scale material characteristics (e.g. growth rate, consistency) are investigated. Specific environmental conditions such as production cessations/restarts, the problem of scale-fragment formation or the distinct role of solid/fluid phase interfaces (e.g. corrosion layers, growth surfaces) and related processes (e.g. crystal nucleation, CO₂/H₂O outgassing, particle mobilization) are highlighted. The formation mechanisms of geologically young veins filling fractures of the Austrian 'Erzberg' iron ore deposit in Styria and their possible relation to gravitational or tectonic mass movements, as well as to variable regional climate conditions in a sensitive Alpine setting are discussed. Karst areas, caves and speleothems were investigated in the context of stalagmite growth dynamics and the reconstruction of past changes in air temperature and meteoric precipitation. Using selected and environmentally well-constrained natural and technical Ca-carbonate materials established as well as newly developed isotope tracers (e.g. clumped isotope thermometer and fluid provenance tracer) can be evaluated and calibrated.

Karbonate in natürlichen und geotechnischen Umfeldern – Chemische Sedimente als Umweltarchiv

Zusammenfassung

Die verschiedenen geowissenschaftlichen Themen dieser Publikation zentrieren sich auf das Karbonatsystem und besonders auf wasserfreie wie wasserhaltige Kalziumkarbonate und die Polymorphe von CaCO₃. Ein breites Spektrum physikochemischer Prozesse von submikroskopischer bis regionaler Größenskala eröffnet einen Zugang zu Grundlagen- wie angewandten Forschungsfragen und verbindet Aspekte der modernen Geochemie mit solchen der Geologie. Die Bildung von Karbonatmineralen in natürlichen und (geo)technischen Umfeldern begründet ein chemisch-sedimentäres Archiv, welches ortsspezifische geogen und anthropogen beeinflusste Umweltbedingungen aufzeichnen kann. Verschiedene sich räumlich und zeitlich ändernde Umweltparameter können aus den in-situ und sukzessiv gebildeten mineralischen Ablagerungen rekonstruiert werden. Ein detailliertes Prozessverständnis der Fluid-Solid (z.B. Wasser-Gestein) Wechselwirkung ermöglicht systematische Einsichten und Anwendungen. Dies beinhaltet ein besseres Verständnis der Karbonatfällung (Wachstumsdynamik) aus wässrigen Lösungen, anorganischer oder mikrobiell beeinflusster Kristallisationsmechanismen und von resultierenden Materialcharakteristika und deren Abhängigkeiten von bestimmten Umweltbedingungen. Zu diesem Zweck werden zumeist räumlich hochauflösende geochemische und bildgebende Analysetechniken und Laborverfahren angewandt. Involviert sind etwa Computer gesteuertes Mikrofräsen und Laserablation mit variablen Beprobungsstrategien von Festphasen in Kombination mit massenspektrometrischen Methoden oder Elektronen- und Röntgenstrahlen basierten Analysen zur Bestimmung von Elementkonzentrationen wie auch der Isotopenverhältnisse und -fraktionierung oder des Kristallwachstums und daraus entstehende Materialtexturen. Radiometrische Uran-Thorium basierte Alter und Raten sowie Messungen mehrfach substituierter Isotopologe (Clumped Isotopes) erbrachten spannende Ergebnisse. Geländebasiertes Umwelt-Monitoring, hauptsächlich von Fluidphasen (Lösungen, Atmosphäre) mittels automatischer Datenlogger, ist ein wesentlicher Bestandteil in manchen der präsentierten Studien.

Die Anwendung geochemischer Ansätze und Werkzeuge auf geotechnische Umfeldern fokussiert in der vorliegenden Arbeit auf unerwünschte Mineralablagerungen – vor allem Karbonat-Scaling (Sinterkrusten i.w.S.) – welche die geothermische Energieproduktion aus tiefen Aquiferen oder die Wasserführung in künstlichen Gerinnen behindern. Gemeint sind reduzierte (Thermal-)Wasser- und Energie-Transfers aus Tiefbohrungen, in Pipelines und Wärmetauschern, wie auch in Tunnel- und Oberflächendrainagen. Diesbezüglich stellt das Konzept der „Scaling Forensik“ einen Multiparameter- und analytisch räumlich-zeitlich hochauflösenden Ansatz der Untersuchung von karbonatischem Scale-Material dar, das zur Evaluierung und Adaption von ungünstigen Orts- (Anlagen-) spezifischen Umwelt- und Betriebsbedingungen herangezogen werden kann. Die maßgeblichen natürlichen und operativen Prozesse und Bedingungen betreffend das variable Fortschreiten und die Materialeigenschaften (z.B. Wachstumsrate, Konsistenz) der Mineralablagerungen werden im Detail untersucht. Rahmenbedingungen im Zusammenhang mit Betriebs-/Förderunterbrechungen, das Problem der Scale-Fragment-Bildung oder die besondere Rolle von Fluid-/Festphasen-Grenzflächen (z.B. Korrosionslagen, Wachstumsoberflächen) und damit einhergehende Prozesse (Kristallnukleation, CO₂/H₂O Entgasen, Partikelmobilisierung) werden diskutiert. Weiters werden die Bildungsmechanismen von geologisch jungen mineralischen Ausfällungen in vertikalen Brüchen der bekannten österreichischen Lagerstätte „Erzberg“ in der Steiermark, sowie die Abhängigkeit solcher Klufthverheilungen von gravitativen oder tektonischen Gesteinsbewegungen und auch von sich verändernden regionalen Klimabedingungen im sensitiven alpinen Raum eruiert. Karstgebiete, Höhlen und Tropfsteine sind mit Blick auf die Stalagmiten-Wachstumsdynamik und die daraus mögliche zeitlich hochaufgelöste Rekonstruktion vergangener Änderungen der Lufttemperatur und des meteorischen Niederschlags ein Untersuchungsgegenstand. Unter Verwendung von ausgewählten und gut charakterisierten Kalziumkarbonaten aus natürlichen oder (geo)technischen Bildungsmilieus können etablierte wie neu entwickelte Isotopen-Tracer (z.B. „Clumped Isotope“ Thermometer und Fluid-Herkunft Tracer) evaluiert und kalibriert werden.

Preface

Carbonate research and its associated technological developments over the last few decades have highlighted the importance of this comprehensive functional and mineral group in various environmental settings on Earth. The wide range of material characteristics of carbonates depend on variable physicochemical conditions during formation. Considering this broad range of settings and conditions, related research and development activities comprise of fundamental scientific as well as applied objectives, e.g. focusing on natural, laboratory experimental, (geo)technical and material science topics. Relying on an evolving

spectrum of field and laboratory analytics, as well as computer modelling techniques utilized to investigate carbonates and their environments, the modern field of carbonate research is highly interdisciplinary. Another principal anchor of carbonate research consists of the detailed examination of fluid-solid interaction, i.e. the intimate association of solid, liquid, and gaseous phases such as carbonate minerals, carbon dioxide, and carbonate alkalinity in aqueous solutions.

Consequently, considering the intention of this piece of work a strong focus is devoted to the advancement in the process understanding of chemical-sedimentary carbonate formation in natural and human-made environmen-

tal settings. This means a detailed and site-specific understanding of the distinct mechanisms and parameters controlling mineralogical, elemental and isotopic compositions. These aims are closely related to carbonate crystallization behaviour, material characteristics, and wanted or unwanted natural as well as technical constraints on highly diverse spatial and temporal scales. Elaborated sampling procedures, state-of-the-art and mostly high-resolution laboratory based analytical techniques, field based environmental monitoring campaigns and experimental setups constitute major building blocks of the carbonate research approach presented here. The recognition of widespread analogies in the determining processes and the transfer of knowledge and analytical skills between the more fundamental (e.g. caves and speleothem formation) and the more applied (e.g. carbonate scale deposition during geothermal energy production) geoscientific topics is exemplified and discussed.

The development of this broad yet selective manuscript is founded on the accompanying chapters of my cumulative habilitation thesis. It is mainly based on an accumulation of selected publications generated during the last few years with own contributions as a first author or as a co-author. I hope that this circumstance can provide some excuse for the occasionally pronounced self-citation. The interested reader, however, might pay attention to the comprehensive reference list provided at the end of this publication.

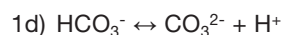
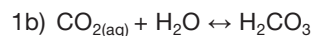
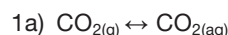


Ronny Boch
April 2019, Graz, Austria

Introduction

From a principal point of view, various carbonate mineral formation is the expression of an acid-base reaction in different environmental conditions, i.e. the salt resulting from the chemical reaction of a weak acid (H_2CO_3) providing the carbonate anion and a base (e.g. $\text{Ca}(\text{OH})_2$) providing the variable cation. Regarding carbonic acid, the widespread occurrence and dissolution of **carbon dioxide** (CO_2) in aqueous solutions is of major importance. The solubility of CO_2 compared to many other gas phases is relatively high, i.e. the equilibrium (Henry's Law) constant $K_{\text{H}} = 10^{-1.47}$ (at 25°C) depends on the partial pressure (fugacity) of the gaseous phase, as well as on temperature and ionic strength (salinity) of the aqueous solution (CARROLL et al., 1991; TRUCHE et al., 2016). In particular, a higher gaseous carbon dioxide partial pressure ($p\text{CO}_{2(\text{g})}$) results in higher CO_2 contents in equilibrium with the aqueous solution ($\text{CO}_{2(\text{aq})}$). CO_2 solubility decreases with increasing temperature and decreases with increasing ionic strength (DUAN & SUN, 2003; MILLERO et al., 2006). At high-pressures (> 100 bar), the solubility of CO_2 reverses, i.e. increases with temperature (DUAN & SUN, 2003). In solution, the hydrated CO_2 , as well as the minor molecular species of carbonic acid (H_2CO_3) possess a strong tendency of partial dissociation towards bicarbonate (HCO_3^-) and the

carbonate anion (CO_3^{2-}) assessed by equilibrium dissociation constants (e.g. MILLERO et al., 2006). These inter-related dissociation equilibria and more generally the **carbonate chemical equilibrium** can be summarized by the following set of equations:

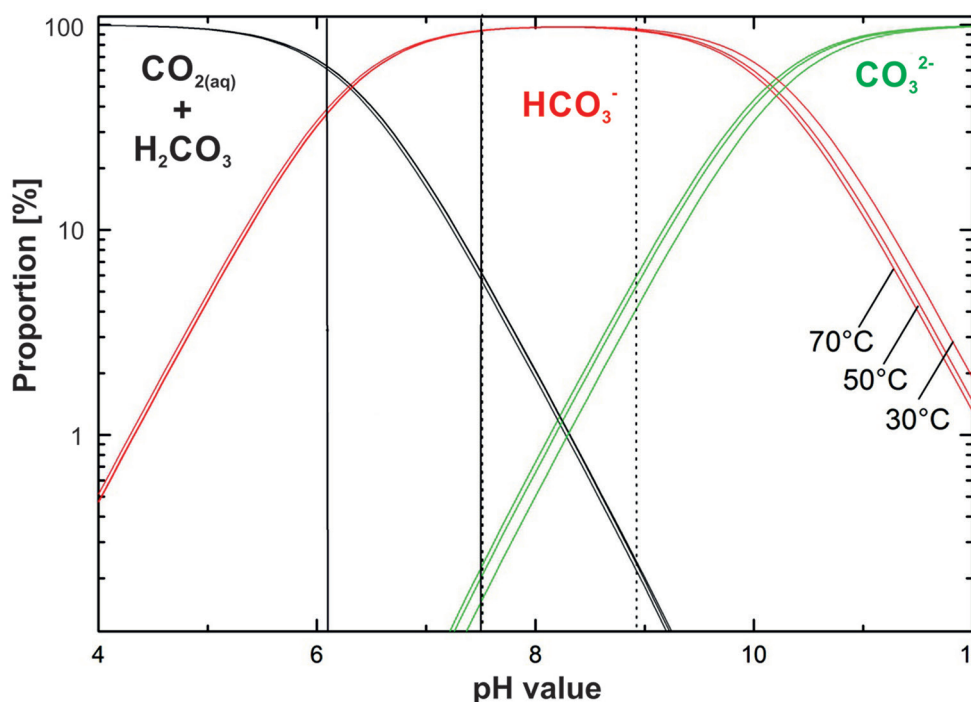


The different carbonate species concentrations in aqueous solution can be summarized by the content of **dissolved inorganic carbon** (DIC):

$$2) \quad [\text{DIC}] = [\text{CO}_{2(\text{aq})}] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

From the fundamental equations noted above, it becomes obvious that the prevailing **pH** conditions in the carbonate chemical system are intimately connected to the dissociation equilibria of the carbonate species, i.e. an acid-base system typically involving the transfer of protons (H^+) in its partial reactions. The proportion of the individual carbonate species in aqueous solution is strongly dependent on the prevailing pH and in turn the content of DIC has a primary effect on the overall solution pH (e.g. in carbonate dominated aquifers, streams and springs; FORD & WILLIAMS, 2007; BOCH et al., 2015; KLUGE et al., 2018). At typical pH ranges in most natural waters ($\sim 6.5\text{--}8.5$), the bicarbonate anion (HCO_3^-) represents the dominant inorganic carbon species in aqueous solution. At lower (acidic) pH conditions, dissolved CO_2 and small fractions of carbonic acid are the main molecular carbon species while at higher (alkaline) pH the carbonate anion prevails (Text-Fig. 1). The latter species is of crucial relevance with regard to the formation of carbonate minerals. Bicarbonate, however, can also be incorporated into the carbonate crystal lattice during rapid carbonate mineral precipitation and favourable kinetic processes (MICHAELIS et al., 1985; MICKLER et al., 2004; EILER et al., 2014). Regarding the carbonate system pH dependencies, the preferred formation of carbonate minerals at increased pH results in a directly coupled pH decrease, while the dissolution of carbonate minerals (salt) results in an overall pH increase, i.e. the carbonate system is also characterized by a pronounced **pH buffering capacity**. Such behaviour is of major importance in various natural as well as human-made environmental settings of carbonate occurrence.

Carbonate mineral formation involves a wide spectrum of possible **cations** combining with the carbonate functional group in a crystal lattice (or a few known amorphous phases). Owing to the divalent negative charge (2^-) of the carbonate anion an arrangement with divalent cations (2^+) of the earth alkaline and transition metals is most common in the carbonate mineral group. Carbonate minerals, however, involve ionic and covalent bonding of the atoms. The electric charge and structural prevalence results in carbonate minerals such as CaCO_3 (three anhydrous polymorphs: calcite, aragonite, vaterite), MgCO_3 (magnesite), SrCO_3 (strontianite), BaCO_3 (witherite), FeCO_3 (siderite), MnCO_3 (rhodochrosite), ZnCO_3 (smithsonite), PbCO_3 (cerussite), $\text{CaMg}(\text{CO}_3)_2$ (dolomite), $\text{Ca}(\text{Fe,Mg})(\text{CO}_3)_2$ (an-



Text-Fig. 1. Proportion of different inorganic carbonate species in aqueous solution depending on pH and a set of temperatures (adapted from KLUGE et al., 2018).

kerite), $\text{Cu}_2\text{CO}_3(\text{OH})_2$ (malachite), $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ (azurite), and several others. Amongst these, calcite and dolomite are the most widespread on Earth accounting for extensive sediment deposits in the ocean basins (e.g. carbonate muds and biogenic compounds) or forming the mass of entire mountain ranges (e.g. the Northern Calcareous Alps and the Dolomites of the Alps; CHANG et al., 1998).

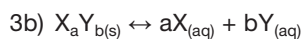
Most of the carbonate minerals mentioned above possess recurrent **structural similarities** (symmetry elements) regarding their atomic bonding and crystallography. A group consists of minerals crystallizing in the **trigonal** (rhombohedral) system (e.g. calcite, magnesite, siderite) in contrast to the **orthorhombic** carbonate group (e.g. aragonite, strontianite, witherite). The former is characterized by a 6-fold coordination of the cation site in the crystal lattice, while orthorhombic carbonates have 9-fold coordinated cation sites. This structural discrepancy results in a significantly different behaviour with regards to the incorporation of cations mostly depending on their respective ionic radius, i.e. divalent cations smaller than Ca (Mg, Zn, Fe, Cu, Mn) are preferred in the rhombohedral crystal lattice while those larger than Ca (Sr, Pb, Ba) show higher average element contents in the orthorhombic ion arrangement (MORSE & MACKENZIE, 1990). The double carbonate dolomite is trigonal-rhombohedral and characterized by a well-ordered and kinetically restricted arrangement of Ca and Mg cations in the crystal lattice. Although there are many similarities and phase relations compared to calcite, the formation of dolomite from direct precipitation or successive dolomitization is a subject of ongoing scientific debate and research activities (MORSE et al., 2007; BALDERMANN et al., 2015). Further considering monovalent alkali metal containing carbonates such as the Na-carbonates natronite ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) and nahcolite (NaHCO_3), their formation also strongly relies on the criteria of ionic radius and ionic charge balance in the crystal lattice according to the prevailing hydrochemical conditions. More specifically, their occurrence is frequently associated with mixing or evaporation in the context of highly saline aqueous solu-

tions (MONNIN & SCHOTT, 1984; COUNCIL & BENNETT, 1993). Carbonates can be further classified as **anhydrous and hydrous minerals**, i.e. those lacking a stoichiometric water component and those comprising water molecules and hydroxyl functional groups (crystal water) as part of their crystal lattice. Relatively common representatives are hydrous carbonates such as monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$), ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$), nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), hydromagnesite ($\text{Mg}_5[\text{CO}_3]_4[\text{OH}]_2 \cdot 4\text{H}_2\text{O}$) and basic calcium carbonate (BCC; $\text{Ca}_3[\text{CO}_3]_2[\text{OH}]_2 \cdot \text{H}_2\text{O}$). Recently, ZOU et al. (2019) reported the existence of monoclinic Ca-carbonate hemihydrate (CCHH; $\text{CaCO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$). These minerals typically form under restricted environmental conditions, e.g. low temperatures, elevated (hydrostatic) pressure or high pH, high saturation states and increased Mg concentrations (KRALJ & BREČEVIĆ, 1995; LANGMUIR, 1997; RODRIGUEZ-RUIZ et al., 2014; RIPKEN et al., 2018). Most of these hydrous carbonates are more or less metastable and show partial or complete dehydration (loss of crystal water) in the event of temperature increase. Consequently, individual idiomorphic crystals or mineral aggregates transform and disintegrate into carbonate minerals of more stable configuration at ambient environmental conditions (BOCH et al., 2015; PURGSTALLER et al., 2017a). For example, the calcium carbonates ikaite and monohydrocalcite are known to destabilize towards calcite or other anhydrous carbonate phases. Regarding the thermal stability of anhydrous carbonates, a critical limit consists in the volatilization of CO_2 at higher temperatures of several hundred degrees centigrade, e.g. thermal decomposition (decarbonation) of calcite at $> 825^\circ\text{C}$ resulting in the formation of calcium oxide (CaO ; burnt lime).

Addressing the general physicochemical characteristics of carbonate minerals, their **solubility** is another parameter of crucial environmental relevance. Compared to other mineral groups (e.g. chlorides, sulphates, sulphides, oxides, silicates) carbonates are of intermediate solubility in aqueous solution. The solubility behaviour is mostly described by the solubility product (equilibrium constant):

$$3a) K_{SP} = [X]^a [Y]^b$$

based on the educt vs. product chemical equilibrium reaction:



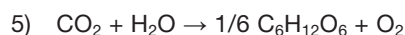
The solubility products of the various carbonate minerals differ significantly, e.g. the $\log_{10} K_{SP}$ values for selected phases at 25° C and 1 bar are: calcite = -8.5 and aragonite = -8.3 (both from PLUMMER & BUSENBERG, 1982), ikaite = -6.6 (BISCHOFF et al., 1993), monohydrocalcite = -7.2 (KRALJ & BREČEVIĆ, 1995), amorphous calcium carbonate = -6.0 (CLARKSON et al., 1992), siderite = -10.9 (REITERER et al., 1981), magnesite = -7.9 (LANGMUIR, 1997) or the double carbonates dolomite $\sim -17.1/2 = -8.6$ and ankerite: $\sim -19.9/2 = -10.0$ (both from MORSE & MACKENZIE, 1990 and depending on stoichiometry). Similar to carbon dioxide and considering moderate environmental conditions, the solubility decreases significantly with increasing temperature (retrograde solubility), increases with increasing pressure, and is further dependent on the ionic strength, specific ion pair and aqueous complex formation with some tendency of increased solubility at higher salinity (LANGMUIR, 1997; MORSE et al., 2007). Based on the solubility of carbonates, the mineral-specific **saturation state** represents another hydrochemical parameter of major environmental relevance. Saturation of an aqueous solution is typically expressed as saturation index defined as the ion activity product of the relevant constituents (mineral assembling ions) versus the solubility product on a logarithmic scale:

$$4) SI = \log [IAP/K_{SP}]$$

where $SI = 0$ indicates saturation (mineral vs. solution in equilibrium), $SI < 0$ indicates undersaturation (mineral dissolution), and $SI > 0$ indicates supersaturation (mineral precipitation) from a thermodynamic (intrinsic energetic) point of view and thus also strongly depending on the prevailing ambient physicochemical conditions. In nature, waters at the surface or underground are typically saturated with respect to $CaCO_3$ and therefore a change in the prevailing environmental conditions results in mineral precipitation or dissolution. The actual mineral precipitation or dissolution behaviour, however, also depends on the reaction kinetics of a particular mineral phase, i.e. the precipitation or dissolution in a specific environmental setting might be promoted or inhibited apart from the thermodynamic saturation state in aqueous solution. Well known examples of such reaction kinetic control on carbonate mineral formation are the restricted crystallization of well-ordered dolomite or the kinetically preferred precipitation of higher soluble Mg-calcite and aragonite instead of thermodynamically more stable low-Mg calcite in the oceans (MORSE & ARVIDSON, 2002; SARKAR et al., 2013). Regarding dolomite formation and the dolomitization of limestones, the precipitation of less ordered and Ca-excess protodolomite constitutes a specific and intensely studied case mostly associated with conditions of high ionic strength solutions, pronounced evaporation or a mediating (catalytic) contribution of bacteria (MORSE et al., 2007; BALDERMANN et al., 2015).

Biological processes are known as major controls of physicochemical reactions during carbonate biomineral-

ization in marine and continental settings (MORSE & MACKENZIE, 1990; MORSE, 2004). Examples are the various types of **exo- and endoskeletons** dominantly consisting of (calcium) carbonate and characterizing organisms such as corals, bivalves, gastropods, echinoderms and foraminifers. Biogenic carbonate mineralization is increasingly recognized in the context of microbial activity represented by numerous species of bacteria, cyanobacteria, algae and fungi. The **microbial communities** are typically present as biofilms or sophisticated networks consisting of distinct organic tissues, precipitated carbonate minerals, and connecting extracellular polymeric substances (EPS; ARP et al., 1999; PEDLEY, 2013; DIAZ et al., 2017). Micrometre- to millimetre-sized filaments, dendritic structures and delicate fibres are common structural elements of such bioecosis (GUO & RIDING, 1992; LANNELUC et al., 2015; JONES, 2017a). The microbes exert either an **active or a passive role** with regard to carbonate mineral formation. A passive role consists in providing a (high specific surface area) substrate for initial mineral nucleation and ongoing crystal growth. In contrast, an active role means the physicochemical alteration of aqueous solution and thus carbonate precipitation conditions in the course of different organism-specific and mostly catalytic (e.g. reduction of activation energies) processes (RIDING, 2000; FOUKE, 2011; LYONS et al., 2015). With respect to the carbonate chemical system, microbial metabolic processes such as photosynthesis and chemoautotroph energy transfers are the most common manifestation of hydrochemical alteration promoting carbonate mineral deposition or dissolution. Photosynthesis utilized by many microbes existing in a diversity of settings on the Earth's surface can be described by the simplified expression:

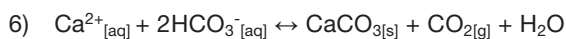


Consequently, various algae or cyanobacteria being common representatives of **photosynthetic microbes** can actively influence the CO_2 budget of their environment and may ultimately trigger carbonate mineral nucleation, or accelerate or reduce local mineral growth (LANGMUIR, 1997; ROGERSON et al., 2008). **Chemoautotroph** life cycles producing their own nutrition and energy gains from selected chemical components and reactions involving aqueous solutions and gases are characteristic of more or less extreme environmental conditions (e.g. thermophile or halophile organisms; TAKAI et al., 2008; LERM et al., 2013). In most cases, the particular energy transfers are based on redox reactions, i.e. redox sensitive chemical constituents being processed in the metabolism of the specialized microbial organism. Examples are the oxidation of organic matter in sediments of the ocean floors or in deep continental reservoirs (sedimentary basins) which liberates CO_2 and therefore provides dissolved carbonate species (alkalinity) in solution and for minerals (MORSE, 2004; VARSÁNYI & KOVÁCS, 2006). Other redox reactions frequently associated with microbial activity are bacterial sulphate reduction (BALDERMANN et al., 2015), sulfide oxidation (LYONS et al., 2015) or iron reduction and oxidation (ZAMMIT et al., 2015). All of these aerobic (e.g. oxidic) or anaerobic (e.g. sulfidic) reaction schemes can have a major influence on carbonate mineral precipitation or dissolution. In this context, the comprehensive topic of burial and maturing carbonate diagenesis and its close interrelation of dissolution and re-precipitation processes should be mentioned.

Microbial processes are further relevant both in natural and human-made (geotechnical) settings of carbonate occurrence (e.g. aquifers; VARSÁNYI et al., 1997; MAYRHOFER et al., 2014), alteration and precipitation (GRENGG et al., 2015; DIAZ et al., 2017; BOCH et al., 2017b).

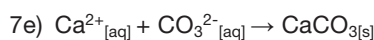
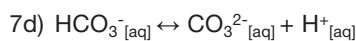
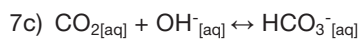
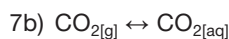
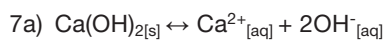
Calcium carbonate – Precipitation and polymorphs

Amongst the numerous carbonate minerals, the Ca-carbonates constitute a division of overwhelming importance, mainly due to their widespread occurrence in natural and human-made environmental settings, their rich chemical and crystallographic variability, and properties depending on distinct environmental conditions, as well as regarding their potential in diverse material scientific and industrial applications. The diverse settings addressing fluid-solid interaction of various planetary hydrogeochemical cycles and Ca-carbonate formation in geotechnical and laboratory synthetic environments will be the subject of a subsequent chapter. Ca-carbonates are involved in purely inorganic, as well as organically mediated processes on different spatial and temporal scales. As for carbonates in general, anhydrous and hydrous phases can be found within the Ca-carbonate division depending on specific and sometimes rare conditions prevailing. Typically, Ca-carbonate mineral formation follows the overall reaction scheme:



This **Ca-carbonate chemical equilibrium** displays the forward reaction of dissolved calcium cations and bicarbonate anions towards anhydrous Ca-carbonate precipitating from aqueous solution, gaseous, or partially dissolved carbon dioxide and water. Examples of this forward directed reaction are the formation of speleothems (dripstones) in caves (FAIRCHILD et al., 2006; BOCH et al., 2011a; DENNISTON & LUETSCHER, 2017), synthetic Ca-carbonate precipitation in laboratory experiments (DIETZEL et al., 2004; TANG et al., 2008a, b; PURGSTALLER et al., 2017b), or unwanted Ca-carbonate precipitation affecting geotechnical and water supply infrastructure (HASSON et al., 2010; SÜRMEHINDI et al., 2013; BOCH et al., 2017a). The inverse reaction (from right to left in equation 6) describes the dissolution of Ca-carbonate via CO_2 and water (carbonic acid) resulting in increased calcium and carbonate species in solution. Typical examples of the latter reaction are the karstification of limestone (FORD & WILLIAMS, 2007; MATTEY et al., 2016), the dissolutional alteration of Ca-carbonate aquifers (HANSHAW & BACK, 1979; SMART & FRIEDERICH, 1986; OTT et al., 2015), or dissolution (vs. re-precipitation) processes during carbonate diagenesis (MORSE & ARVIDSON, 2002; MOORE & WADE, 2013; DE BOEVER et al., 2017). Considering the individual stoichiometric constituents and their equilibrium relation, Ca-carbonate precipitation is promoted by increased initial calcium concentrations and carbonate alkalinity, increased CO_2 outgassing, and/or evaporation of the aqueous solution. The ionic supply strongly depends on site-specific fluid-solid (water-rock) interaction in the case of natural or geotechnical settings (e.g. water residence time and ion exchange in aquifers; LANGMUIR, 1997), or the parent solution ionic compositions in laboratory experiments (e.g. NIEDERMAYR et al., 2013). In addition, the availability of water constitutes a fundamental prerequisite in this chemical equilibrium, next to the

prevailing temperature, pressure, and overall hydrochemical composition (ionic strength and ion association) in line with the principle physicochemical dependencies of carbonates in general. The internal (aqueous solution) versus external (atmospheric) **CO_2 partial pressure** and thus effective gradient is of crucial relevance with regard to either CO_2 outgassing and intimately related Ca-carbonate precipitation or enhanced carbonic acid based Ca-carbonate dissolution. A higher solution CO_2 partial pressure, as well as a higher surface area (e.g. water film or stream surface) results in increased CO_2 diffusion and outgassing to the atmosphere, which in turn controls the amount and rate of CO_2 exchange and carbonate precipitation (DANDURAND et al., 1982; BOCH & SPÖTL, 2011; YAN et al., 2017). The role and variable rate of **CO_2 degassing** are frequently discussed in the context of variable Ca-carbonate precipitation in caves, natural streams, fractures, aqueducts, or thermal water wells and transport pipes (MICKLER et al., 2004; SÜRMEHINDI et al., 2013; BOCH et al., 2017b; JONES, 2017b). In contrast, Ca-carbonate precipitation can also be induced by the **absorption of CO_2** in alkaline (elevated pH) aqueous solutions. The respective set of chemical equilibrium reactions might be summarized as follows:



or alternatively



This mechanism of Ca-carbonate mineral formation is often based on the dissolution of a Ca-rich phase and the simultaneous occurrence of significantly increased pH values. Both conditions can arise from the dissolution of highly soluble portlandite ($\text{Ca}(\text{OH})_2$; equation 7a), e.g. from fresh concrete components (KOSEDNAR-LEGENSTEIN et al., 2008; RINDER et al., 2013; BOCH et al., 2015). The high aqueous solution pH (increased OH^- concentration) results in the predominance of a low internal CO_2 partial pressure (Text-Fig. 1) triggering the absorption of gaseous CO_2 from the surrounding atmosphere. Consequently, the hydroxylation of dissolved CO_2 results in an immediate transformation towards dissolved inorganic carbon species such as bicarbonate (equ. 7c) and the further dissociation towards the carbonate anion (equ. 7d). The latter combines with dissolved calcium ions in order to form Ca-carbonate minerals (equ. 7e). Depending on the specific environmental conditions, anhydrous or hydrous Ca-carbonates may precipitate (equ. 7). For example, the formation of ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) is frequently associated with near-freezing temperatures, particularly high pH, and carbonate supersaturation, and eventually with specific CaCO_3 inhibiting elemental and molecular constituents (DIECKMANN et al., 2008; HU et al., 2014; BOCH et al., 2015; FIELD et al., 2017). In essence, the CO_2 absorption based Ca-carbonate formation mechanism often results in prominently high precipitation rates and associated crystal growth and fabrics.

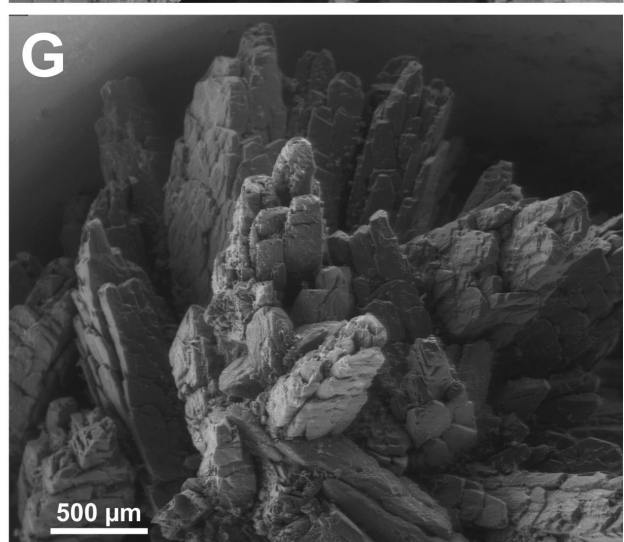
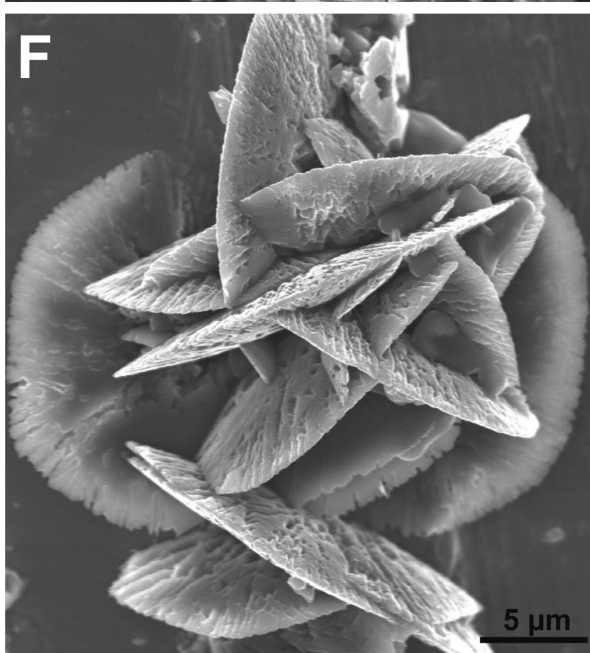
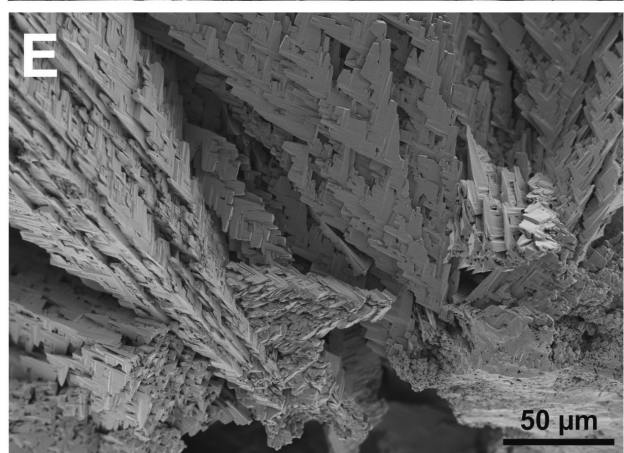
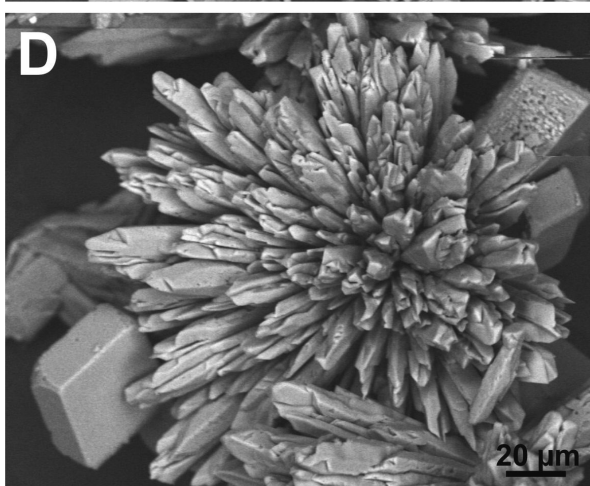
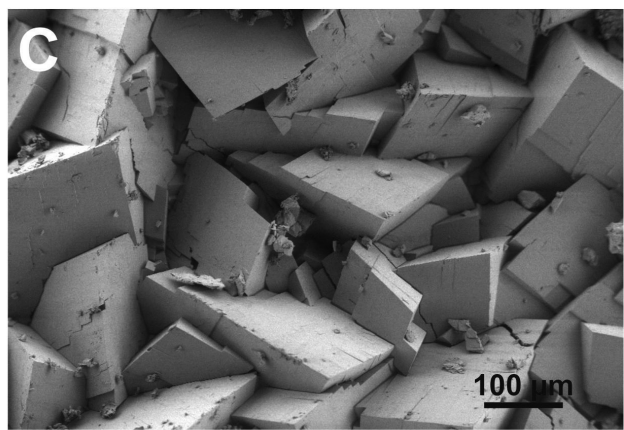
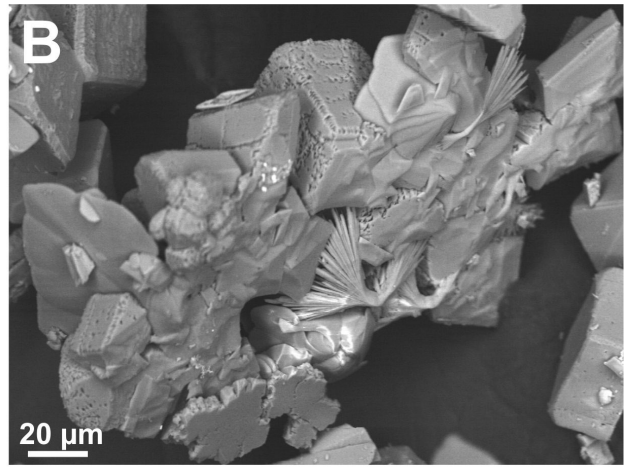
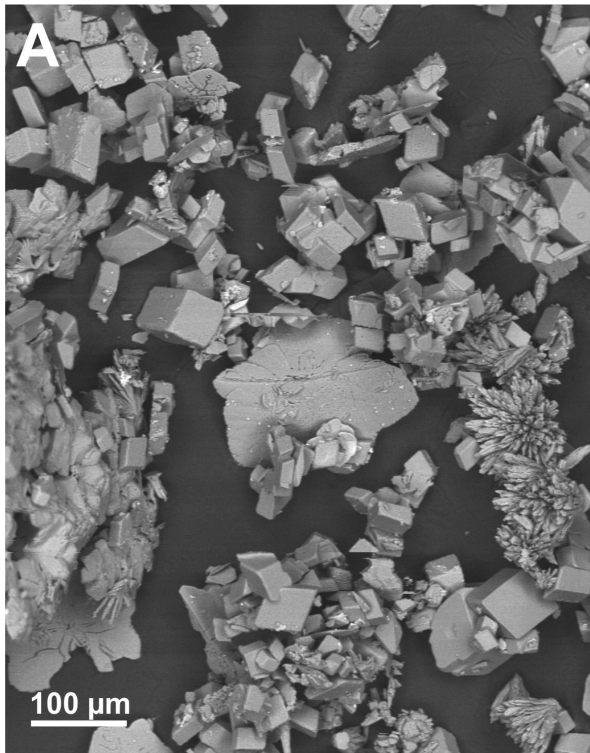
Examining the anhydrous CaCO_3 minerals, **three polymorphs** of significantly different crystallography and geochemistry can be distinguished: **calcite, aragonite and vaterite** (Text-Fig. 2). Their close environmental and material scientific relations are subject of intense research activities (GEBAUER et al., 2009; RODRIGUEZ-NAVARRO & BENNING, 2013; KONRAD et al., 2016). Amongst the most striking differences, the three polymorphs possess different crystal systems, i.e. calcite is trigonal, aragonite is orthorhombic, and vaterite is hexagonal (CHANG et al., 1998; MORSE et al., 2007). Calcite is known as a mineral of extraordinarily rich crystal shapes (over 400 different forms) based on its rhombohedral unit cell in principal related to the NaCl crystal structure (triangular CO_3^{2-} anions instead of Cl⁻). The perfect cleavage (10–11 faces) and typical cleavage rhombohedra of calcite are a direct expression of this structure. Amongst the many forms, rhombohedral and prismatic-scalenohedral calcite habits are characteristic (Text-Figs. 2A–C, E). Aragonite also shows a prominent spectrum of different crystal shapes including radiating-spherical, columnar-pseudo-hexagonal, acicular (needle) and divergent (wheat-sheaf) forms (Text-Figs. 2B, D). In contrast to calcite, its cleavage is imperfect. Vaterite crystals are rare in nature but typically show spherulitic, tabular and fibrous habits or might occur in the form of aggregates consisting of much smaller crystallites (Text-Figs. 2A, F). In these structures, the cationic lattice site is 6-fold coordinated in calcite, 9-fold coordinated in aragonite and 6- to 8-fold coordinated in vaterite (VAN DRIESSCHE et al., 2017). This variable ionic bonding environment substantiates a significantly different physical and chemical behaviour of these polymorphs. The larger cation site makes aragonite a slightly denser, higher pressure, and temperature resistant polymorph, while calcite is typically the stable form at lower temperature and pressure conditions in aqueous systems. Furthermore, the different cation sites entail a significantly different substitutive incorporation of various (mostly alkaline earth) cations instead of intermediate-sized calcium ions. Aragonite favours the incorporation of relatively large cations (with regard to ionic radius), such as Sr, Ba, Pb, and U as uranyl cation, while the smaller Mg cation is strongly avoided in the aragonite crystal lattice. In contrast, Mg is readily substituted into calcite and MgCO_3 proportions of up to 30 mol.% occur in Mg-calcite (CHANG et al., 1998). Fe, Mn, Sr and Ba are also common but minor elemental substitutes in calcites.

In terms of their **thermodynamical stability**, aragonite and vaterite exist as metastable crystalline phases under surface ambient environmental conditions and therefore transform into thermodynamically more stable calcite via dissolution-re-precipitation reactions (BRAND, 1994; VAN DRIESSCHE et al., 2017). For example, aragonite to calcite transformation was investigated in speleothems (FRISIA et al., 2002; PERRIN et al., 2014) and in corals (YOSHIOKA et al., 1986), as well as during ductile deformation processes (SNOW & YUND, 1987) or quasi solid-state transformations based on thermal dehydration of small amounts of fluid inclusions (KOGA et al., 2013). SARKAR et al. (2013) studied the transformation of vaterite to aragonite in a setting potentially relevant for biomineralization. The issue of (meta)stability gets even more obvious for the **hydrous Ca-carbonates** such as **ikaite** and **amorphous calcium carbonate (ACC)**. Ikaite has a monoclinic crystal structure and typically occurs as aggregates of multi-direction-

al, euhedral and square-prismatic, sigmoidal-bended pyramidal crystals (SWAINSON & HAMMOND, 2001; BOCH et al., 2015; Text-Fig. 2G). ACC ($\text{CaCO}_3 \cdot n\text{H}_2\text{O}$) is largely non-crystalline and hydrated and frequently occurs in the form of aggregates assembled from nano-sized and globular shaped crystals (e.g. DEMÉNY et al., 2016a). However, diverse and complex varieties of ACC probably exist (BOTS et al., 2012). For example, GEBAUER et al. (2009) reported a transient form referred to as ACC I, which favoured calcite nucleation, while ACC II resulted in vaterite precipitation. The transformation of ikaite, as well as ACC to more stable and anhydrous forms of CaCO_3 is characterized by more or less complete **dehydration** of the structural water. Various conditions and reaction paths of natural and synthetic ikaite transformation towards calcite (GREINERT & DERKACHEV, 2004), vaterite (TANG et al., 2009) or various Ca-carbonate polymorphs (ITO, 1998; PURGSTALLER et al., 2017a) were studied. Similarly, the transformation of ACC towards aragonite (ZHANG et al., 2012) or vaterite (BOTS et al., 2012) was the subject of laboratory experiments. KONRAD et al. (2016) investigated the transformation of additive-free ACC in air and found a strong dependence of ACC metastability on the physisorption of critical H_2O levels, i.e. relative humidity and thin water films adsorbed around ACC particles. Different experimental H_2O exposure conditions resulted in partial dissolution–re-precipitation of the ACC particles and consequently in different and simultaneously formed anhydrous crystalline Ca-carbonate polymorphs of distinct proportions (KONRAD et al., 2016).

The precipitation of the various Ca-carbonates and the polymorphism of anhydrous CaCO_3 also strongly depend on their respective **solubility and saturation state** in aqueous solution (Text-Fig. 3). Aragonite and vaterite possess a higher solubility compared to calcite and the hydrous Ca-carbonates monohydrocalcite, ikaite and ACC are even more soluble at widespread ambient environmental conditions. In contrast to the other Ca-carbonates, ikaite shows a prograde solubility behaviour, i.e. an increasing solubility with increasing temperature (Text-Fig. 3). Regarding calcite, its solubility also depends on the available and incorporated Mg concentration, i.e. solid solutions of CaCO_3 and MgCO_3 resulting in low- or high Mg-calcite (MORSE et al., 2007). Above 5 to 10 mol.% MgCO_3 in the crystal lattice, the Mg-calcite solubility exceeds the aragonite solubility (e.g. MORSE et al., 2007; ROSSI & LOZANO, 2016). Ikaite, monohydrocalcite and ACC are often the precipitation products of solutions with prominently high Ca-carbonate supersaturation and other related environmental constraints (KRALJ & BREČEVIĆ, 1995; BOCH et al., 2015; PURGSTALLER et al., 2017a).

In addition to the thermodynamic determination on the occurrence of different Ca-carbonates, **reaction kinetic effects** play a crucial role during mineral precipitation or dissolution. The nucleation or inhibition of a particular Ca-carbonate mineral might also rely on the transgression of thermodynamic, as well as kinetic, barriers. For example, initial calcite nucleation (e.g. on substrates) is well known to require aqueous solution $\text{SI}_{\text{calcite}}$ values above ~ 0.3 (multiple supersaturation), depending on additional physicochemical conditions (GEBAUER et al., 2009; VAN DRIESSCHE et al., 2017). Also, the carbonate chemical equilibria consist of several **partial reactions** determining the overall mineral precipitation or dissolution prog-



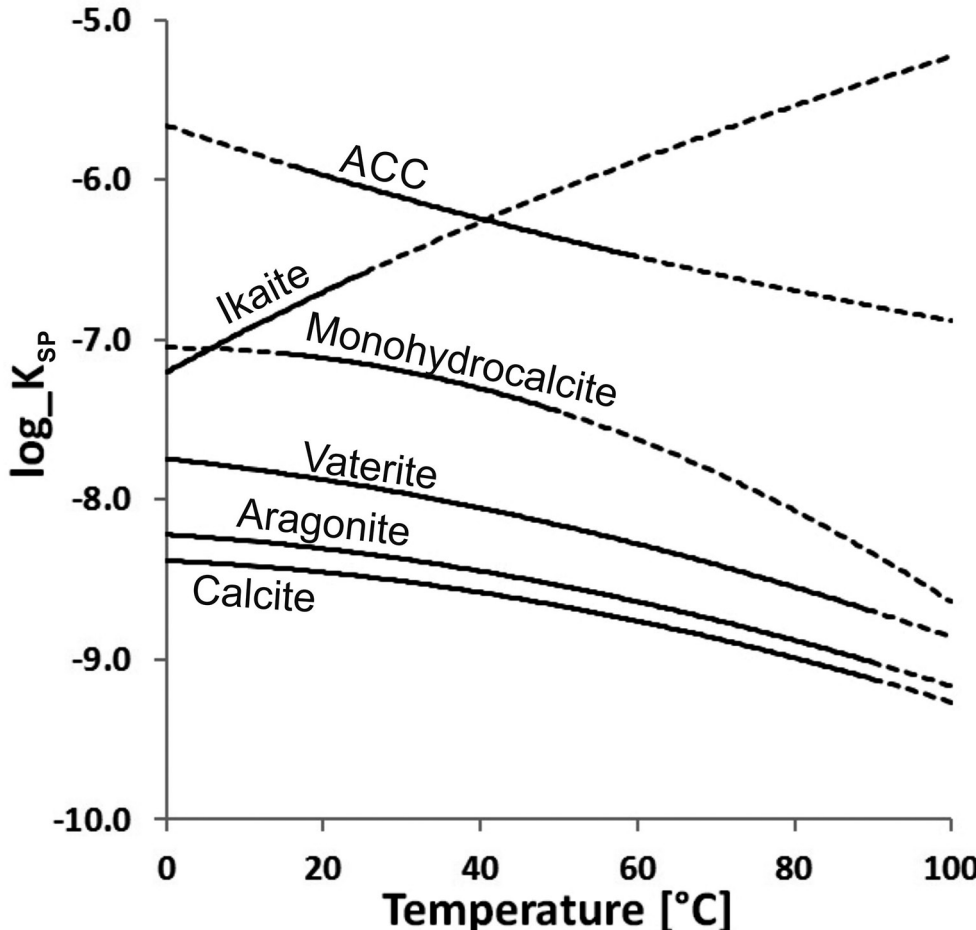
◀Text-Fig. 2.

Electron microscopic (SEM) images of different Ca-carbonates. A) The polymorphs calcite (rhombohedral), aragonite (radiating-spherical) and vaterite (hexagonal discs) in close relation during a laboratory precipitation experiment. B) Microporous rhombohedral calcite, wheat-sheaf aragonite and tabular vaterite. C) Dense calcite rhombohedra forming on a corroded steel substrate (from BOCH et al., 2017a). D) Synthetic radiating-spherical aragonite crystals and E) relatively large hydrothermal dendritic calcite crystals. F) Association of tabular, hexagonal vaterite crystals and G) aggregate of sigmoidal-banded, pyramidal monoclinic ikaite crystals (from BOCH et al., 2015). Note the major differences in crystal shapes and sizes of these Ca-carbonates.

ress. In this context, transport- versus surface-controlled processes, such as diffusional gradients and adsorption or desorption of dissolved species on crystal growth surfaces, might be key (REDDY & NANCOLLAS, 1971; VAN ZUILEN et al., 2016; MAVROMATIS et al., 2017). Dehydration and dehydroxylation partial reactions of different reaction rate might also control the overall reaction progress (DIETZEL et al., 1992; SCHOLZ et al., 2009). The actual precipitation rate of different Ca-carbonate minerals is intimately coupled to these partial chemical reactions, e.g. vaterite nucleation can be promoted by enhanced overall precipitation rates (LANGMUIR, 1997). The occurrence of different Ca-carbonate polymorphs has also been shown to reflect the prevailing pH conditions (SPANOS & KOUTSOUKOS, 1998; HU et al., 2015). Variable pH determines the prevailing carbonate chemical equilibrium and aqueous species distribution (e.g. of DIC), and thus the thermodynamic and kinetic potential of specific carbonate mineral nucleation mechanisms (WOLTERS et al., 2012). Considering the pH dependency, the aqueous solution CO₂ dynamics (outgassing vs. absorption) are of major relevance with respect

to variable Ca-carbonate precipitation. The CO₂ gradients, diffusion, and transfer between phases (e.g. solution vs. atmosphere) may additionally rely on the prevailing water flow or water film thickness (DEINES et al., 1974; BOCH & SPÖTL, 2011; DREYBRODT & ROMANOV, 2016).

The precipitation and polymorphism of Ca-carbonates are further influenced by the occurrence and effects of specific **chemical additives** in aqueous solution. Numerous laboratory experiments and empirical observations clearly support the potential of different molecular species to act as nucleation and crystal growth **inhibitors or stabilizers** of particular mineral phases and different actions and types of additives are distinguished (GEBAUER et al., 2009; KUMAR et al., 2018). In most cases, moderate to very small concentrations of these additives are sufficient to exert a major effect on the resulting mineral formation. With respect to Ca-carbonates, the influence of increased Mg concentrations and Mg/Ca ratios is well established to promote aragonite over calcite nucleation (BERNER, 1975; ROSSI & LOZANO, 2016; FERMANI et al., 2017). The co-occurrence and genetic relationship of aragonite and calcite in various natural settings frequently relies on spatiotemporally variable aqueous Mg contents (SPÖTL et al., 2016; BOCH et al., 2019). Different organic constituents can also affect the crystallization behaviour and thus determine resulting carbonate mineral phases. In this context, effects of humic and fulvic acids, polyaspartic and other amino acids, polyacrylic acid, citric acid, EDTA, aloe vera, olive, fig, and gambier extracts from leaves have been studied (HOCH et al., 2000; OUHENIA et al., 2008; SUHARSO et al., 2011; GOPI & SUBRAMANIAN, 2012; CHAUSSE-



Text-Fig. 3. Solubility product (log₁₀ K_{sp}) of various Ca-carbonates for temperatures ranging from 0 to 100° C (adapted from BOCH et al., 2015 and references therein). The continuous curves represent intervals defined by the underlying experimental works, while the dashed sections are extrapolated values. Most Ca-carbonates display a retrograde solubility behaviour, i.e. being less soluble with increasing temperature.

MIER et al., 2015; JIMOH et al., 2017). For example, NIEDERMAIR et al. (2013) studied the influence of polyaspartic acid and found a prevalence of vaterite over aragonite at certain concentrations of this amino acid. MAVROMATIS et al. (2017) showed that different organic ligands have variable effects on aqueous complexation, Mg incorporation and growth of calcite. Similarly, effects of sulphate, phosphate, and phosphonates with regard to Ca-carbonate precipitation in natural and geotechnical settings have been investigated (BUSENBERG & PLUMMER, 1985; GEBAUER et al., 2009; RODRIGUEZ-NAVARRO & BENNING, 2013). HU et al. (2015) found that significant phosphate concentrations favour ikaite over vaterite nucleation at near-freezing temperatures. Considering geotechnical and industrial applications, inorganic and organic additives play a primary role as carbonate scale inhibitors in the course of geothermal energy production from deep aquifers, petroleum production, or drinking- and wastewater treatment (PARLAKTUNA & OKANDAN, 1989; KETRANE et al., 2009; KUMAR et al., 2018; MPELWA & TANG, 2019). LI et al. (2015), for example, tested six different chemical additives commercially available with regard to their effects on Ca-carbonate scale inhibition and reported a distinct control of aragonite versus calcite precipitation, as well as modifications of crystal shapes and fabrics. In essence, the chemical additives influence critical reaction steps and interfaces during fluid-solid interaction on atomic scale, e.g. the stability, kinetics, and prevalence of aqueous complexes, the hydration shell and potential dehydration of dissolved ionic and molecular constituents, as well as the adsorption and eventual blockage of further ion attachment and step propagation at crystal growth sites. For example, Ca-carbonate precipitation is inhibited due to adsorption of soluble pre-nucleation clusters to polyacrylic acid or other polycarboxylates in aqueous solution resulting in suppressed aggregation (GEBAUER et al., 2009). In some cases, crystal nucleation might be inhibited even under very high supersaturation conditions.

Aside from specific chemical constituents, Ca-carbonate precipitation and different polymorphs might also be affected by physical and biological triggers. Strong **magnetic fields** are long known to have potential to modify the nucleation behaviour and material characteristics of carbonate precipitates and are frequently used for scale mitigation during geothermal energy and oil production from deep boreholes or during desalination of waters (GABRIELLI et al., 2001; WARSINGER et al., 2015). Magnetic treatment of aqueous solutions was shown to influence the proportions of calcite, aragonite, and vaterite crystals mostly depending on the field strength, flow rate and exposure time (KOBÉ et al., 2002; KNEZ & POHAR, 2005). FATHI et al. (2006) discussed the impact of magnetic forces on homogeneous versus heterogeneous crystal nucleation and variable nucleation rates resulting in different particle sizes, distinct crystal shapes, and a preventable or modifiable adhesion to a substrate (e.g. transport pipe, heat exchanger surface). Regarding ionic interaction and the potential of carbonate precipitation, a magnetic field could manipulate the hydration shell thickness around relevant ions via a rearrangement of polar water molecules during magnetic exposure (AL HELAL et al., 2018). Alternatively, **ultrasonic treatment** was reported to increase CaCO₃ precipitation rates in favour of vaterite as a polymorph (SU et al., 2015; VASYLIEV et al., 2018). A major control on mineral precipitation and

polymorphism can further result from various **substrate effects**, i.e. the nucleation of different Ca-carbonates on different solid substrates (D'SOUZA et al., 1999; HASSON et al., 2010). This includes studies of carbonate nucleation on surfaces and seeds of different materials and topography, such as steels and silica (WANG et al., 2013), glass (RIEHELMMANN et al., 2014), or plastics (WANNER et al., 2017). For example, recent experimental work revealed preferential vaterite nucleation on polyamide (WEDENIG et al., 2016). Moreover, a variable degree of corrosion of conventional (low-alloy) steel surfaces also affects the morphology and rates of Ca-carbonate crystal growth (BOCH et al., 2017a; LI et al., 2019). In essence, the availability of a substrate (surface) can significantly change crystallization mechanisms and associated nucleation barriers, surface- and crystal lattice energies (DE YOREO et al., 2015). The metastable and hydrated Ca-carbonate phases ikaite and monohydrocalcite were unexpectedly found to be stabilized at room temperature and without chemical additives in experiments investigating Ca-carbonate supersaturation in tiny (nano-/picoliter) droplet volumes (RODRIGUEZ-RUIZ et al., 2014). Thus, **volume confinement** of aqueous solutions might also be a parameter of interest regarding the occurrence of the different Ca-carbonates in nature and technical settings. The relevance of micro-domains and associated hydrochemical conditions is further increasingly recognized in the context of microbial activity in biofilms (PEDLEY, 2013; DIAZ et al., 2017) or during crystallization of carbonate **endo- and exoskeletal hard parts** (e.g. corals; VAN DRIESSCHE et al., 2017). Considering biomineralization, the widespread occurrence of metastable aragonite next to (Mg-)calcite at ambient (e.g. shallow marine bivalve shells) environmental conditions has long been a subject of research involving Ca-carbonate polymorphism related to vital effects and hydrochemical modification in micro-domains. During formation of skeletal parts, the initial nucleation and subsequent rapid transformation of metastable amorphous calcium carbonate (ACC) towards vaterite, calcite, and aragonite becomes evident by applying high spatial and/or temporal resolution analytical tools (BOTS et al., 2012; DE YOREO et al., 2015). Nano-sized, globular ACC precipitation and its role for the ripening of Ca-carbonate crystals is also manifested in **biofilms** and carbonate crusts of hot springs (JONES & PENG, 2012), as well as during microbially-mediated and relatively rare ooid deposition on carbonate platforms (e.g. Bahamas; DIAZ et al., 2017). In fact, microbial communities possess a broad array of possible metabolic effects in order to sustain their nutrition and to adapt to local physicochemical conditions (TEMPLETON & BENZERARA, 2015). Several of these metabolic pathways can also promote or retard Ca-carbonate crystallization and microbial relicts. Rod-shaped, globular, filamentous, dendritic, or rosette forms are typical expressions of microbial presence during carbonate deposition.

Another topic that reflects the diverse nature of Ca-carbonate precipitation includes the rich variety of **crystal shapes and fabrics**, even when considering individual Ca-carbonate phases. Distinct crystallization mechanisms that describe nucleation and crystal growth have emerged and in recent years the **classical monomer attachment** approach of crystal growth has been challenged by new models including the nucleation of **amorphous precursors** and the (re)arrangement of **clusters** (VAN DRIESSCHE et al., 2017). In essence, the classical crystallization

mechanism interprets crystal growth as an initial nucleus augmentation via successive attachment of ions and molecules on the growing crystal surfaces and defects, kinks, and steps are of major relevance regarding oriented growth progression (e.g. spiral-growth mechanism; TENG, 2013). The state-of-the-art crystallization models consider a variable sequence of ions forming ion clusters (e.g. aqueous complexes), liquid precursors, amorphous intermediates (e.g. ACC), metastable (e.g. vaterite) and stable crystals (e.g. calcite) following the impetus of successive free energy (ΔG) reduction and stepwise transgression of energy barriers and associated phase transformations, i.e. thermodynamic and kinetic constraints (RAO & CÖLFEN, 2017). Multiple pathways from atoms/molecules to euhedral crystals are currently being evaluated and **particle-based mineral formation** mechanisms, e.g. via nanoparticles and amorphous precursors, are the subject of intense research efforts and increasing recognition (DE YOREO et al., 2015). GEBAUER et al. (2008) emphasize the role of pre-nucleation clusters in aqueous solution in the assembly of different types of amorphous Ca-carbonate (ACC) phases subsequently transforming and ripening towards calcite, aragonite, or vaterite. These soluble pre-nucleation clusters are of crucial relevance in a multistep crystal nucleation process. The amorphous particulate carbonate phases are also considered to precede all of the possible crystalline Ca-carbonate polymorphs (GEBAUER et al., 2009). Importantly, the initial aggregation of nano-sized clusters is more or less random and the rearrangement of these basic modules results in an increasing order from amorphous to crystalline and a further reduction of surface and lattice energies during ripening from multiple crystallites to larger euhedral crystals (TENG, 2013). The successive order involves dehydration of the less ordered amorphous phases, dissolution versus re-precipitation, and in some cases also biologically mediated reactions (e.g. in marine organisms; BOTS et al., 2012). The formation and morphologies of the well-ordered anhydrous Ca-carbonate polymorphs obviously depends on different and variable hydro-physicochemical conditions (VAN DRIESSCHE et al., 2017). However, these phases as well as ACC are frequently observed to nucleate and coexist next to each other (NIELSEN & DE YOREO, 2017; Text-Fig. 2). Such observations suggest only subtle differences in the pre-nucleation and clustering of partial reactions to exert a major control on most of the subsequent Ca-carbonate precipitation and final polymorphism.

Regarding the Ca-carbonate mineral- and polymorph-specific **petrography and morphology**, distinct differences in the overall material appearance and consistency arise. Macroscopic **material characteristics**, such as (an)isotropy, intra- and intercrystalline porosity, colouring (e.g. from light scattering), and durability are directly related to crystal nucleation, crystal growth, and dominant crystal faces, and the resulting Ca-carbonate fabrics. In the case of calcite, columnar, palisade, dendritic, or micritic fabrics can result due to variable crystallization preconditions (FREYET & VERRECHIA, 1999; FRISIA, 2015). Aragonite precipitates typically occur as acicular and radiating, (hemi) spherulitic to botryoidal crystal aggregates and vaterite is mostly tabular or spherulitic (SAND et al., 2012; JONES, 2017a). Importantly, these underlying micro- to macroscopic features affect the visual expression and Ca-carbonate material characteristics of higher order, e.g. brittle

consistency or various forms of layering based on crystallite orientation and associated pore spaces (CHAFETZ & GUIDRY, 1999; BOCH et al., 2011a). Such hierarchical order based on successive deposition of Ca-carbonate is also expressed in the speleothem architectural analysis proposed recently (MARTÍN-CHIVELET et al., 2017). In this context, the extensive topic of **carbonate diagenesis** should be addressed. Following deposition from aqueous solution, pristine Ca-carbonate precipitates are frequently transformed or altered, i.e. mineralogical, chemical, and petrographic changes occur spatially and with time during early diagenesis and meteoric alteration or burial diagenesis towards metamorphosis (MORSE, 2004; DE BOEVER et al., 2017). Recrystallization often results in the transformation of aragonite to calcite (DOMÍNGUEZ-VILLAR et al., 2017; PEDERSON et al., 2019) or metastable ikaite to more-stable calcite (PURGSTALLER et al., 2017a). A major mechanism of such diagenetic recrystallization consists in the dissolution and subsequent re-precipitation of solid phases (HANSHAW & BACK, 1979; CASELLA et al., 2017; PEDERSON et al., 2019). During such reactions, the fabrics of recrystallized Ca-carbonate precipitates typically become mosaic and sparry, and thus exhibit larger crystal sizes and more homogeneous fabrics (FRISIA, 2015; BOCH et al., 2019). This evolution is obviously related to processes such as re-nucleation (e.g. number of nuclei) and particular crystal growth mechanisms (e.g. ionic supply). In most cases, the overall intra- and intercrystalline porosity of the altered carbonate precipitates decreases, although it might also increase in cases of significant volume changes (CASELLA et al., 2017). The specific progress of such ripening and recrystallization again depends on multiple physicochemical, as well as metabolic (microbial) conditions, e.g. temperature and pressure, and the effect of specific constituents (e.g. inhibitors) in aqueous solution (BRAND, 1994; MOORE & WADE, 2013). Moreover, the availability of water either in the form of fluid inclusions, fluids associated with organic matter or as later-stage percolating (vadose or phreatic) waters mostly constitutes a crucial prerequisite for dissolution and re-precipitation (DE BOEVER et al., 2017; PEDERSON et al., 2019).

Calcium carbonate – Element and isotope fractionation

Variable Ca-carbonate precipitation conditions and polymorphism are also manifested in distinct chemical and isotopic compositions depending on equilibrium and/or kinetic fractionation patterns. **Minor and trace elemental fractionation** into Ca-carbonates under physicochemical equilibrium conditions can be expressed quantitatively as specific (molar) elemental ratios (e.g. Mg/Ca, Sr/Ca) and related distribution (partition) coefficients, in which particular elements are more compatible in the different Ca-carbonate crystal lattices, i.e. they are readily substituted instead of calcium cations or carbonate anions (BÖTTCHER & DIETZEL, 2010). Apart from structural sites, elemental incorporation is associated with interstitial positions or defect sites in the crystal lattice (MORSE et al., 2007). The knowledge of elemental fractionation behaviour and element-specific partition coefficients is either based on laboratory experiments, thermodynamic-kinetic modelling, or empirical (field) related studies. Next to ionic electric charge and ionic radius, primary environmental conditions, such as temperature and pressure, determine the variable elemental incorporation. In general, low temperatures (e.g. high lati-

tude or altitude) hamper the equilibration of aqueous solution versus solid phase elemental partitioning (BÖTTCHER & DIETZEL, 2010). The aqueous speciation – specific constituents, pH, and ionic strength – also exert major effects on minor and trace elemental distributions (MAVROMATIS et al., 2015). Similarly, the precipitation rate, mineral-specific saturation states, and crystal growth mechanisms have shown distinct influences on different elements. Considering the anhydrous CaCO₃ polymorphism, pronounced differences between aragonite, vaterite, and calcite are well known, as the concentration of most elements strongly depends on the coordination of available ionic lattice sites and the ionic radius of the substitutes (WASSENBERG et al., 2016). For example, the incorporation of **Mg in calcite and aragonite** constitutes a subject of long-lived research (BERNER, 1975; MAVROMATIS et al., 2013). The distinction of low- and high magnesium calcite and the occurrence of CaCO₃-MgCO₃ solid solutions rely on the potential of highly variable Mg contents. The calcite Mg concentrations were also shown to increase with increasing temperature, as well as increasing ionic strength, which is particularly evident in marine settings of Ca-carbonate precipitation (BÖTTCHER & DIETZEL, 2010). In addition, Mg concentrations in calcite have been shown to increase with increasing precipitation rate (MAVROMATIS et al., 2013). Investigations have further focused on the alkaline earth elements **Sr and Ba**. These two elements largely display similar behaviour and their incorporation into calcite revealed some weak to ambiguous temperature dependence, but a strong positive relationship with precipitation rate and also pH (LORENS, 1981; TESORIERO & PANKOW, 1996). This is usually explained by the favoured incorporation of the relatively large Sr and Ba cations during rapid, and therefore less selective, calcite crystal growth, e.g. at higher pH and SI_{calcite} . Sr and Ba concentrations in aragonite also revealed some significant temperature dependence (DIETZEL et al., 2004). New results, however, support a dominant control of Ba incorporation in aragonite and calcite by the precipitation rate, which in turn is mostly related to ionic radii size effects (MAVROMATIS et al., 2018). Regarding the relationship of Mg, Sr, and Ba, some Ca-carbonate precipitates (e.g. speleothems) show a positive co-variation of their concentrations, mainly reflecting a corresponding hydrochemical evolution (e.g. prior CaCO₃ precipitation in the aquifer; McMILLAN et al., 2005). Alternatively, an inverse correlation of Mg versus Sr and Ba primarily depending on precipitation rate and aqueous solution composition can be observed (BOCH et al., 2011a). A dominant role of increased precipitation rate was also inferred with regards to higher **sodium** and **sulphate** contents in calcite (BUSENBERG & PLUMMER, 1985). Conversely, the concentrations of **manganese, cobalt, and cadmium** in calcite decreased at higher precipitation rate (LORENS, 1981). In recent years, the fractionation and varying incorporation of **numerous other elements** (B, P, S, Fe, Cu, Zn, Br, Y, Pb, U) in Ca-carbonate have been studied and implications on aqueous speciation, pH, sorption and transport processes and overall soil and aquifer hydrological conditions have been drawn (BORSATO et al., 2007; LANGER et al., 2018). In particular, the highly variable incorporation of **uranium** in the dominant form of uranyl cations (UO₂²⁺) into calcite and aragonite has gained some attention related to (paleo) hydrological process understanding and radiometric U-Th dating of Ca-carbonates (REEDER et al., 2000; LACHNIET et

al., 2012). Applications of minor and trace elemental fractionation include paleo- and modern environmental (hydrological and climate) studies of diverse natural settings of carbonate precipitation (FAIRCHILD & TREBLE, 2009; BOCH et al., 2011a), anthropogenic settings (SÜRMELEHINDI et al., 2013; BOCH et al., 2017a), inorganic vs. biotic relationships during water-rock interaction (SAUNDERS et al., 2014), or the removal (co-precipitation) of problematic (e.g. heavy metal contaminants such as Cd) or wanted (e.g. Li) elements with Ca-carbonate (KÖHLER et al., 2007).

Varying environmental conditions of Ca-carbonate formation from aqueous solutions are further reflected in distinct **isotope fractionation** patterns of different elements primarily based on physicochemical transitions between gaseous, liquid, and solid phases of the relevant partial reactions. More specifically, isotopes can be fractionated during mineral precipitation and dissolution, evaporation, sorption, diffusion, redox, and aqueous complexation reactions. In many of the chemical reactions an **isotopic equilibrium** between individual phases is attained, which can be described by fractionation factors determined from experimental, modelling, or empirical approaches (FRIEDMAN & O'NEIL, 1977). At ambient environmental conditions, typical stable isotopic fractionation is sensitive to the prevailing temperature, i.e. the partitioning of the relatively light and heavy isotope(s) of a chemical element reflects the thermodynamic conditions during phase transitions (EPSTEIN et al., 1953). Apart from equilibrium conditions, isotopic fractionation can also be controlled by dominant kinetic influences determining the direction and extent of the resulting isotope separation (MICKLER et al., 2004; DAËRON et al., 2019). These **kinetic effects** are mainly based on the different vibrational frequencies and chemical bonding characteristics between isotopes of distinct masses resulting in different reaction rates during isotope exchange (HOEFS, 2015; GUSSONE et al., 2016). The relatively light and heavy isotopes of an element behave kinetically different during chemical reactions, e.g. light isotopes being kinetically favoured during transition from the liquid to the gaseous state. The latter is manifested in the enrichment of the relatively light stable ¹²C and ¹⁶O isotopes in the course of CO₂ outgassing of dissolved inorganic carbon and evaporation of water (SCHOLZ et al., 2009). **Metabolic (vital) effects** during biological cycles and biomineralization of carbonates are also known as potential fractionation mechanism, e.g. the preferential enrichment of light C isotopes during photosynthesis and associated Ca-carbonate and organic tissue formation (GUO et al., 1996; LIU et al., 2015). Isotope fractionation processes can be further affected by **mixing** of isotopic compositions from different reservoirs (sources). The fractions of the endmembers and resulting isotopic signature might then be described by a mixing model (WIEDERHOLD, 2015). Alternatively, the isotopic evolution of a reservoir in which a fraction of isotopes is physically removed from the reservoir during a directed reaction can follow a **Rayleigh fractionation** model, i.e. light or heavy isotopes are preferentially removed from the reservoir and isotopic re-equilibration is prevented (WIEDERHOLD, 2015). Based on the underlying mechanisms and models of isotope fractionation and evolution, various isotope systems open the door for tracing the sources of constituents, as well as numerous inorganic and biotic processes. Importantly, the isotopic compositions contain both qualitative

(provenance signature) and quantitative (extent of chemical/isotopic reaction) environmental information. Typical applications of isotopic fractionation therefore include mineral and fluid provenance studies (RINDER et al., 2013), paleo(geo)thermometry in natural (KLUGE et al., 2014) and geotechnical settings (BOCH et al., 2017a), mineral alteration (GRENGG et al., 2015) and diagenesis (CASELLA et al., 2017), origin and trajectories of air masses (LUETSCHER et al., 2015; HAGER & FOELSCHKE, 2015), seasonal and multi-annual climate evolution (FAIRCHILD et al., 2006; BOCH et al., 2011b), and other processes sensitive to isotope fractionation that occur in a variety of natural and anthropogenic environmental settings.

In the context of Ca-carbonate precipitates, diverse **traditional** (light elements, relatively large mass discrimination) and **non-traditional** (heavier metals, subtle mass differences) **isotope systems** have been measured by various techniques of mass spectrometry and have been evaluated for their systematic fractionation behaviour. Considering the carbonate functional group, valuable environmental information is captured in the **oxygen** isotopic composition. The $^{18}\text{O}/^{16}\text{O}$ isotope ratio in carbonate minerals depends on factors such as the temperature of crystallization, the source and isotopic evolution of the precipitating fluid, and eventually kinetic (e.g. evaporation), catalytic (e.g. microbial), and diagenetic effects (e.g. recrystallization). An established utilization consists in the oxygen isotope thermometer of carbonate formation (EPSTEIN et al., 1953) relying on equilibrium O isotope fractionation factors derived from laboratory experiments (KIM & O'NEIL, 1997; DIETZEL et al., 2009) or empirical observations (COPLEN, 2007; TREMAINE et al., 2011). This isotopic thermometer was applied in various natural (BOCH et al., 2009; KELE et al., 2015) and human-made settings (BOCH et al., 2017a). The carbonate O isotope signature can further reflect the source and trajectories of meteoric precipitation and related groundwater, e.g. Atlantic versus Mediterranean sources of moisture advected to the Alps (LUETSCHER et al., 2015). Systematic differences also depend on the CaCO_3 polymorph formed, e.g. aragonite is enriched in ^{18}O vs. ^{16}O by $\sim 0.5\text{--}1\text{‰}$ relative to calcite at similar conditions (CLARK & FRITZ, 1997; BOCH et al., 2005). Another traditional isotope system with respect to environmental process understanding and reconstruction consists in the stable **carbon** isotope composition of carbonate minerals. The $^{13}\text{C}/^{12}\text{C}$ isotope ratio primarily depends on the source(s) and (hydro)chemical evolution of the relevant carbon species (e.g. dissolved inorganic carbon) in conjunction with parameters and processes determining CO_2 exchange reactions (temperature, pH) and related C isotopic fractionation. Major contributions to C isotope variation might therefore derive from the interaction of atmospheric, biogenic, pedogenic, and host rock carbon sources (DEINES et al., 1974), vadose and phreatic aquifer dynamics (e.g. dissolution vs. prior CaCO_3 precipitation; BAJO et al., 2017), dynamic CO_2 exchange during CO_2 outgassing or absorption (RINDER et al., 2013; DREYBRODT & ROMANOV, 2016), the crystallization temperature and precipitation rate (CLARK & FRITZ, 1997). At similar environmental conditions, aragonite is relatively enriched in ^{13}C vs. ^{12}C by $1.5\text{--}2.5\text{‰}$ compared to calcite supporting a major effect of crystal structure (MOOK, 1986; BOCH et al., 2005). Amongst the non-traditional stable isotopes, $^{44}\text{Ca}/^{40}\text{Ca}$ ratios of calcite, vaterite, and ikaite showed some positive

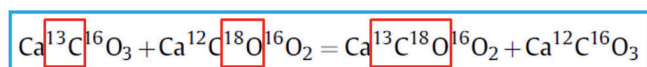
correlation to precipitation rate, i.e. increased ^{44}Ca vs. ^{40}Ca fractionation at increased precipitation rate (TANG et al., 2008b; GUSSONE et al., 2011, 2016). The **calcium** isotopes further revealed an ambiguous (insignificant) relation to formation temperature with a tendency of decreased ^{44}Ca vs. ^{40}Ca fractionation at higher temperatures (GUSSONE et al., 2003; TANG et al., 2008b). $^{44}\text{Ca}/^{42}\text{Ca}$ ratios can be used as a proxy for meteoric paleo-precipitation based on variable prior calcite precipitation in the course of increased recharge or aridity (OWEN et al., 2016). Monitoring of different **magnesium** reservoirs associated with a cave system revealed a dominant relationship of $^{26}\text{Mg}/^{24}\text{Mg}$ isotope ratios to speleothem calcite precipitation (growth) rate (IMMENHAUSER et al., 2010). Likewise, laboratory experiments yielded favoured ^{24}Mg concentration in calcite and a decreasing fractionation at higher precipitation rate (MAVROMATIS et al., 2013). This atypical behaviour might be explained by a kinetically inhibited dehydration of aqueous Mg^{2+} in combination with crystal surface entrapment (IMMENHAUSER et al., 2010). SAENGER & WANG (2014) found a major influence on Mg isotope fractionation related to different carbonate minerals (aragonite, dolomite, magnesite, calcite) and growth mechanisms. Moreover, temperature has a primary influence at higher Mg/Ca ratios and respective SI values, while precipitation rate was dominant with regard to Mg isotope fractionation at low Mg/Ca ratios and SI values. Radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios in carbonate constitute a more established isotope system frequently applied in material provenance studies (rocks, artefacts), seawater carbonate-based Sr chronostratigraphy over extended geological time intervals, and in connection with the stable **strontium** isotopes $^{88}\text{Sr}/^{86}\text{Sr}$ can also provide information on weathering and orogenic processes (NEBEL & STAMMEIER, 2016). The focused application of **boron** isotopes ($^{11}\text{B}/^{10}\text{B}$) as a promising proxy of (sea)water pH and coupled variation of atmospheric CO_2 concentrations is based on the pH dependent fixation of $\text{B}(\text{OH})_4^-$ (borate anion) and isotopically heavier $\text{B}(\text{OH})_3$ (boric acid) from aqueous solution into carbonate (BALAN et al., 2018). Further regarding non-traditional (higher atomic mass) Ca-carbonate relevant isotope systems, stable **barium** isotopes ($^{137}\text{Ba}/^{134}\text{Ba}$) have been used as a geochemical parameter reflecting oceanic circulation, weathering, and paleoproductivity in which carbonates preferentially incorporate the lighter Ba isotopes (VAN ZUILEN et al., 2016). However, MAVROMATIS et al. (2016) have shown that Ba isotopic equilibria are subject to dynamic re-equilibration after mineral formation and thus their paleoenvironmental interpretation should be considered with caution. **Iron** isotopes ($^{56}\text{Fe}/^{54}\text{Fe}$) in carbonates and various other minerals are strongly influenced by kinetic fractionation at lower temperatures and are most sensitive to distinct redox conditions ($\text{Fe}[\text{II}]\text{--}\text{Fe}[\text{III}]$), inorganic vs. microbial processes (e.g. bacterial iron and sulphate reduction), as well as diagenesis (HOEFS, 2015). **Zinc** isotope fractionation ($^{66}\text{Zn}/^{64}\text{Zn}$) between aqueous solutions and calcite was recently proposed as a non-traditional pH-sensitive isotope system and paleo-proxy based on experiments using mixed-flow reactors under controlled laboratory conditions (MAVROMATIS et al., 2019). Considering unstable isotopes, **uranium** ($^{234}\text{U}/^{238}\text{U}$) isotopic compositions of Ca-carbonates were used as a tracer of hydrological processes, such as differentiated water infiltration areas, aqueous solute provenance, rock weathering, and groundwater flow and

evolution (RIOTTE & CHABAUX, 1999). U isotope ratios are primarily sensitive to the prevailing aqueous speciation and redox state, as well as strongly dependent on isotopic disequilibrium during α -recoil processes (preferential leaching of ^{234}U ; PACES et al., 2002). The application of U isotopes in carbonate precipitates in the context of radiometric age determination will be discussed in a separate chapter (SHEN et al., 2012; SPÖTL & BOCH, 2012). Finally, recent developments of Ca-carbonate isotope analysis include stable **hydrogen ($^2\text{H}/^1\text{H}$)** isotope ratios of tiny fluid inclusions trapped in the mineral precipitates (e.g. speleothems; DUBLYANSKY & SPÖTL, 2009). These can be liberated, chemically separated and purified via thermal decrepitation or mechanical vacuum crushing (DEMÉNY & SIKLÓSY, 2008). In connection with the carbonate oxygen isotopes and established H vs. O isotope relationships such as the Global Meteoric Water Line (CRAIG, 1961), valuable information regarding formation temperature and water source can be inferred.

Another major progress in isotope analysis includes the recent measurement and interpretation of rare **multiply-substituted isotopologues (clumped isotopes)** in various carbonates (EILER, 2007; EILER et al., 2014). The clumped isotopic composition of carbonates relies on the determination of relatively rare and heavy stable ^{13}C and ^{18}O isotopes bound together in the carbonate functional group ($^{13}\text{C}^{18}\text{O}^{16}\text{O}_2^{2-}$; Text-Fig. 4). This quantity mainly depends on kinetic and molecular bonding (binding energy) differences of the isotopes involved and thus on the prevailing temperature during mineral (e.g. Ca-carbonate) formation. In particular, more ^{13}C and ^{18}O isotopes are clumped in the carbonate crystal lattice at lower temperature in comparison to a fully stochastic distribution (SCHAUBLE et al., 2006). Consequently, **formation (crystallization) temperatures** can be derived from analysis of the clumped isotopic composition of a carbonate mineral without the necessity of knowing the associated (original) aqueous solution stable isotopic composition. The temperature dependence is captured in a single-phase equilibrium (Text-Fig. 4), in contrast to two-phase equilibria, e.g. the established carbonate/solution oxygen isotope thermometer (DAËRON et al., 2019).

Technically, clumped isotopes are measured by **multi-collector gas source isotope ratio mass spectrometry** involving state-of-the-art high sensitivity (high electric resistance) Faraday detectors (EILER et al., 2013). More specifically, CO_2 is extracted from the carbonate mineral via phosphoric acid digestion, further separated, and purified in a multi-step laboratory procedure (KLUGE et al., 2015). Based on the relevant isotope ratios measured simultaneously, the deviation of the measured δ^{47} value – mainly represented by the rare clumped $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ molecule – from a stochastic δ^{47} distribution (in a $\sim 1,000^\circ\text{C}$ CO_2 reference gas) results in a characteristic Δ_{47} value (big delta). The latter decreases with increasing temperature. Next to Δ_{47} , the mass spectrometric

analysis determines the carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. In connection with the Δ_{47} -based temperature, the mineral stable O isotopic composition allows for a calculation of the mineral forming fluid (aqueous solution) $\delta^{18}\text{O}$ value based on the application of established temperature dependent O isotope fractionation factors (e.g. KIM & O'NEIL, 1997; COPLEN, 2007). Thus, apart from (paleo)thermometry, clumped isotope analyses constitute a promising tool with regard to the **provenance of (paleo)fluids** (LUETKEMEYER et al., 2016; BOCH et al., 2019). Considering the **accuracy and precision** of the temperature estimates, unaltered sample materials, the absolute mineralization temperature, the calibration function of Δ_{47} vs. temperature used, the laboratory and analytical protocols applied, and the number of replicate (sub)sample measurements are probably most relevant. The carbonate minerals should not have undergone reordering of their (clumped) isotopes, e.g. during diagenetic or metamorphic recrystallization processes and subsequent cooling below a mineral-specific blocking temperature (SHENTON et al., 2015; LLOYD et al., 2017). Moreover, at higher absolute temperatures ($> 150\text{--}200^\circ\text{C}$) the precision of the temperature estimates decreases rapidly due to the intrinsically decreasing differences in the Δ_{47} values vs. temperature changes (KLUGE et al., 2015). Regarding the numerical calibration functions of the geothermometer, a multitude of existing and ongoing efforts are based on experimental, empirical, and modelling studies and the clumped isotope community seeks for universal (broad temperature range, mineral (in)dependent) and laboratory independent calibrations (GHOSH et al., 2006; TANG et al., 2014; BONIFACIE et al., 2017). This also includes critical analytical steps such as the phosphoric acid digestion temperature (e.g. 25 vs. 90°C), statistical procedures, and correction terms applied (DAËRON et al., 2016; KELSON et al., 2017). An accurate implementation further involves the investigation of potentially relevant effects influencing clumped isotope fractionation during variable carbonate mineral precipitation. This comprises an evaluation of equilibrium vs. kinetic fractionation effects (DAËRON et al., 2011; LEVITT et al., 2018), and more specifically temperature, precipitation rate, pH and DIC speciation effects (TRIPATI et al., 2015; KLUGE & JOHN, 2015). For example, KLUGE et al. (2018) used natural travertine and geotechnical scale samples from geothermal facilities to investigate the role of pH and DIC speciation effects on calcite formation. Their results revealed a possible underestimation of Δ_{47} -based formation temperatures from true formation temperatures under environmental conditions that include very high mineral precipitation rates, high pH, and/or low temperatures (slow equilibration), i.e. only relevant quantitatively in specific environmental settings. More generally, however, observational evidence suggests that most Earth-surface calcite precipitates form out of oxygen and clumped isotopic equilibrium to a variable degree (DAËRON et al., 2019), i.e. potential (kinetic) isotope fractionation effects have to be evaluated with caution for specific environmental settings and applications. Most recent analytical developments further involve the utilization of **laser absorption spectroscopy** for determining the relevant multiply-substituted isotopologues (e.g. of CO_2 ; PROKHOROV et al., 2019). This optical method of clumped isotope thermometry facilitates a simplified sample preparation, more rapid sample throughput and the circumvention of some isobaric interference problems. Further,



Text-Fig. 4. Single-phase equilibrium describing the temperature dependent “clumping” of relatively rare and heavy ^{13}C and ^{18}O isotopes during Ca-carbonate precipitation.

considering the overall lower instrumentation costs and reduced space requirements, the laser spectroscopic technique might outcompete mass spectrometric analysis in a foreseeable future.

Diverse environmental settings

Carbonates constitute a major **carbon reservoir** participating in the Earth's carbon cycle, i.e. the largest carbon reservoir of the lithosphere (MORSE et al., 2007). In the relation of CO₂ and carbonate minerals, the lithosphere (and mantle), hydrosphere (and cryosphere), pedosphere, biosphere, and atmosphere are coupled in an array of complex albeit few dominant physico-bio-chemical processes determining carbon exchange and carbonate occurrence. The latter processes **spatially** extend from the macroscale (e.g. mountain ranges/landscapes and marine platforms) to the microscale (e.g. crystal nucleation and diagenesis) and **temporally** extend from geological timescales to nearly instantaneous mineral formation. Carbonates in general and Ca-carbonates in particular shape paleo- and modern environmental settings, natural (geogenic), and human-made (anthropogenic, e.g. geotechnical) environments. In addition, Ca-carbonate minerals represent the most abundant mineral group with regard to biomineralization (GEBAUER et al., 2009).

Sedimentary carbonates form from cycles and events of autochthonous and allochthonous carbonate deposition depending on tectonic, climate, and various other environmental factors. Limestones, marls, calcareous sandstones, and dolomite rocks are voluminous manifestations of such foregoing sedimentation. In the **marine realm**, deep and shallow water carbonates are of frequent occurrence including oceanic basin muds (MORSE & MACKENZIE, 1990) and lagoonal sands (e.g. ooids; DIAZ et al., 2017), as well as different types of platform carbonate and coral reefs (DUNBAR, 2000). In this context, coccolithophores, foraminifera, mollusks, red algae, and echinoderms are the most important organisms precipitating Ca-carbonate skeletal parts in the oceans (MORSE, 2004). These sedimentary components of variable fragment- and grain sizes typically undergo burial, hydrothermal, and microbial **diagenetic processes** including the precipitation of carbonate cements in pore spaces (MOORE & WADE, 2013) and/or dolomitization (BALDERMANN et al., 2015). Considering the diverse environmental settings and temporal evolution of sedimentary carbonates, many of these mineral deposits can serve as a valuable chemical-sedimentary archive. Pristine **corals**, for example, are of interest with respect to inorganic versus biochemical carbonate nucleation and as an environmental archive capturing past global sea-level variations affecting coastal areas (SIDALL et al., 2003). Similarly, **bivalves and brachiopods** are studied in the light of Ca-carbonate polymorphism and biomineralization, and to decipher paleoclimate information from their exoskeletal chemical composition (DETTMAN et al., 1999). In the marine and freshwater sedimentary environment, **stromatolites and microbial mats** constitute a shallow water and mostly laminated mineral formation that is organically-mediated (cyanobacteria, algae) and results in Ca-carbonate precipitation, particle entrapment, and cementation (FREYET & VERRECCHIA, 1998; RIDING, 2000). Ca-carbonates of micritic to structurally complex growth morphology are also of frequent occurrence in **lake sediments**

of different regions and hydrochemistry and in some cases display rhythmic (seasonal, varve) successions (COUNCIL & BENNETT, 1993; OEHLERICH et al., 2013). Freshwater Ca-carbonates such as typically compact and well-laminated **travertines** and porous, more heterogeneous **calcareous tufa** are either associated with thermal or ambient temperature water streams in connection with strongly localized (neo)tectonic or volcanic activity, or other specific sedimentary settings influenced by deep water circulation and carbonate mobilization (BOCH et al., 2005; BROGI et al., 2012). Similar freshwater Ca-carbonate growth successions were also investigated in **historic** (e.g. Roman) **aqueducts and water cisterns** (PASSCHIER et al., 2016a, b). The interplay of Ca-carbonate dissolution (mobilization) and precipitation additionally characterizes the widely distributed **karst areas and caves** involving karstification processes and **speleothem** mineralization (FAIRCHILD & BAKER, 2012). The latter carbonate formations have shown to provide a spatiotemporally attractive chemical-sedimentary archive of diverse (multi-proxy) paleoenvironmental information anchored with precise radiometric (uranium-series) chronologies (BOCH et al., 2011b; CHENG et al., 2016). Similar capabilities can be attributed to the investigation and environmental interpretation of carbonate precipitates in **fractures and faults**, i.e. these deposits might capture chemical and petrographic information on paleoclimate conditions, as well as (neo)tectonic or gravitational mass movements (HAUSEGGER et al., 2010; BOCH et al., 2019). Secondary **carbonate cements** consolidating limestone and dolomite fragments (e.g. boulders) from major mass movements have been used to provide absolute radiometric age constraints (minimum ages) of **rock falls** (OSTERMANN et al., 2007). **Concretions and nodules** in (paleo)**soils** consisting of Ca-carbonate have also been utilized in (paleo)environmental studies targeting meteoric conditions (e.g. loess dolls; BARTA, 2014) or uplift of mountainous terranes (GHOSH et al., 2006). The diverse settings of carbonate occurrence further include **cryogenic precipitates in sea ice** (e.g. ikaite; FISCHER et al., 2013) or **cave ice** (COLUCCI et al., 2017). Such ice-hosted carbonates are indicators of distinct and often extreme hydrochemical and atmospheric conditions.

Considering **natural environmental settings** of carbonate occurrence, some **magmatic rocks** can contain carbonate minerals, i.e. mostly calcite (OKRUSCH & MATTHES, 2010). Typical host rocks are alkaline or ultramafic igneous rocks, such as **carbonatites and kimberlites**. For example, the lava and explosive ejection materials of volcano Lengai located in the East African Rift Zone are known for their Ca-(Na)-carbonate mineral content (WEIDENDORFER et al., 2017). In association with regional magmatic processes, carbonates may also precipitate in **hydrothermal veins**, i.e. mostly calcite and iron and magnesium carbonates deriving from deep and hot water circulation (PIRAJNO, 2009). These carbonates are of interest with regard to their source and evolution and in particular regarding their formation temperature, thermal fluid composition (e.g. brines), and absolute and relative (vs. host rock) age distributions (MASKENSKAYA et al., 2014). For example, LUETKEMEYER et al. (2016) studied calcite veins in the San Andreas Fault system focusing on stable C, O, and clumped isotope signatures in order to trace fluid sources, specific fluid-rock interactions and related mechanisms of frequent seismic events. Networks of calcite veins in con-

nection with fractures and faults in the Oman mountains were elaborated focusing on variable fluid pathways and hydraulic connectivity (ARNDT et al., 2014). A detailed geochemical investigation of vein carbonates is further of interest regarding prospective nuclear waste disposal sites (YARDLEY et al., 2016). Fluid inclusions captured in calcite at Yucca Mountain (Nevada) revealed hypogene hydrothermal activity during the young geological past (DUBLYANSKY & SPÖTL, 2010). Some carbonate minerals characterize regional settings of relevance with regard to economic **raw material** production. **Siderite** has Fe concentrations high enough to be explored as an iron ore for the steel industry, e.g. the major siderite-ankerite iron ore deposit at Erzberg, Austria (PROCHASKA, 2016; BOCH et al., 2019). Similarly, **magnesite** constitutes a (hydrothermal) carbonate of material-specific relevance, e.g. as an ore of refractory Mg sinters (Breitenau, Austria; HENJES-KUNST et al., 2014). In the context of natural carbonate settings, **metamorphic rocks** should also be considered. **Marbles** represent recrystallized Ca-carbonates of variable metamorphic overprint (anchimetamorphous to blueschist facies) and resulting petrography (SEATON et al., 2009). **Carbonate-rich (calcareous) shales** are widespread metamorphic rocks in the Alps (e.g. Bündnerschiefer Formation; SCHMID et al., 2004) and might even host caves and speleothem carbonate precipitation (BOCH & SPÖTL, 2011). Interestingly, carbonate concretions that have formed at relatively low temperature and with chemical zonation were also found in **meteorites** from Mars (VALLEY et al., 1997). Hydrous carbonates such as ikaite and monohydrocalcite are considered prospective minerals of high scientific interest on the **Mars** surface (HARNER & GILMORE, 2015). In this regard, the natural occurrence of carbonates might even be expected from other (exo)planets.

The diverse environmental settings further comprise of **synthetic carbonate** formation in the **laboratory** targeting fundamental, as well as material scientific and industrial applications. This includes **precipitation and alteration experiments** of various carbonate minerals under controlled physicochemical conditions in order to study basic mechanisms of crystal (re)nucleation and growth, and elemental and isotopic fractionation (DIETZEL et al., 2009). The experimental setup might either consist of more or less static steel autoclaves (CASELLA et al., 2017) or various adaptations of dynamic flow reactors (MAVROMATIS et al., 2017). Further, carbonate precipitation from an aqueous reaction solution can be triggered by simple mixing of parent solutions or by the membrane CO₂ diffusion technique (DIETZEL et al., 2004; TANG et al., 2012). In addition, some experimental setups mimic specific chemical-sedimentary environmental conditions, e.g. inorganic stalagmite growth (DAY & HENDERSON, 2013) or biologically mediated freshwater travertine and calcareous tufa deposition (PEDLEY, 2013). Experiments and laboratory based analyses were further dedicated to **historic building materials** involving carbonate mineralization, e.g. **lime mortar, plaster, or concrete** of ancient Greek, Roman, or Medieval times (KOSEDNAR-LEGENSTEIN et al., 2008). The archaeological carbonate utilization also includes geochemical and archaeometrical investigations of ancient artefacts by laser ablation mass spectrometry (LA-ICP-MS; DEGRYSE & VANHAECKE, 2016), as well as radiocarbon dating of calcite formed from atmospheric CO₂ absorption in concrete (DIETZEL & BOCH, in press). Likewise, complex fluid-sol-

id interaction involving various carbonates amongst other curing and/or dissolving phases is intensely studied in **modern concrete constructional settings** (MITTERMAYR et al., 2017; GRENGG et al., 2018; GALAN et al., 2019).

Settings of (Ca-)carbonate mineralization also include chemical-sedimentary environments strongly influenced both by **natural and human-made** (operational) conditions. In principal, however, most natural environments involving carbonate (oceans, lakes, rivers, mountain territories, soils, sea ice, etc.) might be more or less affected by human impacts (e.g. global warming, pollution). More specifically, carbonate formation and mobilization in **geo-technical settings** strongly rely on a geogenic versus anthropogenic relationship. For example, Ca-carbonates precipitated from saline (thermal) waters produced from deep reservoirs and boreholes often constitute a major challenge in the course of **geothermal energy production**, as well as in the **oil and gas industry** (BJØRNSTAD & STAMATAKIS, 2006; ZARROUK & MOON, 2014). The occurrence of unwanted **carbonate scaling** mostly depends on the natural reservoir rock and water chemical preconditions in combination with the human-made disturbance of natural physicochemical equilibrium conditions (e.g. pressure/temperature changes; HAKLIDIR & HAKLIDIR, 2017). Typical expressions of these carbonate scale deposits are reduced inner diameters and clogging of **well casings and transport pipelines** (DEMIR et al., 2014; BOCH et al., 2016) or an ongoing blockage and reduced heat and energy transfers in thermal water **heat exchangers** (HASSON et al., 1968; BOCH et al., 2017a). Various forms of scaling and fouling including Ca-carbonates are also major obstacles in many cases of **water treatment**, such as **desalination** during potable or industrial water production (WARSINGER et al., 2015). Unwanted carbonate scales are also common mineral precipitates at low temperature ambient conditions in **artificial channels**, such as **drainages in tunnels** (DIETZEL et al., 2013; CHEN et al., 2019) or bypassing concrete stream beds (BOCH et al., 2015). However, selected geotechnical carbonate scale materials of well constrained environmental conditions have also shown attractive hydro- and geochemical characteristics with regards to fundamental research on isotope (and element) fractionation mechanisms, i.e. a benefit from the otherwise unwanted deposits (KLUGE et al., 2018). Last but not least, considering that **CO₂** as a major and increasingly problematic greenhouse gas, its **geotechnical and industrial sequestration**, i.e. CO₂ capture and storage by dissolution in deep sedimentary basin formation waters and/or by solid-phase carbonation are also a subject of modern carbonate research (SANNA et al., 2014). In this context, complex gas-water-rock interactions and mineral dissolution versus precipitation reactions in carbonate, sandstone, or ophiolite reservoirs are evaluated by laboratory experimental, modelling, and field based approaches (KHARAKA et al., 2006; TUTOLO et al., 2015). KELEMEN & MATTER (2008), as an example, investigated geologically young carbonate veins in ophiolites hosting peridotite and found high reaction rates, and therefore geochemical potential, for in-situ conversion of CO₂ and peridotite (weathering) to Ca-Mg-carbonate minerals. More generally, the uptake and conversion of CO₂ exerts a primary role in global **silicate weathering** and in the transformation of silicates (e.g. feldspars, pyroxenes) into clay minerals in association with dissolved inorganic carbon or carbonate minerals (DEPAOLO et al., 2013).

Caves, Speleothems and Climate Reconstruction

Speleothems (dripstones, cave decoration) – in particular stalagmites and flowstones – have emerged as an attractive, and therefore intensely investigated, chemical-sedimentary archive that captures environmental information in diverse ways. The closely related research fields and topics constitute a **multidisciplinary approach** primarily focused around the geoscientific disciplines of geochemistry and Quaternary geology, but further including specialized knowledge from mineralogy, hydro(geo)logy, speleology, climate research and meteorology, material sciences, and (micro)biology. Speleothem formations consisting of Ca-carbonate (dominantly calcite) can form in different caves. **Karst caves** in limestone and dolomite host rocks (aquifers), however, clearly outnumber cave settings of metamorphic (e.g. marbles, calcareous schists) or magmatic (e.g. hydrothermal fractures, lava tunnels) provenance. Regarding their geographic and climate regime **distribution**, caves are a widespread natural phenomenon within the geological wealth of landforms. Consequently, caves represent a (paleo)environmental archive located in areas populated by humans, as well as in remote karst areas (FORD & WILLIAMS, 2007). This circumstance is a spatial advantage compared to other established but locally less diverse environmental (climate) archives, such as ice cores from Greenland and Antarctica (KAWAMURA et al., 2007; BARKER et al., 2011) or sediment cores from the deep ocean basins (LISIECKI & RAYMO, 2005). Another spatial advantage consists in the location of cave settings **underground**, i.e. the environmentally sensitive but fragile speleothem formations are protected from most of the destructive atmospheric, sedimentary, and diagenetic processes shaping the Earth's surface and sedimentary spaces (environmental archives) in particular. Considering the **temporal extension** of caves and speleothems, the time interval associated with the **Quaternary** period (the last ~2.6 millions of years) can be easily covered, although major cave systems and chambers do not constitute a landform of high stability in geological time and space, i.e. caves undergo maturity processes and stages from initial pores and mostly through partly dissolution enlarged fractures in the carbonate host rock towards the phreatic evolution of cave chambers, vadose water percolation, and speleothem deposition, and finally undergo gravitational collapse or erosion at the Earth's surface. Older cave systems may date back to the younger or perhaps middle Tertiary period. In this regard, speleothems constitute an environmental archive of the more recent geological past and its prevailing climate conditions. Importantly, typical speleothem carbonate material of variable age has shown to be well suited for absolute **radiometric age determination** based on uranium-series geochemistry (EDWARDS et al., 1987; RICHARDS & DORALE, 2003; SPÖTL & BOCH, 2012). This potential of establishing precise and accurate **chronologies and growth models** for individual speleothem samples and related environmental information constitutes another prominent strength of this mineral archive in relation to other (bio)chemical sediments susceptible to environmental variability. Although situated underground, caves and successively growing speleothems possess several **interconnections** to the prevailing climate and atmospheric conditions at the **Earth's surface** (FAIRCHILD et al., 2006). The most

important are chemical, isotopic, and particle composition signatures transferred by the seepage water (dripwater), a variable cave air exchange (ventilation) influencing air- and hydrochemical gradients and compositions and the multi-annual thermal assimilation (equilibration) of the cave interior versus outer atmosphere. **Stalagmites and flowstones** are of primary importance as paleoenvironmental mineral archives owing to their relatively simple growth geometries compared to other forms of speleothems, such as stalactites, stalagnates (columns), curtains, pool formations, and helictites (WHITE & CULVER, 2012). During ongoing speleothem precipitation from aqueous solution, variable environmental parameters have an influence on the chemical and petrographic dripstone composition, and this variability that is captured in the solid carbonate can be reconstructed in a **multi-proxy** (representative variables) approach (BOCH, 2008; FAIRCHILD & BAKER, 2012). In this context, **cave monitoring** programs have shown of great value regarding the fundamental, as well as site-specific, understanding of speleothem growth dynamics and its environmental dependencies (MATTEY et al., 2008; BOCH et al., 2011a). In the following sections, some of the major speleothem based and climate research dedicated requirements will be presented focusing on the author's own scientific experiences.

Uranium-Thorium based speleothem chronologies

The reliable age determination of speleothem carbonates constitute the backbone of this field's rapid scientific development and increasing value in the context of (paleo) climate research. The extraordinary dating capability of typical speleothems is based on selected **uranium-series isotopes** incorporated and evolving in the speleothem Ca-carbonate. Radiometric radiocarbon (^{14}C) dating was applied in the early history of speleothem based paleoclimate research – and still can be of additional value – but suffers from several geochemical restrictions (FOHLMESTER et al., 2017). The time (age) elapsed after speleothem carbonate (calcite) deposition is reflected in the isotope (and activity) ratios of unstable uranium and thorium parent (^{238}U) and daughter nuclides (^{234}U , ^{230}Th) establishing over time in the speleothem carbonate based on the natural ^{238}U decay chain (IVANOVICH & HARMON, 1992; CHENG et al., 2013). Importantly, the radiogenic ^{230}Th is exclusively derived from the decay of the preceding ^{238}U and ^{234}U isotopes and its relative amount in the carbonate (sub)sample is therefore a precise measure of time depending on well-known half-lives of the relevant unstable nuclides. In principle, the U in the carbonate precipitates available for radioactive decay with time, results from specific dissolved U species (mainly aqueous uranyl – UO_2^{2+} complexes), while Th species are virtually insoluble and expelled from the aqueous solution (adsorbed to solids) and thus not incorporated into the speleothem calcite crystal lattice. An efficient hydrochemical separation of U and Th is essential with regard to the radiometric clock in speleothems. Minor amounts of detrital ^{230}Th (not from in-situ decay) being incorporated in the carbonate precipitated from aqueous solution (seepage water) are corrected for using the measured ^{232}Th isotope ($^{230}\text{Th}/^{232}\text{Th}$ ratio). In general, the potential and achievable precision of the U-Th ages and chronologies strongly depend on the local **geochemistry and geology** associated with the particular cave setting and speleothem formation (SPÖTL & BOCH, 2012). Depending on the local carbonate

host rocks (e.g. marble vs. dolomite vs. pure limestone), the karst processes (fluid-solid interaction), available U concentrations, detrital (Th) contributions, and speleothem growth are significantly different. Also, carbonate host rock mobilization from carbonic acid based dissolution reacts different from sulfide oxidation and sulfuric acid based carbonate dissolution and subsequent Ca-carbonate precipitation (HOLZKÄMPER et al., 2005; BOCH et al., 2009; BAJO et al., 2017). Consequently, some speleothem and other Ca-carbonate precipitate **^{238}U - ^{234}U - ^{230}Th dating** efforts and dating precisions might suffer from low initial U concentrations (also very young samples), heavy detrital contamination, or later-stage (diagenetic) alteration (RICHARDS & DORALE, 2003). In most cases, however, absolute ages of speleothem formation can be inferred up to a dating limit of ~700,000 years based on U-Th. Select uranium and lead (^{204}Pb , ^{205}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb) isotopes of the natural ^{238}U and ^{235}U decay chains measured against synthetic isotope tracers (technical spikes) allow speleothems to be dated millions of years in age, in the case of favourable geochemical preconditions (WOODHEAD et al., 2006; MEYER et al., 2011). Critical issues with regard to **U-Pb dating** are the initial (common) Pb concentrations (contamination), very low radiogenic Pb concentrations (relatively young samples), and disturbed mineral closed system and therefore secular equilibrium conditions (volatile daughter nuclides).

Regarding the age determination of stalagmites, a first classification might be based on some direct observations, e.g. location in the cave system, and stalagmite size and colouring. Ahead of collecting the entire **stalagmite** sample, it might also be reasonable to extract a small drillcore from the thicker stalagmite base in order to constrain its growth inception and potential time interval of scientific interest based on U-Th (or U-Pb). In the case of massive **flowstones**, the **sampling** is mostly restricted to surface samples or multiple and distributed drillcores of variable diameter (cm-range) and length (meter-range; BOCH & SPÖTL, 2011). The collected stalagmites and flowstone drillcores are typically cut and polished (to enhance visual contrast) for multiple extractions of subsamples across the speleothem growth axis using band- or circular saws or handheld drills. These chunks and powders are then acid digested and processed in a multi-step wet-chemical procedure in a high-level clean laboratory using ion exchange columns and organic resins (chromatography) and various chemicals (SHEN et al., 2012). This multi-step process includes the **separation and enrichment** of tiny amounts of U and Th from the sample carbonate. Subsequently, the separate U and Th fractions and their isotopic compositions are analysed applying thermal-ionization **mass-spectrometry** (TIMS) or, more commonly, multi-collector inductively-coupled-plasma mass-spectrometry (MC-ICP-MS). Due to the small isotope concentrations and resulting ion beams, the ionization efficiency and magnet-optical transfers, and therefore the instrument setup, calibration, tuning and backgrounds, are all critical issues. The relevant isotope mass ranges, resolution, and interferences depend on the measurement protocol and machine setup (e.g. electron multiplier vs. faraday ion detectors), as well as the clean laboratory procedure (e.g. control spikes added) and – based on personal experience – these analytical conditions are significantly different in several aspects between dating laboratories. High-resolution subsampling

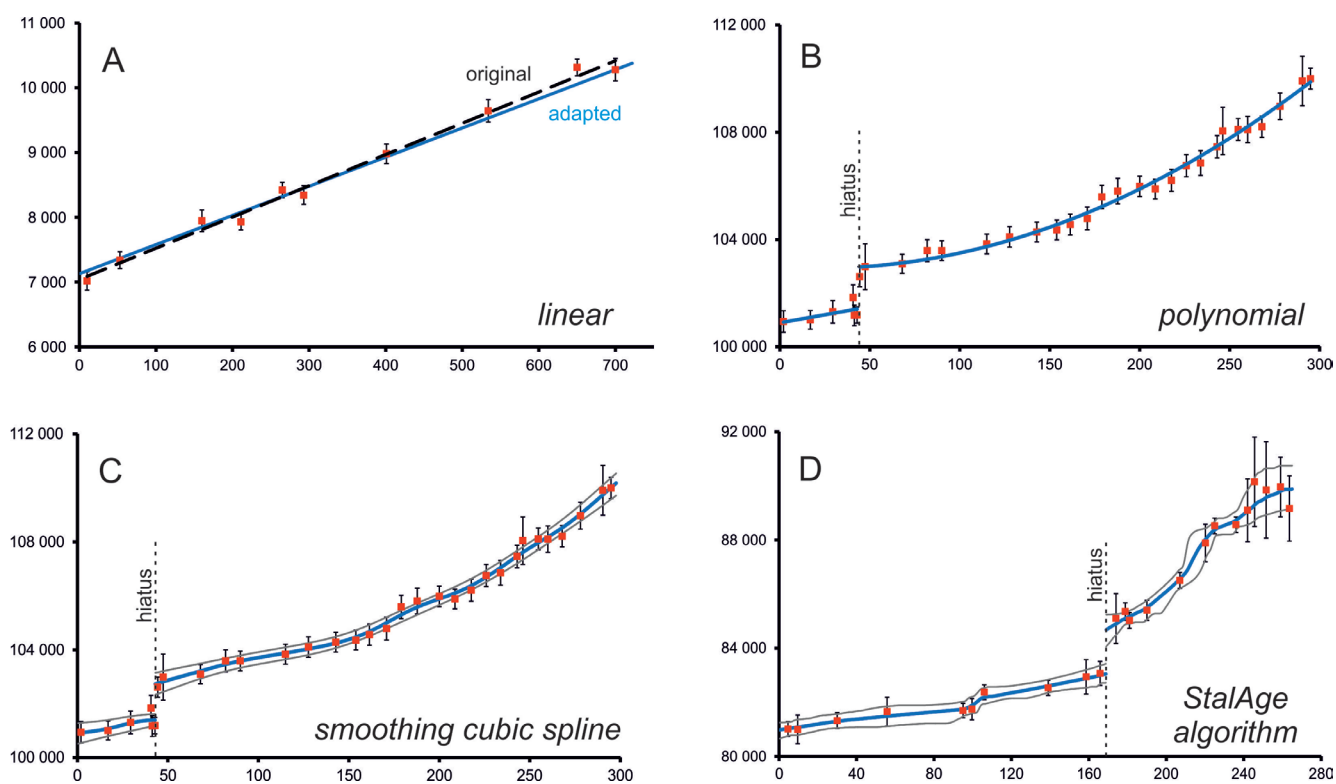
for U-Th and U-Pb age determination can also be performed by laser ablation coupled to multi-collector mass-spectrometry and the ages might then be calculated online (EGGINS et al., 2005; SMITH, 2014). The precision (age errors) of these measurements, however, is typically significantly lower. Depending on the geochemical preconditions and absolute age of a speleothem sample, relative **age uncertainties** (2-sigma) of 0.2 to 2 % are state-of-the-art for most U-Th dating laboratories, i.e. a radiometric dating technique of high precision in the context of paleoenvironmental studies. Considering very young samples (up to few thousands of years), as well as old samples (half a million years and older), the achievable precision decreases significantly (several percent) and in the case of detritally contaminated sample material the mandatory ^{232}Th correction applied during isotope data processing results in major measured versus corrected age corrections and thus larger age uncertainties (sometimes tens of percent; BOCH et al., 2019). The accuracy of the absolute ages is primarily related to the reliability of the established, but continuously improved, radioactive **decay constants** (half-lives) of the unstable U and Th isotopes (CHENG et al., 2013). SPÖTL & BOCH (2012) provide a compact introduction to uranium-series dating of speleothems.

Interconnecting radiometric ages measured from the speleothem bottom (oldest part) to the top (youngest) or multiple ages distributed across the speleothem growth axis, can be accomplished using sample-specific **age (growth) models**. These **numerical** models interpolate and eventually extrapolate trends inferred from the individual data points (ages) of the radiometric datasets, thereby constituting an integral part of speleothem based **chronologies** that allows for paleoenvironmental information to be tightened to their temporal evolution. Moreover, the particular **speleothem growth rate** (carbonate precipitation rate) is a direct numerical result of such age models. The preferred numerical approach of a specific age dataset strongly depends on the number and distribution of the individual age data points, the overall and variable age uncertainties (error bars), as well as complicating features such as age inversions (within monotonic stratigraphic order), outliers, abrupt growth rate variations, and growth interruptions (hiatuses). These age versus depth characteristics are often evaluated in close connection with available petrographic information from the speleothem sample (e.g. visual indication of growth interruptions, (ir)regular lamination). In any case, the age-depth relationship has to satisfy the criterion of a monotonic slope (e.g. steadily decreasing age with increasing distance from stalagmite base). In the case of a simple stalagmite or flowstone drillcore bottom-top relationship, or an even distribution of multiple ages measured across the respective growth axis, a **simple linear function** might be applied as a numerical age model reflecting the speleothem growth evolution (Text-Fig. 5A; BOCH et al., 2009). These simple models, however, can oversimplify the real growth pattern and minor but environmentally meaningful variations are not reflected. In the case of numerous and closely spaced age data points, these could also be **straightly connected**, i.e. a form of simple linear pointwise interpolation characterizing a more variable but spatially well constrained age model (DYKOSKI et al., 2005). Unfortunately, the latter age models entail somewhat artificial growth rate variations resulting from the sharp changes of slopes at the anchor-

ing age data points, i.e. in nature changes in speleothem growth might be more gradual and not be characterized by partially sampling-dependent kinks. Age-depth distributions of limited complexity can also be represented by various **polynomial functions** of least-squares (SPÖTL & MANGINI, 2002). More detailed growth variations are to be expected in natural speleothem specimen, and are again neglected in such age models. With respect to high temporal resolution paleoclimate records, this deficiency has to be considered. In some cases, however, these numerical solutions might be reasonable within the analytical age uncertainties (Text-Fig. 5B). A more fluent approach supporting the occurrence of significant growth variations consists in various regressions by **smoothing cubic spline functions** (HEEGAARD et al., 2005; SPÖTL et al., 2006). Most spline functions and associated statistics underlying speleothem chronologies are calculated using the open-source programming package “R” (R DEVELOPMENT CORE TEAM, 2018). Utilizing predefined keywords, selected parameters (e.g. degree of freedom) can be modified by the user, and the age and spline-dependent confidence limits (e.g. 2σ) can easily be calculated (Text-Fig. 5C). The manipulation, however, is still of some subjective decision and a combination of trial-and-error and best-case scenario might define the final speleothem chronology. In order to counteract such manipulation, SCHOLZ & HOFFMANN (2011) developed the **StalAge algorithm** based on a Monte-Carlo simulation successively fitting ensembles of linears with variable slopes to subsets of age data points and their respective uncertainties, while also including basic stratigraphic information. This approach of age-depth

modelling, including the calculation of confidence intervals (2σ), is suitable for challenging datasets and the lack of adjustable parameters ensures high reproducibility (Text-Fig. 5D). An increasing number of paleoclimate records are temporally constrained by StalAge calculations (BOCH et al., 2011b; PEREZ-MEJIAS et al., 2017). **OxCal** is another **algorithm** of high acceptance and mostly used in radiocarbon dating (BRONK RAMSEY & LEE, 2013). This approach is based on random Poisson processing and only some rigidity parameters of the age model can be modified by the user. Owing to its satisfying flexibility of tracing the age data, automatic calculation of associated age uncertainties (2σ), and user-friendly implementation, it is increasingly used in paleoclimate studies (MOSELEY et al., 2016; PEREZ-MEJIAS et al., 2017). A **comparison** of different speleothem age modelling approaches that considers typical as well as challenging U-Th age datasets is provided by SCHOLZ et al. (2012).

Importantly, the **selected numerical approach** of age-depth modelling has a major influence on the final speleothem chronology, which temporally constrains the captured environmental information. The influence is particularly large for those paleoenvironmental records that are less constrained by the available U-Th data, i.e. being characterized by higher age uncertainties (lower precision), few data points, potential growth interruptions, distributions suggesting unreasonable growth rate variations, outliers and/or age inversions. More specifically, the absolute and relative **timing, duration, and temporal progress** of archived rare or recurrent climate events and cycles on



Text-Fig. 5. Different age (growth) modelling approaches applied to typical U-Th based data points and their respective age uncertainties (2σ error bars). A) Simple linear function proposed by software (e.g. MS Excel) inherent statistics and adapted manually within the age errors. B) Least-squares polynomial fit to relatively evenly distributed age data points including a speleothem growth interruption (hiatus). C) Same dataset as in B but applying a smoothing cubic spline function calculated in the programming software “R” for the two separate growth sections. D) StalAge algorithm developed by SCHOLZ & HOFFMANN (2011) based on approximate Monte-Carlo simulation of piecewise linear fits to age data subsets. Note the variable flexibility of the resulting age models in tracing the measured age data (blue curves) and the variable 95 % (2σ) confidence limits (thin grey curves). The age-depth models also differ in terms of their reproducibility.

short- and longer-term timescales are directly inferred from the calculated age models (BOCH et al., 2011b; CHENG et al., 2016). Consequently, the temporal expression and scientific interpretation of environmental variation is strongly dependent on the – more or less objective – chronology of the individual paleoclimate records and their relation to other absolutely dated chronologies. For example, speleothem U-Th based chronologies are related to ice core based (lamina counting and ice flow modelling) chronologies, which in turn may reveal rapid spatiotemporal variations that include socio-politically critical variables such as air temperature, meteoric precipitation, mean sea level, and greenhouse gas concentrations (KAWAMURA et al., 2007; BARKER et al., 2011). In this context, testing the analytical precision, reliability, and reproducibility of the radiometric ages and superimposed age models is of highest relevance in order to minimize **subjective constraints**. In addition to a comprehensive disclosure of the measurement and data evaluation procedures performed, a favourable speleothem sample geochemistry allowing of precise age data is critical with regards to reliable, and perhaps internationally relevant, chronologies. Additional temporal constraints from detailed petrographic inspection of growth segments or regular minor/trace element variations can be of value, e.g. refining age models between measured U-Th data points by annual lamina counts and/or element cycles (ASRAT et al., 2007; BOCH et al., 2011a).

Speleothem stable oxygen isotope records

Regarding the paleoenvironmental information captured in speleothem carbonates, the stable O isotopic composition constitutes a proxy (representative parameter) of particular relevance. This is manifested in the numerous research publications reporting variable O isotope values in the course of speleothem growth, i.e. mostly isotope curves across the growth axis of a speleothem sample reflecting **spatiotemporal variations** of different origin and magnitude (FAIRCHILD & BAKER, 2012). The stable O isotopes are most relevant considering their occurrence in water and (carbonate) minerals, their often well-known fractionation processes, and their sensitivity to environmental variation on different spatial and temporal scales (HOEFS, 2015). These attributes and resulting potential in the light of paleoclimate investigation are not restricted to speleothems, but to several environmental archives involving stable O isotope analyses, e.g. ice cores, corals, marine and lake carbonate sediments and others. In all of these cases, identifying the variable **reservoirs and isotope fractionation processes** of oxygen are crucial, as they differ significantly between terrestrial and marine settings (CLARK & FRITZ, 1997). Further considering the widespread terrestrial speleothem archive, the carbonate O isotopic compositions capture **environmental information** related to the source and transport routes (trajectories) of air masses and moisture, time and space of meteoric precipitation, the prevailing air temperature, meteoric and carbonate precipitation conditions, and other isotope reservoir specific alternative processes. In particular, the O isotopic signature of atmospheric moisture depends on the source region (e.g. Atlantic vs. Mediterranean), as well as sea surface temperature, and evaporation conditions. The transport distances (advection of moisture), variable latitude (climate zonation) and altitude (ascent/descent of moisture), as well as (re) evaporative and condensation processes affect the specific

rainout, O isotopic evolution and signature. Further, the regional climate, meteorological conditions, and season of the year determine the O isotope compositions, while the respective air temperature and meteoric precipitation amounts have a strong effect on condensation and associated O isotopic fractionation (CRAIG, 1961). At the surface and underground, the O isotopic signatures are altered by evapo(transpi)ration from plants and storage reservoirs (lakes, rivers) and various effects from water-rock interaction in soils and aquifers. Finally, equilibrium and kinetic effects control O isotope fractionation between aqueous solutions (e.g. seepage water) and related carbonate precipitates (e.g. speleothems; MICKLER et al., 2004; DAÉRON et al., 2019).

Based on this multitude of dominantly physicochemical processes and effects that determine O isotopic compositions, specific **environmental relationships** can be studied qualitatively and quantitatively. In the realm of (paleo) climate research, the O isotope signatures are mainly a proxy parameter for variable air- and water temperatures and meteoric precipitation amounts and sources (FAIRCHILD et al., 2006; HOEFS, 2015). These principal meteorological and climate variables differ significantly on regional and temporal scales and such variability can be archived in the speleothem carbonate at variable degrees of signal to noise. This is expressed in the increasingly available stable O isotope curves of variable timing and **temporal resolution**, resulting from speleothem carbonate subsample transects extracted at variable **spatial resolution**. Depending on spatiotemporal resolution (e.g. high-resolution micromilling) and the overall time interval and growth rates of a particular speleothem, environmental information of diverse implication and detail might be reconstructed. Critically, the environmental and related O isotopic signals are **transferred and altered** between the different reservoirs of relevance, i.e. atmosphere, hydrosphere, pedosphere, aquifer, and cave system. Next to the atmospheric fractionation processes (CRAIG, 1961; HAGER & FOELSCHKE, 2015), the stable O isotope processing involves soil water and CO₂ isotope exchanges, as well as typical fluid-solid reactions in the karst aquifers influencing the hydrochemistry of the seepage- and subsequent drip waters (e.g. water mixing from different flow routes, outgassing, prior CaCO₃ precipitation; SMART & FRIEDERICH, 1986; MATTEY et al., 2016). Conditions within the cave, particularly atmospheric conditions, can affect the hydrochemistry, including O isotopic compositions, of the water and dissolved inorganic carbonate due to variable gradients, e.g. temperatures and partial pressure differences promoting outgassing of CO₂ and H₂O (MATTEY et al., 2008; BOCH et al., 2011a). The speleothem carbonate O isotope compositions reflect this **cascade** of dominant processes and consequently constitute some **filtering, attenuating, and amplifying** variable (TREMAINE et al., 2011).

The stable O isotope records from speleothems therefore often reflect the prevailing meteorological conditions and principal **atmospheric circulation patterns** on different timescales at the cave site. In this context, the existence of pronounced **seasons** in the mid and high latitudes, or lack thereof in tropical low-latitude climate zones, have a strong effect on speleothem growth and O isotope compositions. Some regions and speleothem O isotope records show a distinct sensitivity to variable **monsoonal winds**

and rains and related shifts in the Inter-Tropical Convergence Zone (CRUZ et al., 2005; CHENG et al., 2016). Likewise, O isotopes in stalagmites have recorded variations of the **El Niño Southern Oscillation** (WANG et al., 2017). **Storm events**, such as tropical cyclones (FRAPPIER et al., 2007) or influences of Mediterranean cyclone activity (DEMÉNY et al., 2017), might also be recorded. For major parts of Europe, the positioning and strength of the **westerlies** and seasonal atmospheric circulation patterns such as the **North Atlantic Oscillation** can exert a major influence on the recorded O isotope values (BOCH & SPÖTL, 2011; FOHLMEISTER et al., 2017). In this respect, the extent of **snow** precipitation and subsequent **snowmelt** can significantly impact the karst aquifer recharge and water mixing, and thus the annually averaged isotopic composition of speleothems (FORD & WILLIAMS, 2007). Importantly, the recurrent (cycles) or irregular (events) environmental conditions operate from daily, seasonal, multi-annual to millennial timescales, which strongly affect the final captured isotopic compositions, as well as their magnitude (e.g. weighing of seasonal contributions; BOCH et al., 2011a; DOMÍNGUEZ-VILLAR et al., 2018). For example, in investigating two selected stalagmites from the Swiss Alps, LUETSCHER et al. (2015) found major **storm track and advective moisture transport** changes during the **Last Glacial Maximum** (LGM) dated to 26.5–23.5 kyr BP. Based on a precise U-Th chronology and high-resolution O isotope records, LUETSCHER et al. (2015) built a conceptual model of isotope fractionation derived from meteoric precipitation trajectories and associated O isotopic depletion during a Rayleigh fractionation process. Their results revealed a strongly enhanced advection of moisture from the South towards the Alps. This southward shift is interpreted to be the result of ice sheet expansion in the Atlantic Ocean, which, consequently, precluded common (e.g. modern) advection of moisture from the north-western Atlantic Ocean. The implications from the conceptual model are in line with field evidence of prominent glacier advances in the southern part of the Alps during that time, and an O isotope-based mixing model allowed quantifying S-Alps meteoric precipitation amounts being two or three times higher during LGM compared to today (LUETSCHER et al., 2015). In some places and for some speleothem samples, **quantitative environmental information** might be derived. Relying on long-term meteorological data and cave monitoring observations, BOCH et al. (2009) calculated relative air temperature decreases of $\sim -3^\circ\text{C}$ for an abrupt decadal-scale climate event at 8.2 kyr BP, and slightly less cooling for another prominent event at 9.1 kyr BP. These temperature variation determinations are again based on O isotope fractionation, i.e. the positively correlated O isotopic composition of meteoric precipitation with air temperature, as well as O isotope equilibrium fractionation between drip water and speleothem calcite. While the quantitative paleoclimate reconstructions of temperature and meteoric precipitation are the aim of some speleothem studies (e.g. LACHNIET, 2009), overall these studies are relatively scarce.

Broadly, the qualitative interpretation of high-resolution speleothem O isotope profiles are used in combination with precisely dated U-Th data in order to improve our process understanding of principal and often global climate relationships, such as the influence of the North Atlantic realm on Asian monsoon patterns (CHENG et al., 2016). In particular, the speleothem (mostly stalagmite) isotope sig-

nals and chronologies can be used to **improve the chronology and timing** of proxy signals from other climate archives, e.g. ice cores or marine sediment cores (BARKER et al., 2011; LISIECKI & STERN, 2016). For example, BOCH et al. (2011b) published a stable O isotope record of the Last Glacial period covering the time interval from 120 to 60 kyr BP at a temporal resolution of 2 to 22 years and typical U-Th based age uncertainties (2σ) of 200 to 500 years. **The NALPS record** is a composite isotope record from several geochemically selected stalagmites from different caves located at the northern rim of the Alps. The record consist of a relatively long time interval at high temporal resolution, and reveals pronounced and detailed paleoclimate variations including the prominent Last Glacial **Dansgaard-Oeschger (D-O) cycles**, as well as recurrent short-lived climate events (precursor-, rebound-, intermittent-type events). The latter climate anomalies were not reported outside Greenland (ice cores) before. D-O oscillations and probably also the minor climate anomalies are mostly explained by rapid (decadal-scale) **air temperature increases and decreases** in connection with the reorganization of major oceanic (e.g. thermo-haline circulation) and atmospheric (e.g. wind fields) variables in the North Atlantic region (JOHNSEN et al., 2001; WUNSCH, 2006). Considering the large amplitudes (up to 4.5 ‰) of the stable O isotope signals recorded in the NALPS curves, temperature control alone seems unlikely (BOCH et al., 2011b). Instead, these stalagmites capture an O isotopic composition strongly influenced by the **seasonal variation of meteoric precipitation** and infiltration next to air temperature. In the Alps, typical seasonal amplitudes in $\delta^{18}\text{O}$ of precipitation amount to $\sim 10\text{‰}$ between summer and winter (HAGER & FOELSCHKE, 2015), and the timing and amounts therefore strongly affect the overall seepage/drip water compositions. Changes in the timing and duration of seasonal temperature amplitudes, rainfall amounts, and snow cover are thus archived in the speleothems from the N-Alps. Moreover, the observed cycles and events clearly demonstrate regional versus global teleconnections, which can be utilized to compare and refine existing Greenland ice core chronologies by corresponding Greenland versus NALPS stable O isotope signals and the more precise and accurate speleothem U-Th chronology (RASMUSSEN et al., 2014; BARKER et al., 2015; LISIECKI & STERN, 2016). In particular, the absolute and relative timing, durations, temporal progress, and spatial amplitudes can be evaluated in many details. The principal teleconnections in the Earth's climate system can also be reflected in stable O isotope curves on much **longer timescales**, e.g. Quaternary glacial (ice age) and interglacial (warm epochs) cycles. Several drill cores were extracted from subaqueous calcite precipitated over hundred thousands of years in an extensional fracture of **Devils Hole** in Nevada, USA (MOSELEY et al., 2016). Stable O isotopic compositions measured from the drill cores of different length and depth in the fracture reflect the major warm-cold transitions of the last $\sim 200,000$ years. In addition, the well constrained U-Th time series strongly supports a tight connection of **ice age terminations** and variable **atmospheric CO_2** concentrations to **northern hemispheric summer insolation**, and thus, **orbital forcing** from the Earth's elliptical orbit (eccentricity), as well as tilt (obliquity), and unstable orientation (precession) of the axis of the Earth (BERGER & LOUÏRE, 2002; SARNTHEIN et al., 2009; MOSELEY et al., 2016).

Multi-proxy approach of climate parameters

Speleothems provide many ways of archiving variable environmental – and in particular climate – conditions **in the carbonate material** they consist of. The different ways and chemical-sedimentary mechanisms are reflected in distinct **proxy variables** representing major climate parameters, such as air temperature, the seasonal distribution and amounts of meteoric precipitation, as well as climate related changes of the vegetation above the cave. The availability of multiple proxy parameters enabling more diverse but also more concise constraints on past environmental conditions constitutes another strength of speleothems within the variety of paleoclimate archives. Regarding the reconstruction of climate parameters from the speleothem carbonate, the general but also cave site-specific **transfer mechanisms of the climate signals** to the speleothems depend on the coupling of the cave interior versus exterior environmental conditions. In this context, the translating mechanisms and their partial reactions provide different sensitivities underground with respect to climate changes at the surface, i.e. some proxy parameters might reflect seasonal or even daily changes while others capture a smoothed multi-annual trend (FAIRCHILD & BAKER, 2012). Consequently, the temporal resolution of the climate proxy parameter, as well as the spatial resolution and **sampling strategy applied** are critical ingredients in a speleothem based climate reconstruction. For example, proxy measurements applying modern imaging techniques, computer-controlled micromilling, and electron microprobe or laser ablation provide significantly higher resolution paleoclimate information compared to point-wise and handheld sampling tools (SPÖTL & MATTEY, 2006; BOCH, 2008). Also, some speleothem proxies are of **indicative** character regarding a specific environmental parameter reflected while others rely on more **complex** environmental controls and transfer relationships.

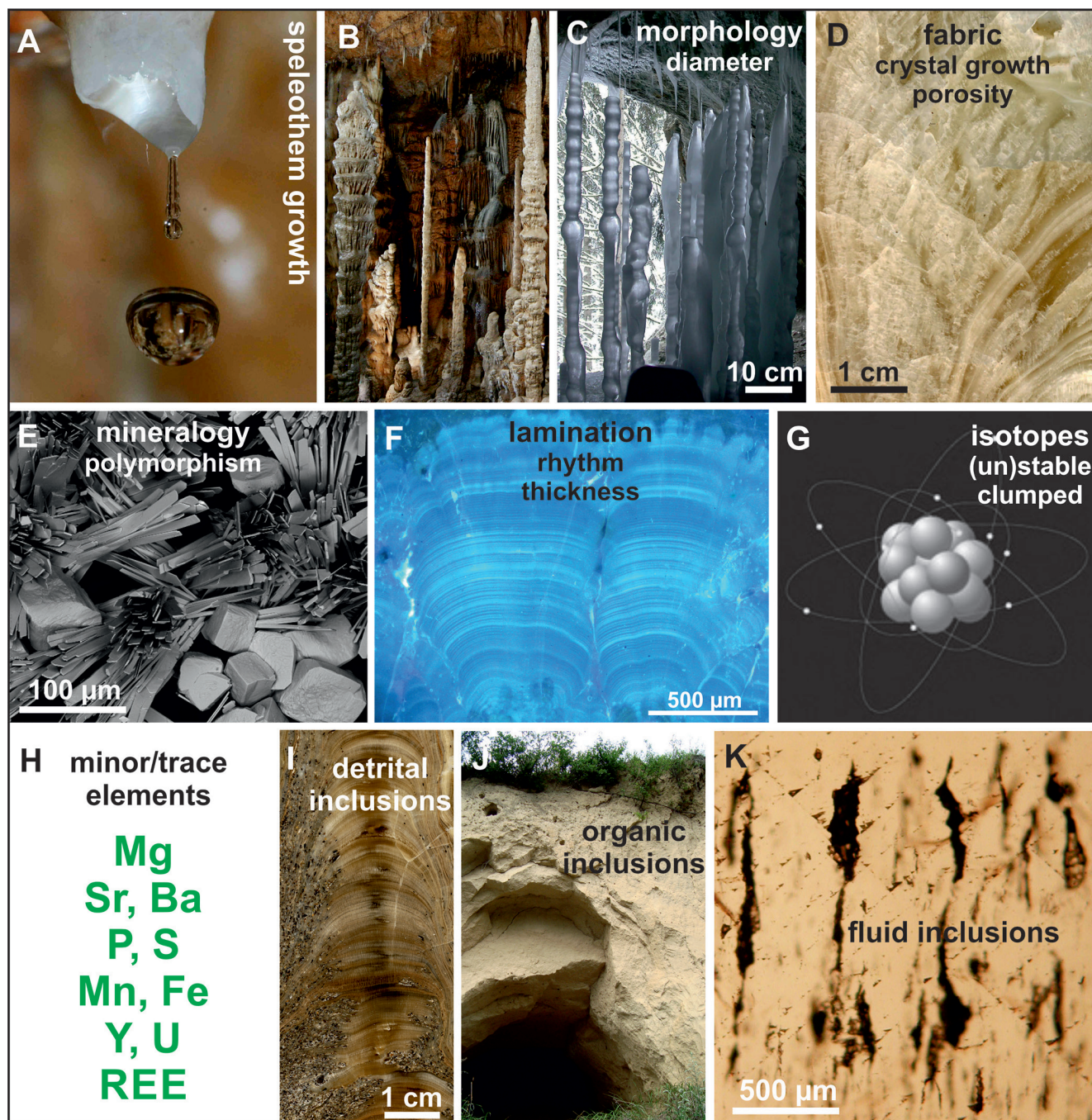
A principal climate proxy consists in the **occurrence or absence of speleothem growth** during a particular time (climate) interval or region (cave system). Radiometric age constraints and in particular the determination of the growth inception (e.g. stalagmite base), growth cessation (stalagmite top) and eventually growth interruptions (hiatus within stalagmite) of an individual or multiple speleothem samples therefore constitute indicative climate information concerning the **availability of (drip) water** (Text-Fig. 6A). The latter could be restricted by pronounced aridity (drought) conditions (VAKS et al., 2006) or temperatures below freezing (SPÖTL & MANGINI, 2007). Furthermore, a hydrochemistry favourable of speleothem deposition constitutes an essential requirement, i.e. soil and karst processes resulting in vadose waters of sufficient Ca-carbonate supersaturation. Alternatively, speleothem growth might be periodically restricted by excess water availability, e.g. flooding of cave chambers in the course of sea-level oscillations or storm events (DENNISTON & LUETSCHER, 2017). Distinct and variable speleothem growth intervals were used as a climate proxy in different regions hosting karst caves (FLEITMANN et al., 2007; BOCH et al., 2010). Another macroscopic climate proxy consists in the variable **morphology of speleothems** and in particular of stalagmites (Text-Figs. 6B, C). Changing **diameters** along the growth axis and the resulting **shapes** are mainly dependent on water discharge (drip rate), as well as the actual CO₂ gradients (outgassing, growth kinetics) and hy-

drochemistry (CaCO₃ supersaturation; BOCH et al., 2011a and references therein). For example, an increased vadose water supply from higher meteoric precipitation amounts can be manifested in overall broader stalagmites and the evolution of increasing diameters and conical shapes. In contrast, reduced drip rates and a hydrochemistry favourable of speleothem growth might result in slim carbonate formations, such as the widespread candle-stick type stalagmites (MARTÍN-CHIVELET et al., 2017). The vertical versus horizontal growth of stalagmites depending on the prevailing physicochemical conditions was also investigated based on conceptual models and mathematical approaches (MÜHLINGHAUS et al., 2007). Strongly variable atmospheric and cave climate conditions can further be reflected in a changing speleothem **mineralogy** (Text-Fig. 6E). Typical examples are variable proportions of the Ca-carbonate polymorphs calcite and aragonite in speleothems of different age or within individual samples (WASSENBURG et al., 2016), as well as the occurrence of Ca-sulphates such as gypsum (PLAN et al., 2012). The latter is frequently associated with hypogenic cave formation in the course of sulphide oxidation and sulphuric acid based carbonate dissolution, mobilization and subsequent Ca-carbonate and Ca-sulphate precipitation in characteristic hypogenic cave chambers (DUBLYANSKY, 2012). Apart from diagenetic transformations, mineralogical changes often reflect extreme environmental conditions, e.g. dryness promoting increased evaporation, mineral-specific supersaturation and increased prior CaCO₃ precipitation during vadose water flow (MCMILLAN et al., 2005). For example, BOCH et al. (2019) reported a principal control of variable aragonite versus calcite in flowstone-like precipitates of vertical fractures (veins) from variable water flow routes and a hydrochemical evolution involving irregular variations in the Mg/Ca ratio and Ca-carbonate supersaturation in the fissured carbonate aquifer. Often pronounced climate sensitivity is further ascribed to the **speleothem petrography** (Text-Figs. 6D, F). This includes spatiotemporal changes of the fabrics (oriented crystal growth, porosity) and various rhythmic (e.g. annual) or event lamination and zonation patterns along the speleothem growth axis (FRISIA, 2015; MARTÍN-CHIVELET et al., 2017). Importantly, changes in the speleothem growth rate are reflected in the variable fabrics and layer thicknesses depending on (un)favourable climate and speleothem growth conditions (BAKER et al., 2008; BOCH & SPÖTL, 2011). In other words, the seasonally and longer-term variable temperatures and meteoric precipitation amounts translate into drip water and ion supply and consequently into mass, volume (density depending on calcite fabric) and cave site-specific progress of speleothem build-up.

High-resolution climate information is further archived in the variable speleothem carbonate **minor and trace elemental compositions** (Text-Fig. 6H). Mg, Sr and Ba might be considered of particular relevance due to their common occurrence in calcite and/or aragonite and the elements P, S, Mn, Fe, Y, U and the rare earth elements (REE) were also investigated in some detail (FAIRCHILD & TREBLE, 2009; BOCH et al., 2011a; TREMAINE & FROELICH, 2013). The elemental concentrations reflect numerous underlying mechanisms of fluid-solid interaction including the aquifer host rock, seepage water infiltration and residence time, mixing and phase separation, as well as specific elemental fractionation mainly depending on temperature and speleo-

them growth rate. BORSATO et al. (2015) studied sulphate concentrations in drip water and speleothems as a proxy of volcanic eruptions, soil and aquifer processes, as well as anthropogenic atmospheric SO₂ emissions. Incorporation of selected elements was also investigated by cave-analogue experiments in the laboratory (DAY & HENDERSON, 2013). Environmental changes of variable complexity are also captured in distinct **isotope ratios** of O, C, S, Mg, Ca, Sr, U and several other (trace) elements (Text-Fig. 6G). The stable and unstable isotopes of typically rare versus more common nuclides reflect even subtle variations in the karst water cycle and related processes of speleothem

formation. Stable C and O isotope signals represent the most applied isotope proxies in speleothem carbonate and are mainly sensitive to temperature, meteoric precipitation composition, as well as dissolved vs. gaseous CO₂ dynamics (TREMAINE et al., 2011; DEMÉNY et al., 2017). In this context, **equilibrium and kinetic C and O isotope fractionation** processes have gained special attention (MICKLER et al., 2006; DREYBRODT & ROMANOV, 2016) and clumped isotope values (Δ_{47}) might be particularly sensitive proxies of these processes during speleothem growth (DAÉRON et al., 2011, 2019; AFFEK et al., 2014). Stable isotopic compositions of the common elements Ca and Mg are increasingly



Text-Fig. 6. Variable environmental (climate) conditions can be reconstructed from multiple proxies archived in speleothems including the occurrence or absence of speleothem growth (A, B), the growth morphologies (shapes) of stalagmites (B, C), speleothem petrography and mineralogy (D, E), rhythmic or event layering (F), various Ca-carbonate (un)stable isotopic (G) and minor/trace elemental compositions (H), as well as detrital (siliciclastic; I), organic (acids or pollen; J) and fluid (water/air, K) inclusions.

studied in speleothems and are mostly related to variable carbonate precipitation rates and aridity (IMMENHAUSER et al., 2010; OWEN et al., 2016). Unstable Pb and U isotope systematics were repeatedly discussed as a hydrological proxy of water recharge vs. discharge and thus past meteoric precipitation (ZHOU et al., 2005; YANG et al., 2015).

A climate proxy of indicative character consists in various forms of **inclusions** eventually being incorporated in the speleothem carbonate (Text-Figs. 6I–K). **Detrital inclusions** such as sand grains or clay minerals of variable chemistry might be transported to the speleothem surface in the course of major discharge (flushing) from the soil zone and karst aquifer or alternatively from unconsolidated sediment mobilization during major water level rises, i.e. phreatic flooding of otherwise vadose cave sections (Text-Fig. 6I). In this regard, detrital layers are typically a proxy of extreme meteorological events, such as periodical flood waters (SPÖTL et al., 2011; DENNISTON & LUETSCHER, 2017). **Organic inclusions** of highly variable size typically reflect the vegetation cover in the cave area (above the cave; Text-Fig. 6J). In few cases, strongly indicative pollen might be captured in the speleothem carbonate (MEYER et al., 2009). More commonly, allochthonous organic compounds from progressive degradation processes in the soil zone, as well as autochthonous organic matter from microbial communities in the aquifer and cave constitute variable organic contributions (BLYTH et al., 2016). Many of these organic inclusions show fluorescence in UV-microscopy (BOCH & SPÖTL, 2011). Finally, **fluid inclusions** comprising of variable amounts of drip water and cave air reflect the prevailing environmental conditions in a rather direct fashion (Text-Fig. 6K). More specifically, the stable H and O isotopic compositions of the water inclusions represent an attractive proxy of the seepage- and meteoric water source and evolution (DUBLYANSKY & SPÖTL, 2009). Their measurement, however, is highly challenging due to the small sample amounts and potential alteration effects (DEMÉNY et al., 2016b). For example, JOHNSTON et al. (2018) conducted fluid inclusion stable H and O isotope analyses of stalagmite and flowstone samples in comparison with the respective calcite O isotope values and known equilibrium fractionation factors in order to calculate the climate dependent past speleothem formation temperatures.

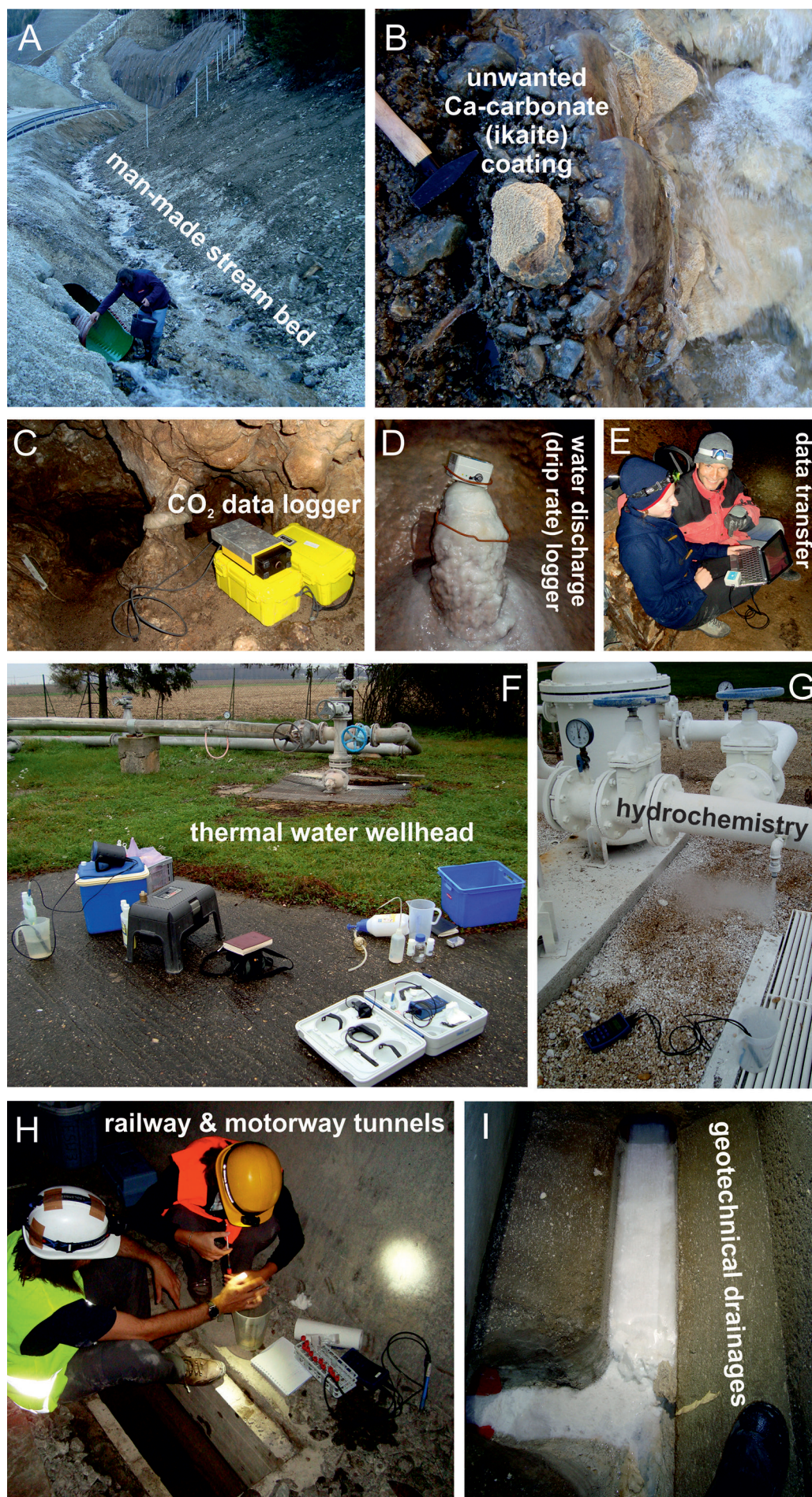
The actual benefit of a multi-proxy approach from speleothems in comparison to other climate archives strongly relies on the scientific development of an **in-depth process understanding** of the different **proxy dependencies** in relation to often highly variable environmental conditions on different spatial and temporal scales. An increased understanding of elemental and isotopic fractionation processes during phase transitions in the atmosphere, soil zone and karst aquifer, as well as during speleothem crystal growth and potential diagenetic alteration might be of particular relevance (WASSENBURG et al., 2016). The critical question of qualitative versus quantitative climate reconstruction from the proxies also gains in importance, in particular with regard to numerical (computer) models processing and delivering numbers of past and future climate change (NOAA, 2018). Considering that most speleothem based paleoclimate records provide **qualitative** environmental information in principal (warmer/colder, wetter/drier), a replication of the proxy variability in multiple speleothem samples from a particular location (cave) or even different places in

a region should be envisaged. Thus, temporally well constrained coeval and composite speleothem stable isotope and elemental records can be of reliable value regarding pronounced climate variations, e.g. the prominent 8.2 kyr cooling event (BOCH et al., 2009; MISCHEL et al., 2016). Regarding the target of more **quantitative** speleothem based climate reconstructions, O isotopes in the carbonate and in fluid inclusions are promising proxies, e.g. for calculating absolute calcite formation temperatures and temperature changes (JOHNSTON et al., 2018). Clumped isotopic compositions should also be mentioned in this context of absolute temperature constraints (MECKLER et al., 2015). Major efforts, however, have to be pursued in order to establish more reliable **proxy calibrations and site-specific transfer functions** of the external climate parameters to the speleothem proxy parameters, i.e. numerical relationships of the prevailing temperature (in °C) and meteoric precipitation amounts (in mm) being captured in the respective values of the proxy parameters. In this respect, an increasing number of speleothem paleoclimate studies provide selected and calibrated proxy records of (semi) quantitative information. OWEN et al. (2016), for example, utilized **stable Ca isotope fractionation** measured in the host rock, drip water and calcite on artificial substrates, as well as in stalagmites from Heshang Cave, China. Based on relatively simple calibration functions and an aquifer model, they inferred a dominant control of the $^{44}\text{Ca}/^{42}\text{Ca}$ isotope ratios by variable prior calcite precipitation and directly related Ca removal. During the 8.2 kyr cooling event archived in a stalagmite sample, increased prior calcite precipitation and Ca removal were determined to reflect a mean annual **rainfall decrease** of ca. 30 %, i.e. a drop to **~700 mm/yr** for ~80 years duration. In Postojna Cave (Slovenia), a high-resolution stable O isotope record of a young stalagmite measured by ion microprobe was calibrated against the O isotope composition of regional meteoric precipitation (DOMÍNGUEZ-VILLAR et al., 2018). The calibrated stalagmite proxy $\delta^{18}\text{O}$ record allowed to **reproduce the variable $\delta^{18}\text{O}$ signature of cave drip waters** collected and further to reconstruct the regional inter-annual precipitation variability filtered by the aquifer. In addition, the proxy calibration revealed average karst aquifer **water residence times of ~11 months** and growth of the analysed stalagmite interval in the years 1984 to 2003. Importantly, these more or less quantitative environmental reconstructions from caves and speleothems are mostly based on multi-annual **cave monitoring** programs of different extent and resolution in combination with various **instrumental meteorological data**.

Environmental Monitoring

In principle, all kinds of environments can be the subject of some physical, chemical or biological monitoring activities applying appropriate analytical techniques in order to understand specific environmental relationships and their implications. Thus, environmental monitoring is also conducted in the attempt of an **increased process understanding** of widespread **carbonate formation and alteration** depending on strongly variable environmental conditions. The variations occur within a broad spatial and temporal range and consequently the monitoring approaches

and associated analytical techniques differ significantly. Amongst the great variety of natural and human-made environmental settings to be monitored, the **human to regional scale** systems represent typical subjects of environmental monitoring. Examples are monitoring efforts of various natural and geotechnical springs and streams, cave systems, geothermal and hydrocarbon production wells and deep aquifers or drainages of different implementation in railway and motorway tunnels (Text-Fig. 7). Depending on the particular setting and the **natural site- or installation-specific** characteristics, geologically and anthropogenically influenced (e.g. operational) environmental conditions determine the relevance and magnitude of related processes on different spatiotemporal scales in a system, e.g. effects from global warming, industrial pollution, water recharge and discharge, variable (water, energy) production or mineral formation conditions. In essence, environmental monitoring approaches target an evaluation and more or less detailed



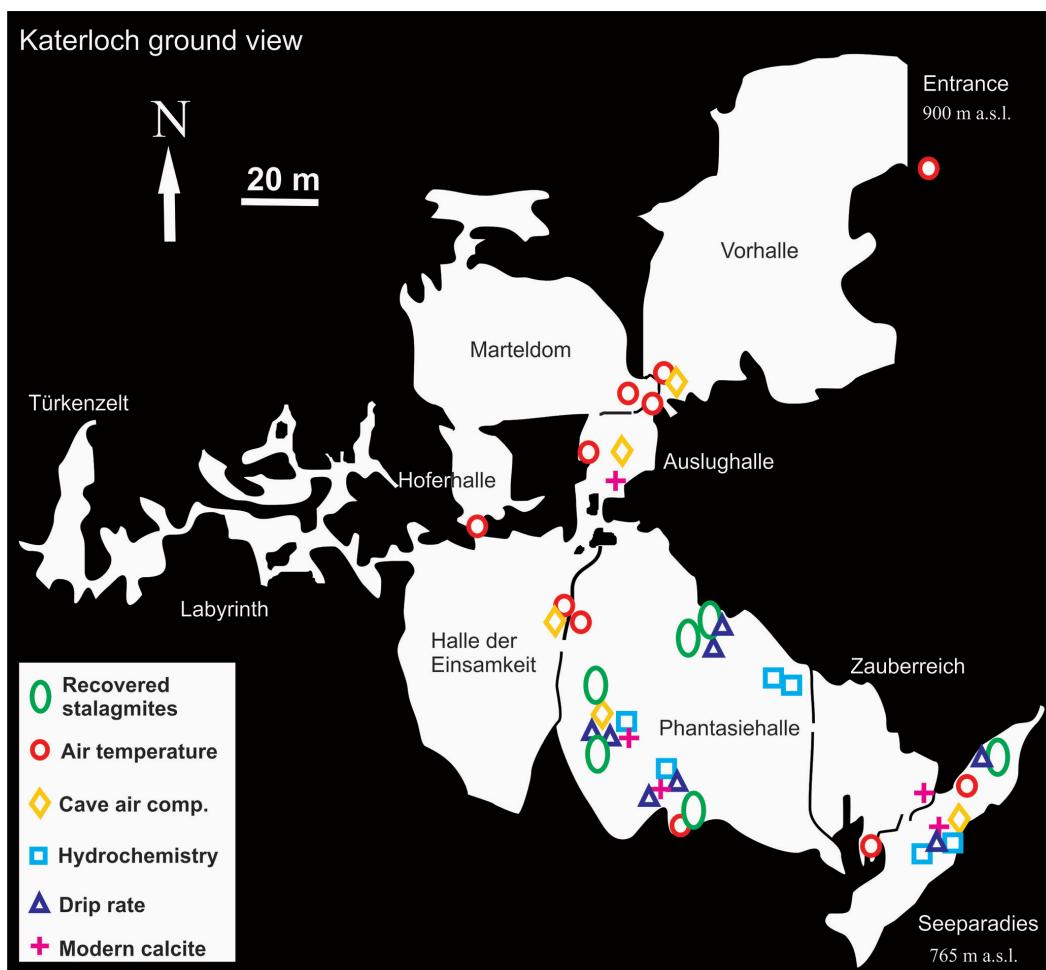
Text-Fig. 7. Impressions from natural and geotechnical settings of environmental monitoring. A, B) Regular monthly monitoring and process understanding of unwanted Ca-carbonate precipitation and associated hydrochemical alteration in a human-made stream bed. C, D, E) Multi-annual bi-monthly (cave visits) and continuous (data loggers) cave monitoring including cave air, seepage waters and solid precipitates (speleothems) in different cave chambers. F, G) Observation of fluid-solid interaction targeting scaling and corrosion processes impairing deep wells for geothermal energy production. H, I) Monitoring of site-specific mineral precipitates clogging drainages in different tunnels.

classification of the dominant relationships. More specifically, the environmental monitoring programs on macroscopic (living) scale can be distinguished from the typically **laboratory based** monitoring of specific processes in **confined environments**, e.g. monitoring of experimental conditions of fluid-solid interaction on a microscopic scale. The in-situ Raman spectroscopic monitoring of Ca-carbonate transformation reactions in the context of natural biomineralization or industrial material development could be mentioned here (PURGSTALLER et al., 2016). In all of these cases, the **monitoring strategies** applied depend on multiple factors and basic vs. comprehensive, partial vs. holistic approaches might be considered. However, environmental monitoring always involves expert knowledge and various physical-chemical-biological analytical techniques are a key element in order to investigate the complex relationships of natural and/or technical parameters (Text-Fig. 7). In this respect, the broad field of environmental monitoring is clearly an **analytical technology driven undertaking** within the geosciences and other disciplines. This comprises methods and tools applied in the field, in the laboratory and eventually also in computer simulations. In view of the rapid technological development in that area, the state-of-the-art is difficult to define and a combination of established and very new monitoring tools and approaches characterizes environmental monitoring studies providing new insights, e.g. regarding meteorological/climate parameter vs. proxy relationships in the course of Ca-carbonate precipitation dynamics. Also, monitoring of particular parameters and processes is always based

on **data acquisition of limited spatial and temporal extension**, e.g. more or less continuous in selected sections within a few hours or years. The interpolation and/or extrapolation of numerical relationships is common practice during the envisaged environmental interpretation and implications inferred. Accordingly, this raises the question on the reliability and detail of the process understanding gained in the course of a monitoring approach. Nevertheless, next to experimental and modelling approaches environmental monitoring constitutes a serious attempt of a more comprehensive and in-depth knowledge on carbonate formation and its various dependencies. Only considering the recent geoscientific literature on this topic would easily exceed the intention of this chapter and the settings discussed in this publication.

Periodical sampling and data loggers

Monitoring of environmental processes in specific settings and over time is intrinsically tied to the spatial and temporal **resolution of the measurements** performed during a monitoring campaign. The analyses of environmental parameters (e.g. temperature, water discharge, mass concentration) can be done in regular or irregular time intervals at one or multiple sampling points of the system observed (e.g. cave; Text-Fig. 8). In most cases, punctual one-time or repeated measurements result in datasets of different spatiotemporal extent and their significance with regard to specific process understanding strongly depends on the spatial and temporal extension of the environmental processes of interest. Consequently, the selective distribution



Text-Fig. 8. Location of cave air, seepage water and Ca-carbonate sampling sites in Katerloch Cave, Styria. The selected positions and technical infrastructure (data loggers) constitute an ongoing multi-annual (since 2005) and partially high temporal resolution (hourly) cave monitoring program in order to investigate the variable cave climate and speleothem growth dynamics in relation to meteorological/climate changes.

and density (spacing) of the sampling sites (e.g. in different cave sections; Text-Fig. 8) and the frequency of the sampling intervals (e.g. seconds to annual) has to be arranged in compliance with the carbonate precipitation dynamics and associated fluid-chemical reactions of interest independent of monitoring natural or human-made (e.g. geotechnical) environmental settings. More importantly, the **timing, duration, progress** and therefore shifts and delays of the relevant environmental variables determining carbonate formation should be captured by the monitoring efforts. For example, an investigation of the prevailing weather conditions (e.g. low air pressure fields and storms) in relation to a karst aquifer and cave system and its short-term effects on speleothem growth should be based on a relatively high temporal (and spatial) resolution monitoring approach, i.e. daily, hourly or less (CELLE-JEANTON et al., 2001; BALDINI et al., 2008). Likewise, the evolution of longer-term environmental trends (e.g. global warming) affecting a particular system of fluid-solid interaction might not necessarily require a high-resolution monitoring approach, i.e. resolving seasonal or inter-annual differences is sufficient. The latter could be the case for monitoring water recharge and discharge of aquifers in sedimentary basins or crystalline rock formations (STRAUHAL et al., 2016; MECHAL et al., 2017). Karst aquifers, in contrast, are typically highly dynamic and responsive with regard to changing atmospheric and meteoric precipitation conditions and a higher resolution monitoring might therefore be necessary inherently (OZYURT et al., 2014). The monitoring should further be adapted in the light of more **cyclic** (e.g. seasons, snow-melt) versus **event-like** (e.g. storms, flooding, drought) recurrent variations, i.e. the nature and expression of the environmental trigger motivates irregular or regular observation intervals and the overall resolution recommended. However, the distinction of causes versus effects controlling various Ca-carbonate precipitation mechanisms and occurring either in strictly periodical cycles or irregular (e.g. stochastic) events is obviously a floating transition. In essence, the spatiotemporal strategy has to be well balanced with regard to the environmental processes targeted. A coarse resolution monitoring program runs the risk of an oversimplification or even misguided process understanding. A very high resolution monitoring approach can suffer from an unfavourable signal to noise detection of environmental information, i.e. the relevant processes of a particular research question could be masked in the overwhelming data acquisition. Apart from the critical specialist area constraints, the extension – resolution and duration – of an environmental monitoring program in the course of scientific and applied (e.g. consulting) activities is often restricted by the available time, costs, human resources and overall conditions at the setting (e.g. danger, construction progress; BOCH et al., 2015).

Regarding environmental **data acquisition** widespread **punctual sampling** at selected spots of a specific setting (e.g. stream, tunnel, cave, well; Text-Fig. 7) during visits of the site typically requires the field based deployment of specific and mostly handheld analytical instruments in combination with different sampling procedures and preparation techniques for later laboratory based measurements. This comprises analyses of aqueous solutions such as various types of fresh and contaminated waters or brines, gases of variable partial pressure in a confined soil air, cave, well, pipeline or the free atmosphere

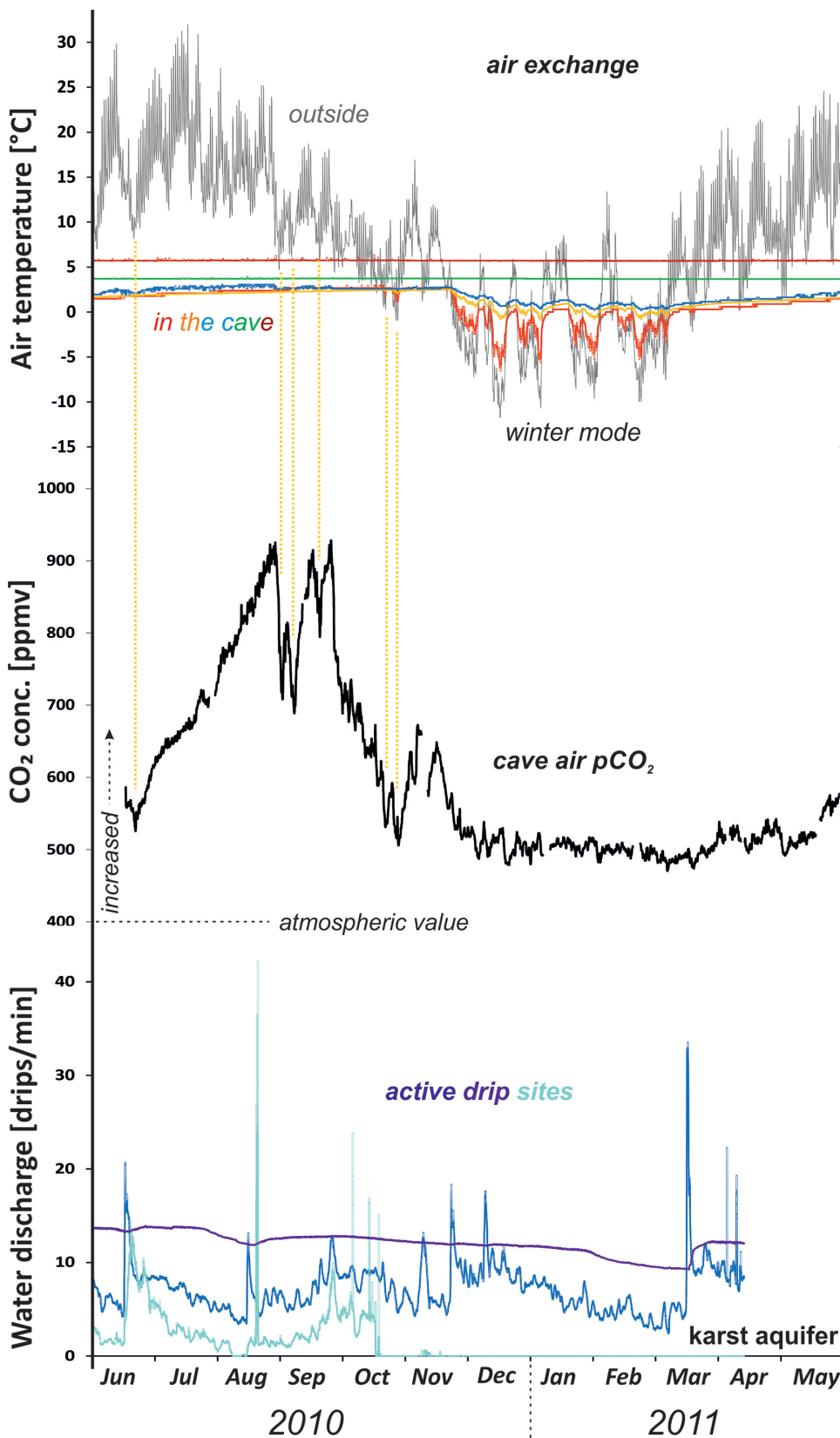
volume, as well as solid phases forming under very different conditions at distinct rates and being accessible to punctual sampling. The latter includes a multitude of minerals in the context of natural chemical-sedimentary archives (e.g. Ca-carbonate and accessory minerals in speleothems, travertine, lake and marine sediments, veins), unwanted scale deposits in technical settings (e.g. geothermal and oil producing wells and pipelines, tunnel and processing water drainages, drinking water treatment) or corrosion products of various steel components in industrial or geotechnical applications. Common electronic instrumentation for hydrochemical analysis in the field includes pH-, electric conductivity-, redox- and oximeters and might be combined with a broad range of physical environmental analyses (e.g. thermometer, flow meter, distance meter, anemometer). For all of these instruments, the achievable analytical accuracy, precision, and resolution of the measurements have to be considered and careful calibration in method-specific intervals constitutes an integral part of professional data acquisition. An **adequate sampling procedure** further involves flexibilities and constraints regarding sample amounts and sample preparation. In some settings, the available sample volumes are strongly restricted, e.g. slow drip water supply in a cave or little mineral precipitate collected on an artificial substrate. The sample amount often determines the possible utilization of laboratory analytical techniques, as well as possible replicate measurements and consequently the reliability of the results and process understanding inferred. A wide range of sample vessels – bottles of various materials for liquids or different bags for gases – are used and play a critical role with regard to sample transport, practical storage life and alteration. Potential sample alteration concerns partial mineral precipitation from altered saturation states due to temperature changes or outgassing, as well as element specific leaching or adsorption effects related to the storage medium. Sample preparation further includes filtering (e.g. using 0.45 µm mesh size cellulose acetate filters), aqueous solution acidification for conservation (e.g. adding nitric acid for ICP-OES based elemental analysis) or permanent cooling during sample transport (cf. BOCH et al., 2015). The various avenues of chemical or biological sample contamination should also be considered and avoided. An immediate sample analysis after sampling (e.g. same day) is recommended whenever feasible.

Environmental data acquisition at different spatial and temporal resolution can also be executed by various types of **automated data loggers**. These mostly electronic instruments typically consist of one or more specific sensors connected to a data processing and data storage unit and some power supply. The **sensor** might be based on an electrochemical reaction, such as a pair of electrodes wired to a voltmeter, e.g. measuring electric conductivity, pH or redox potential. Sensors can also be based on optical (e.g. measuring gas concentrations) or acoustic (e.g. drip counting) signals. **Data processing** strongly relies on the particular environmental parameter monitored and data loggers of different complexity range from established and commercially available to scientific prototypes. Considering **data storage** units, such as memory cards the rapid development and miniaturization in recent years is clearly tied to the ongoing evolution in the computer electronic realm, e.g. increased data storage capac-

ities with concurrently decreased storage medium size. Likewise, the **power supply** requirements strongly benefit from recent developments, such as partially decreased energy consumption of more efficient sensors, the rapid evolution of various kinds of (Li-)batteries, and the general public interest in mobile electronics, i.e. independent of a wired power supply. Many data loggers, however, are still in need of a higher voltage energy source and their flexibility might therefore be restricted, e.g. mobile instruments measuring stable isotopic compositions. The **data transfer** from the logger data storage unit is achieved in different ways including shuttle components typically provided with the data logger, USB and memory card based transfers or plug-in connections for laptops and smartphones. Modern developments further comprise the **wireless** and mostly **online** data transfer from local monitoring stations to the user via telecommunication networks, e.g. meteorological stations or hydrochemical and scaling monitoring in geotechnical settings. As for conventional punctual and mostly manual environmental measurements – for example using handheld analytical instruments – the spatial distribution and spacing, as well as temporal resolution of the data logging is of crucial importance and strongly depends on the technical specification and adaptable measurement protocols of the monitoring instrument. Many data loggers stay online and a more or less continuous monitoring of one or more dedicated environmental variables is possible, resulting in numerical environmental records of narrow time intervals (e.g. minute-range datasets).

Continuous monitoring and data storage in distinct short-term intervals are logging tasks implemented in a growing number of **air- and water-temperature loggers** applied in a broad range of different settings including water streams and stagnant bodies, caves, tunnels, deep wells and industrial environments. State-of-the-art temperature loggers cover an attractive range of negative to high temperatures allowing for a multi-annual autonomous registration of higher amplitude temperature changes, while also providing high accuracy and precision of the measurements. Some of these loggers provide a high sensitivity and temperature resolution for capturing even subtle variations (e.g. 0.02°C ; Onset HOBO Water Temp Pro v2 data logger used by BOCH et al., 2011a). Text-Figure 9 (upper diagram) shows atmospheric (outside) versus cave interior air temperature variation at a high temporal resolution (two-hour intervals) for a one year monitoring period. The temperature logging revealed distinct warm versus cold seasonal modes of cave air exchange (ventilation), as well as changes from daily fluctuation and the prevailing weather conditions. Moreover, the air temperatures increase with depth underground and distance from the cave entrance and the deepest chambers show stable temperatures, although small seasonal amplitudes ($\sim 0.1^{\circ}\text{C}$) can still be resolved owing to this monitoring approach. In comparison to, e.g. monthly or even weekly measurements, such data clearly promote a more detailed understanding of environmental relationships (exterior/interior climate) and processes (speleothem growth). Recent developments in autonomous and continuous data logging further comprise of different **gas analysers**, e.g. for CO_2 and CH_4 concentrations. These loggers differ significantly in terms of their measurement range, resolution, accuracy and applicability to demanding natural environments, but most are based on nondispersive infrared absorption of the gases analysed

(e.g. instruments of the LI-COR company). LUETSCHER & ZIEGLER (2012) developed a logger (CORA) for longer-term monitoring of variable **CO_2 concentration, air pressure** and temperature even in cold and humid environments (e.g. caves). The hand-sized logger (Text-Fig. 7C) is powered by an internal and additional external battery pack and air CO_2 contents up to 2 vol.% can be measured at high temporal resolution (e.g. every 10 min) with relatively high accuracy ($\pm 3\%$). Depending on the selected measurement interval, the mobile power supply lasts for a few months up to several years. CO_2 measurements in four-hour intervals conducted in a major chamber of Katerloch Cave (Austria) over a year (Text-Fig. 9, middle diagram) revealed significantly increased cave air CO_2 concentrations compared to average atmospheric values. The contents further display pronounced seasonal, as well as small daily fluctuations and are commonly related to larger outside vs. inside air temperature changes and eventually to some transient impact from small sized groups of cave visitors (exhaling CO_2). Importantly, the variable CO_2 fluxes are a sensitive record of the variable cave ventilation mainly depending on the prevailing meteorological conditions and further affecting physicochemical processes of fluid-solid interaction in this cave (BOCH et al., 2011a). Considering overall **water discharge monitoring**, several techniques including mechanical measurements (e.g. propeller), radar, ultrasound, tipping buckets and acoustic detection are available and their application often depends on the dimension and expected variability of water discharge. Vadose seepage (drip) water supply, for example, can be measured by acoustic counting, e.g. STALAGMATE data logger (COLLISTER & MATTEY, 2008; Text-Figs. 7D, E). The latter small sized ($\sim 5 \times 5 \text{ cm}$, 300 g), Li-battery powered and thus autonomous monitoring instrument is based on the registration of falling water drops by a sealed microphone and ongoing (multi-annual) counting and periodical data storage (e.g. logging intervals of hours to seconds). These highly sensitive monitoring tools provide information on variable **drip rates** (e.g. in caves, tunnels, buildings) in relation to the prevailing (meteoric) environmental conditions. Text-Figure 9 (lower diagram) shows about one year of continuous and high temporal resolution (30 min intervals) monitoring of drip water supply at three different sites in Katerloch Cave. The selected drip sites revealed many similarities regarding their response to meteoric precipitation (recharge) conditions, i.e. contemporaneous rapid increases and more gradual decreases. Regarding their absolute rates and degree of variability, however, the sites react differently and represent markedly different flow regimes in the overlying karst aquifer. The site-specific water discharge thus depends on inter-annual, seasonal (e.g. snowmelt in spring) to daily (e.g. storm events) meteoric and karst aquifer saturation conditions. Next to gaseous and liquid phases, solid materials such as mineral precipitates can be monitored continuously by placing **artificial substrates** in the fluid flow. For example, active speleothem growth can be studied by mounting convex or plain, smooth or roughened **glass** substrates on the top of different stalagmites and drip sites distributed in a cave (BOCH, 2008; TREMAINE et al., 2011). These glass slides are then recovered regularly (e.g. bimonthly) or after some definite time interval (e.g. eight years in Katerloch Cave). The collected Ca-carbonate can be analysed at high spatiotemporal resolution across the growth axis similar to a stalag-



Text-Fig. 9. Example of environmental monitoring in a cave system (Katerloch, Styria) at high temporal resolution over one year duration using data loggers. Exterior and cave interior air temperature (2 h intervals), CO₂ partial pressure (4 h) and water discharge (sum of drips every 30 min) show pronounced daily to seasonal variations. A cold season mode of enhanced cave air exchange (ventilation) can be distinguished from a warm season mode with higher pCO₂ and little temperature fluctuation. Cave air compositions are affected by major atmospheric (outside) temperature changes (yellow lines). Deeper cave sections show higher and stable temperatures although the small seasonal amplitudes can still be resolved (~0.1 °C). Rapid increases in seepage water discharge are observed after several days of rainy weather and during snowmelt in spring. The drip sites reflect different karst aquifer flow regimes of variable sensitivity to meteoric precipitation and karst aquifer recharge.

mite. Additional environmental information from punctual or continuous monitoring of the drip water and cave air in combination with meteorological data is of high value. Alternatively, round glass substrates can be mounted at the upper end of boreholes drilled from an actively growing flowstone or travertine deposit or short drill cores capturing modern precipitation conditions might be extracted after some time of site-specific monitoring (BOCH & SPÖTL, 2011). Comparable approaches might also be conducted in more applied settings of monitoring mineral precipitation, e.g. various geotechnical drainages, wells and pipelines. Likewise, corrosion and material alteration processes are monitored by placing **coupons** of different material (carbon steel, alloys, plastics) in the fluid flow and their mass loss and later visual inspection can help in the understanding of critical fluid-solid interaction (NOGARA & ZARROUK, 2014).

New developments of on-site and online environmental data logging comprise the measurement of different **stable isotopes** of common gases and aqueous solutions. This includes the analysis of stable C isotope ratios and gas concentrations of carbon dioxide and methane, stable H and O ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$) in water and vapour, and stable N ($\delta^{15}\text{N}$) isotopic compositions and gas concentrations of nitrous oxide in the atmosphere (MAHER et al., 2014; ERLER et al., 2015). These traditional isotope systems provide valuable insights regarding sources and transfer processes of the major water, carbon and nitrogen cycles. Companies such as Thermo Scientific and Picarro develop instruments that are based on mid-infrared absorption of the respective gas phases, i.e. **isotope ratio infrared spectrometry** (IRIS; Thermo Scientific) or **laser-light interactive cavity ring-down spectroscopy** (CRDS; Picarro). Importantly, these techniques are

increasingly sensitive to different stable isotope compositions of the fluids analysed and enable an online (real-time) and local monitoring of the isotope signals. This implies significantly reduced size and weight compared to conventional isotope ratio mass spectrometers and consequently a portable and robust construction scheme with regard to an anticipated application in the field. Also, some of these instruments facilitate multiple input channels in order to monitor isotopic compositions from several sampling sites in a natural or geotechnical environmental setting simultaneously. Most instruments further provide a possible connection to laboratory or field based peripheral instruments for measuring isotope ratios of, e.g. dissolved inorganic and organic carbon or carbonate minerals. Typical applications in the modern environmental realm include the high-resolution analysis of variable **greenhouse gas fluxes**, e.g. spatial and temporal variations of CO₂ and CH₄ concentrations and the respective stable C isotopic compositions emitted from natural gas production wells to the atmosphere (MAHER et al., 2014). Online and on-site stable C and O isotope and gas concentration monitoring of ambient air CO₂ was conducted in cave systems in order to trace transient environmental conditions and associated processes at minute-range temporal resolution over a whole year (TÖCHTERLE et al., 2017).

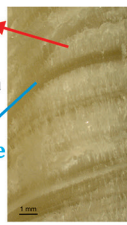
Monitoring carbonate precipitation dynamics

Extended and detailed environmental observation of various natural and human-made settings hosting **modern carbonate formation** promotes an understanding of the dominant processes and parameters and implications of major environmental or material related relevance might be inferred from such monitoring efforts. The approaches of clarifying environmental controls on mineral precipitation are highly site-specific. However, increasing scientific and practical knowledge on the (un)favourable (pre)conditions of (un)wanted precipitation of minerals, as well as the associated evolution of fluids, result in an advanced process understanding of the **precipitation mechanisms** and potential **controlling measures**. The latter includes natural and technical possibilities of environmental parameter variation. For example, an environmental monitoring campaign conducted recently targeted the process understanding of unwanted, rapidly precipitated and several centimeter thick **mineral deposits in a human-made concrete river bed** (~1.5 km length) bypassing a repository of excavation materials from a major infrastructure project in Austria (BOCH et al., 2015). The periodical on-site sampling and measurements in combination with laboratory and modelling based data enabled to constrain the prominent but rare precipitation of ikaite (CaCO₃·6H₂O) crusts in the upper and middle stream sections and more compact but thinner calcite crusts covering the refilled river sediments (colluvium) of the lower stream. Also, the highly anomalous hydrochemical conditions and evolution were evaluated in space (along the stream and tributary inlets) and time (over a year). The hydrochemical analyses revealed pH values up to 12.9 (instead of natural 7.5–8.5), calcium concentrations up to 200 mg/l (instead of 10–20 mg/l) and calcite supersaturation (SI values) up to 2.5 in the otherwise low ionic strength waters at this location (metamorphic host rocks). Ikaite could only be measured in the laboratory (by XRD, FT-IR and ESEM) after solid sample recovery from the river bed in its ambient

aqueous solution, transport in refrigerated boxes and careful handling during analysis. The first ikaite samples recovered in plastic bags disintegrated into a loose powder consisting of microscopic calcite crystals within hours to few days. Mainly based on distinct relationships of hydrochemical parameters monitored, e.g. pH, electric conductivity, CO₂ partial pressure and concentrations of dissolved ions, the environmental conditions favourable of ikaite nucleation and rapid crystal growth could be constrained. In essence, enhanced portlandite (Ca[OH]₂) dissolution from the human-made concrete river bed resulted in a strong increase of Ca concentrations and pH and concomitantly decreased aqueous solution pCO₂. This in turn facilitated an efficient Ca-carbonate precipitation mechanism relying on the continuous absorption of CO₂ from the atmosphere and persistently increased dissolved inorganic carbon and Ca-carbonate (ikaite) supersaturation (RINDER et al., 2013; BOCH et al., 2015). The **concrete leaching** and associated anomalous water chemistry were promoted by a restricted compaction and hardening of the river concrete basement in the course of cold (winter) water temperatures and time pressure, i.e. a higher porosity than usual, slower reaction kinetics during cement hydration and carbonation, as well as increased reactive surfaces and water access in the concrete. Owing to the efficiency of the determining Ca-carbonate precipitation mechanism and the sizes of the principal chemical reservoirs involved (concrete bed, atmosphere, streaming water), up to 2 kg/m²/d of ikaite deposition were calculated for the early stage of the aqueous solution monitoring. Importantly, the spatiotemporal monitoring in this **“field-based laboratory”** allowed for a better understanding of ikaite versus calcite formation. The few preconditions favouring ikaite include the prevailing cold water temperatures and prominently high Ca-carbonate supersaturation due to high pH, Ca contents and carbonate alkalinity supplied from large reservoirs. A major influence of calcite nucleation inhibitors (e.g. phosphate, organic constituents), strongly elevated ionic strength (saline conditions) or water mixing discussed in the scientific literature (e.g. HU et al., 2015) could not be confirmed. However, based on the observed spatial and temporal relationships of ikaite and calcite also expressed in the different river sections, the **occurrence of metastable ikaite** could be restricted to temperatures ≤ 6° C, highly alkaline pH > 11, elevated Ca concentrations > 30 mg/l and Ca-carbonate saturation states clearly exceeding the solubility of ikaite. Regarding the temporal evolution of the ikaite precipitates, the monthly monitoring campaign showed a rapid vanishing of the ikaite crusts during a pronounced temperature rise > 6° C in springtime, i.e. most likely thermal decomposition and mobilization of metastable ikaite in the turbulent water flow occurred. In contrast, some hydrochemical parameters showed a more gradual change (e.g. decreasing pH and elemental concentrations) indicative of diminishing concrete leaching. In this respect, the monitoring also allowed some forecasting with regard to the return to geogenic hydrochemical conditions after a limited time of anthropogenic (construction related) impact. It should also be noted, that anomalously altered water chemistries hold the potential of leaching critical constituents (e.g. heavy metals) and thus of an environmental hazard, which was also evaluated in this particular case study.

Environmental monitoring further comprises **cave monitoring of speleothem growth dynamics** in order to utilize these mineral precipitates as paleoclimate archives (MATTEY et al., 2008; BOCH et al., 2011a; RIECHELMANN et al., 2013). These monitoring approaches of a natural system are of diverse complexity with regard to their spatial and temporal extent in the particular cave system and also regarding the application of automated in-situ instrumentation in combination with periodical cave visits. The majority of the case studies target a site-specific and detailed understanding of short- and long-term fluid-solid interaction determining the growth and composition of the speleothems. Consequently, aqueous solutions, gases and solid phases are typically monitored as well as the inter-related subsystems comprising of the cave atmosphere, seepage water, carbonate precipitates, soil zone and karst aquifer in relation to the prevailing regional meteorological and climate conditions on different timescales. In this respect, the daily to inter-annual variable hydrochemistry, water discharge, outside vs. inside temperature and air exchange, as well as the extent of modern Ca-carbonate precipitation are of principal interest. Temperature and meteoric precipitation amounts are the meteorological/climate parameters of major relevance regarding speleothem deposition and paleoenvironmental information archived. In many caves, the outside mean annual air temperature is reflected in a very similar average cave air temperature. However, exterior versus interior temperature gradients of variable spatial and temporal extent control the **cave air exchange** ranging from subtle cave breathing to pronounced cave winds (FAIRCHILD & BAKER, 2012). This cave ventilation is mostly relevant in regions possessing distinct seasons of the year and further strongly depends on the specific geometry of a cave system, i.e. the number, size and relative position of cave entrances and chambers. Based on these few preconditions, many caves exhibit some distinct cave ventilation dynamics, which can be traced by continuous measurements of air temperature, CO₂ and radon gas concentrations or air pressure (FERNANDEZ-CORTES et al., 2009; VIETEN et al., 2016). The ventilation pattern might either be constrained by some seasonally changing bidirectional chimney effect in the case of two or more cave openings (SPÖTL et al., 2005) or by intermittent trapping of cold (dense) and descending air (BOCH et al., 2011a) or warm and ascending air (BOCH & SPÖTL, 2011) through a single upper or lower entrance. Importantly, the air exchange has a strong effect on the cave air composition and the prevailing CO₂ partial pres-

sure and gradients. This in turn affects the intensity of CO₂ outgassing and the hydrochemistry (e.g. pH) of the cave drip waters (SPÖTL et al., 2005; MATTEY et al., 2016; MICKLER et al., 2019). In **Katerloch Cave** (Styria), multi-annual cave monitoring revealed a dominant control of the common stalagmite fabrics (lamination), stable C isotopes and minor elements (Mg, Sr, Ba) in the calcite by seasonal contrasts in air temperature determining the intensity of unidirectional cave ventilation and further the rate of CO₂ degassing and the chemistry of the drip waters (e.g. Ca-carbonate saturation state) and finally the amount, geometry and porosity of the precipitated calcite on the growing speleothems (BOCH et al., 2011a). In other words: "The air forms the rock" in Katerloch Cave. Interestingly, all of the investigated stalagmites in Katerloch (n = 22) show the same binary lamination pattern consisting of white, porous, fluid inclusion-rich layers with some tendency of enhanced (thicker) calcite deposition on the stalagmite central growth axis versus thinning towards the flank, as well as translucent, compact (dense) layers and more equally distributed calcite deposition across the growing stalagmite top. The recurrent pattern is intimately connected to distinct **warm and cold season modes** in this cave, which also affect other environmental proxies recorded in the stalagmite next to its petrography (Text-Fig. 10). These implications are mainly based on periodical hydrochemical analyses, as well as automated and highly-resolved temperature and CO₂ concentration data logging in comparison to meteorological data from weather stations nearby. Meteoric precipitation in the form of rainfall or snow acts as the principal atmospheric parameter controlling **water recharge** to the karst aquifer and thus **discharge** (drip rate) in Katerloch Cave has shown to exert an additional amplifying or attenuating influence on the seasonally prevailing and mainly temperature dependent speleothem growth mechanism. This is based on hourly drip logger and daily meteorological data in comparison to the periodically monitored hydrochemistry. Available multi-annual drip logger measurements from two active stalagmite precipitating drip sites in combination with petrographic evidence from these samples and older stalagmites support two major types of stalagmites in Katerloch, i.e. those of more regular seasonal lamination forming from more rhythmic (conservative) drip sites and those of more irregular inter-annual fabrics (high variability in lamina thickness) from sites of more individual sensitivity to karst water excess (SAKOPARNIG et al., 2016). Some **amplifying vs. attenuating effects** of variable drip water supply in relation to more

Environmental Proxies Layer type, δ ¹³ C, minor elements	Season	Ventilation	Cave air		Drip water chemistry				Drip rate	CO ₂ outgassing
			pCO ₂	δ ¹³ C	SI _{cc}	pH	δ ¹³ C _{DIC}	EC		
<p>white, porous inclusion-rich calcite low δ¹³C low Mg, high Sr, Ba</p> 	warm (late spring - early autumn)	reduced	high	low	rel. low	low	low	high	typ. high	reduced
<p>translucent, dense compact calcite high δ¹³C high Mg, low Sr, Ba</p>	cold (late autumn - early spring)	intensified	low	high	rel. high	high	high	low	typ. low	enhanced

Text-Fig. 10.

Based on multi-annual cave monitoring, the origin of layer formation and principal environmental dependencies of minor elemental and carbon isotope incorporation in stalagmite calcite could be constrained. These proxies revealed a distinct site-specific relation to seasonally prevailing physicochemical conditions reflected in variable cave air and drip water parameters. The process understanding of cave climate and speleothem growth allows for a reconstruction of paleoenvironmental information from the measured stalagmite carbonate proxies (adapted after BOCH et al., 2011a).

rhythmic cave air exchange has also been observed for lamination, zonation and stable C and O isotope patterns archived in an active flowstone in the past (drillcores) and during a dedicated cave monitoring campaign (BOCH & SPÖTL, 2011). In both cases, meteoric precipitation and typically related water discharge result in a variable water film thickness on the actively growing stalagmite or flowstone growth surface, which partially controls the effective CO₂ diffusion and outgassing rates from the water to the cave atmosphere. As mentioned earlier, this is further controlled by the prevailing CO₂ partial pressures and gradients in the course of a variable soil zone, karst aquifer and cave atmospheric state and evolution of free vs. dissolved CO₂ (MATTEY et al., 2016; MICKLER et al., 2019).

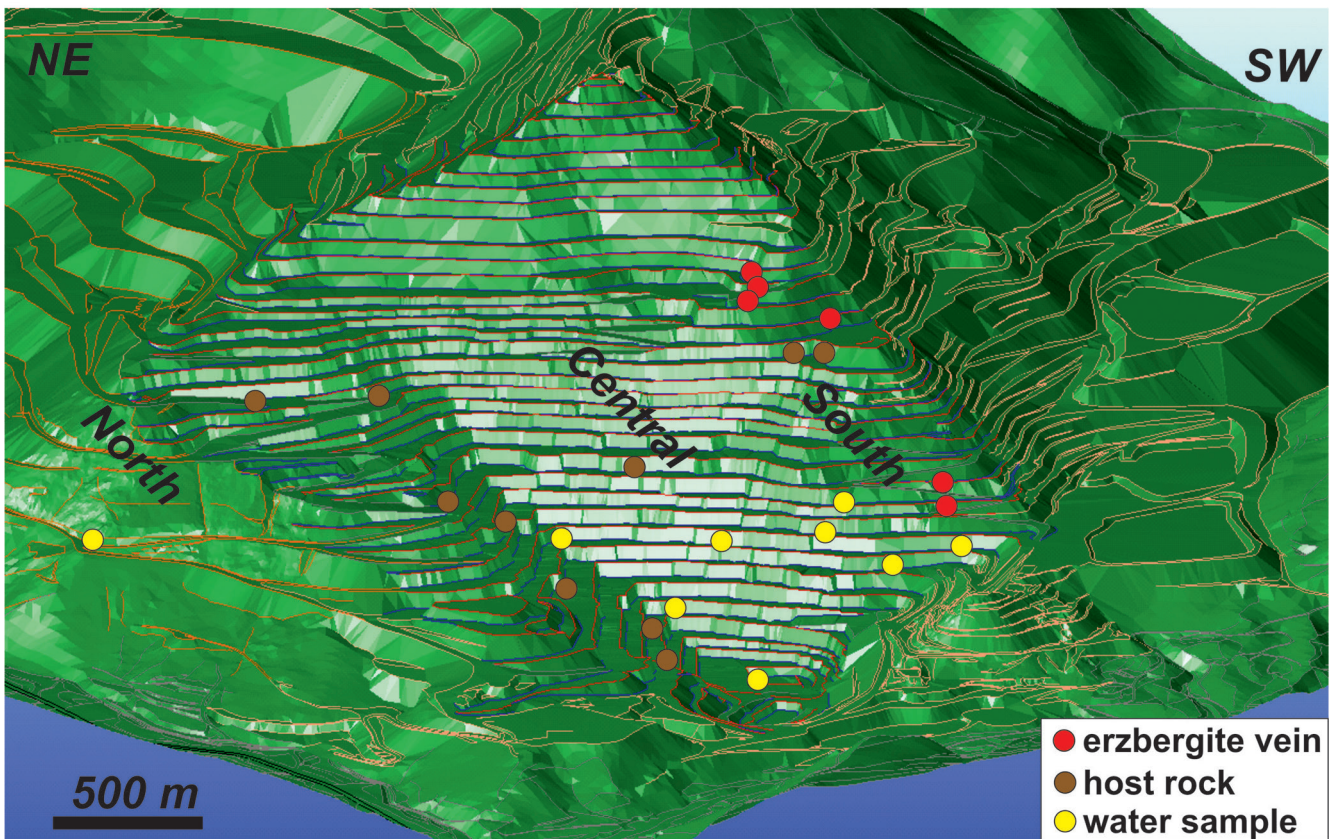
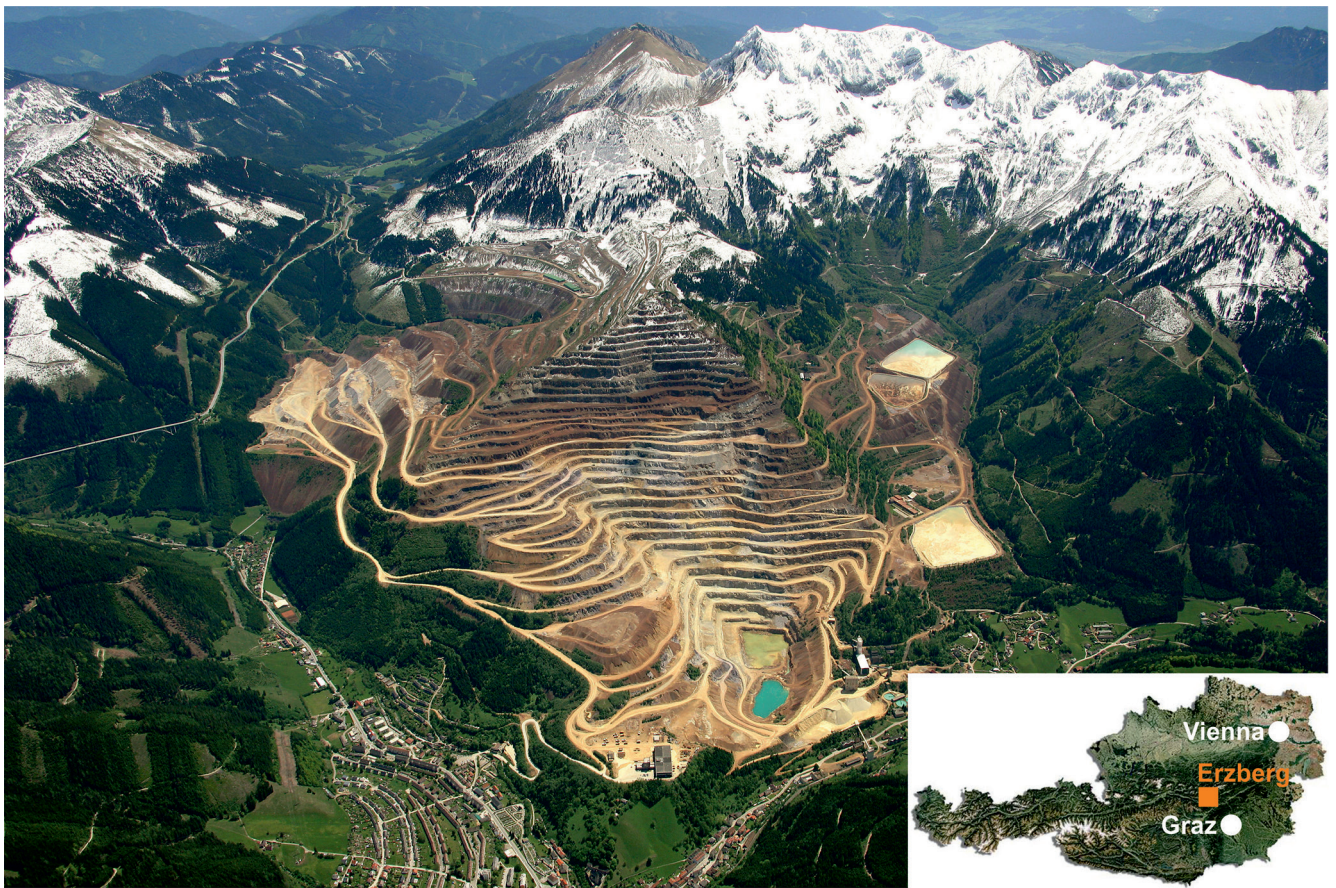
From the detailed monitoring of site-specific and in many cases widely distributed carbonate precipitation dynamics, distinct environmental proxy dependencies can be inferred. These constitute a promising starting point for qualitative and quantitative paleoenvironmental reconstructions from the mineral precipitates. In Katerloch Cave, the process understanding of lamina development and selected elemental and isotopic compositions in relation to the prevailing atmospheric conditions promotes an array of possible investigations with regard to climate change of the recent to ancient past (Text-Fig. 10). Based on a **multi-proxy approach**, this includes potential regional reconstructions and overall implications on air temperatures, as well as meteoric precipitation amounts and distributions. Even in the case of comprehensive monitoring efforts, a modern calibration of temperature and precipitation dependencies is challenging, although key to numerical environmental transfer functions (TREMAINE et al., 2011; MICKLER et al., 2019). Nevertheless, valuable insights into fundamental processes of carbonate crystallization, equilibrium vs. kinetically influenced elemental and isotope fractionation can result from the periodical or high spatiotemporal resolution monitoring in different settings.

Next to more or less purely inorganic hydrochemical variations and related carbonate mineralization, high-resolution environmental monitoring also includes **biological** and mostly **microbial processes** in diverse natural and man-made settings. For example, using a **CO₂-flux monitoring chamber**, the states of dissolved CO₂ and O₂ in connection with variable aquatic photosynthesis, dissolved inorganic carbon contents and autochthonous organic matter were monitored in 15 min intervals over a daily cycle (LIU et al., 2015). SEVILGEN et al. (2019) monitored coral calcification in vivo applying microsensors and fluorescent dyeing tracers in order to spatiotemporally constrain the vital Ca-carbonate chemical constituents during biomineralization. Microbial metabolic processes were further monitored with regard to unwanted scaling and corrosion impairing geothermal wells and heat exchangers (WÜRDEMANN et al., 2014). In this context, site-specific biofilm formation and in particular microbes of the sulphur, nitrogen and iron redox-chemical cycles can be monitored by connecting a **mobile bypass system** to the hydrothermal fluid flow. Regarding geothermal installations, intermittent stagnant conditions in the course of production cessations have shown to be of major relevance due to microbial activity enhancing temperature effects and unfavourable oxygen ingress (WÜRDEMANN et al., 2014). Further considering anthropogenic settings, on-site and online monitor-

ing of dominant carbonate precipitation affecting technical (e.g. tunnel) drainages constitutes a field of interesting developments. For example, the concept and prototype of a **“Sinterwächter”** (scale guard) seeks for an automatization in monitoring hydrochemical scaling potentials based on principal and reliable parameters (e.g. EC, pH; DIETZEL et al., 2013). This high temporal resolution and spatially flexible monitoring approach includes a telecommunication based data transfer from the geotechnical infrastructure and new field- and laboratory based test environments (e.g. Koralmtunnel) and technical improvements constitute some promising work in progress. The latter also involves an increased process understanding of scale material characteristics deriving from complex fluid-solid interaction (see respective chapter), as well as the inclusion of efficient and automated countermeasures.

Carbonates from the ‘Erzberg’ Iron Ore Mine (Austria)

The **iron ore deposit** “Erzberg” might be Austria’s most prominent geo-site based on its historic, socio-economic and geoscientific standing. It represents the largest siderite (FeCO₃) occurrence worldwide and the conspicuous pyramid shape of the iron-rich mountain range (1,532 m a.s.l. originally; 1,466 m today) and current open pit mine results from 30 successive stages of 24 meters height (Text-Fig. 11). Up to now, ~245 million tons of iron ore carbonate were processed by the VOEST-Alpine steel industry at Erzberg (up to 3 million tons/year) and ~150 million tons future reserves are available for delivery to the manufacturing sites in Linz and Donawitz (PROCHASKA, 2012). Erzberg hosts **various carbonate minerals** including widespread siderite, ankerite, dolomite, calcite, aragonite and several others, which make it an interesting location for carbonate research. Aside from the dominant Ca-carbonates (calcitic limestone) and Fe-carbonates (siderite, ankerite) a broad range of accessory sulfide minerals (pyrite, chalco- and arsenopyrite, sphalerite, galenite, fahlore, cinnabar), as well as silica minerals (muscovite, quartz) are characteristic of the local rocks (THALMANN, 1979; SCHULZ et al., 1997). Geologically, the iron ore deposit belongs to the Greywacke zone at the base of the Northern Calcareous Alps and was involved in Variscan nappe stacking of dominant Devonian limestones and Carboniferous dark siliceous schists followed by a Permo-Triassic transgression- al phase and Alpine synclinal tectonic deformation during Cretaceous times (BRYDA et al., 2013). Silurian/Devonian limestones and dolostones host the closely related siderite and ankerite ([Ca,Fe,Mg]₂[CO₃]₂) iron concentrating mineralization, which was further (partially) overprinted during Alpine metamorphism. The **source of the iron** and genetic evolution of the ore deposit constitute a subject of ongoing geoscientific debate involving the two principal ideas of a marine-volcanic-exhalative-synsedimentary formation versus a metasomatic-epigenetic origin (SCHULZ et al., 1997; PROCHASKA, 2012). In recent times, a later-stage metasomatic-epigenetic alteration of the original Silurian/Devonian host rock carbonate (Sauberberger Kalk) by buried hypersaline (evaporitic) brines and Late Triassic (based on Sm/Nd radiometric dating) hydrothermal fluid mobilization under redox reductive and acidic hydrogeochemical condi-



Text-Fig. 11. Overview and sample locations at Erzberg. Upper image: Aerial impression of the Erzberg open pit iron ore mine and the surrounding Alpine area located in Austria between Graz and Vienna (small map). Lower image: Digital terrain model of Erzberg showing the sampling positions of erzbergite veins, various host rock carbonates, as well as water from small fracture and surface streams (adapted from Boch et al., 2019). Note the preferred occurrence of the CaCO_3 vein samples in the more southern Erzberg section.

tions is promoted as the most plausible explanation (PROCHASKA, 2016). Erzberg carbonate host rocks further allow for the local mineralization of prominent CaCO_3 (aragonite, calcite) **veins filling vertical fractures** of centimeter to several decimeters width and often tens of meters length (HATLE, 1892; BOCH et al., 2019). The mostly layered (laminated) and visually outstanding precipitates are addressed as **“Erzbergite”** in private and museum mineral collections, some decorative contexts and the sparse scientific literature (ANGEL, 1939). In the vast majority of erzbergite material encountered on-site, the respective fractures are completely filled (sealed) by these mineral precipitates and their thickness typically reflects the local fracture extension (Text-Figs. 12A–C). In a study published recently, their origin and depositional dynamics, ages and temperatures of formation, as well as related environmental preconditions and implications have been evaluated in detail based on state-of-the-art geochemical and petrographic analytical tools (BOCH et al., 2019). In addition, the so-called **“Eisenblüte”** (iron flower) carbonate precipitates represent fragile dendritic and aragonitic mineral formations in rare open fractures and are often closely associated with the flowstone-like erzbergite veins (HATLE, 1892; ANGEL, 1939). These prominent and wanted mineral formations resemble helictites (eccentriques) forming under specific conditions in some karst caves (ONUİK et al., 2014). Interestingly, these aragonite dendrites have not been studied in detail, i.e. they might hold some promising scientific potential regarding an increased understanding of aragonite nucleation during purely inorganic versus possible microbially mediated processes.

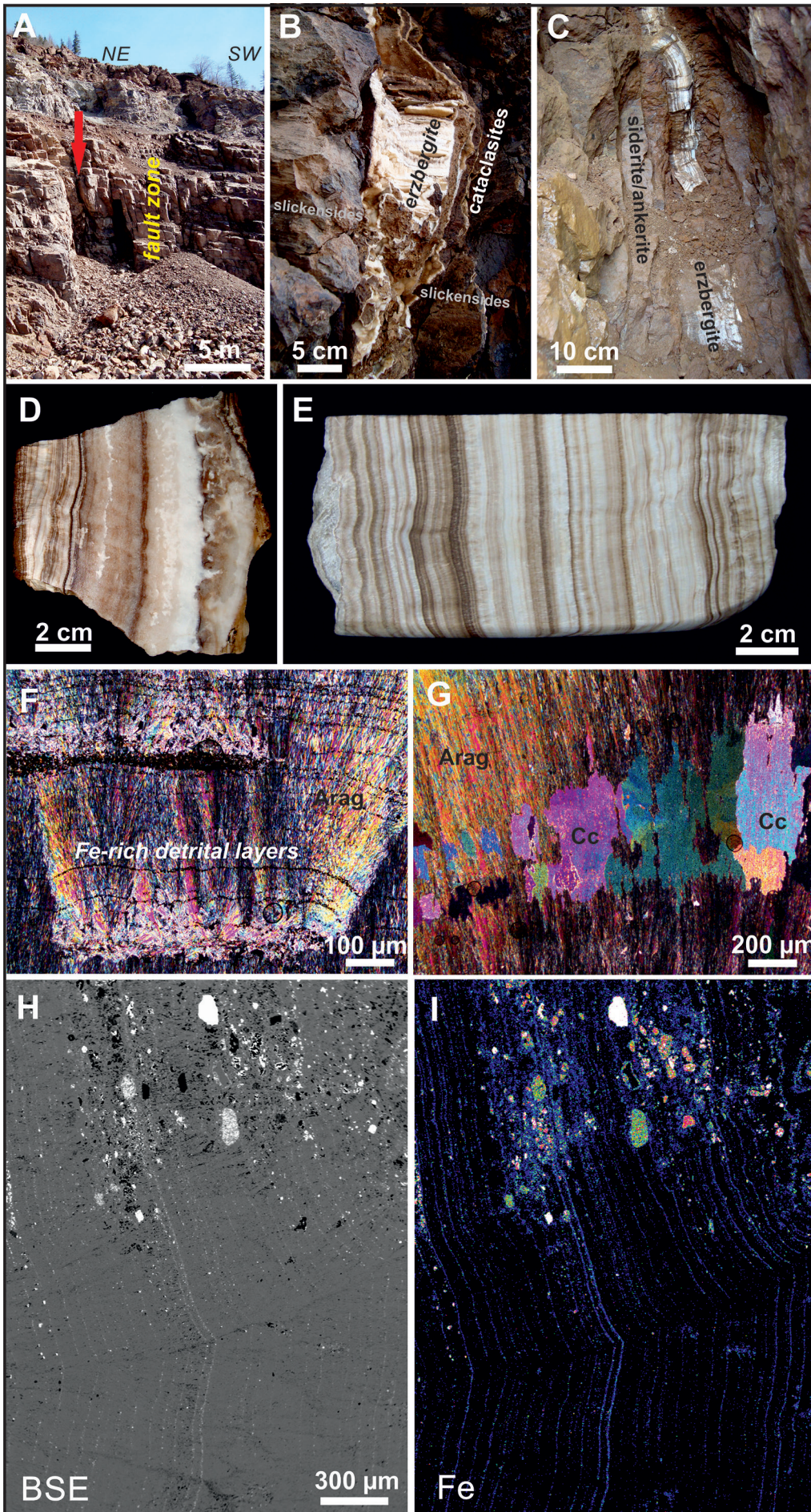
In an attempt of **(re)evaluation and increased process understanding** of the carbonate occurrences at Erzberg, new sampling campaigns, field- and laboratory based and often high-resolution and sensitive analytical techniques were recently applied and further work is currently in progress. The sampling included the **major carbonate host rocks**, such as siderite and ankerite dominated sections of the iron ore body, as well as variably altered limestone and dolostone samples recovered on-site from different levels of the open pit mine (Text-Fig. 11). In addition, reworked and partially iron-rich basal breccia material (Permian age; SCHULZ et al., 1997) was sampled, as well as some specimens of localized pyrite mineralization. The investigation of these samples was mainly focused on genetic and geochemical aspects of the local iron enrichment at Erzberg and also regarding their role as source rocks of the prominent erzbergite vein formation in fractures. **Selected representative erzbergite samples** ($n = 25$) were collected on-site from the rare veins currently accessible and being mostly located in the southern part of Erzberg (Text-Fig. 11). Interestingly, some of the fractures filled with erzbergite also showed slickenside striations and distinct cataclastic rocks and the latter were also sampled in oriented fashion for further microstructural and chemical analysis. In addition, erzbergite samples from our university collection and private collectors were analysed. The detailed evaluation was mainly focused on the origin and spatiotemporal growth dynamics of the aragonite-calcite veins and their potential value as a chemical-sedimentary environmental archive. In this context, radiometric U-Th dating, high-resolution electron microprobe elemental mapping, as well as stable (C, O) and clumped isotope measurements were conducted for the first time (BOCH et

al., 2019). In order to better constrain the site-specific water-rock interaction at Erzberg, **modern waters** were collected and analysed in July 2015 and April 2016 from fracture and surface flows of different sections (Text-Fig. 11). The analyses included a broad range of hydrochemical and stable isotopic (H, C, O, S) parameters, as well as aqueous solution modelling (BOCH et al., 2019).

Considering the principal research questions, scientific approach and new insights envisaged, the **current research activities at Erzberg** can provide contributions to different geoscientific aspects of regional to fundamental relevance. A detailed evaluation of the prominent erzbergite veins contributes to a better understanding of **vein mineralization** and of associated (brittle) fracture formation and filling and further of the widespread aragonite-calcite relationship. In the realm of vein formation, a growing interest is mainly boosted by the investigation of wanted as well as unwanted carbonate precipitation in deep porous sediment or fissured rock reservoirs (aquifers). For example, the fostered precipitation of long-lasting carbonate minerals in the course of geotechnical CO_2 sequestration (CCS – carbon capture and storage, e.g. in peridotite or basaltic rocks; KELEMEN & MATTER, 2008; MATTER et al., 2016), CO_2 -based geothermal energy production (RANDOLPH & SAAR, 2011; BUSCHEK et al., 2014), reinjection of saline fluids (RIVERA DIAZ et al., 2016) or the determination of paleofluid sources and effects in fault zones and Earthquake areas (LUETKEMEYER et al., 2016; PAGEL et al., 2018) constitute major research fields interested in vein mineralization. Also, genetic aspects of layering (lamination) and carbonate diagenesis can be targeted next to an application of the spatiotemporally evolving veins as a regional chemical-sedimentary archive capturing paleoenvironmental information and the timing and progress of past or recent (neo)tectonic and gravitational mass movements dissecting the Erzberg mountain range. Similarly, new geochemical information based on non-traditional isotopic techniques, could shed light into genetic aspects of the **iron ore formation**. This involves the regional source and concentration of iron and other metals, the potential role and chemistry of paleofluids, the timing of the processes and the metasomatic or metamorphic alteration of the ore deposit. Further, a reliable connection to other locations and episodes of Alpine ore formation (e.g. magnesite deposits) might be established.

Growth dynamics of aragonite-calcite veins (“Erzbergite”)

The principal hydrogeochemical mechanisms and environmental dependencies of erzbergite vein formation were analysed in a comprehensive field- and laboratory based investigation (BOCH et al., 2019). In particular, new and detailed insights have arisen from the application of high-resolution petrographic and elemental imaging, as well as non-traditional (clumped, U-Th) isotopic techniques. Mineralogical and chemical characterization of different erzbergite veins revealed a clear **dominance of aragonite precipitation** in comparison to pristine **calcite**, i.e. initial calcite crystallization is typically restricted and in fact relatively rare in the fractures at Erzberg. Rather, most of the calcite observed in several of the samples is obviously of **diagenetic origin** following the replacement of former aragonite and the later-stage diagenetic alteration pref-



erentially occurs across layers of different thickness and lateral extension (Text-Fig. 12D). Elemental distribution mapping of selected erzbergite sample sections in combination with hydrochemical analysis of modern fracture and surface waters at Erzberg strongly support a major control of the aragonite-calcite polymorphism by conspicuously high aqueous molar **Mg/Ca ratios** (2 up to 26 measured) – inhibiting calcite nucleation – as well as overall high CaCO_3 supersaturation (SI_{Arag} up to 1.3; BOCH et al., 2019). Only few of the samples showed some indication of scarce microbial presence, i.e. playing an ac-

Text-Fig. 12. Characteristics of erzbergite veins precipitating in fractures at Erzberg. A) Brittle fault zone of the southern section including two major vertical fractures filled with erzbergite and cataclasite (position of image B marked by red arrow). Slickensides indicate a sinistral strike-slip movement. C) Typical Ca-carbonate vein entirely sealing a formerly open fracture of the surrounding Fe(Ca,Mg)-carbonate host rocks. D) Erzbergite sample collected on-site showing characteristic layering comprising of a mm-scale lamination, broader (cm) zonation, recurrent brownish stained layers and localized carbonate fabrics indicative of partial diagenetic alteration (Arag → Cc). E) Nicely laminated sample from a mineral collection. F) Thin section transmitted-light image (crossed polars) displaying a typical radial fascicular aragonite section in erzbergite interrupted by multiple thinner but variable intra-crystalline particle layers. G) Common diagenetic replacement of pristine and dominant acicular/fascicular aragonite towards mosaic calcite crystals. The diagenetic alteration starts as patches and progresses preferentially across layers. Note the horizontal (vs. in-situ) orientation of erzbergite in the images F) and G). H) Back-scattered electron microprobe image supporting the detrital particulate character of the brownish stained layers within erzbergite. In most vein samples, these detrital layers show more irregular recurrence intervals and thicknesses. I) Electron microprobe based iron concentration distribution indicative of Fe-rich (Fe-carbonates, Fe-[hydr]oxides) detrital particle layers.

tive or passive role in the course of erzbergite deposition. Regarding the mineralogy, the iron mineral goethite and the siliciclastic minerals muscovite and quartz were detected in the brownish-stained layers. Further considering their particulate (different grain sizes) and variably thick character, these stained layers can be interpreted as detrital and **Fe-rich particle layers** within the aragonite-calcite succession. They are sourced by the oxidative corrosion of the widespread Fe-carbonate host rocks (siderite, ankerite) and accessory Fe-sulfides (pyrite) and subsequent detrital mobilization and local sedimentation in the vertical fractures. Regarding the erzbergite petrography, **layering** is a widespread textural feature, which can be differentiated into a narrow (mm-scale) lamination and a broader zonation (cm-scale banding) pattern (Text-Figs. 12D, E). The laminae represent an original growth feature primarily based on the visually outstanding and repeated deposition of the brownish-stained Fe-rich detrital particle layers and the zonation mainly depends on the predominance of either snow-white aragonite or more beige coloured and mostly diagenetic calcite. A regular (e.g. seasonal) alternation of aragonite and calcite proposed in earlier studies (HATLE, 1892; ANGEL, 1939) could not be confirmed from the vein samples studied (BOCH et al., 2019). Additionally, high-resolution petrographic and chemical analysis in combination with radiometric U-Th dating revealed a typically **irregular (episodic) nature of the layering**, i.e. only few erzbergite sample sections showed some closely spaced and most likely periodical deposition of thin detrital particle layers (e.g. from snowmelt; Text-Figs. 12F–I).

Considering the driving mechanism of carbonate dissolution, mobilization and erzbergite vein mineralization, analyses of modern waters at Erzberg in connection with solid-phase mineralogical and stable isotopic analyses strongly support **sulfide oxidation** of the widespread accessory sulfide minerals in the host rocks as a major geochemical precondition. Increased dissolved sulphate concentrations (up to 226 mg/l) in the modern waters, sulphate $\delta^{34}\text{S}$ values ranging from -4.9 to +2.5 ‰ (VCDT), increased $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC; +2.4 to +3.8 ‰ VPDB), as well as persistently high erzbergite $\delta^{13}\text{C}$ compositions (up to +6.8 ‰ VPDB) are the most striking features of common sulfide oxidation and related **sulfur acidic** carbonate host rock and accessory mineral dissolution, i.e. an efficient aqueous mechanism involving a relatively strong acid. Stable C and O isotope analyses of the principal host rock carbonates at Erzberg and of numerous erzbergite aragonite-calcite samples yielded limestone/dolostone (Sauburger Kalk), as well as ankerite being the **main source rocks** of vein mineralization in fractures, i.e. the local lithology is reflected in the erzbergite isotopic composition to a variable degree (BOCH et al., 2019). In addition, the spatially and temporally variable **hydrochemical evolution** in the dominantly fissured carbonate aquifer results in significant local differences with regard to the aqueous solution chemistry and directly related potential for erzbergite formation. Based on a limited number ($n = 10$) of modern water analyses, systematic **local differences** between the more **southern, central and northern Erzberg sections** could be claimed. More specifically, from a modern hydrochemical point of view, CaCO_3 precipitation should be more pronounced in the southern part and this is in line with the majority of erzbergite samples encountered on-site in the southern Erzberg section today (Text-Fig. 11).

These findings are probably related to spatially distinct sources and flow paths of the vein precipitating aqueous solutions. In this context, the hydrogeochemical analyses conducted revealed the occurrence of some characteristic mechanisms of fluid-solid interaction at Erzberg. This includes the prevalence of **prior CaCO_3 precipitation** mostly for water flows in the southern section, i.e. the hydrochemical evolution strongly depends on the successive loss (precipitation) of Ca-Carbonate (aragonite or calcite) during water percolation. Such a fractionating mechanism is indicated by the prominently enriched molar Mg/Ca ratios, the Mg/Ca vs. Ca concentration distribution (inverse relationship), strongly increased $\delta^{13}\text{C}$ of DIC and erzbergite, and the preferred depletion of Sr, Ba and U concentrations in aqueous solution in the case of prior aragonite precipitation. Furthermore, hydrochemical processes such as **evolving CO_2 outgassing** and pH buffering are of major relevance at Erzberg and are intimately connected to prior and vein CaCO_3 precipitation. An enhanced potential of CO_2 degassing arising from principal chemical reactions, such as siderite/ankerite oxidation, sulfur acidic dissolution of limestone/dolostone or ankerite and the different forms of Ca-carbonate precipitation at Erzberg is supported by increased CO_2 partial pressures calculated for the aqueous solutions ($\log_{10} P_{\text{CO}_2}$ of -3.2 to -2.3), compared to the overall prominently elevated C isotopic signatures (BOCH et al., 2019). Pronounced **pH buffering** of the evolving waters imprinted by sulfide oxidation and sulfur acidic dissolution, is strongly suggested by the overall high pH values (8.1–8.8) measured and further by the high CaCO_3 supersaturation (SI_{Arag} of 0.7 to 1.3; SI_{Cc} of 0.8 to 1.4) calculated based on the local water analyses from different sections at Erzberg. This can be explained by the dominance of various and in principal alkaline carbonate host rocks constituting the fissured carbonate aquifer and thus interacting with the variably acidic solutions. Based on distinct aqueous speciation plots (e.g. Mg vs. Ca. vs. sulphate), the occurrence of some **incongruent dissolution** (e.g. dedolomitization) is suggested with focus on the more central Erzberg section. This hydrochemical mechanism well known from carbonate aquifers relies on the different solubility behaviour and the counteracting crystallization potential of the involved carbonate minerals, e.g. slow dissolution of ankerite or dolomite and the concurrent supersaturation and kinetically-favoured precipitation of aragonite or calcite in fissures and fractures of the Erzberg aquifer.

The first clumped isotope measurements conducted at Erzberg, as well as the typical stable O isotope compositions of the vein carbonates (-11.5 to -5.1 ‰ VPDB) support a **meteoric origin of the erzbergite precipitating aqueous solutions**, i.e. the waters evolving in the fissured aquifer originate from a spatiotemporally variable infiltration of rain or snow. The $\delta^{18}\text{O}$ signatures of the original fluids calculated from the Ca-carbonate clumped isotope analyses (Δ_{47} based temperature vs. $\delta^{18}\text{O}_{\text{carb}}$) range from -11.8 to -8.7 ‰ (VSMOW) and are thus similar to values measured in modern waters at Erzberg ($\delta^{18}\text{O}$: -11.2 to -7.7 ‰; BOCH et al., 2019) and values based on the Austrian Network of Isotopes in Precipitation (observation station Wildalpen; altitude corrected mean annual $\delta^{18}\text{O}$ values of -13.1 ‰ and warm season values of -10.7 ‰; HAGER & FOELSCHKE, 2015). Stable H and O isotope measurements of the modern waters further suggest a different meteor-

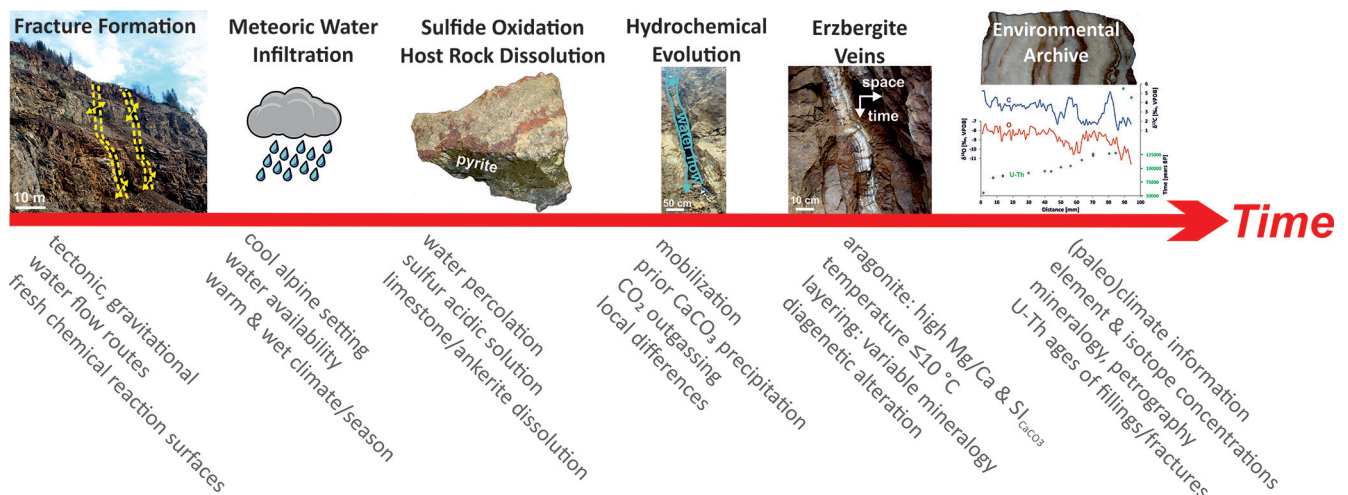
ic water infiltration area for the southern vs. central and northern sections, i.e. the latter might be sourced from an infiltration area of higher altitude and a higher proportion of cold season precipitation (overall lower $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values). Along with the O isotopic paleofluid composition, the clumped isotope analyses also provided reliable and relatively precise constraints on the **formation temperatures of the erzbergite vein precipitates**. Replicated measurements from multiple samples ($n = 7$) yielded crystallization temperatures from +2 to +9° C (~5° C on average) involving uncertainties of $\pm 2\text{--}8^\circ\text{C}$ based on the temperature calibration of KLUGE et al. (2015). Therefore, the erzbergite veins represent a rare case of dominant aragonite nucleation at cool to near-freezing temperatures and the elevated altitude Alpine setting is reflected in these meteoric (in contrast to hydrothermal hypogenic) carbonate precipitates. These mineral deposits also show some systematic variation depending on their timing of formation (BOCH et al., 2019). Regarding the site-specific formation conditions, the initial **opening of fractures** constitutes an essential prerequisite providing preferential water flow routes and fresh chemical reaction surfaces for pronounced fluid-solid interaction involving sulphide oxidation and the various hydrochemical mechanisms mentioned before (Text-Fig. 13). The dominantly vadose flow regime in the fissured carbonate aquifer results in a uni- or bidirectional growth of erzbergite in the vertical fractures, i.e. vein mineralization progressing from one or both adjacent fracture walls towards complete sealing (Text-Figs. 12A–C). Based on a rich dataset of radiometric $^{238}\text{U}\text{--}^{234}\text{U}\text{--}^{230}\text{Th}$ age determination of erzbergite samples, the typical **growth rates of these veins** can be constrained to some tens of micrometres per year. For example, considering a typical fracture of 10 cm width and a conservative growth rate of 0.02 mm/year in combination with progressive unidirectional erzbergite deposition, it would only take ~5,000 years to entirely seal the void. This corresponds well to the U-Th dating results obtained for many of the samples analysed and a bidirectional growth evident in some erzbergite samples might even proceed more rapidly. Regarding the **absolute ages and their distribution in time**, the erzbergite samples dated so far ($n = 20$) yielded ages from 285.1 ± 3.9 to

1.03 ± 0.04 kyr BP (thousands of years before 1950 A.D.), i.e. a relatively broad range during the late Pleistocene with some samples as new as the historical age (BOCH et al., 2019). In most cases, the relative age uncertainties (2σ) are of high precision and range within 0.5 to 1 % of the absolute age and thus within \pm few hundreds of years mostly depending on the highly variable initial U concentrations (^{238}U from 7 to 3,120 ppb) and detrital Th contamination (^{232}Th from 20 to 96,180 ppt). Most samples revealed a rather continuous growth from their base(s) to top(s) and consequently represented a relatively narrow time interval of deposition (some thousands of years). Only few erzbergite samples showed longer-term growth interruptions and thus captured a large time range. Interestingly, all of the erzbergite samples recovered from currently accessible fractures on-site yielded U-Th ages younger than the Last Glacial Maximum ($< \sim 20$ kyr BP) in the Alps, i.e. these carbonate veins are of unexpectedly young geological age. Furthermore, the age distribution strongly supports a preferred erzbergite vein formation during favourable – warm and wet – environmental conditions (Text-Figs. 14, 15). This prominent environmental dependency is clearly related to the hydrogeochemical mechanisms and elevated altitude Alpine setting of erzbergite formation. A conceptual model of the spatiotemporally variable vein growth dynamics at Erzberg is summarized in Text-Figure 13.

Environmental implications on fracture formation and paleoclimate

Based on the new **geochemical investigations** at Erzberg and the more detailed process understanding gained (e.g. erzbergite growth dynamics), various modern and past **environmental dependencies** can be inferred. In particular, implications and potentials with regard to studies on fracture formation and distribution, paleoclimate information from the erzbergite chemical-sedimentary archive and genetic aspects of the iron ore carbonates arise in the context of the recent and ongoing research activities.

The **opening of fractures** constitutes an essential prerequisite with regard to water flow in the fissured carbonate aquifer and related erzbergite vein deposition at Erzberg. Importantly, the open fractures of different width and ver-



Text-Fig. 13. Conceptual model of spatiotemporal erzbergite vein formation at Erzberg. The growth dynamics can be illustrated by an essentially stepwise evolution starting with the opening of fractures and associated fresh chemical reaction surfaces towards a potential application of the chemical-sedimentary deposits as a (paleo)environmental archive.

tical extension provide fresh chemical reaction surfaces of the various host rock carbonates and accessory sulphides promoting a distinct hydrochemical evolution of the infiltrating meteoric waters. As seen in the previous chapter, this involves an array of chemical reactions, such as sulphide oxidation and Fe²⁺-carbonate corrosion, sulphur acidic vs. pH buffered aqueous solutions, (incongruent) carbonate host rock dissolution and mobilization, prior CaCO₃ precipitation and CO₂ outgassing, and finally Ca-carbonate vein precipitation and **sealing of the fractures** (BOCH et al., 2019). An overall high efficiency and rapid rates of these physicochemical processes is supported by the radiometric U-Th dating results from erzbergite samples, i.e. the aragonite-calcite veins typically represent relatively short time intervals (some thousands of years) of complete fracture filling and average growth rates of a few tens of micrometres per year were inferred. Analyses of modern waters collected at Erzberg clearly showed a high potential for ongoing Ca-carbonate vein precipitation, i.e. high total dissolved solid contents, high aragonite and calcite supersaturation states, high aqueous solution pCO₂ and thus outgassing and pH increasing tendencies (BOCH et al., 2019). In principle, the mechanism of erzbergite vein mineralization in fractures at Erzberg is still at work based on the modern hydrochemistry, however, the open pit mining activities and in particular the frequent mobilization of dust might exert some disturbing (inhibiting) effect on currently precipitating carbonates in fractures near the surface (dust coatings observed by the author). In essence, these observations and underlying mechanisms of fluid-solid interaction, the consistently young age (< 20 kyr BP) of erzbergite sampled on-site and the typically rapid and complete sealing of the fractures strongly support a **geologically young age of the fractures**. It seems highly unlikely that the vertical fractures have remained open over extended geological time intervals (e.g. hundred thousands or millions of years) and were then filled more or less instantaneously in the recent past. More likely, the opening of a fracture, as well as the occurrence of relatively warm and wet environmental conditions promoting erzbergite growth in this overall cool Alpine Erzberg climate setting, marks the initiation and often rapid progress of fracture sealing.

Evaluating the principal **origin of the fractures** filled with young erzbergite veins, the associated rock movements could either be the expression of gravitational or (neo) tectonic and seismic forces. Regarding a **gravitationally induced** rock failure and displacement, the repeated occurrence of warm climate intervals (interglacials) versus ice ages and related ice cover of mountain ranges and ice streams in valleys should be considered in the Alpine realm during the Late Pleistocene, i.e. the time interval represented by erzbergite samples dated so far (VAN HUSEN, 2009; LUETSCHER et al., 2015). In particular, rock movements could be initiated in the course of glacier and permafrost ice melting and eventually by some regional isostatic rebound after relief of strain or by oversteepened mountain flanks after glacier retreat. The last glaciation (Würm) and its glacial maximum (LGM) in the Erzberg area, however, only featured a relatively minor ice cover, i.e. patches of ice on high mountain tops east of the major connected ice-stream network and the basin of Eisenerz has not been glaciated (VAN HUSEN, 2009; BRYDA et al., 2013). In principal, the aforementioned possi-

ble gravitational mass movements should be characterized by dominantly **vertical rock movements**. In some of the fractures filled with erzbergite, however, indications of **lateral movements** including slickensides, cataclasites, kirkite and adjacent damage zones were encountered and these fractures can thus be classified as **fault zones** (Text-Fig. 14). The cataclastic rocks appear mostly in original position (on vertical fracture walls) and can be traced for several meters. Thin section inspection revealed a matrix supported fabric hosting radially disrupted and displaced fragments, elongated and rotated clasts, as well as mm-scale secondary carbonate veins. Importantly, the cataclasites are also cemented by the erzbergite Ca-carbonate precipitates. The orientation of the sinistral slickenside striations on the fracture walls hosting the cataclasites strongly supports directed **strike-slip faulting** and therefore a potential **tectonic origin** (Text-Fig. 14). In connection with the consistently young U-Th ages of erzbergite veins sampled in the field, this raises the principal question of a correspondingly young age of the cataclastic rocks and the slickensides, i.e. a possible origin from some neotectonic activity. These unexpected findings are further supported by the hydrogeochemical mechanism of typically rapid erzbergite infilling and the comparatively soft (immature) material consistency of the formerly more or less uncemented cataclastic rocks adhering to the vertical fracture walls makes it unlikely for these rocks to be spatially stable in an open fracture over extended time intervals. From a regional tectonic and structural geology point of view, the Erzberg area is encircled by major and minor Alpine fault systems, e.g. the two major and sinistral SEMP (Salzach-Ennstal-Mariazell-Puchberg; main strand ~10 km from Erzberg) and Mur-Mürz fault systems, the Trofaiach fault, Palten-Liesingtal fault and Gesäuse fault (BRYDA et al., 2013). Some evidence for potential neotectonic activity also comes from the displacement of relatively young speleothems constrained to Last Glacial times in Hirschgruben Cave (Hochschwab mountain range; PLAN et al., 2010). In a recent publication, BAROŇ et al. (2019) report the registration of active displacements in selected cave systems of that region based on two years of monitoring applying Moiré extensometers. The nearby "Rockslide of Wildalpen" event was dated to ~5800 yr BP and a minor local earthquake or major regional earthquake associated with the fault systems listed before was discussed as a trigger (VAN HUSEN & FRITSCH, 2007). Further, modern earthquakes are relatively frequent in the wider Erzberg area, e.g. a major earthquake in Leoben in 1794 or a minor seismic event in Eisenerz in 1964 (magnitude 2.7; LENHARDT et al., 2007). In principle, the fractures/faults at Erzberg could be part of a conjugated system, i.e. sub-faults of the dominant – mostly sinistral and strike-slip – regional fault regimes not recognized as such at Erzberg so far. For example, brittle tectonic conjugated faults involving cataclasites and affecting carbonate host rocks were reported from three locations relatively close to Erzberg and were related to the major SEMP fault system (HAUSEGGER & KURZ, 2013). First measurements of the principal orientations of vertical faces and slickenside striations in some of the prominent erzbergite filled fractures/faults also support a possible connection to the SEMP fault system. In this tectonic context, these fractures could therefore be another expression of an ongoing uplift and eastward lateral extrusion of the Eastern Alps (DECKER et al., 2005; PLAN et al.,

2010; BAROŇ et al., 2019). Moreover, some fractures and associated erzbergite vein samples show indications of a possible **reactivation of the faults** (episodic slip). Sample EB9 from a fracture accessible in the southern Erzberg section on level Schuchart (~1,110 m a.s.l.; Text-Fig. 14) precipitated in close spatial relation to two different generations of cataclastic rocks, which are probably the expression of two distinct tectonic events. Multiple and precise radiometric U-Th measurements of the adjacent erzbergite aragonite yielded ages ranging from 19.21 ± 0.10 to 13.11 ± 0.09 kyr BP (Text-Fig. 14). Interestingly, the oldest ages (orange in Text-Fig. 14) came from aragonite closest

to the fracture wall hosting the cataclasites, while another group of subsamples (red in Text-Fig. 14) shows systematically younger ages towards complete sealing. Possible reactivation and associated opening of fractures is also supported by sample EB2 (cf. BOCH et al., 2019 and Text-Fig. 15). The vein sample shows an older interval dated to 285.1 ± 3.9 and 229.6 ± 2.1 kyr BP characterized by bidirectional growth towards complete filling of the void and a much younger interval starting from $\sim 128.16 \pm 0.66$ to 55.54 ± 0.27 kyr BP and being characterized by unidirectional growth (on one fracture wall) towards complete fracture sealing. These observations are supported by the

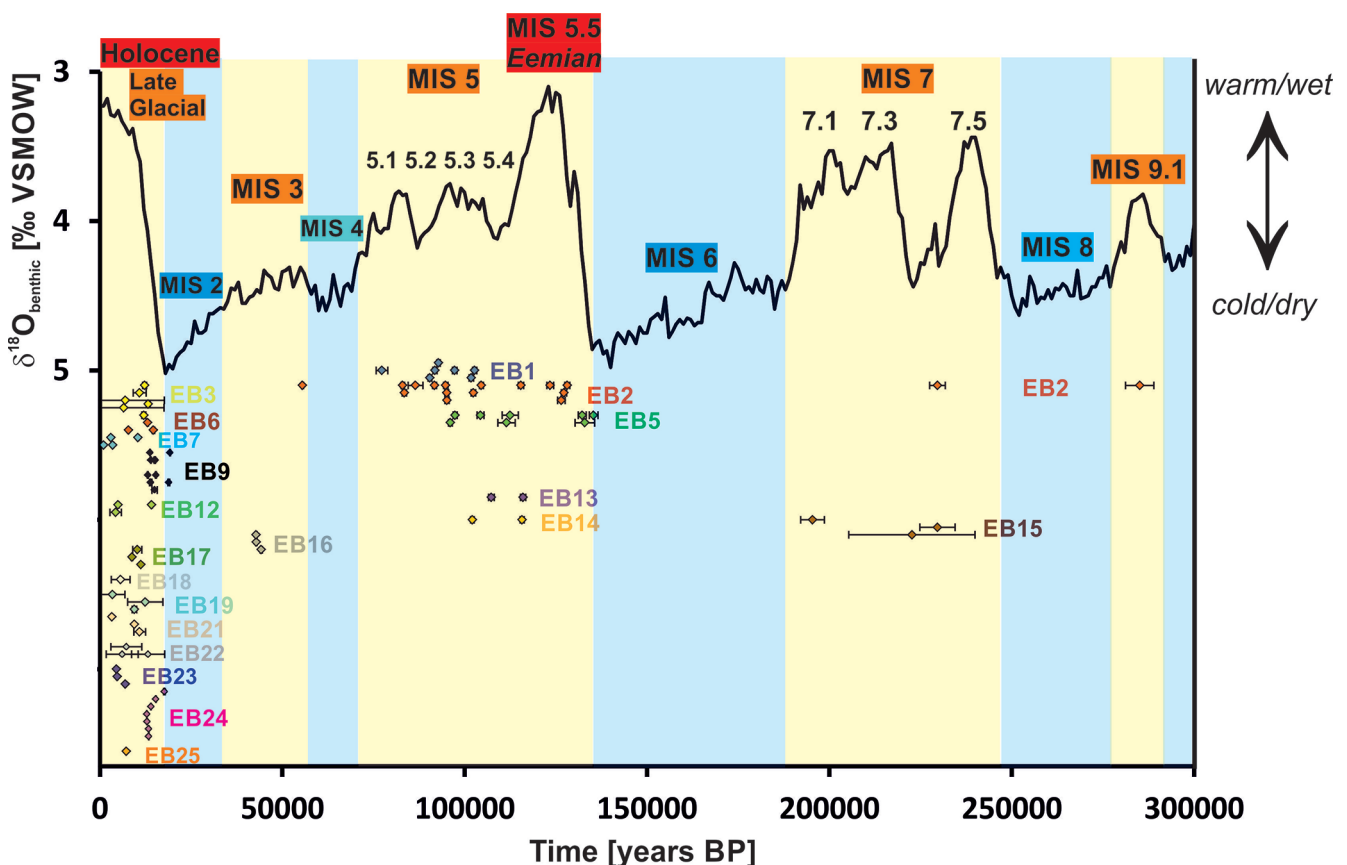


Text-Fig. 14. Brittle fault (damage) zone hosting two major vertical fractures in the southern part of Erzberg both entirely sealed with erzbergite carbonate (level Schuchart, ~1,110 m a.s.l.). The northern (left) fracture features slickensides and two generations of cataclastic rocks. Multiple and precise ^{238}U - ^{234}U - ^{230}Th age data of the aragonite precipitates support young ages (< 20 kyr BP) and rapid deposition of the CaCO_3 filling the fracture and cementing the cataclasites. The latter are mostly in original position and can be traced for several meters in the downwards narrowing fracture. The petrographic and structural characteristics of this place in combination with the radiometric dating results raise questions on a geologically young age of the fractures/faults and cataclastic rocks, as well as the possible reactivation of directed rock movements.

dating results, as well as by detailed petrographic analysis. In principle, the recurrent opening of fractures and closely related erzbergite deposition at Erzberg within the recent geological past could also result from preferential gravitational movements across much older brittle tectonic structures (e.g. strike-slip faults), i.e. a **reactivation of the damaged and weakened zones** in some relation to specific (paleo)environmental conditions. In essence, the origin of the fractures/faults hosting relatively young erzbergite seems a promising field of ongoing research activities and more field- and microstructural data of the faults and its cataclastic rocks in combination with petrographic and geochemical constraints should be targeted.

Apart from fracture formation and structural geology, the vein mineralizations at Erzberg can further contribute to research activities in the field of **Quaternary geology** and paleoclimate reconstruction in the Alps. Based on their timing of formation (Text-Fig. 15) and distinct environmental dependencies (BOCH et al., 2019), the spatiotemporally variable deposition of the erzbergite veins represents a **chemical-sedimentary environmental archive** of potentially high temporal resolution in a climatically sensitive Alpine setting. In the context of modern climate change and more specifically global warming, the Alps have shown to be a region of increased sensitivity regarding the magnitude and rate of climate variation (AUER et al., 2007). Considering the preservation of environmental changes in the

past and the potential for paleoclimate reconstruction, the erzbergite deposits are comparable to other continental Ca-carbonate precipitates, such as stalagmites and flowstones in karst caves (BOCH & SPÖTL, 2011; FAIRCHILD & BAKER, 2012), travertines and calcareous tufa (CAPEZZUOLI et al., 2014; TOKER et al., 2015) and lake deposits (BRAUER et al., 2007; OEHLERICH et al., 2013). In all of these cases, the capability of precise ^{238}U - ^{234}U - ^{230}Th radiometric dating constitutes a major prerequisite in order to reliably constrain the specific time intervals, rates and progress of carbonate growth and related paleoenvironmental changes manifested in the carbonate mineral deposits. In the first instance, the **presence or absence of erzbergite** forming during a particular time interval has shown to provide some valuable paleoclimate information. Aragonite-calcite precipitation in fractures at Erzberg is clearly favoured during relatively warm and wet climate intervals and is virtually absent during cold and dry periods (Text-Fig. 15). In other words, erzbergite growth is strongly focused on the warm/wet interglacials (e.g. Holocene, Eemian; red labels in Text-Figure 15) and interstadials (orange labels in Text-Figure 15) and did not occur during pronounced cold and dry ice ages (e.g. Marine Isotope Stages 2 and 6; blue labels in Text-Figure 15) and cool stadials (e.g. MIS 4). This can be explained by the cool formation (water) temperatures inferred from the erzbergite aragonite clumped- and stable oxygen isotope measurements, i.e. formation conditions restricted by recurrent freezing and/or dryness in



Text-Fig. 15. Timing of erzbergite formation based on precise radiometric U-Th dating of numerous individual vein samples (n = 20; selection from EB1 to EB25) in comparison to the marine oxygen isotope evolution of the past 300 kyr (after LISIECKI & RAYMO, 2005). Erzbergite deposition is clearly favoured during warm and wet climate intervals (yellow bars; MIS – marine isotope stages of low $\delta^{18}\text{O}$; interglacials and interstadials) and restricted or absent (freezing) during cold and dry intervals (blue bars; high $\delta^{18}\text{O}$; ice ages and cool stadials) at Erzberg. For most erzbergite samples basal (growth initiation), top (growth cessation – fracture filled) and intermittent U-Th ages were measured and the small age uncertainties (2σ errors) are commonly lower than the symbol size. The majority of erzbergite veins is younger than the last glacial maximum (MIS 2) and most samples represent short time intervals, i.e. rapid fracture sealing.

the higher elevation Alpine setting of the Erzberg meteoric water infiltration area and aquifer (BOCH et al., 2019). Thus, water recharge and discharge and a hydrochemical evolution supporting erzbergite vein mineralization were repeatedly suppressed during the last ~300 kyr BP (Text-Fig. 15) and probably much longer. The occurrence of erzbergite obviously represents a robust indication of overall favourable (mild) regional climate conditions, i.e. more or less comparable to today. It might therefore serve as a promising paleoclimate proxy of such environmental conditions over time and its full potential could be elaborated in future investigations at Erzberg.

Regarding further paleoclimate information from the erzbergite veins and more specifically from the relatively warm and humid time intervals covered, several other **proxy parameters** can be analysed from this mineral archive in fractures. Multiple and replicated measurements of clumped isotopic compositions of erzbergite subsamples from different age dated growth intervals could provide valuable constraints on the **absolute temperatures** prevailing during specific periods in the past, i.e. erzbergite constitutes an interesting target for the clumped isotope geothermometer. In combination with the Ca-carbonate stable O isotope values and established temperature dependent O isotope fractionation factors (e.g. COPLIN, 2007), the clumped isotope measurements can further provide a calculation of the original erzbergite precipitating aqueous solution stable O isotopic composition. The latter strongly reflects **genetic aspects of the vein depositing waters**, e.g. the source and eventual altering effects. At Erzberg, both past and modern waters in the fractures revealed a distinct meteoric origin and their locally differentiated isotopic signatures and hydrochemical evolution reflected seasonal and spatial variations of water infiltration and flow in the fissured carbonate aquifer (BOCH et al., 2019). Likewise, the CaCO₃ stable O isotope values capture environmental information on the **timing** (e.g. warm vs. cold climate period or season) and **source** (e.g. trajectories of moist air masses) of the carbonate forming aqueous solutions. Importantly, state-of-the-art micro-sampling (e.g. micro-milling) and mass spectrometric analytical techniques (see respective chapter) facilitate **high-resolution O isotope transects** reflecting longer- and short-term trends or rare events of the variable paleoclimate conditions. A similar approach might also be chosen with regard to environmental information from the CaCO₃ stable C isotopic compositions. The **erzbergite carbon isotope values** were found to mainly reflect the carbonate source rock (Fe-carbonates vs. Ca-Mg-carbonates), as well as site-specific processes of fluid-solid interaction determining the hydrochemical evolution of the aqueous solutions. The latter comprises of processes such as sulfide oxidation, incongruent carbonate dissolution, prior CaCO₃ precipitation and CO₂ outgassing in the aquifer (BOCH et al., 2019). In this context, the C isotopes represent a sensitive proxy to water recharge and discharge and in particular to differentiated flow routes and associated erzbergite formation. This is also the case with respect to the spatiotemporally variable vein petrography, i.e. the **lamination and zonation patterns** based on a variable mineralogy. The occurrence of aragonite, (Mg)-calcite and brownish stained detrital particle layers during specific time (climate) intervals can also be interpreted in a high-resolution analytical approach. Most likely, the mineralogy and petrography

strongly rely on meteoric precipitation and the directly related water saturation conditions in the fissured aquifer. Extreme seasonal and/or climate variations might result in varying water residence times ranging from **nearly complete drying to pronounced flushing events**, which are then further expressed in a more variable erzbergite appearance. In conclusion, the erzbergite vein fillings constitute a potential high-resolution paleoclimate archive of changing air- and related water temperatures, as well as of varying amounts and seasonal distributions of regional meteoric precipitation. Key to this paleoenvironmental application is the climate sensitive Alpine setting, the geochemically favourable material characteristics (pristine aragonite) allowing for precise radiometric (U-Th) age determination and the multi-proxy approach of major atmospheric (climate) variables.

Carbonate Scales forming during Geothermal Energy Production

The **knowledge** of fluid-solid interaction and variable mineral growth dynamics in the carbonate system gained from the detailed investigation of selected natural settings (e.g. speleothems in caves, veins at Erzberg) can be **transferred** to carbonate mineralization occurring in human-made (geotechnical) settings, e.g. geothermal power plants, railway and motorway tunnels. Importantly, the same underlying physicochemical mechanisms determine the carbonate crystallization pathways, their dominant environmental dependencies and consequently the spatio-temporal progress of mineral growth and the closely related material characteristics (e.g. consistency, anisotropy). In contrast to the diverse natural settings of carbonate precipitation, the technical settings primarily consider the **current (modern) and shorter-term state** of chemical-sedimentary deposition instead of longer-term paleoenvironmental considerations. In most geotechnical settings carbonate formation is typically undesired and highly problematic as it impairs fluid flow (e.g. thermal waters) and energy (e.g. heat) transfers in the technical components.

Scaling – unwanted mineral deposits

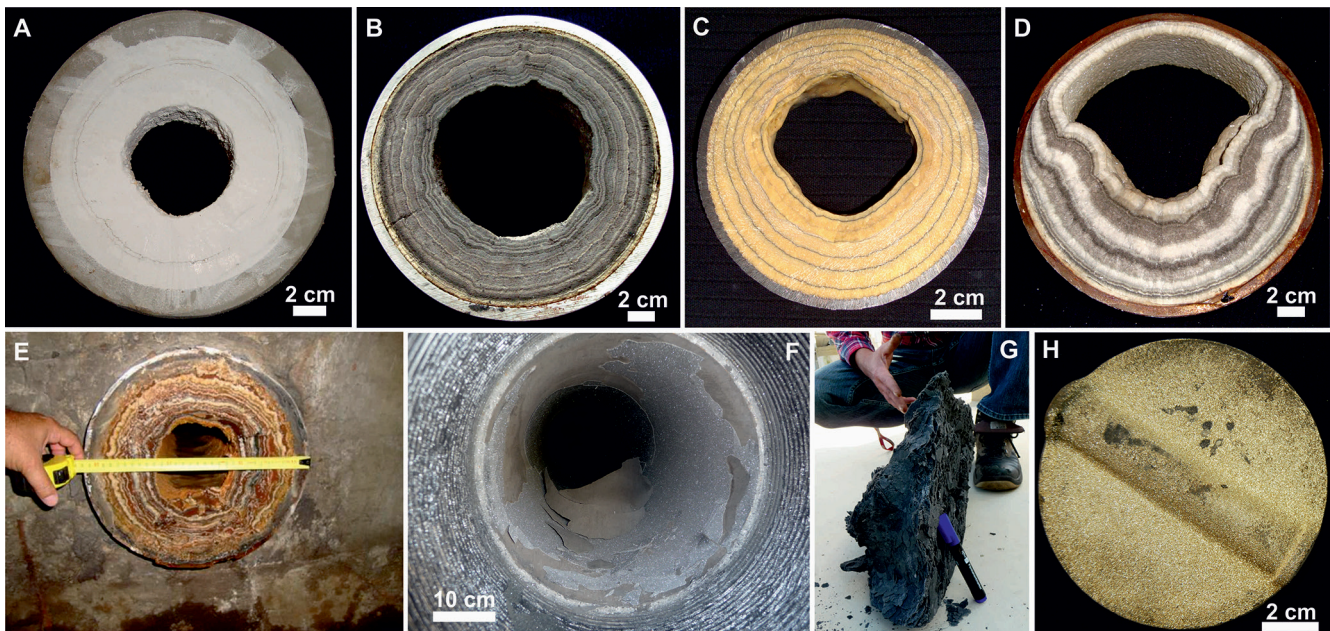
Unwanted mineral deposition (scaling) constitutes a **common obstacle** during geothermal heat and electric power production from deep thermal water reservoirs. The production of aqueous fluids from depth is typically associated with increased gas and total dissolved solid contents in equilibrium with the surrounding aquifer and more specifically its host rocks and elevated temperature and pressure conditions. In this context, deep geothermal wells (e.g. production and reinjection wells of hydrothermal doublet systems) tapping an aquifer of typically high water residence times lead to a major **disturbance** of the naturally prevailing physicochemical conditions. The pressure, temperature and chemical gradient changes introduced consequently entail an increased potential of mineral precipitation, as well as frequently related material corrosion processes deriving from the saline aqueous fluids. Depending on the natural geological and hydrogeochemical preconditions, the mineral precipitates include various carbonates, sulphates, sulphides, (hydr)oxides, chlorides and silica phases (CORSI, 1986; FINSTER et al., 2015).

These minerals depositing from the thermal fluid can lead to problematic inner-diameter reductions, disturbed flow regimes and clogging of the deep wells, pumps, pipelines, filters, valves, heat exchangers and other components of geothermal installations (Text-Fig. 16). Regarding mineral formation and material alteration from corrosive mechanisms, sulfidic and oxidic phases of various heavy metals – e.g. Fe, Cu and Zn supplied from steel – are the most common minerals encountered and strongly depend on the locally prevailing redox- and temperature conditions (VALDEZ et al., 2009; NOGARA & ZARROUK, 2017). Important constituents of enhanced corrosion are elevated H₂S, CO₂, O₂ and H₂ gas concentrations, chloride and sulphate contents, and a high constituent supply (flow rate). The particular manifestation and scaling and/or corrosion progress depends both on natural and human-made (operational) environmental conditions. Thus, next to the local natural hydrogeological setting **multiple operational parameters** are involved, such as variable physicochemical gradients, flow rates, flow geometries, mixing, materials used and other technical regulations. Importantly, the natural conditions encountered and operational parameters applied are distinct **site- (installation-) specific** prerequisites but adaptable to variable degrees. The unique appearance of (Ca-)carbonate scale materials found in different geothermal installations is an expression of the site-specific character of geothermal scaling and corrosion processes (Text-Fig. 16; BOCH et al., 2017b). Further, these processes are highly variable within an individual installation, i.e. they vary in space and time and different sections of the thermal fluid circuit might be affected constantly or temporarily (e.g. during production cessations). In essence, a better **process understanding of scaling and corrosion** related mineral deposition, as well as economically feasible **strategies and countermeasures** are the subject of ma-

ior efforts within the deep geothermal energy exploration community. Key elements in this complex field of interdisciplinary and applied research might be more elaborate approaches of resolving fluid-solid interactions and the variable scale material characteristics, the development of new construction materials being in contact with the demanding thermal fluids, the realistic monitoring of scaling and corrosion processes at high spatial and temporal resolution (on-site, online), and sophisticated approaches involving site-specific computer based modelling of multiple engineering and chemical components.

Scaling Forensics – Reconstructing site-specific production conditions

Based on the fact that scale deposits forming in different technical components of geothermal installations with time capture site-specific natural and operational production conditions in their chemical and petrographic (fabric) compositions, these chemical-sedimentary archives can be interpreted in a **scaling forensic approach** (BOCH et al., 2017b). In other words, these bodies evolving in pipes and on other substrates represent solid records of favourable vs. unfavourable production conditions with regard to variable effects on the aqueous solution chemistry resulting in variable scaling and corrosion processes. In contrast to the purely natural settings of mineral deposition in paleoenvironmental studies, the geothermal scale materials reflect a combination of natural as well as technical (operational) environmental conditions determining their **site-specific growth dynamics**. In particular, the natural physical and hydrochemical conditions of thermal fluids produced from major deep aquifers are often relatively stable on the relevant timescales (years to few decades), i.e. the extended fluid residence times and enhanced fluid-solid interaction underground provides a well equilibrated



Text-Fig. 16.

Unwanted mineral precipitates impairing energy extraction from deep thermal waters. A) to D) Ca-carbonate scales of different site-specific appearance (colour, layering, consistency, growth progress, substrate material). Scale D) resulted from a separate two-phase (water + gas) thermal fluid streaming in a horizontal steel pipeline. E) Prominent scale sample (calcite, aragonite and Fe-oxhydroxides) deposited over 45 years in a pipeline draining a storage tank of a thermal spa in Hungary. F) Scale-fragments made of Mg-calcite and accessory sulphide minerals evolving in conventional steel pipes of a geothermal power plant in Germany and further resulting in G) highly problematic massive blocks of accumulated and cemented flakes clogging tube bundle heat exchangers (cf. BOCH et al., 2017a). H) Pyrite (FeS₂) mineralization on a valve flap impairing its functionality with time.

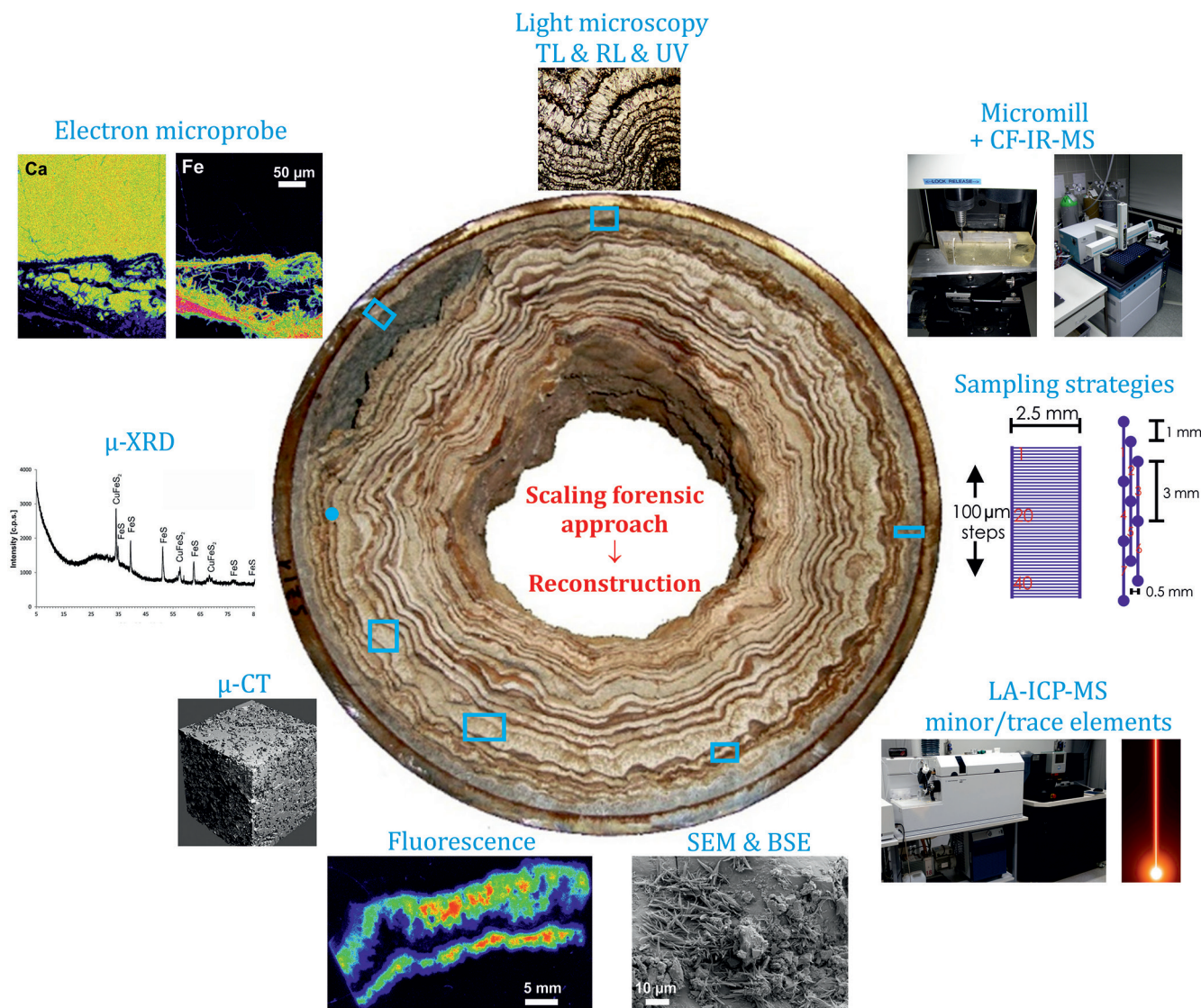
and therefore rather stable temperature, pressure, hydrochemical and hydraulic regime. In this regard, the possible short-term variation of human-made operational conditions might exert a stronger control on unwanted scaling and corrosion processes and their progress in most geothermal installations facing such problems. Nevertheless, the natural preconditions encountered are often decisive with respect to the overall potential, rates and volumes of scale deposits or material alterations to be expected and in some cases, the local handicaps might remain challenging for a given site of geothermal energy exploitation. Considering the **frequency of maintenance intervals** and the established **mechanical and chemical cleaning procedures** which can be applied for removing the scale deposits from different components and positions (CANDIDO & ZARROUK, 2017), the scales might be distinguished based on more wanted vs. unwanted material characteristics. Amongst the many possible distinctions mostly depending on genetic aspects of scale formation and fluid-solid interaction (see subsequent chapter), the scale material consistency and resulting durability with regard to its removal constitute a critical parameter. For example, compact and brittle carbonate scales strongly adhering to the underlying substrate material over longer distances (e.g. across pipes; Text-Fig. 16) are more difficult to remove mechanically (and chemically) compared to loose carbonate mud from nucleation in suspension being locally accumulated at obstacles (e.g. filter, heat exchanger). The latter might be removed regularly (e.g. daily) using a pressurized water hose, while the former has to be handled by workers in a time consuming laborious procedure (e.g. with a hammer and chisel or other exhausting mechanical means). Scales with increased porosity (lower density) typically result in a more rapid scaling progress compared to compact (dense) and relatively thinner scales, i.e. inner diameters of wells and pipelines are narrowed more rapidly impairing fluid flow and geothermal energy extraction and the frequency of maintenance intervals must be increased adequately. Importantly, the relevant scale material characteristics and growth dynamics are clearly site-specific and can vary extensively depending on the technical and operational conditions prescribed during thermal water production (BOCH et al., 2017a; HAKLIDIR & HAKLIDIR, 2017). The latter, however, represent an interesting subject for ongoing research activities and for potential site-specific adaptations, i.e. the scale material characteristics and progress could be controlled (operated) in a favourable manner (reduced growth and easy to remove).

The concept of Scaling Forensics is based on the application of a **broad laboratory analytical approach** involving state-of-the-art and mostly high spatial – and consequently temporal – resolution mineralogical/geochemical and imaging techniques (Text-Fig. 17). A **detailed reconstruction** of the spatiotemporally variable **carbonate scale growth dynamics** depending on the site-specific and longer- vs. shorter-term prevailing natural and technical (operational) geothermal production conditions is targeted. This includes an in-depth physicochemical process understanding of favourable (reduced scale deposition) vs. unfavourable (increased scale deposition) thermal water production conditions with regard to the site-specific scaling (and corrosion) progress. Essentially, the scaling forensic approach constitutes a **multi-proxy approach** combining multiple analytical techniques in order to gain environmen-

tal information on multiple physical and chemical parameters during thermal water production and consequently geothermal energy extraction. This involves environmental parameters and processes such as temperature and pressure changes, fluid flow rate, CO₂ and H₂O (steam) outgassing, pH and pe (redox) changes, the mobilization of specific elements and particles, mixing of fluids, the role of production cessations and restarts, material specific (e.g. steels, plastics) observations, and others. All of these variables can exert a major or minor, continuous or intermittent effect on the scale growth dynamics and the intimately related scale material characteristics. The laboratory analytical methods of choice include **powder- or micro-X-ray diffraction** measurements of selected subsamples (drilled powders) or spots in order to determine variable mineralogical compositions of the scale deposits (Text-Fig. 17). XRD analyses might also be performed on remaining mineral residua (e.g. sulphide and silica minerals) extracted from the bulk (carbonate) scale materials after chemically-selective procedures of **acid digestion** (e.g. BOCH et al., 2016). Detailed **petrographic information** including mineralogical and textural (fabric) changes can be derived by applying various **light microscopic techniques** to thin-sections prepared from the scales. This includes transmitted-, reflected- and epifluorescence (e.g. UV-activated) microscopy, as well as cathodoluminescence. A higher spatial resolution (µm size) can be achieved by **scanning electron microscopic techniques** (SEM) utilizing secondary electron (SE) or back-scattered electron (BSE) imaging. The latter has shown to be of particular value in evaluating the local presence of microbes (e.g. bacteria, fungi) in scale materials. In the **BSE images**, organic tissues appear in prominently blackish colour compared to the surrounding carbonate matrix or accessory minerals based on their distinct low-density contrast. The occurrence and distribution of microbial communities can further be studied by **fluorescence staining and imaging** of fresh scale material surfaces. This method uses mixed dyes resulting in fluorescence of the stained material when they are bound to nucleic acids (DNA, RNA) eventually being present. The scale surfaces of interest are investigated before and after staining and fluorescent signals can be detected by an epifluorescence microscope or other imaging systems (cf. GRENGG et al., 2017). Significant scale material contrasts mainly comprising of changes in **porosity and fabrics** can also be distinguished based on **micro-computer tomography** (µ-CT; Text-Fig. 17). This high spatial resolution method is typically focused on small volumes (cm³ size) represented in cylinders of sample material extracted from the bulk samples (e.g. rocks, scales; cf. OTT et al., 2012). High-resolution petrographic insights and simultaneous **major and minor element chemical distribution mapping** (µm-scale) is facilitated by **electron probe microanalysis** (EPMA). This tool is of particular value for resolving distinct mineralogical and material specific contrasts, for example across interfaces (substrate vs. scale) or in layered sample sections (BOCH et al., 2017a). In addition, precise quantitative elemental compositions of selected constituents can be determined by spot analysis of energy-dispersive X-ray spectra (EDX; MITTERMAYR et al., 2017). Regarding the measurement of **minor and trace elemental compositions** in the solid scale materials, **laser ablation coupled to mass spectrometry** (LA-ICP-MS) can provide highly-resolved (10s of µm spot size)

and sensitive (ppb range) chemical information (JOCHUM et al., 2009). Typical **sampling strategies** include point-wise or continuous transects across the spatiotemporally evolving sample materials, as well as more sophisticated sampling grids. In the context of carbonate scales, high-resolution LA-ICP-MS based concentration profiles of the elements **Mg, Sr and Ba** can provide valuable proxy information on the variable scale growth dynamics and therefore progress. In particular, the incorporation of the relatively large cations Sr^{2+} and Ba^{2+} into CaCO_3 is well known to strongly depend on the prevailing precipitation rate and varying Mg concentrations often reflect spatial changes of dominant Ca-carbonate (scale) deposition as a result of prior CaCO_3 precipitation and related Mg fractionation (enrichment) along the flow path (see Erzberg chapter). Different spatial but mostly high-resolution sampling strategies are further applied for **stable C and O isotope analyses** of the scale carbonate. This is typically accomplished by the extraction of tiny sample powders (~0.3 mg) from the scale material using a **computer-controlled micromill device** in combination with subsequent **mass spec-**

trometric analysis (CF-IR-MS; Text-Fig. 17). The C and O isotope signatures have shown to be a sensitive proxy for outgassing of CO_2 and H_2O (bubbling/steam formation) from the thermal water (BOCH et al., 2017a). More specifically, the isotopically relatively light $^{12}\text{C}^{16}\text{O}_2$ and $^1\text{H}_2^{16}\text{O}$ molecules are preferentially enriched (Rayleigh fractionation) in the separating gas phases and therefore the related $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the concomitantly precipitating CaCO_3 are relatively enriched in the heavier and rare ^{13}C and ^{18}O isotopes. Importantly, the **magnitude and rate of CO_2 and H_2O outgassing** are directly related to the **amount and rate of Ca-carbonate precipitation** based on the carbonate chemical equilibrium (equation 6) and thus the overall scaling progress in a pipeline or other components. The multi-proxy scaling forensic approach of the solid mineral deposits can further be extended by process oriented hydrogeochemical computer modelling, e.g. using the thermodynamic and aqueous speciation based numerical calculations provided in the software PHREEQC (PARKURST & APPELO, 2013; AKIN & KARGI, 2019).



Text-Fig. 17. Concept of Scaling Forensics based on the application of various high spatiotemporal resolution geochemical and imaging analytical techniques. Carbonate scale deposits constitute an evolving chemical-sedimentary environmental archive capturing site-specific natural and technical (operational) thermal water production conditions in their chemical and petrographic compositions. A reconstruction of favourable vs. unfavourable production conditions and process understanding of the variable scaling progress is targeted.

In a **recent case study**, a **scaling forensic approach** of unwanted mineral deposits increased the site-specific process understanding significantly (BOCH et al., 2017a). Two geothermal facilities for district heating and electric power production with similar construction schemes and located close to each other in S-Germany showed rapid deposition (within weeks to few months) of scale-fragments resulting in massive clogging of the tube bundle heat exchangers which consequently disturbed energy transfers and caused repeated shutdowns of the power plants. A detailed – high-resolution scaling forensic – investigation of solid scale materials from different sections of the plants in combination with comprehensive hydrochemical and technical data revealed the occurrence of partially unfavourable natural as well as human-made physicochemical conditions. This included an intimate connection of H₂S (sulfidic) based steel corrosion and enhanced CaCO₃ crystal growth, a critical role of thermal water production cessations and restarts, and the relevance of increased CO₂ concentrations that might be associated with fault zones frequently targeted for hydrogeothermal energy exploitation (BOCH et al., 2017a). The specific character and progress of carbonate scaling and problematic **scale-fragment mobilization** strongly relied on the presence and effects of distinct interfaces (substrate vs. scale vs. fluid flow), the materials used (conventional steel pipes), the scale material consistency (euhedral crystalline, brittle), as well as self-reinforcing feedback mechanisms. It is therefore an example of site-specific fluid-solid interaction. Some of the most relevant processes and effects promoting carbonate scaling will be discussed in the next chapter.

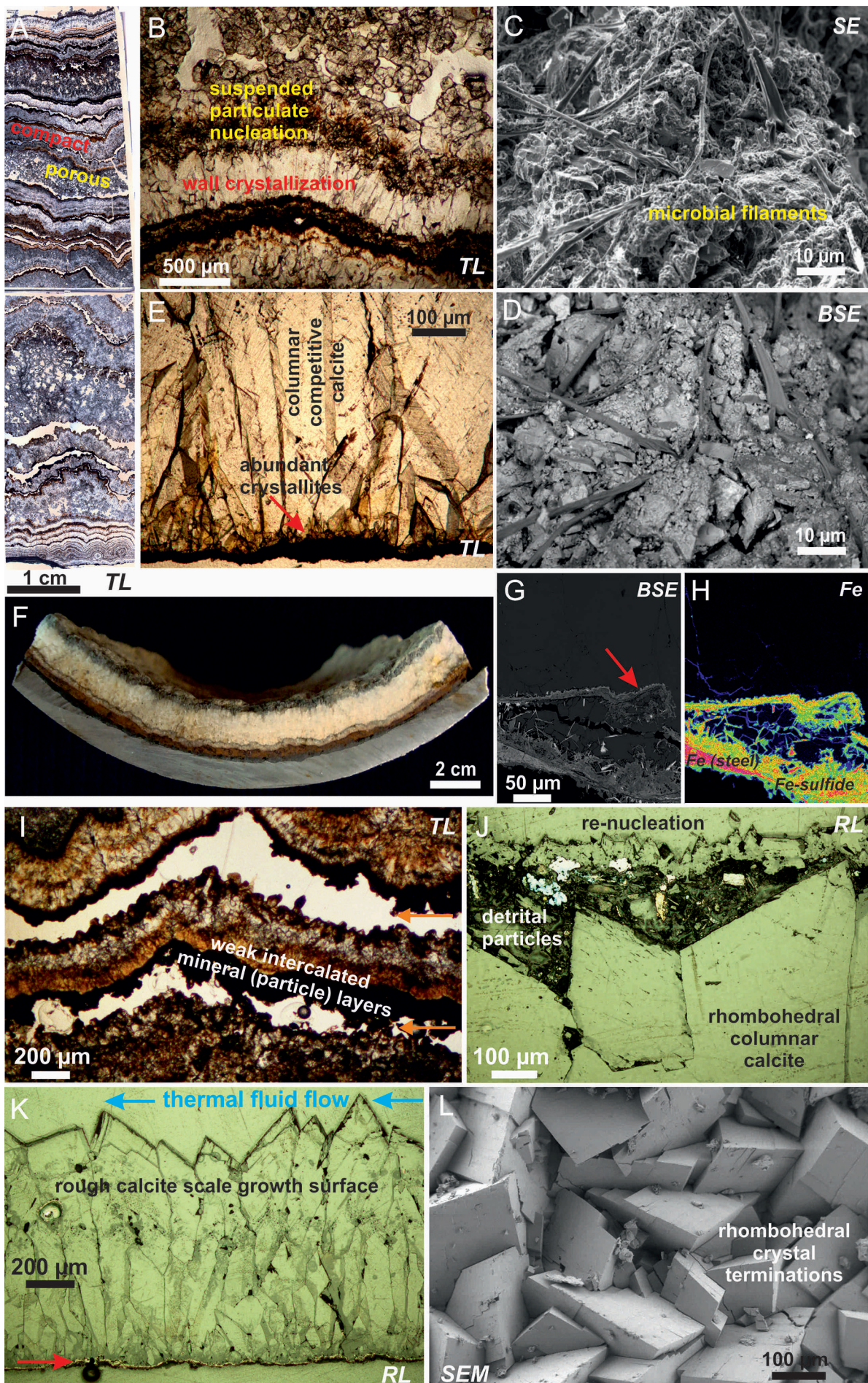
Considering an **application of Scaling Forensics in practice**, this might not be limited to a **late stage clarification** of critical and unwanted processes leading to major scaling and corrosion problems. Rather, it could be implemented in an **early stage evaluation** of potential geogenic and human-made problems and a concomitant site-specific optimization of technical/operational parameters with regard to the most efficient thermal water and energy production. In the future, it could be implemented as a part of a **site-specific testing program** comparable to the well-established hydraulic pumping tests. More specifically, the high spatiotemporal resolution (micrometre range) forensic approach presented facilitates a detailed investigation of even relatively **thin scale coatings** (e.g. millimetre thickness) precipitated within **few days or weeks** only (test phase). These mineral deposits, however, still represent a valuable chemical-sedimentary archive capturing the variable and potentially (un)favourable physicochemical production conditions. The latter could be tested and optimized in a dedicated test series also involving **on-site and online monitoring** of select relevant environmental parameters (e.g. temperature, pressure, flow rate, electric conductivity, pH, pe, pCO₂, particle load, etc.). Importantly, intentionally varied production parameters will be reflected in the precipitated scales, which will effectively allow for a better assessment of site-specific issues (e.g. how the scaling is affected by changes in the aforementioned parameters) and hence allow for optimization of the operating conditions by establishing systematic **countermeasures** to reduce the impact of scaling.

Processes determining carbonate scale material characteristics

Multiple physicochemical processes and related environmental conditions determine the character and extent of mineral deposition in the context of hydrogeothermal scaling and the alteration of materials (e.g. steel corrosion). Focusing on carbonate scaling, the temporally and spatially variable scaling progress and resulting consistencies of the scale materials determine the frequency at which maintenance should be conducted, as well as on the mechanical and chemical cleaning or material treatment procedures that are practical for resolving scaling and/or corrosion problems. Moreover, **different crystallization and depositional mechanisms** yield a broad range of scale materials with different consistencies, from hard and compact to soft and porous. Rhythmic growth successions (layering) and variable material consistencies are a common feature in many scale deposits (Text-Fig. 18; BOCH et al., 2017b).

Carbonate scales can be placed into three major groups based on the dominant depositional mechanism that produced them, these are i) inorganic crystallization, ii) microbially mediated deposition, and iii) particle/fragment mobilization and accumulation. Scale production via **inorganic crystallization** mainly depends on the prevailing hydrochemical production conditions, as well as the chemical and physical properties of the substrate in contact with the thermal water. Inorganic scale formation can be further separated into two sub-groups: i) wall crystallization (heterogeneous scale growth) and ii) suspended particulate nucleation (homogeneous crystallization). **Wall crystallization** refers to crystal nucleation and scale growth on some substrate material (e.g. pipe or heat exchanger surface), whilst **suspended particulate nucleation** of solid phases occurs rather spontaneously in highly supersaturated, gas-rich (bubbling) and/or turbulent water flows (Text-Figs. 18A, B; BRAMSON et al., 1995; BOCH et al., 2016). Regarding inorganic carbonate precipitation in hydrogeothermal settings, the process of variable **CO₂ outgassing** was recognized as highly relevant for scale deposition (ALT-EPPING et al., 2013; WANNER et al., 2017). In principle, CO₂ absorption constitutes another process of potential dissolved inorganic carbonate evolution and subsequent carbonate mineral formation (see equation 7). The latter, however, is restricted to strongly elevated pH (ca. > 10) and strongly reduced CO₂ partial pressure conditions (much lower than atmospheric) of the aqueous solution and is therefore irrelevant for geothermal scaling.

Apart from inorganic controls on crystal growth and fabrics, **microbially mediated processes** can exert a major influence on scale deposition (Text-Figs. 18C, D). These influences comprise of either i) passive or ii) active contributions from the microbial species and communities involved. Typically, extensive microbial presence results in relatively porous fabrics and consequently softer scale consistencies. In various tempered geothermal settings, different bacteria and fungi might be most common (TEMPLETON & BENZERARA, 2015; OSVALD et al., 2017). The distinction and relevance of more passive and more active roles, however, is not strict. **Passive functions of microbial presence** include the availability of an attractive substrate for initial crystal nucleation or particle entrapment owed to the typically large specific surface area and irregularly shaped topography of the filamentous and high-



◀Text-Fig. 18.

Overview on principal depositional mechanisms and specific interfaces affecting the carbonate scale growth dynamics, fabrics and material consistency. A) Transmitted-light (TL) thin section composite image showing a multi-annual Ca-carbonate scale sample comprised of compact vs. porous layers of highly variable thickness reflecting different depositional (growth) mechanisms. B) Compact and brittle calcite scale fabric resulting from wall crystallization (on a substrate) vs. porous and softer fabric resulting from CaCO_3 (calcite and aragonite) crystallite nucleation in suspension preceding agglomeration and cementation. C) Secondary electron (SE) and D) back-scattered electron (BSE) images of microbial communities (biofilms) influencing scale deposition and consistencies in some geothermal facilities. Note the indicative colour contrast in BSE mode based on the relatively low density of the preserved organic tissue. E) Distinct iron-rich mineral layer (red arrows) resulting from steel corrosion at the base of a carbonate scale and constituting an attractive substrate for abundant crystallite nucleation and ongoing columnar and competitive (dense) calcite crystal growth. F) Prominent corroded interface between a conventional steel pipe and the overgrowing calcite scale material. G) Electron microprobe based BSE image and H) Fe concentration distribution at the base of a carbonate scale-fragment (from BOCH et al., 2017a). Progressive H_2S based steel corrosion promotes Fe-sulfidic mineral layers of reduced mechanical strength (cracks, exfoliation). I) Recurrent intercalated (Fe- and Si-rich) loose particle layers within a scale affecting Ca-carbonate crystal growth and the overall mechanical strength (scale consistency). J) Reflected-light (RL) image of intercalated detrital particles flushed onto an euhedral calcite scale growth surface and having an effect on subsequent calcite (re)nucleation. K) RL and L) scanning electron microscope (SEM) images of a rough calcite scale growth surface influencing the streaming thermal fluid (blue arrows) flow resistance and favouring the local occurrence of (micro)turbulences. This interface therefore affects the extent of potential CO_2 and H_2O (steam) outgassing and directly related CaCO_3 precipitation (scaling progress).

ly porous biofilms which they form (RIDING, 2000; JONES & RENAUT, 2010). The nature of these biofilms further influences ongoing crystal growth and possible cementation of trapped particles. The most important **active roles of microbes** regarding scale deposition are their ability to significantly alter chemical gradients in the reactive solution and to catalyse scaling and/or corrosion processes. The former involves hydrochemical adjustments of pH gradients and carbonate alkalinity or the channeling and gradation of specific ionic constituents (e.g. Ca^{2+}) in aqueous solution (PEDLEY, 2013; DIAZ et al., 2017). Concerning catalytic processes, distinct microbes can enable or accelerate carbonate scale growth or corrosive and mostly redox state related reactions (WÜRDEMANN et al., 2016; WESTPHAL et al., 2019). In geothermal installations, chemoautotroph sulphur, iron, manganese, carbon or nitrogen cycling bacterial species dominate the microbial activity and communities and these redox sensitive elements are either oxidized or reduced during specific energy delivering redox reactions (LANNELUC et al., 2015; NOGARA & ZARROUK, 2017). It should be noted, that the occurrence, extent and speciation of microbial influences might not be accurately reflected in the recovered carbonate scale samples, as in many cases only sparse microbial remnants are preserved. Further, scale deposition can occur in the form of **particle/fragment mobilization and accumulation** (Text-Figs. 16F, G, 18J). Based on the high and often turbulent thermal fluid flow conditions, components of diverse sizes – micrometre crystals to centimetre scale-fragments – can be mobilized and subsequently deposited in wells, pipelines or at obstacles (e.g. filter, heat exchanger, pump). The solid particulate components originate from the corrosion of steel pipes, displacement from the aquifer host rocks, defect well casings, homogeneous particle (crystal) nucleation in suspension or the exfoliation of scale-fragments (WOLFGRAMM et al., 2011; BOCH et al., 2017b). Thus, the well sorted or variably sized particles/fragments typically occur as a loose agglomeration in layers or in local traps but might undergo massive (carbonate)

cementation in the course of ongoing thermal fluid flow (Text-Fig. 16G). Processes favouring particle/fragment mobilization are obviously strongly dependent on the geogenic and operational production conditions and are often episodic in their contribution to scale deposits (e.g. after production cessations and restarts).

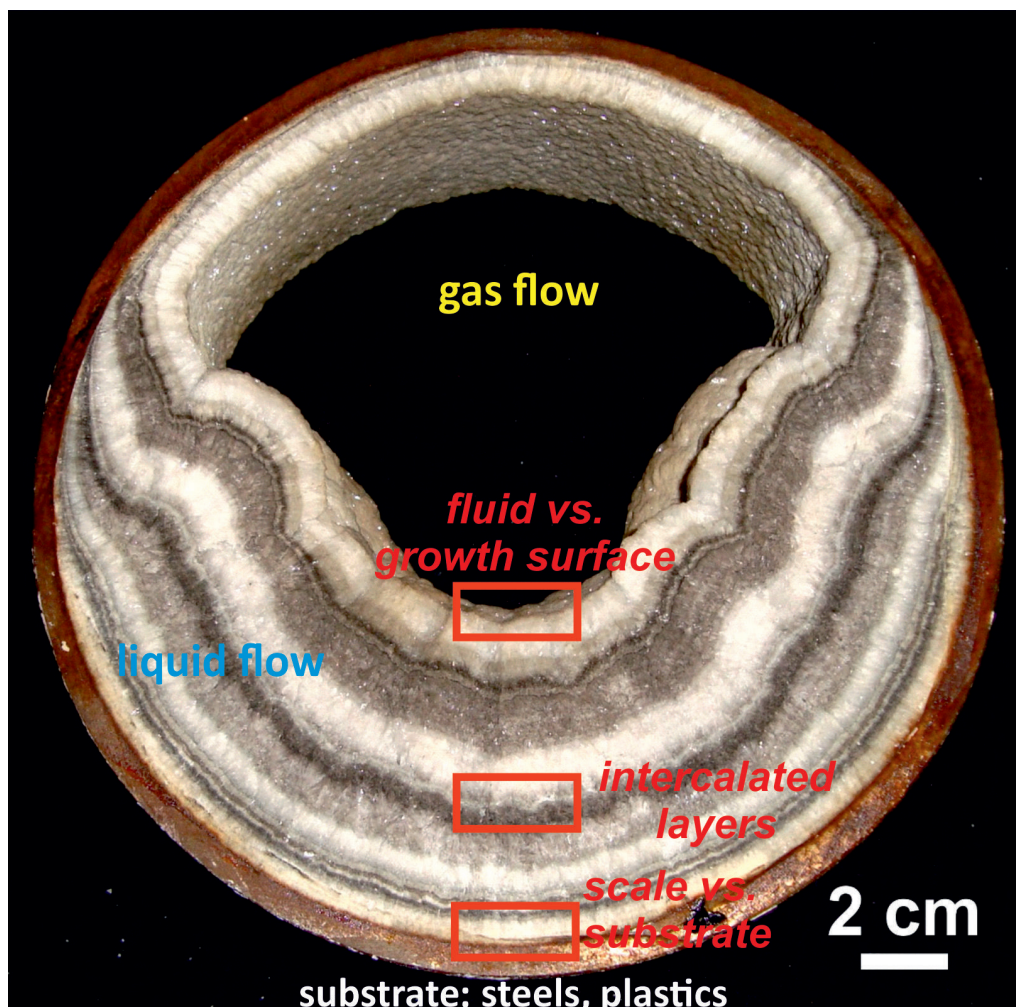
The forensic approach of geothermal production and scaling conditions presented in this chapter further strongly supports **major effects of distinct interfaces** with regard to carbonate scale initiation, growth and related material characteristics. The interfaces primarily addressed comprise of i) the layer or zone between carbonate scale and the underlying substrate material, ii) intercalated mineral (particle) or biofilm layers within the carbonate scales and iii) the scale growth surface versus thermal fluid flow (Text-Fig. 19). Starting with the **interface between carbonate scale and its substrate** (Text-Figs. 18E–H), the initial scale deposition and ongoing crystal growth is strongly affected by the substrate material, i.e. different types of steel (conventional, alloyed) or plastics (PVC, PE, PP) forming the pipes, heat exchangers and other components and surfaces being exposed to the thermal fluid. In particular, distinct mineral layers between steel substrates and scale deposit are of common occurrence and represent mineral formation in the course of different **sulfidic or oxidic steel corrosion mechanisms** (CHOI et al., 2011; LIU et al., 2014). Next to the substrate materials used, the occurrence and character of these **corrosion layers** thus mainly depends on the inorganic – and mostly redox state related – hydrochemical conditions, as well as on potential microbially induced (catalytic) processes enhancing steel corrosion (VALDEZ et al., 2009; NOGARA & ZARROUK, 2017; WESTPHAL et al., 2019). The phenomena of carbonate scaling and steel corrosion have already been recognized as closely interrelated physicochemical processes (STÁHL et al., 2000; MUNDHENK et al., 2013; LI et al., 2019). More specifically, detailed investigations of carbonate scales from Germany and Hungary revealed favoured calcite scale nucleation and crystal growth on the basal corrosion layers (BOCH et al., 2017a, b). This can be explained by the low degree of crystallinity, numerous defect sites, high specific surface area and possible electric charges of typical corroded steel surfaces. Consequently, they constitute an attractive substrate favouring abundant initial crystallite nucleation and crystal growth. Furthermore, the corrosion derived mineral layers made of iron- and other metal (Cu, Zn, Ni) sulphides and (hydr)oxides at the base of the variably thick Ca-carbonate scale deposits provide an interface of reduced mechanical strength. This in turn promotes the evolution of material deteriorating processes such as pitting, cracking, flaking and eventually local scale fragmentation and mobilization (Text-Figs. 18G, H). Considering different substrate materials in contact with the aqueous solution and hosting the scale deposits, **selective leaching of compounds** from fresh or corroded steel components or different types of plastic pipes and coatings, as well as concrete casings could also have an effect on the hydrochemistry and resultant carbonate scaling (HEWITT, 1989; BOCH et al., 2015; GALAN et al., 2019).

In some scale deposits, **recurrent intercalated mineral (particle) or biofilm layers** constitute another distinct interface which can exert some influence on progressive scale growth and the scale material characteristics (Text-Figs. 18I, J). These layers within the scales are of variable

thickness and particle sizes and the mostly iron-rich or siliceous minerals assemble a loose agglomeration of crystals without preferred orientation. Considering their origin, they can be an episodic expression of **allochthonous input** from corroded steel components or of particle displacement from deep aquifer host rocks and through defect borehole casings. Detrital flushing in the course of major production cessations and restarts was observed to be of particular relevance for particle transport (WOLFGRAMM et al., 2011). Alternatively, intercalated layers can also result from **autochthonous microbial activity**, e.g. specific (e.g. iron sulphides/(hydr)oxides) mineral precipitation within temporary biofilms on the scale surface in contact with the thermal fluid (LERM et al., 2013; WÜRDEMANN et al., 2016). The often microbially induced mineral precipitates forming during chemoautotroph redox reactions might remain after the decay of the local biofilms. Regarding the scaling progress and consistency, these intercalated mineral layers have a similar effect compared to the basal corrosion layers: an overall reduced mechanical strength and thus a potential of enhanced scale fragmentation and mobilization, providing an attractive substrate for carbonate scale (re)nucleation and growth, and the release of abrasive particles harming smooth material surfaces (e.g. heat exchangers), coatings (e.g. protective plastic layers) and functional components (e.g. pumps).

Last but not least, the critical interface represented by the **carbonate scale growth surface versus stream-**

ing thermal fluid flow also determines a variable scaling progress, as well as the resulting scale material character (Text-Figs. 18K, L, 19). Depending on the site-specific production conditions and fluid-solid interaction, some scale deposits possess prominently rough growth surfaces as a result of distinct crystal nucleation, competitive crystal growth and ultimately euhedral (e.g. rhombohedral) and oriented crystal terminations and relatively large crystal sizes (Text-Fig. 18K). Importantly, the rough scale growth surface entails an increased flow resistance and the occurrence of (micro)turbulences at this interface, which consequently favours significant CO₂ and H₂O outgassing (bubble/steam formation) and directly related enhanced carbonate (CaCO₃) precipitation (cf. equation 6). This constitutes an in-situ (local small spatial scale turbulences) self-reinforcing mechanism and under conditions of elevated aqueous solution pCO₂ interrelated carbonate (super)saturation and scale formation can be promoted even at elevated operational pressures (e.g. 18 bar) during thermal water production (BOCH et al., 2017a). Moreover, the increased flow-resistance and accompanying shearing forces favour the exfoliation and mobilization of scale-fragments damaging and clogging critical components of the thermal fluid circuit (e.g. filters, heat exchangers). In some geothermal wells and pipelines exhibiting a high gas to water ratio, a two-phase fluid flow might occur, i.e. thermal water and gases (CO₂, H₂O, N₂, CH₄, etc.) as separate but closely related streams (Text-Fig. 19). This typically results in pulsating flow conditions and enhanced turbu-



Text-Fig. 19. Distinct interfaces exerting a major control on carbonate scale initiation, growth and related material characteristics. This involves different substrate (pipe) materials, intercalated mineral (particle) and biofilm layers, as well as the scale growth surface versus fluid flow. In some cases, separated two-phase fluid flows (thermal water + gases) occur and strongly influence the locations and rates of variable scale deposition.

lences. Own investigations on diverse carbonate scales from the Hungarian Pannonian Basin have revealed prominently high average growth rates of such scale materials forming during two-phase pulsating flow conditions. Consequently, these unfavourable geogenic as well as operational conditions should be reduced or avoided, e.g. by increasing the overall working pressures and adjusted flow geometries.

In essence, the distinct scale depositional mechanisms and the specific roles of interfaces contrasting adjacent materials, growth layers and phase transitions strongly influence the overall scaling progress and scale material consistency (durability) and thus the necessary maintenance intervals and cleaning procedures. For example, heterogeneous wall crystallization mostly results in densely packed parallel crystal formation, compact fabrics and a **brittle carbonate scale consistency**, while homogeneous crystallization in suspension is typically manifested in the accumulation of a **loose carbonate mud** (Text-Figs. 18A, B). In some cases, the randomly oriented crystals (c-axis) of the latter might undergo some further compaction and cementation. However, the suspended particulate depositional mechanism typically produces **porous scale fabrics** and a comparatively **rapid scaling progress** (e.g. inner diameter reduction in pipes; Text-Fig. 16). This is also the common case, when extensive microbial biofilms participate in scale deposition, i.e. the resulting scales are often porous and sometimes soft. Nevertheless, the thicker carbonate scales from transport in suspension and subsequent agglomeration or from microbial interaction, might be much easier to **remove mechanically or chemically**. This includes the utilization of a simple or pressurized water hose or the better ingress and interaction of acidified cleaning solutions with regard to softer and more porous scale deposits.

Further, considering the site-specific fluid-solid interaction determining the scale material characteristics, the occurrence and relevance of **interrelated processes** becomes obvious. As an example, a case study on scale-fragment formation in pipelines severely and recurrently clogging the heat exchangers of two major geothermal power plants in Germany revealed the close interrelation of H₂S based steel corrosion and enhanced CaCO₃ crystal growth (BOCH et al., 2017a). The **complex cascade** of interacting processes comprises of various substrate effects on scale nucleation, ongoing crystal growth and fabric development, and the morphology of the scale growth surface mechanically and chemically interacting with the circulating thermal fluid. More specifically, distinct corrosion layers at the scale base have shown to provide an attractive substrate for abundant Ca-carbonate crystallite nucleation and rapid crystal growth but are also the place of preferred mechanical failure and particle/fragment mobilization. In this context, the site-specific role of thermal water **production cessations and abrupt restarts** should be elaborated more critically. This mainly concerns the temporary physicochemical (e.g. redox states) changes accompanying stagnant fluids in the wells and other technical components, the thermal contraction of materials (e.g. steel → cracking and subsequent exfoliation) and potential microbial (re)settlement (habitable environment) during cooling, and the cumulative mobilization of erosive particles, scale- and steel fragments.

Summary and Outlook

The chapters presented in this publication discuss broad, although still select aspects within the extensive field of **modern carbonate research**. Its focus is constrained to a closely related interaction of research questions and methodological approaches situated between **geochemistry and geology**. On several occasions wider interdisciplinary connections to other geoscientific fields (e.g. mineralogy), as well as adjacent scientific and technical fields (e.g. climate research, construction engineering) are established. Considering the carbonate chemical system, the **Ca-carbonates** and more specifically the anhydrous polymorphs calcite and aragonite (CaCO₃), as well as the rarely documented hydrous form ikaite (CaCO₃·6H₂O) constitute mineral formations of primary relevance. Further, Fe-carbonates such as siderite (FeCO₃) and ankerite ([Ca,Fe,Mg]₂[CO₃]₂) are involved in the chapter presenting new investigations of the Erzberg iron ore mine. These carbonate minerals are associated with a highly diverse range of **natural and (geo)technical environmental settings** being exemplified in different chapters. Another principle focus of this work is the critical reflection on the variable **environmental conditions and dependencies** and an advanced **process understanding** of fluid-solid interaction in the course of carbonate precipitation and alteration. The wanted (e.g. speleothem growth in caves) or unwanted (e.g. calcite scaling in geothermal wells) processes are evaluated on strongly **differentiated spatial and temporal scales**. Some of the major conclusions inferred from the selected chapters include:

- The rapid modern development of **in-situ and high-resolution laboratory analytical techniques** (e.g. imaging, chemical composition, isotopic analyses), material- and site-specific **sampling strategies** and field based **on-site and online environmental monitoring** campaigns (e.g. using data loggers) have emerged as important knowledge pacemakers regarding carbonate growth dynamics in natural and human-made environmental settings.
- **Fundamental and applied research** questions and approaches are often closely related and benefit from each other. Regarding distinct chemical-sedimentary processes of carbonate occurrence and characteristics, **widespread analogies** can be recognized. A promising **transfer of knowledge and analytical skills** from fundamental research (e.g. carbonate climate archives) to more applied problems and settings (e.g. carbonate deposition affecting geotechnical infrastructure) is currently evolving. For example, geochemical knowledge and analytical tools associated with natural and site-specific stalagmite growth and cave monitoring have been applied to unwanted and installation-specific carbonate mineralization and its determining natural as well as operational environmental conditions in deep geothermal wells, concrete beds, tunnel drainages and other human-made settings.
- An advanced understanding of **element and isotope fractionation** mechanisms during carbonate precipitation based on laboratory experimental, computer modelled and empirical studies and the utilization of

new (trace) element/isotope chemical systems and analytical techniques increases our knowledge on carbonate mineral-specific crystal nucleation and growth, fabric types and the resulting material consistencies on (geo)technically relevant spatial and temporal scales.

- **Speleothems** made of Ca-carbonate and of diverse age forming in various caves of the Central European Alps constitute a successively deposited archive of the variable **regional climate conditions**. Based on a multi-proxy and mostly high spatial resolution sampling approach of the speleothem carbonate and the cave site-specific growth conditions, valuable paleoclimate information has been extracted, e.g. from the geochemically selected NALPS (northern Alps) stalagmites presented. Precise radiometric **uranium-thorium isotope based chronologies** and high temporal resolution **stable oxygen isotope records** have shown their particular value with regard to distinct climate changes in the past.
- The detailed investigation of typically layered **aragonite-calcite veins** (“Erzbergite”) sealing vertical fractures of the **Erzberg iron ore mine** (Austria) revealed the controlling chemical-sedimentary processes and environmental dependencies of these secondary mineral deposits. This included their formation ages and temperature, precipitation rates, carbonate source rocks, origin and hydrochemical evolution of parent waters, their episodic layering and Ca-carbonate polymorphism, as well as their relation and possible constraints on local fracture formation and their application as a climate archive in an environmentally-sensitive Alpine region. Seemingly well-known rock forming minerals and sediments of the Alps (e.g. at Erzberg) are still **worth to be (re)evaluated**.
- **Unwanted carbonate scaling** frequently impairs hydrogeothermal heat and electric energy exploitation from deep reservoirs relying on natural and human-made (operational) thermal water production conditions. In a **scaling forensic approach** the dominant physicochemical processes determining the **scaling progress** and **scale material characteristics** can be evaluated and adapted. This involves a detailed process understanding of various mineral formation in relation to the local (hydro)geological and technical conditions. **Specific interfaces** within and between solid and fluid phases (e.g. corrosion layers vs. carbonate scale) as well as **production cessations** are of particular relevance. “Scaling Forensics” helped to elucidate facility-specific problems such as ongoing scale-fragment formation and severe blockage of heat exchangers.

Based on the geoscientific topics investigated and discussed in this publication, a large variety of **consecutive and extending research questions** arise. A somewhat subjective outlook with regard to possible fundamental and applied research activities includes the following topics:

- The rapid development of high spatial resolution, in-situ and increased sensitivity laboratory analytical techniques for fluid and solid phase measurements advances our process understanding of **Ca-carbonate**

nucleation and growth dynamics. Ongoing research on the **crystallization mechanisms** of amorphous versus crystalline carbonate phases therefore constitutes a promising field, e.g. investigating controls of the manifold calcite morphologies. This also includes the relevance of **substrate effects** for Ca-carbonate precipitation, e.g. different substrate materials such as various steels, plastics, corrosion layers and coatings and their effects on scaling progress and (un)wanted material consistencies in technical settings.

- Ongoing research efforts further comprise of process-oriented investigations on various **trace element and isotope fractionation behaviours** based on different approaches. This includes the increased understanding of **equilibrium versus kinetic fractionation** with regard to traditional stable isotopes (e.g. C, O), as well as clumped isotopes measured in carbonates. Considering the fundamental **evaluation and calibration** of element and isotope systems, carbonate scale materials deposited in technical settings have shown some attractive potential based on their diverse formational characteristics. In applied settings such as geothermal energy extraction, stable carbon and oxygen isotopes might be used as a **quantitative proxy** for significant changes in fluid temperature, CO₂ and H₂O outgassing and the closely related precipitation (scaling) rate.
- Next to an increased understanding of the depositional dynamics and advanced hydrogeochemical computer modelling, **efficient and sustainable countermeasures** to reduce unwanted carbonate scaling in geotechnical settings are targeted. This includes the preventive future deployment of **field based and automated environmental monitoring tools**, i.e. on-site and online sensors, data loggers and scale guards operating in geothermal wells and pipelines or technical drainages (e.g. in motorway and railway tunnels). The site-specific application and foregoing laboratory based testing of different kinds (additives) of promising **“green inhibitors”** constitute a more intervening although (bio)degradable and environmentally friendly chemical measure suppressing carbonate scale deposition. This also includes the development of systematic and compact (spatial requirements, short duration) field based testing procedures of different commercial and/or blended products and optimized dosages.
- **Scaling Forensics** could be implemented in a **site-specific test phase and procedure** lasting a few days or weeks in the case of thermal water production from deep wells, depending on the local hydrochemistry and rates of scale deposition. In combination with in-situ fluid and operational monitoring this would contribute to a valuable **early stage evaluation** of the specific production conditions in contrast to later stage clarification and problem solving strategies. Thus, it serves major socio-economic interests, i.e. regarding the time, labour input, costs and technical problems associated with maintenance intervals and cleaning procedures in geotechnical infrastructure.
- Considering further fundamental research activities at the **Erzberg iron ore mine**, the application of **new geochemical and mostly isotopic techniques** in-

cluding clumped isotopes (multiply-substituted isotopologues) and non-traditional isotope systems (e.g. $^{56}\text{Fe}/^{54}\text{Fe}$, $^{26}\text{Mg}/^{24}\text{Mg}$) would advance our knowledge on **genetic aspects of the iron ore carbonate**, which still is an ongoing subject of debate. Based on the new and partially unexpected results from the erzbergite veins, the proposed **fracture and fault formation** during young geological times should be assessed critically and a continuation of this work is suggested. Moreover, modern aqueous solutions (e.g. water flows in fractures) encountered at Erzberg revealed an unexpected hydrochemical diversity which could be evaluated in the context of this specific carbonate aquifer and the temporally restrictive (Alpine) hydrogeological and climate conditions.

- **Caves and speleothems** have established as valuable chemical-sedimentary archives mainly relying on their multiple ways of recording paleoenvironmental information, their wide geographical distribution and their geochemical potential for precise chronologies. In most studies published, however, they still suffer from providing only **qualitative climate information** and their compatibility with the **quantitative demand of computer models** calculating past and future climate scenarios is therefore limited. Regardless of the natural complexity and labour intense realization, cave-specific and sophisticated monitoring programs, atmospheric parameter to carbonate **proxy transfer functions and calibrations** might be an obvious way to go.

Acknowledgements

I would like to express my deep gratitude to MARTIN DIETZEL (Graz University of Technology) for the numerous and extensive discussions and invaluable mentoring time on diverse fundamental and applied scientific and interdisciplinary topics. Many thanks to WERNER E. PILLER (Karl-Franzens-University, Graz) for promoting the publication of this manuscript and for being the chairman during my habilitation process. In the latter context, I would like to thank the habilitation committee at TU Graz represented by DANIEL SCOTT KIEFFER, DOROTHEE HIPPLER, MICHAEL WEDENIG, MARTIN DIETZEL, and the dean of the faculty of construction engineering, GERALD ZENZ. The reviewers of my cumulative habilitation thesis (involving chapters of this publication), ANTON EISENHAUER (Geomar, Kiel), INGRID STOBER (Karlsruhe Institute of Technology) and ADRIAN IMMENHAUSER (Ruhr-University Bochum), are also acknowledged accordingly. CHRISTOPH SPÖTL (University of Innsbruck) is acknowledged for his guidance during my PhD studies and earlier scientific career at the Institute of Geology in Innsbruck. ALBRECHT LEIS (JR-AquaConSol

GmbH, Graz) helped in providing his expert knowledge and state-of-the-art stable isotope analyses of carbonates and water samples on many occasions. RICHARD LAWRENCE EDWARDS (University of Minnesota, USA) and HAI CHENG (now at Xi'an Jiaotong University, China) facilitated and guided my Postdoc research activities focusing on uranium-thorium isotope geochemistry at the Department of Earth Sciences in Minneapolis. My sincerest appreciation to JAN KRAMERS (University of Bern, Switzerland; now at University of Johannesburg, South Africa) for his advice during multiple research stays with the isotope geology group in Bern. MICHAEL SARNTHEIN (Christian-Albrechts-University in Kiel) supported my earlier scientific development and provided access to a scientific ocean cruise for drilling sediment cores between Australia and Indonesia (SO-185 VITAL, research vessel SONNE). Further, I would like to thank my professional collaborators in diverse research projects and analytical techniques of the last years, namely TOBIAS KLUGE (University of Heidelberg, Germany), XIANFENG WANG and LIN KE (both at Earth Observatory of Singapore), ANDREA MINDSZENTY (Eötvös Loránd University, Hungary), JÁNOS SZANYI (University of Szeged, Hungary), JÓZSEF DEÁK (GWIS Ltd., Hungary), EDITH HASLINGER (Austrian Institute of Technology, Vienna) and JOHANN E. GOLDBRUNNER (Geoteam GmbH, Graz). GINA E. MOSELEY and MARC LUETSCHER (both at University of Innsbruck) and SILVIA FRISIA (University of Newcastle, Australia) cooperated on cave and speleothem based paleoclimate research partially reported in this publication. Further thanks go to my Institute of Applied Geosciences (IAG) colleagues and collaborators ANDRE BALDERMANN, DOROTHEE HIPPLER, CYRILL GRENGG, STEFANIE EICHINGER and to FLORIAN MITTERMAYR (Institute of Technology & Testing of Building Materials, Graz), WALTER KURZ and CHRISTOPH A. HAUZENBERGER (both at Karl-Franzens-University in Graz). DANIEL SCOTT KIEFFER and DIETMAR KLAMMER, as well as their team consisting of PETER SCHREIBER, DANIELA SOBIAN, ANNA MARIA PENDL and EVELYN REITERER are acknowledged for their support in various IAG organizational skills and works. Special thanks to JUDITH JERNEJ, MARIA HIERZ, ANDREA WOLF and SYLVIA PERCHTHOLD considering their dedicated and often prompt analytical work in our institute's laboratories. OTHMAR NESTROY and HANS ZOJER (both at IAG) provided experienced and friendly advice on scientific and other topics. RALF BENISCHKE (IAG) and PETER REICHL (Amt der Steirischen Landesregierung, Graz) are acknowledged for their help during several field operations. My best thanks to FRITZ GEISLER (Katerloch Cave, Weiz) and HANNES M. PLUCH (VA Erzberg GmbH) for providing access and operational skills at the respective study sites. Many thanks also to KATHLEEN A. WENDT (University of Innsbruck) and ISAAC J. KELL DUIVESTEIN for English language proofreading of selected chapters. Finally, I would like to thank my partner in life ALEXANDRA KILARSKI for many great moments and experiences living in Innsbruck, Graz and Vienna.

References

- AFFEK, H.P., MATTHEWS, A., AYALON, A., BAR-MATTHEWS, M., BURSTYN, Y., ZAARUR, S. & ZILBERMAN, T. (2014): Accounting for kinetic isotope effects in Soreq Cave (Israel) speleothems. – *Geochimica et Cosmochimica Acta*, **143**, 303–318, New York.
- AKIN, T. & KARGI, H. (2019): Modeling the geochemical evolution of fluids in geothermal wells and its implication for sustainable energy production. – *Geothermics*, **77**, 115–129, Amsterdam.
- AL HELAL, A., SOAMES, A., GUBNER, R., IGLAUER, S. & BARIFCANI, A. (2018): Influence of magnetic fields on calcium carbonate scaling in aqueous solutions at 150°C and 1 bar. – *Journal of Colloid and Interface Science*, **509**, 472–484, Amsterdam.
- ALT-EPPING, P., WABER, H.N., DIAMOND, L.W. & EICHINGER, L. (2013): Reactive transport modeling of the geothermal system at Bad Blumau, Austria: Implications of the combined extraction of heat and CO₂. – *Geothermics*, **45**, 18–30, Amsterdam.
- ANGEL, F. (1939): Unser Erzberg. – *Mitteilungen des Naturwissenschaftlichen Vereines für Steiermark*, **75**, 227–321, Graz.
- ARNDT, M., VIRGO, S., COX, S.F. & URAI, J.L. (2014): Changes in fluid pathways in a calcite vein mesh (Natih Formation, Oman Mountains): insights from stable isotopes. – *Geofluids*, **14**, 391–418, Oxford.
- ARP, G., THIEL, V., REIMER, A., MICHAELIS, W. & REITNER, J. (1999): Biofilm exopolymers control microbialite formation at thermal springs discharging into the alkaline Pyramid Lake, Nevada, USA. – *Sedimentary Geology*, **126**, 159–176, Amsterdam.
- ASRAT, A., BAKER, A., MOHAMMED, M.U., LENG, M.J., CALSTEREN, P.V. & SMITH, C. (2007): A high-resolution multi-proxy stalagmite record from Mechara, Southeastern Ethiopia: palaeohydrological implications for speleothem palaeoclimate reconstruction. – *Journal of Quaternary Science*, **22**, 53–63, Chichester.
- AUER, I., BÖHM, R., JURKOVIC, A., LIPA, W., ORLIK, A., POTZMANN, R., SCHÖNER, W., UNGERSBÖCK, M., MATULLA, C., BRIFFA, K., JONES, P., EFTHYMIADIS, D., BRUNETTI, M., NANNI, T., MAUGERI, M., MERCALDI, L., MESTRE, O., MOISSELIN, J.-M., BEGERT, M., MÜLLER-WESTERMEIER, G., KVETON, V., BOCHNICEK, O., STASTNY, P., LAPIN, M., SZALAI, S., SZENTIMREY, T., CEGNAR, T., DOLINAR, M., GAJIC-CAPKA, M., ZANINOVIC, K., MAJSTOROVIC, Z. & NIEPLOVA, E. (2007): HISTALP – historical instrumental climatological surface time series of the Greater Alpine Region. – *International Journal of Climatology*, **27**, 17–46, Chichester.
- BAJO, P., BORSATO, A., DRYSDALE, R., HUA, Q., FRISIA, S., ZANCHETTA, G., HELLSTROM, J. & WOODHEAD, J. (2017): Stalagmite carbon isotopes and dead carbon proportion (DCP) in a near-closed-system situation: An interplay between sulphuric and carbonic acid dissolution. – *Geochimica et Cosmochimica Acta*, **210**, 208–227, New York.
- BAKER, A., SMITH, C.L., JEX, C., FAIRCHILD, I.J., GENTY, D. & FULLER, L. (2008): Annually Laminated Speleothems: a Review. – *International Journal of Speleology*, **37**, 193–206, Tampa.
- BALAN, E., NOIREAUX, J., MAVROMATIS, V., SALDI, G., MONTQUILLIOUT, V., BLANCHARD, M., PIETRUCCHI, F., GERVAIS, C., RUSTAD, J.R., SCHOTT, J. & GAILLARDET, J. (2018): Theoretical isotopic fractionation between structural boron in carbonates and aqueous boric acid and borate ion. – *Geochimica et Cosmochimica Acta*, **222**, 117–129, New York.
- BALDERMANN, A., DEDITIUS, A.P., DIETZEL, M., FICHTNER, V., FISCHER, C., HIPPLER, D., LEIS, A., BALDERMANN, C., MAVROMATIS, V., STICKLER, C.P. & STRAUSS, H. (2015): The role of bacterial sulfate reduction during dolomite precipitation: Implications from Upper Jurassic platform carbonates. – *Chemical Geology*, **412**, 1–14, Amsterdam.
- BALDINI, J.U.L., MCDERMOTT, F., HOFFMANN, D.L., RICHARDS, D.A. & CLIPSON, N. (2008): Very high-frequency and seasonal cave atmosphere PCO₂ variability: Implications for stalagmite growth and oxygen isotope-based paleoclimate records. – *Earth and Planetary Science Letters*, **272**, 118–129, Amsterdam.
- BARKER, S., KNORR, G., EDWARDS, R.L., PARRENIN, F., PUTNAM, A.E., SKINNER, L.C., WOLFF, E. & ZIEGLER, M. (2011): 800,000 Years of Abrupt Climate Variability. – *Science*, **334**, 347–351, Washington, D.C.
- BARKER, S., CHEN, J., GONG, X., JONKERS, L., KNORR, G. & THORNALLEY, D. (2015): Icebergs not the trigger for North Atlantic cold events. – *Nature*, **520**, 333–336, London.
- BAROŇ, I., PLAN, L., SOKOL, L., GRASEMANN, B., MELICHAR, R., MITROVIC, I. & STEMBERK, J. (2019): Present-day kinematic behaviour of active faults in the Eastern Alps. – *Tectonophysics*, **752**, 1–23, Amsterdam.
- BARTA, G. (2014): Paleoenvironmental reconstruction based on the morphology and distribution of secondary carbonates of the loess-paleosol sequence at Süttő, Hungary. – *Quaternary International*, **319**, 64–75, Oxford.
- BERGER, A. & LOUTRE, M.F. (2002): An Exceptionally Long Interglacial Ahead? – *Science*, **297**, 1287–1288, Washington, D.C.
- BERNER, R.A. (1975): The role of magnesium in the crystal growth of calcite and aragonite from sea water. – *Geochimica et Cosmochimica Acta*, **39**, 489–504, New York.
- BISCHOFF, J.L., FITZPATRICK, J.A. & ROSENBAUER, R.J. (1993): The Solubility and Stabilization of ikaite (CaCO₃·6H₂O) from 0 °C to 25 °C: Environmental and Paleoclimatic Implications for Thinolite Tufa. – *The Journal of Geology*, **101**, 21–33, London.
- BJØRNSTAD, T. & STAMATAKIS, E. (2006): Mechanisms of mineral scaling in oil and geothermal wells studied in laboratory experiments by nuclear techniques. – *Czechoslovak Journal of Physics*, **56**, 405–416, Prague.
- BLYTH, A.J., HARTLAND, A. & BAKER, A. (2016): Organic proxies in speleothems – New developments, advantages and limitations. – *Quaternary Science Reviews*, **149**, 1–17, Amsterdam.
- BOCH, R. (2008): Stalagmites from Katerloch Cave, Austria: Growth dynamics and high-resolution records of climate change. – PhD thesis, University of Innsbruck, 223 pp., Innsbruck.
- BOCH, R. & SPÖTL, C. (2011): Reconstructing palaeoprecipitation from an active cave flowstone. – *Journal of Quaternary Science*, **26**, 675–687, Chichester.
- BOCH, R., SPÖTL, C., REITNER, J.M. & KRAMERS, J. (2005): A Late-glacial travertine deposit in Eastern Tyrol (Austria). – *Austrian Journal of Earth Sciences*, **98**, 78–91, Wien.
- BOCH, R., SPÖTL, C. & KRAMERS, J. (2009): High-resolution isotope records of early Holocene rapid climate change from two coeval stalagmites of Katerloch Cave, Austria. – *Quaternary Science Reviews*, **28**, 2527–2538, Amsterdam.
- BOCH, R., SPÖTL, C. & KRAMERS, J. (2010): Wachstumsphasen von Stalagmiten im Katerloch (2833/59). – *Die Höhle*, **61**, 48–56, Wien.
- BOCH, R., SPÖTL, C. & FRISIA, S. (2011a): Origin and palaeoenvironmental significance of lamination in stalagmites from Katerloch Cave, Austria. – *Sedimentology*, **58**, 508–531, Amsterdam.
- BOCH, R., CHENG, H., SPÖTL, C., EDWARDS, R.L., WANG, X. & HÄUSELMANN, P. (2011b): NALPS: a precisely dated European climate record 120–60 ka. – *Climate of the Past*, **7**, 1247–1259, Göttingen.

- BOCH, R., DIETZEL, M., REICHL, P., LEIS, A., BALDERMANN, A., MITTERMAYR, F. & PÖLT, P. (2015): Rapid ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) crystallization in a man-made river bed: Hydrogeochemical monitoring of a rarely documented mineral formation. – *Applied Geochemistry*, **63**, 366–379, Amsterdam.
- BOCH, R., SZANYI, J., LEIS, A., MINDSZENTY, A., DEÁK, J., KLUGE, T., HIPPLER, D., DEMÉNY, A. & DIETZEL, M. (2016): Geothermal Carbonate Scaling: Forensic Studies Applying High-Resolution Geochemical Methods. – Proceedings of the European Geothermal Congress, paper #111, 1–10, Strasbourg.
- BOCH, R., LEIS, A., HASLINGER, E., GOLDBRUNNER, J.E., MITTERMAYR, F., FRÖSCHL, H., HIPPLER, D. & DIETZEL, M. (2017a): Scale-fragment formation impairing geothermal energy production: interacting H_2S corrosion and CaCO_3 crystal growth. – *Geothermal Energy*, **5**: 4, <https://dx.doi.org/10.1186/s40517-017-0062-3>
- BOCH, R., LEIS, A., MINDSZENTY, A., GOLDBRUNNER, J.E., SZANYI, J., DEÁK, J., HASLINGER, E., VIRÁG, M., MITTERMAYR, F. & DIETZEL, M. (2017b): Scaling Forensics: Evaluating geothermal production conditions from scales as chemical-sedimentary archives. – Proceedings of the German Geothermal Congress 2017, paper #P6, 1–12, Munich.
- BOCH, R., WANG, X., KLUGE, T., LEIS, A., LIN, K., PLUCH, H., MITTERMAYR, F., BALDERMANN, A., BÖTTCHER, M.E. & DIETZEL, M. (2019): Aragonite–calcite veins of the ‘Erzberg’ iron ore deposit (Austria): Environmental implications from young fractures. – *Sedimentology*, **66**, 604–635, Amsterdam.
- BONIFACIE, M., CALMELS, D., EILER, J.M., HORITA, J., CHADUTEAU, C., VASCONCELOS, C., AGRINIER, P., KATZ, A., PASSEY, B.H., FERRY, J.M. & BOURRAND, J.-J. (2017): Calibration of the dolomite clumped isotope thermometer from 25 to 350°C, and implications for a universal calibration for all (Ca, Mg, Fe) CO_3 carbonates. – *Geochimica et Cosmochimica Acta*, **200**, 255–279, New York.
- BORSATO, A., FRISIA, S., FAIRCHILD, I.J., SOMOGYI, A. & SUSINI, J. (2007): Trace element distribution in annual stalagmite laminae mapped by micrometer-resolution X-ray fluorescence: Implications for incorporation of environmentally significant species. – *Geochimica et Cosmochimica Acta*, **71**, 1494–1512, New York.
- BORSATO, A., FRISIA, S., WYNN, P.M., FAIRCHILD, I.J. & MIORANDI, R. (2015): Sulphate concentration in cave dripwater and speleothems: long-term trends and overview of its significance as proxy for environmental processes and climate changes. – *Quaternary Science Reviews*, **127**, 48–60, Amsterdam.
- BOTS, P., BENNING, L.G., RODRIGUEZ-BLANCO, J.-D., RONCAL-HERRERO, T. & SHAW, S. (2012): Mechanistic Insights into the Crystallization of Amorphous Calcium Carbonate (ACC). – *Crystal Growth and Design*, **12**, 3806–3814, Washington, D.C.
- BÖTTCHER, M.E. & DIETZEL, M. (2010): Metal-ion partitioning during low-temperature precipitation and dissolution of anhydrous carbonates and sulphates. – *EMU Notes in Mineralogy*, **10**, 139–187.
- BRAMSON, D., HASSON, D. & SEMIAT, R. (1995): The roles of gas bubbling, wall crystallization and particulate deposition in CaSO_4 scale formation. – *Desalination*, **100**, 105–113, Amsterdam.
- BRAND, U. (1994): Morphochemical and replacement diagenesis of biogenic carbonates. – *Developments in Sedimentology*, **51**, 217–282, Amsterdam.
- BRAUER, A., ALLEN, J.R.M., MINGRAM, J., DULSKI, P., WULF, S. & HUNTLEY, B. (2007): Evidence for last interglacial chronology and environmental change from Southern Europe. – *Proceedings of the National Academy of Sciences*, **104**, 450–455, Allahabad.
- BROGI, A., CAPEZZUOLI, E., BURACCHI, E. & BRANCA, M. (2012): Tectonic control on travertine and calcareous tufa deposition in a low-temperature geothermal system (Sarteano, Central Italy). – *Journal of the Geological Society*, **169**, 461–476, London.
- BRONK RAMSEY, C. & LEE, S. (2013): Recent and planned developments of the program OxCal. – *Radiocarbon*, **55**, 720–730, Cambridge.
- BRYDA, G., VAN HUSEN, D., KREUSS, O., KOUKAL, V., MOSER, M., PAVLIK, W., SCHÖNLAUB, H.P. & WAGREICH, M. (2013): Erläuterungen zu Blatt 101 Eisenerz. – 223 pp., Geologische Bundesanstalt, Wien.
- BUSCHEK, T.A., BIELICKI, J.M., CHEN, M., SUN, Y., HAO, Y., EDMUNDS, T.A., SAAR, M.O. & RANDOLPH, J.B. (2014): Integrating CO_2 Storage with Geothermal Resources for Dispatchable Renewable Electricity. – *Energy Procedia*, **63**, 7619–7630, Amsterdam.
- BUSENBERG, E. & PLUMMER, L.N. (1985): Kinetic and thermodynamic factors controlling the distribution of SO_4^{2-} and Na^+ in calcites and selected aragonites. – *Geochimica et Cosmochimica Acta*, **49**, 713–725, New York.
- CANDIDO, C.A.S. & ZARROUK, S.J. (2017): Scaling Mitigations for the Binary Plant Vaporizer: Upper Mahiao, the Philippines. – Proceedings 39th New Zealand Geothermal Workshop, Rotorua, 1–8, Rotorua, New Zealand.
- CAPEZZUOLI, E., GANDIN, A. & PEDLEY, M. (2014): Decoding tufa and travertine (fresh water carbonates) in the sedimentary record: The state of the art. – *Sedimentology*, **61**, 1–21, Amsterdam.
- CARROLL, J.J., SLUPSKY, J.D. & MATHER, A.E. (1991): The Solubility of Carbon Dioxide in Water at Low Pressure. – *Journal of Physical and Chemical Reference Data*, **20**, 1201–1209, Melville, N.Y.
- CASELLA, L.A., GRISSHABER, E., YIN, X., ZIEGLER, A., MAVROMATIS, V., MÜLLER, D., RITTER, A.C., HIPPLER, D., HARPER, E.M., DIETZEL, M., IMMENHAUSER, A., SCHÖNE, B.R., ANGIOLINI, L. & SCHMAHL, W.W. (2017): Experimental diagenesis: insights into aragonite to calcite transformation of *Arctica islandica* shells by hydrothermal treatment. – *Biogeosciences*, **14**, 1461–1492, Washington, D.C.
- CELLE-JEANTON, H., TRAVI, Y. & BLAVOUX, B. (2001): Isotopic typology of the precipitation in the Western Mediterranean Region at three different time scales. – *Geophysical Research Letters*, **28**, 1215–1218, Washington, D.C.
- CHAFETZ, H.S. & GUIDRY, S.A. (1999): Bacterial shrubs, crystal shrubs, and ray-crystal shrubs: bacterial vs. abiotic precipitation. – *Sedimentary Geology*, **126**, 57–74, Amsterdam.
- CHANG, L.L.Y., DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1998): *Rock-Forming Minerals – Non-silicates: Sulphates, Carbonates, Phosphates and Halides*. – 2nd edition, 383 pp., Geological Society of London, London.
- CHAUSSEMIER, M., POURMOHTASHAM, E., GELUS, D., PÉCOUL, N., PERROT, H., LÉDION, J., CHEAP-CHARPENTIER, H. & HORNER, O. (2015): State of art of natural inhibitors of calcium carbonate scaling – A review article. – *Desalination*, **356**, 47–55, Amsterdam.
- CHEN, Y., CUI, Y., GUIMOND BARRETT, A., CHILLE, F. & LASSALLE, S. (2019): Investigation of calcite precipitation in the drainage system of railway tunnels. – *Tunnelling and Underground Space Technology*, **84**, 45–55, Oxford.
- CHENG, H., LAWRENCE EDWARDS, R., SHEN, C.-C., POLYAK, V.J., ASMEROM, Y., WOODHEAD, J., HELLSTROM, J., WANG, Y., KONG, X., SPÖTL, C., WANG, X. & CALVIN ALEXANDER JR, E. (2013): Improvements in ^{230}Th dating, ^{230}Th and ^{234}U half-life values, and U–Th isotopic measurements by multi-collector inductively coupled plasma mass spectrometry. – *Earth and Planetary Science Letters*, **371/372**, 82–91, Amsterdam.
- CHENG, H., EDWARDS, R.L., SINHA, A., SPÖTL, C., YI, L., CHEN, S., KELLY, M., KATHAYAT, G., WANG, X., LI, X., KONG, X., WANG, Y., NING, Y. & ZHANG, H. (2016): The Asian monsoon over the past 640,000 years and ice age terminations. – *Nature*, **534**, 640–646, London.
- CHOI, Y.-S., NESIC, S. & LING, S. (2011): Effect of H_2S on the CO_2 corrosion of carbon steel in acidic solutions. – *Electrochimica Acta*, **56**, 1752–1760, Kidlington.
- CLARK, I.D. & FRITZ, P. (1997): *Environmental Isotopes in Hydrogeology*. – CRC Press LLC, 1st ed., 352 pp., Boca Raton.

- CLARKSON, J.R., PRICE, T.J. & ADAMS, C.J. (1992): Role of metastable phases in the spontaneous precipitation of calcium carbonate. – *Journal of the Chemical Society, Faraday Transactions*, **88**, 243–249, London.
- COLLISTER, C. & MATTEY, D. (2008): Controls on water drop volume and speleothem drip sites: An experimental study. – *Journal of Hydrology*, **358**, 259–267, Amsterdam.
- COLUCCI, R.R., LUETSCHER, M., FORTE, E., GUGLIELMIN, M., LENAZ, D., PRINCIVALLE, F. & VITA, F. (2017): First alpine evidence of in situ coarse cryogenic cave carbonates (CCC_{coarse}). – *Geografia Fisica e Dinamica Quaternaria*, **40**, 53–59, Torino.
- COPLEN, T.B. (2007): Calibration of the calcite–water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory. – *Geochimica et Cosmochimica Acta*, **71**, 3948–3957, New York.
- CORSI, R. (1986): Scaling and corrosion in geothermal equipment: problems and preventive measures. – *Geothermics*, **15**, 839–856, Amsterdam.
- COUNCIL, T.C. & BENNETT, P.C. (1993): Geochemistry of ikaite formation at Mono Lake, California: Implications for the origin of tufa mounds. – *Geology*, **21**, 971–974, Washington, D.C.
- CRAIG, H. (1961): Isotopic variations in meteoric waters. – *Science*, **133**, 1702–1703, Washington, D.C.
- CRUZ, F.W., BURNS, S.J., KARMANN, I., SHARP, W.D., VUILLE, M., CARDOSO, A.O., FERRARI, J.A., DIAS, P.L.S. & VIANA, O. (2005): Insolation-driven changes in atmospheric circulation over the past 116,000 years in subtropical Brazil. – *Nature*, **434**, 63–66, London.
- DAÉRON, M., GUO, W., EILER, J., GENTY, D., BLAMART, D., BOCH, R., DRYSDALE, R., MAIRE, R., WAINER, K. & ZANCHETTA, G. (2011): ¹³C/¹⁸O clumping in speleothems: Observations from natural caves and precipitation experiments. – *Geochimica et Cosmochimica Acta*, **75**, 3303–3317, New York.
- DAÉRON, M., BLAMART, D., PERAL, M. & AFFEK, H.P. (2016): Absolute isotopic abundance ratios and the accuracy of Δ_{47} measurements. – *Chemical Geology*, **442**, 83–96, Amsterdam.
- DAÉRON, M., DRYSDALE, R.N., PERAL, M., HUYGHE, D., BLAMART, D., COPLEN, T.B., LARTAUD, F. & ZANCHETTA, G. (2019): Most Earth-surface calcites precipitate out of isotopic equilibrium. – *Nature Communications*, **10**: 429, London. <https://dx.doi.org/10.1038/s41467-019-08336-5>
- DANDURAND, J.L., GOUT, R., HOEFS, J., MENSCHER, G., SCHOTT, J. & USDOWSKI, E. (1982): Kinetically controlled variations of major components and carbon and oxygen isotopes in a calcite-precipitating spring. – *Chemical Geology*, **36**, 299–315, Amsterdam.
- DAY, C.C. & HENDERSON, G.M. (2013): Controls on trace-element partitioning in cave-analogue calcite. – *Geochimica et Cosmochimica Acta*, **120**, 612–627, New York.
- DE BOEVER, E., BRASIER, A.T., FOUBERT, A. & KELE, S. (2017): What do we really know about early diagenesis of non-marine carbonates? – *Sedimentary Geology*, **361**, 25–51, Amsterdam.
- DECKER, K., PERESSON, H. & HINSCH, R. (2005): Active tectonics and Quaternary basin formation along the Vienna Basin Transform fault. – *Quaternary Science Reviews*, **24**, 305–320, Amsterdam.
- DEGRYSE, P. & VANHAECKE, F. (2016): Status and prospects for quasi-non-destructive analysis of ancient artefacts via LA-ICP-MS. – *Elements*, **12**, 341–346, Québec.
- DEINES, P., LANGMUIR, D. & HARMON, R.S. (1974): Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. – *Geochimica et Cosmochimica Acta*, **38**, 1147–1164, New York.
- DEMÉNY, A. & SIKLÓSY, Z. (2008): Combination of off-line preparation and continuous flow mass spectrometry: D/H analyses of inclusion waters. – *Rapid Communications in Mass Spectrometry*, **22**, 1329–1334, Chichester.
- DEMÉNY, A., NÉMETH, P., CZUPPON, G., LEÉL-ŐSSY, S., SZABÓ, M., JUDIK, K., NÉMETH, T. & STIEBER, J. (2016a): Formation of amorphous calcium carbonate in caves and its implications for speleothem research. – *Scientific Reports*, **6**: 39602, London. <https://dx.doi.org/10.1038/srep39602>
- DEMÉNY, A., CZUPPON, G., KERN, Z., LEÉL-ŐSSY, S., NÉMETH, A., SZABÓ, M., TÓTH, M., WU, C.-C., SHEN, C.-C., MOLNÁR, M., NÉMETH, T., NÉMETH, P. & ÓVÁRI, M. (2016b): Recrystallization-induced oxygen isotope changes in inclusion-hosted water of speleothems – Paleoclimatological implications. – *Quaternary International*, **415**, 25–32, Oxford.
- DEMÉNY, A., KERN, Z., CZUPPON, G., NÉMETH, A., LEÉL-ŐSSY, S., SIKLÓSY, Z., LIN, K., HU, H.-M., SHEN, C.-C., VENNEMANN, T.W. & HASZPRA, L. (2017): Stable isotope compositions of speleothems from the last interglacial – Spatial patterns of climate fluctuations in Europe. – *Quaternary Science Reviews*, **161**, 68–80, Amsterdam.
- DEMIR, M.M., BABA, A., ATILLA, V. & INANLI, M. (2014): Types of the scaling in hyper saline geothermal system in northwest Turkey. – *Geothermics*, **50**, 1–9, Amsterdam.
- DENNISTON, R.F. & LUETSCHER, M. (2017): Speleothems as high-resolution paleoflood archives. – *Quaternary Science Reviews*, **170**, 1–13, Amsterdam.
- DEPAOLO, D.J., COLE, D.R., NAVROTSKY, A. & BOURG, I.C. (2013): Geochemistry of Geologic Carbon Sequestration: An Overview. – *Reviews in Mineralogy and Geochemistry*, **77**, 1–14, Washington, D.C.
- DETTMAN, D.L., REISCHE, A.K. & LOHMANN, K.C. (1999): Controls on the stable isotope composition of seasonal growth bands in aragonitic fresh-water bivalves (unioniëe). – *Geochimica et Cosmochimica Acta*, **63**, 1049–1057, New York.
- DE YOREO, J.J., GILBERT, P.U.P.A., SOMMERDIJK, N.A.J.M., PENN, R.L., WHITELAM, S., JOESTER, D., ZHANG, H., RIMER, J.D., NAVROTSKY, A., BANFIELD, J.F., WALLACE, A.F., MICHEL, F.M., MELDRUM, F.C., CÖLFEN, H. & DOVE, P.M. (2015): Crystallization by particle attachment in synthetic, biogenic, and geologic environments. – *Science*, **349**, 6247, aaa6760.
- DIAZ, M.R., EBERLI, G.P., BLACKWELDER, P., PHILLIPS, B. & SWART, P.K. (2017): Microbially mediated organomineralization in the formation of ooids. – *Geology*, **45**, 771–774, Washington, D.C.
- DIECKMANN, G.S., NEHRKE, G., PAPADIMITRIOU, S., GÖTTLICHER, J., STEININGER, R., KENNEDY, H., WOLF-GLADROW, D. & THOMAS, D.N. (2008): Calcium carbonate as ikaite crystals in Antarctic sea ice. – *Geophysical Research Letters*, **35**: L08501, Washington, D.C. <https://dx.doi.org/10.1029/2008GL033540>
- DIETZEL, M. & BOCH, R. (2018): Radiometrische Altersdatierung von historischem Kalkmörtel – Geochemische Voraussetzungen und Ansätze zur Interpretation. – in press.
- DIETZEL, M., USDOWSKI, E. & HOEFS, J. (1992): Chemical and ¹³C/¹²C- and ¹⁸O/¹⁶O-isotope evolution of alkaline drainage waters and the precipitation of calcite. – *Applied Geochemistry*, **7**, 177–184, Amsterdam.
- DIETZEL, M., GUSSONE, N. & EISENHAUER, A. (2004): Co-precipitation of Sr²⁺ and Ba²⁺ with aragonite by membrane diffusion of CO₂ between 10 and 50 °C. – *Chemical Geology*, **203**, 139–151, Amsterdam.
- DIETZEL, M., TANG, J., LEIS, A. & KÖHLER, S.J. (2009): Oxygen isotopic fractionation during inorganic calcite precipitation. – Effects of temperature, precipitation rate and pH. – *Chemical Geology*, **268**, 107–115, Amsterdam.
- DIETZEL, M., PURGSTALLER, B., LEIS, A., REICHL, P., STADLER, H., NIEDERMAIR, A., RINDER, T. & WAGNER, H. (2013): Current challenges for scaling of tunnel drainage systems – Modelling approaches, monitoring tools and prevention strategies. – *Geomechanics and Tunneling*, **6**, 743–753, Berlin.

- DOMÍNGUEZ-VILLAR, D., KRKLEC, K., PELICON, P., FAIRCHILD, I.J., CHENG, H. & EDWARDS, L.R. (2017): Geochemistry of speleothems affected by aragonite to calcite recrystallization. – Potential inheritance from the precursor mineral. – *Geochimica et Cosmochimica Acta*, **200**, 310–329, New York.
- DOMÍNGUEZ-VILLAR, D., LOJEN, S., KRKLEC, K., KOZDON, R., EDWARDS, R.L. & CHENG, H. (2018): Ion microprobe $\delta^{18}\text{O}$ analyses to calibrate slow growth rate speleothem records with regional $\delta^{18}\text{O}$ records of precipitation. – *Earth and Planetary Science Letters*, **482**, 367–376, Amsterdam.
- DREYBRODT, W. & ROMANOV, D. (2016): The evolution of ^{13}C and ^{18}O isotope composition of DIC in a calcite depositing film of water with isotope exchange between the DIC and a CO_2 containing atmosphere, and simultaneous evaporation of the water. Implication to climate proxies from stalagmites: A theoretical model. – *Geochimica et Cosmochimica Acta*, **195**, 323–338, New York.
- D'SOUZA, S.M., ALEXANDER, C., CARR, S.W., WALLER, A.M., WHITCOMBE, M.J. & VULFSON, E.N. (1999): Directed nucleation of calcite at a crystal-imprinted polymer surface. – *Nature*, **398**, 312–316, London.
- DUAN, Z. & SUN, R. (2003): An improved model calculating CO_2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. – *Chemical Geology*, **193**, 257–271, Amsterdam.
- DUBLYANSKY, Y.V. (2012): Hydrothermal Caves. – In: WHITE, W.B. & CULVER, D.C. (Eds.): *Encyclopedia of Caves*, Chennai Academic Press, 2nd ed., 391–397, Amsterdam.
- DUBLYANSKY, Y.V. & SPÖTL, C. (2009): Hydrogen and oxygen isotopes of water from inclusions in minerals: design of a new crushing system and on-line continuous-flow isotope ratio mass spectrometric analysis. – *Rapid Communications in Mass Spectrometry*, **23**, 2605–2613, Chichester.
- DUBLYANSKY, Y.V. & SPÖTL, C. (2010): Evidence for a hypogene paleohydrogeological event at the prospective nuclear waste disposal site Yucca Mountain, Nevada, USA, revealed by the isotope composition of fluid-inclusion water. – *Earth and Planetary Science Letters*, **289**, 583–594, Amsterdam.
- DUNBAR, R.B. (2000): Clues from corals. – *Nature*, **407**, 956–958, London.
- DYKOSKI, C.A., EDWARDS, R.L., CHENG, H., YUAN, D., CAI, Y., ZHANG, M., LIN, Y., QING, J., AN, Z. & REVENAUGH, J. (2005): A high-resolution, absolute-dated Holocene and deglacial Asian monsoon record from Dongge Cave, China. – *Earth and Planetary Science Letters*, **233**, 71–86, Amsterdam.
- EDWARDS, R.L., CHEN, J.H. & WASSERBURG, G.J. (1987): ^{238}U - ^{234}U - ^{230}Th - ^{232}Th systematics and the precise measurement of time over the past 500,000 years. – *Earth and Planetary Science Letters*, **81**, 175–192, Amsterdam.
- EGGINS, S.M., GRÜN, R., MCCULLOCH, M.T., PIKE, A.W.G., CHAPPELL, J., KINSLEY, L., MORTIMER, G., SHELLEY, M., MURRAY-WALLACE, C.V., SPÖTL, C. & TAYLOR, L. (2005): In situ U-series dating by laser-ablation multi-collector ICPMS: new prospects for Quaternary geochronology. – *Quaternary Science Reviews*, **24**, 2523–2538, Amsterdam.
- EILER, J.M. (2007): “Clumped-isotope” geochemistry – The study of naturally-occurring, multiply-substituted isotopologues. – *Earth and Planetary Science Letters*, **262**, 309–327, Amsterdam.
- EILER, J.M., CLOG, M., MAGYAR, P., PIASECKI, A., SESSIONS, A., STOLPER, D., DEERBERG, M., SCHLUETER, H.-J. & SCHWIETERS, J. (2013): A high-resolution gas-source isotope ratio mass spectrometer. – *International Journal of Mass Spectrometry*, **335**, 45–56, Amsterdam.
- EILER, J.M., BERGQUIST, B., BOURG, I., CARTIGNY, P., FARQUHAR, J., GAGNON, A., GUO, W., HALEVY, I., HOFMANN, A., LARSON, T.E., LEVIN, N., SCHAUBLE, E.A. & STOLPER, D. (2014): Frontiers of stable isotope geoscience. – *Chemical Geology*, **372**, 119–143, Amsterdam.
- EPSTEIN, S., BUCHSBAUM, R., LOWENSTAM, H. & UREY, H.C. (1953): Revised carbonate-water isotopic temperature scale. – *Geological Society of America Bulletin*, **64**, 1315–1326, Boulder.
- ERLER, D.V., DUNCAN, T.M., MURRAY, R., MAHER, D.T., SANTOS, I.R., GATLAND, J.R., MANGION, P. & EYRE, B.D. (2015): Applying cavity ring-down spectroscopy for the measurement of dissolved nitrous oxide concentrations and bulk nitrogen isotopic composition in aquatic systems: Correcting for interferences and field application. – *Limnology and Oceanography: Methods*, **13**, 391–401, Oxford.
- FAIRCHILD, I.J. & BAKER, A. (2012): *Speleothem Science – From Process to Past Environments*. – 1st ed., 450 pp., Chichester (Wiley-Blackwell).
- FAIRCHILD, I.J. & TREBLE, P.C. (2009): Trace elements in speleothems as recorders of environmental change. – *Quaternary Science Reviews*, **28**, 449–468, Amsterdam.
- FAIRCHILD, I.J., SMITH, C. L., BAKER, A., FULLER, L., SPÖTL, C., MATTEY, D., McDERMOTT, F. & E.I.M.F. (2006): Modification and preservation of environmental signals in speleothems. – *Earth-Science Reviews*, **75**, 105–153, Amsterdam.
- FATHI, A., MOHAMED, T., CLAUDE, G., MAURIN, G. & MOHAMED, B.A. (2006): Effect of a magnetic water treatment on homogeneous and heterogeneous precipitation of calcium carbonate. – *Water Research*, **40**, 1941–1950, Amsterdam.
- FERMANI, S., NJEGIC DZAKULA, B., REGGI, M., FALINI, G. & KRALJ, D. (2017): Effects of magnesium and temperature control on aragonite crystal aggregation and morphology. – *CrystEngComm*, **19**, 2451–2455, London.
- FERNANDEZ-CORTES, A., SANCHEZ-MORAL, S., CUEZVA, S., CANAVERAS, J.C. & ABELLA, R. (2009): Annual and transient signatures of gas exchange and transport in the Castanar de Ibor cave (Spain). – *International Journal of Speleology*, **38**, 153–162, Tampa.
- FIELD, L.P., MILODOWSKI, A.E., SHAW, R.P., STEVENS, L.A., HALL, M.R., KILPATRICK, A., GUNN, J., KEMP, S.J. & ELLIS, M.A. (2017): Unusual morphologies and the occurrence of pseudomorphs after ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) in fast growing, hyperalkaline speleothems. – *Mineralogical Magazine*, **81**, 565–589, London.
- FINSTER, M., CLARK, C., SCHROEDER, J. & MARTINO, L. (2015): Geothermal produced fluids: Characteristics, treatment technologies, and management options. – *Renewable and Sustainable Energy Reviews*, **50**, 952–966, Oxford.
- FISCHER, M., THOMAS, D.N., KRELL, A., NEHRKE, G., GÖTTLICHER, J., NORMAN, L., MEINERS, K.M., RIAUX-GOBIN, C. & DIECKMANN, G.S. (2013): Quantification of ikaite in Antarctic sea ice. – *Antarctic Science*, **25**, 421–432, Cambridge.
- FLEITMANN, D., BURNS, S.J., MANGINI, A., MUDELSEE, M., KRAMERS, J., VILLA, I., NEFF, U., AL-SUBBARY, A.A., BUETTNER, A., HIPPLER, D. & MATTER, A. (2007): Holocene ITCZ and Indian monsoon dynamics recorded in stalagmites from Oman and Yemen (Socotra). – *Quaternary Science Reviews*, **26**, 170–188, Amsterdam.
- FOHLMEISTER, J., PLESSSEN, B., DUDASHVILI, A.S., TJALLINGII, R., WOLFF, C., GAFUROV, A. & CHENG, H. (2017): Winter precipitation changes during the Medieval Climate Anomaly and the Little Ice Age in arid Central Asia. – *Quaternary Science Reviews*, **178**, 24–36, Amsterdam.
- FORD, D. & WILLIAMS, P. (2007): *Karst Hydrogeology and Geomorphology*. – 2nd ed., 562 pp., Chichester (John Wiley & Sons Ltd, UK).

- FOUKE, B.W. (2011): Hot-spring Systems Geobiology: abiotic and biotic influences on travertine formation at Mammoth Hot Springs, Yellowstone National Park, USA. – *Sedimentology*, **58**, 170–219, Amsterdam.
- FRAPPIER, A.B., SAHAGIAN, D., CARPENTER, S.J., GONZALEZ, L.A. & FRAPPIER, B.R. (2007): Stalagmite stable isotope record of recent tropical cyclone events. – *Geology*, **35**, 111–114, Washington, D.C.
- FREYET, P. & VERRECCHIA, E.P. (1998): Freshwater organisms that build stromatolites: a synopsis of biocrystallization by prokaryotic and eukaryotic algae. – *Sedimentology*, **45**, 535–563, Amsterdam.
- FREYET, P. & VERRECCHIA, E.P. (1999): Calcitic radial palisadic fabric in freshwater stromatolites: diagenetic and recrystallized feature or physicochemical sinter crust? – *Sedimentary Geology*, **126**, 97–102, Amsterdam.
- FRIEDMAN, I. & O'NEIL, J.R. (1977): Compilation of stable isotope fractionation factors of geochemical interest. – In: FLEISCHER, M. (Ed.): *Data of Geochemistry*, 6th ed. – Geological Survey Professional Paper, 440–KK, Washington.
- FRISIA, S. (2015): Microstratigraphic logging of calcite fabrics in speleothems as tool for palaeoclimate studies. – *International Journal of Speleology*, **44**, 1–16, Tampa.
- FRISIA, S., BORSATO, A., FAIRCHILD, I.J., MCDERMOTT, F. & SELMO, E.M. (2002): Aragonite-calcite relationships in speleothems (Grotte De Clamouse, France): Environment, fabrics, and carbonate geochemistry. – *Journal of Sedimentary Research*, **72**, 687–699, Tulsa.
- GABRIELLI, C., JAOUHARI, R., MAURIN, G. & KEDDAM, M. (2001): Magnetic water treatment for scale prevention. – *Water Research*, **35**, 3249–3259, Amsterdam.
- GALAN, I., BALDERMANN, A., KUSTERLE, W., DIETZEL, M. & MITTERMAYER, F. (2019): Durability of shotcrete for underground support—Review and update. – *Construction and Building Materials*, **202**, 465–493, Oxford.
- GEBAUER, D., VÖLKELE, A. & CÖLFEN, H. (2008): Stable prenucleation calcium carbonate clusters. – *Science*, **322**, 1819–1822, Washington, D.C.
- GEBAUER, D., CÖLFEN, H., VERCH, A. & ANTONIETTI, M. (2009): The multiple roles of additives in CaCO₃ crystallization: A quantitative case study. – *Advanced Materials*, **21**, 435–439, Weinheim.
- GHOSH, P., ADKINS, J., AFFEK, H., BALTA, B., GUO, W., SCHAUBLE, E.A., SCHRAG, D. & EILER, J.M. (2006): ¹³C–¹⁸O bonds in carbonate minerals: A new kind of paleothermometer. – *Geochimica et Cosmochimica Acta*, **70**, 1439–1456, New York.
- GOPI, S.P. & SUBRAMANIAN, V.K. (2012): Polymorphism in CaCO₃ – Effect of temperature under the influence of EDTA (di sodium salt). – *Desalination*, **297**, 38–47, Amsterdam.
- GREINERT, J. & DERKACHEV, A. (2004): Glendonites and methane-derived Mg-calcites in the Sea of Okhotsk, Eastern Siberia: implications of a venting-related ikaite/glendonite formation. – *Marine Geology*, **204**, 129–144, Amsterdam.
- GRENGG, C., MITTERMAYER, F., BALDERMANN, A., BÖTTCHER, M.E., LEIS, A., KORAIMANN, G., GRUNERT, P. & DIETZEL, M. (2015): Microbiologically induced concrete corrosion: A case study from a combined sewer network. – *Cement and Concrete Research*, **77**, 16–25, Oxford.
- GRENGG, C., MITTERMAYER, F., KORAIMANN, G., KONRAD, F., SZABÓ, M., DEMENY, A. & DIETZEL, M. (2017): The decisive role of acidophilic bacteria in concrete sewer networks: A new model for fast progressing microbial concrete corrosion. – *Cement and Concrete Research*, **101**, 93–101, Oxford.
- GRENGG, C., MITTERMAYER, F., UKRAINCZYK, N., KORAIMANN, G., KIENESBERGER, S. & DIETZEL, M. (2018): Advances in concrete materials for sewer systems affected by microbial induced concrete corrosion: A review. – *Water Research*, **134**, 341–352, Amsterdam.
- GUO, L.I. & RIDING, R. (1992): Microbial micritic carbonates in uppermost Permian reefs, Sichuan Basin, southern China: some similarities with recent travertines. – *Sedimentology*, **39**, 37–53, Amsterdam.
- GUO, L., ANDREWS, J., RIDING, R., DENNIS, P. & DRESSER, Q. (1996): Possible microbial effects on stable carbon isotopes in hot-spring travertines. – *Journal of Sedimentary Research*, **66**, 468–473, Tulsa.
- GUSSONE, N., EISENHAEUER, A., HEUSER, A., DIETZEL, M., BOCK, B., BÖHM, F., SPERO, H.J., LEA, D.W., BIJMA, J. & NÄGLER, T.F. (2003): Model for kinetic effects on calcium isotope fractionation ($\delta^{44}\text{Ca}$) in inorganic aragonite and cultured planktonic foraminifera. – *Geochimica et Cosmochimica Acta*, **67**, 1375–1382, New York.
- GUSSONE, N., NEHRKE, G. & TEICHERT, B.M.A. (2011): Calcium isotope fractionation in ikaite and vaterite. – *Chemical Geology*, **285**, 194–202, Amsterdam.
- GUSSONE, N., SCHMITT, A.-D., HEUSER, A., WOMBACHER, F., DIETZEL, M., TIPPER, E. & SCHILLER, M. (2016): Calcium Stable Isotope Geochemistry. – 1st ed., 260 pp., Berlin–Heidelberg (Springer).
- HAGER, B. & FOELSCHKE, U. (2015): Stable isotope composition of precipitation in Austria. – *Austrian Journal of Earth Sciences*, **108**, 2–13, Wien.
- HAKLIDIR, F.T. & HAKLIDIR, M. (2017): Fuzzy control of calcium carbonate and silica scales in geothermal systems. – *Geothermics*, **70**, 230–238, Amsterdam.
- HANSHAW, B.B. & BACK, W. (1979): Major geochemical processes in the evolution of carbonate – Aquifer systems. – *Journal of Hydrology*, **43**, 287–312, Amsterdam.
- HARNER, P.L. & GILMORE, M.S. (2015): Visible-near infrared spectra of hydrous carbonates, with implications for the detection of carbonates in hyperspectral data of Mars. – *Icarus*, **250**, 204–214, New York.
- HASSON, D., AVRIEL, M., RESNICK, W., ROZENMAN, T. & WINDREICH, S. (1968): Calcium carbonate scale deposition on heat transfer surfaces. – *Desalination*, **5**, 107–119, Amsterdam.
- HASSON, D., SIDORENKO, G. & SEMIAT, R. (2010): Calcium carbonate hardness removal by a novel electrochemical seeds system. – *Desalination*, **263**, 285–289, Amsterdam.
- HATLE, E. (1892): Fünfter Beitrag zur mineralogischen Topographie der Steiermark. – *Mitteilungen des Naturwissenschaftlichen Vereines für Steiermark*, **28**, 294–308, Graz.
- HAUSEGGER, S. & KURZ, W. (2013): Cataclastic faults along the SEMP fault system (Eastern Alps, Austria) – A contribution to fault zone evolution, internal structure and paleo-stresses. – *Tectonophysics*, **608**, 237–251, Amsterdam.
- HAUSEGGER, S., KURZ, W., RABITSCH, R., KIECHL, E. & BROSCHE, F.-J. (2010): Analysis of the internal structure of a carbonate damage zone: Implications for the mechanisms of fault breccia formation and fluid flow. – *Journal of Structural Geology*, **32**, 1349–1362, Oxford.
- HEEGAARD, E., BIRKS, H.J.B. & TELFORD, R.J. (2005): Relationships between calibrated ages and depth in stratigraphical sequences: an estimation procedure by mixed-effect regression. – *The Holocene*, **15**, 612–618, Los Angeles.
- HENJES-KUNST, F., PROCHASKA, W., NIEDERMAYER, A., SULLIVAN, N. & BAXTER, E. (2014): Sm-Nd dating of hydrothermal carbonate formation: An example from the Breitenau magnesite deposit (Styria, Austria). – *Chemical Geology*, **387**, 184–201, Amsterdam.

- HEWITT, A.D. (1989): Leaching of metal pollutants from four well casings used for ground-water monitoring. – CRREL Special Report 89–32, US Army Corps of Engineers, 11 pp., Hannover.
- HOCH, A.R., REDDY, M.M. & AIKEN, G.R. (2000): Calcite crystal growth inhibition by humic substances with emphasis on hydrophobic acids from the Florida Everglades. – *Geochimica et Cosmochimica Acta*, **64**, 61–72, New York.
- HOEFS, J. (2015): *Stable Isotope Geochemistry*. – 7th ed., 389 pp., Berlin–Heidelberg (Springer).
- HOLZKÄMPER, S., SPÖTL, C. & MANGINI, A. (2005): High-precision constraints on timing of Alpine warm periods during the middle to late Pleistocene using speleothem growth periods. – *Earth and Planetary Science Letters*, **236**, 751–764, Amsterdam.
- HU, Y.-B., WOLF-GLADROW, D.A., DIECKMANN, G.S., VÖLKER, C. & NEHRKE, G. (2014): A laboratory study of ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) precipitation as a function of pH, salinity, temperature and phosphate concentration. – *Marine Chemistry*, **162**, 10–18, Miami.
- HU, Y.-B., WOLTERS, M., WOLF-GLADROW, D.A. & NEHRKE, G. (2015): Effect of pH and phosphate on calcium carbonate polymorphs precipitated at near-freezing temperature. – *Crystal Growth and Design*, **15**, 1596–1601, Washington, D.C.
- IMMENHAUSER, A., BUHL, D., RICHTER, D., NIEDERMAYR, A., RIECHELMANN, D., DIETZEL, M. & SCHULTE, U. (2010): Magnesium-isotope fractionation during low-Mg calcite precipitation in a limestone cave. – Field study and experiments. – *Geochimica et Cosmochimica Acta*, **74**, 4346–4364, New York.
- ITO, T. (1998): Factors controlling the transformation of natural ikaite from Shiowakka, Japan. – *Geochemical Journal*, **32**, 267–273, Tokyo.
- IVANOVICH, M. & HARMON, R.S. (1992): *Uranium-series Disequilibrium: Applications to Earth, Marine Environmental Sciences*. – 910 pp., Oxford (Clarendon Press).
- JIMOH, O.A., OKOYE, P.U., ARIFFIN, K.S., HUSSIN, H.B. & BAHARUN, N. (2017): Continuous synthesis of precipitated calcium carbonate using a tubular reactor with the aid of aloe vera (*Aloe barbadensis* Miller) extract as a green morphological modifier. – *Journal of Cleaner Production*, **150**, 104–111, Amsterdam.
- JOCHUM, K.P., STOLL, B., FRIEDRICH, J.M., AMINI, M., BECKER, S., DÜCKING, M., EBEL, D.S., ENZWEILER, J., HU, M., KUZMIN, D., MERTZKRAUS, R., MÜLLER, W.E.G., REGNER, J., SOBOLEV, A., WANG, X. & ZHAN, X. (2009): Laser ablation-inductively coupled plasma-mass spectrometry and its application in geochemistry, cosmochemistry and environmental research. – *Rock and Mineral Analysis*, **28**, 53–68.
- JOHNSEN, S.J., DAHL-JENSEN, D., GUNDESTRUP, N., STEFFENSEN, J.P., CLAUSEN, H.B., MILLER, H., MASSON-DELMOTTE, V., SVEINBJÖRNSDOTTIR, A.E. & WHITE, J. (2001): Oxygen isotope and palaeotemperature records from six Greenland ice-core stations: Camp Century, Dye-3, GRIP, GISP2, Renland and NorthGRIP. – *Journal of Quaternary Science*, **16**, 299–307, Chichester.
- JOHNSTON, V.E., BORSATO, A., FRISIA, S., SPÖTL, C., DUBLYANSKY, Y., TÖCHTERLE, P., HELLSTROM, J.C., BAJO, P., EDWARDS, R.L. & CHENG, H. (2018): Evidence of thermophilisation and elevation-dependent warming during the Last Interglacial in the Italian Alps. – *Scientific Reports*, **8**: 2680, London. <https://dx.doi.org/10.1038/s41598-018-21027-3>
- JONES, B. (2017a): Review of calcium carbonate polymorph precipitation in spring systems. – *Sedimentary Geology*, **353**, 64–75, Amsterdam.
- JONES, B. (2017b): Review of aragonite and calcite crystal morphogenesis in thermal spring systems. – *Sedimentary Geology*, **354**, 9–23, Amsterdam.
- JONES, B. & PENG, X. (2012): Amorphous calcium carbonate associated with biofilms in hot spring deposits. – *Sedimentary Geology*, **269–270**, 58–68, Amsterdam.
- JONES, B. & RENAULT, R.W. (2010): Calcareous spring deposits in continental settings. – *Developments in Sedimentology*, **61**, 177–224, Amsterdam.
- KAWAMURA, K., PARRENIN, F., LISIECKI, L., UEMURA, R., VIMEUX, F., SEVERINGHAUS, J.P., HUTTERLI, M.A., NAKAZAWA, T., AOKI, S., JOUZEL, J., RAYMO, M.E., MATSUMOTO, K., NAKATA, H., MOTOYAMA, H., FUJITA, S., GOTO-AZUMA, K., FUJII, Y. & WATANABE, O. (2007): Northern Hemisphere forcing of climatic cycles in Antarctica over the past 360,000 years. – *Nature*, **448**, 912–916, London.
- KELE, S., BREITENBACH, S.F.M., CAPEZZUOLI, E., NELE MECKLER, A., ZIEGLER, M., MILLAN, I.M., KLUGE, T., DEÁK, J., HANSELMANN, K., JOHN, C.M., YAN, H., LIU, Z. & BERNASCONI, S.M. (2015): Temperature dependence of oxygen- and clumped isotope fractionation in carbonates: a study of travertines and tufas in the 6–95°C temperature range. – *Geochimica et Cosmochimica Acta*, **168**, 172–192, New York.
- KELEMEN, P.B. & MATTER, J. (2008): In situ carbonation of peridotite for CO_2 storage. – *Proceedings of the National Academy of Sciences*, **105**, 17295–17300, Allahabad.
- KELSON, J.R., HUNTINGTON, K.W., SCHAUER, A.J., SAENGER, C. & LECHLER, A.R. (2017): Toward a universal carbonate clumped isotope calibration: Diverse synthesis and preparatory methods suggest a single temperature relationship. – *Geochimica et Cosmochimica Acta*, **197**, 104–131, New York.
- KETRANE, R., SAIDANI, B., GIL, O., LELEYTER, L. & BARAUD, F. (2009): Efficiency of five scale inhibitors on calcium carbonate precipitation from hard water: Effect of temperature and concentration. – *Desalination*, **249**, 1397–1404, Amsterdam.
- KHARAKA, Y.K., COLE, D.R., HOVORKA, S.D., GUNTER, W.D., KNAUSS, K.G. & FREIFELD, B.M. (2006): Gas-water-rock interactions in Frio Formation following CO_2 injection: Implications for the storage of greenhouse gases in sedimentary basins. – *Geology*, **34**, 577–580, Washington, D.C.
- KIM, S.-T. & O'NEIL, J.R. (1997): Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. – *Geochimica et Cosmochimica Acta*, **61**, 3461–3475, New York.
- KLUGE, T. & JOHN, C.M. (2015): Effects of brine chemistry and polymorphism on clumped isotopes revealed by laboratory precipitation of mono- and multiphase calcium carbonates. – *Geochimica et Cosmochimica Acta*, **160**, 155–168, New York.
- KLUGE, T., AFFEK, H.P., DUBLYANSKY, Y. & SPÖTL, C. (2014): Devils Hole paleotemperatures and implications for oxygen isotope equilibrium fractionation. – *Earth and Planetary Science Letters*, **400**, 251–260, Amsterdam.
- KLUGE, T., JOHN, C.M., JOURDAN, A.-L., DAVIS, S. & CRAWSHAW, J. (2015): Laboratory calibration of the calcium carbonate clumped isotope thermometer in the 25–250 °C temperature range. – *Geochimica et Cosmochimica Acta*, **157**, 213–227, New York.
- KLUGE, T., JOHN, C.M., BOCH, R. & KELE, S. (2018): Assessment of Factors Controlling Clumped Isotopes and $\delta^{18}\text{O}$ Values of Hydrothermal Vent Calcites. – *Geochemistry, Geophysics, Geosystems*, **19/6**, 1844–1858, Washington, D.C.
- KNEZ, S. & POHAR, C. (2005): The magnetic field influence on the polymorph composition of CaCO_3 precipitated from carbonized aqueous solutions. – *Journal of Colloid and Interface Science*, **281**, 377–388, Amsterdam.
- KOBE, S., DRAZIC, G., CEFALAS, A.C., SARANTOPOULOU, E. & STRAZISAR, J. (2002): Nucleation and crystallization of CaCO_3 in applied magnetic fields. – *Crystal Engineering*, **5**, 243–253, Oxford.

- KOGA, N., KASAHARA, D. & KIMURA, T. (2013): Aragonite crystal growth and solid-state aragonite-calcite transformation: A physico-geometrical relationship via thermal dehydration of included water. – *Crystal Growth and Design*, **13**, 2238–2246, Washington, D.C.
- KÖHLER, S.J., CUBILLAS, P., RODRIGUEZ-BLANCO, J.D., BAUER, C. & PRIETO, M. (2007): Removal of cadmium from wastewaters by aragonite shells and the influence of other divalent cations. – *Environmental Science and Technology*, **41**, 112–118, Washington, D.C.
- KONRAD, F., GALLIEN, F., GERARD, D.E. & DIETZEL, M. (2016): Transformation of amorphous calcium carbonate in air. – *Crystal Growth and Design*, **16**, 6310–6317, Washington, D.C.
- KOŠEDNAR-LEGENSTEIN, B., DIETZEL, M., LEIS, A. & STINGL, K. (2008): Stable carbon and oxygen isotope investigation in historical lime mortar and plaster. – Results from field and experimental study. – *Applied Geochemistry*, **23**, 2425–2437, Amsterdam.
- KRALJ, D. & BREČEVIĆ, L. (1995): Dissolution kinetics and solubility of calcium carbonate monohydrate. – *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **96**, 287–293, Amsterdam.
- KUMAR, S., NAIYA, T.K. & KUMAR, T. (2018): Developments in oilfield scale handling towards green technology – A review. – *Journal of Petroleum Science and Engineering*, **169**, 428–444, Amsterdam.
- LACHNIET, M.S. (2009): Climatic and environmental controls on speleothem oxygen-isotope values. – *Quaternary Science Reviews*, **28**, 412–432, Amsterdam.
- LACHNIET, M.S., BERNAL, J.P., ASMEROM, Y. & POLYAK, V. (2012): Uranium loss and aragonite-calcite age discordance in a calcitized aragonite stalagmite. – *Quaternary Geochronology*, **14**, 26–37, Amsterdam.
- LANGER, G., SADEKOV, A., NEHRKE, G., BAGGINI, C., RODOLFO-METALPA, R., HALL-SPENCER, J.M., CUOCO, E., BIJMA, J. & ELDERFIELD, H. (2018): Relationship between mineralogy and minor element partitioning in limpets from an Ischia CO₂ vent site provides new insights into their biomineralization pathway. – *Geochimica et Cosmochimica Acta*, **236**, 218–229, New York.
- LANGMUIR, D. (1997): Carbonate Chemistry. – In: LANGMUIR, D.: *Aqueous Environmental Geochemistry*, 193–230, Upper Saddle River (Prentice Hall).
- LANNELUC, I., LANGUMIER, M., SABOT, R., JEANNIN, M., REFAIT, P. & SABLÉ, S. (2015): On the bacterial communities associated with the corrosion product layer during the early stages of marine corrosion of carbon steel. – *International Biodeterioration and Biodegradation*, **99**, 55–65, Barking.
- LENHARDT, W.A., FREUDENTHALER, C., LIPPITSCH, R. & FIEGWEL, E. (2007): Focal-depth distributions in the Eastern Alps based on macroseismic data. – *Austrian Journal of Earth Sciences*, **100**, 66–79, Wien.
- LERM, S., WESTPHAL, A., MIETHLING-GRAFF, R., ALAWI, M., SEIBT, A., WOLFGGRAMM, M. & WÜRDEMANN, H. (2013): Thermal effects on microbial composition and microbiologically induced corrosion and mineral precipitation affecting operation of a geothermal plant in a deep saline aquifer. – *Extremophiles*, **17**, 311–327, Tokyo.
- LEVITT, N.P., EILER, J.M., ROMANEK, C.S., BEARD, B.L., XU, H. & JOHNSON, C.M. (2018): Near equilibrium ¹³C-¹⁸O bonding during inorganic calcite precipitation under chemo-stat conditions. – *Geochemistry, Geophysics, Geosystems*, **19/3**, 901–920, Washington, D.C.
- LI, H., YANG, J., ZHANG, L., ZOU, H., LI, D., WANG, Q., MENG, D. & LU, M. (2019): Influence of thermophilic sulfate-reducing bacteria and deposited CaCO₃ on the corrosion of water injection system. – *Engineering Failure Analysis*, **95**, 359–370, Oxford.
- LI, X., GAO, B., YUE, Q., MA, D., RONG, H., ZHAO, P. & TENG, P. (2015): Effect of six kinds of scale inhibitors on calcium carbonate precipitation in high salinity wastewater at high temperatures. – *Journal of Environmental Sciences*, **29**, 124–130, Amsterdam.
- LISIECKI, L.E. & RAYMO, M.E. (2005): A Pliocene-Pleistocene stack of 57 globally distributed benthic δ¹⁸O records. – *Paleoceanography*, **20**: PA1003, Washington, D.C. <https://dx.doi.org/10.1029/2004PA001071>
- LISIECKI, L.E. & STERN, J.V. (2016): Regional and global benthic δ¹⁸O stacks for the last glacial cycle. – *Paleoceanography*, **31**, 1368–1394, Washington, D.C.
- LIU, H., LIU, Z., MACPHERSON, G.L., YANG, R., CHEN, B. & SUN, H. (2015): Diurnal hydrochemical variations in a karst spring and two ponds, Maolan Karst Experimental Site, China: Biological pump effects. – *Journal of Hydrology*, **522**, 407–417, Amsterdam.
- LIU, Z.Y., WANG, X.Z., LIU, R.K., DU, C.W. & LI, X.G. (2014): Electrochemical and sulfide stress corrosion cracking behaviors of tubing steels in a H₂S/CO₂ annular environment. – *Journal of Materials Engineering and Performance*, **23**, 1279–1287, New York.
- LLOYD, M.K., EILER, J.M. & NABELEK, P.I. (2017): Clumped isotope thermometry of calcite and dolomite in a contact metamorphic environment. – *Geochimica et Cosmochimica Acta*, **197**, 323–344, New York.
- LORENS, R.B. (1981): Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate. – *Geochimica et Cosmochimica Acta*, **45**, 553–561, New York.
- LUETKEMEYER, P.B., KIRSCHNER, D.L., HUNTINGTON, K.W., CHESTER, J.S., CHESTER, F.M. & EVANS, J.P. (2016): Constraints on paleofluid sources using the clumped-isotope thermometry of carbonate veins from the SAFOD (San Andreas Fault Observatory at Depth) borehole. – *Tectonophysics*, **690**, Part A, 174–189, Amsterdam.
- LUETSCHER, M. & ZIEGLER, F. (2012): CORA – a dedicated device for carbon dioxide monitoring in cave environments. – *International Journal of Speleology*, **41**, 275–283, Tampa.
- LUETSCHER, M., BOCH, R., SODEMANN, H., SPÖTL, C., CHENG, H., EDWARDS, R.L., FRISIA, S., HOF, F. & MÜLLER, W. (2015): North Atlantic storm track changes during the Last Glacial Maximum recorded by Alpine speleothems. – *Nature Communications*, **6**: 6344, London. <https://dx.doi.org/10.1038/ncomms7344>
- LYONS, T.W., FIKE, D.A. & ZERKLE, A. (2015): Emerging biogeochemical views of Earth's ancient microbial worlds. – *Elements*, **11**, 415–421, Québec.
- MAHER, T.D., SANTOS, I.R. & TAIT, D.R. (2014): Mapping methane and carbon dioxide concentrations and δ¹³C values in the atmosphere of two Australian coal seam gas fields. – *Water, Air and Soil Pollution*, **225**: 2216, Dordrecht. <https://dx.doi.org/10.1007/s11270-014-2216-2>
- MARTÍN-CHIVELET, J., MUÑOZ-GARCÍA, M.B., CRUZ, J.A., ORTEGA, A.I. & TURRERO, M.J. (2017): Speleothem Architectural Analysis: Integrated approach for stalagmite-based paleoclimate research. – *Sedimentary Geology*, **353**, 28–45, Amsterdam.
- MASKENSKAYA, O.M., DRAKE, H., BROMAN, C., HOGMALM, J.K., CZUPPON, G. & ÅSTRÖM, M.E. (2014): Source and character of syntaxial hydrothermal calcite veins in Paleoproterozoic crystalline rocks revealed by fine-scale investigations. – *Geofluids*, **14**, 495–511, Oxford.
- MATTER, J.M., STUTE, M., SNÆBJÖRNSDÓTTIR, S.Ó., OELKERS, E.H., GISLASON, S.R., ARADÓTTIR, E.S., SIGFUSSON, B., GUNNARSSON, I., SIGURDARDÓTTIR, H., GUNNLAUGSSON, E., AXELSSON, G., ALFREDSSON, H.A., WOLFF-BOENISCH, D., MESFIN, K., TAYA, D.F.D.L.R., HALL, J., DIDERIKSEN, K. & BROECKER, W.S. (2016): Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. – *Science*, **352**, 1312–1314, Washington, D.C.
- MATTEY, D., LOWRY, D., DUFFET, J., FISHER, R., HODGE, E. & FRISIA, S. (2008): A 53 year seasonally resolved oxygen and carbon isotope record from a modern Gibraltar speleothem: Reconstructed drip water and relationship to local precipitation. – *Earth and Planetary Science Letters*, **269**, 80–95, Amsterdam.

- MATTEY, D.P., ATKINSON, T.C., BARKER, J.A., FISHER, R., LATIN, J.P., DURELL, R. & AINSWORTH, M. (2016): Carbon dioxide, ground air and carbon cycling in Gibraltar karst. – *Geochimica et Cosmochimica Acta*, **184**, 88–113, New York.
- MAVROMATIS, V., GAUTIER, Q., BOSCH, O. & SCHOTT, J. (2013): Kinetics of Mg partition and Mg stable isotope fractionation during its incorporation in calcite. – *Geochimica et Cosmochimica Acta*, **114**, 188–203, New York.
- MAVROMATIS, V., MONTOUILLOUT, V., NOIREAUX, J., GAILLARDET, J. & SCHOTT, J. (2015): Characterization of boron incorporation and speciation in calcite and aragonite from co-precipitation experiments under controlled pH, temperature and precipitation rate. – *Geochimica et Cosmochimica Acta*, **150**, 299–313, New York.
- MAVROMATIS, V., VAN ZUILEN, K., PURGSTALLER, B., BALDERMANN, A., NÄGLER, T.F. & DIETZEL, M. (2016): Barium isotope fractionation during witherite (BaCO₃) dissolution, precipitation and at equilibrium. – *Geochimica et Cosmochimica Acta*, **190**, 72–84, New York.
- MAVROMATIS, V., IMMENHAUSER, A., BUHL, D., PURGSTALLER, B., BALDERMANN, A. & DIETZEL, M. (2017): Effect of organic ligands on Mg partitioning and Mg isotope fractionation during low-temperature precipitation of calcite in the absence of growth rate effects. – *Geochimica et Cosmochimica Acta*, **207**, 139–153, New York.
- MAVROMATIS, V., GOETSCHL, K.E., GRENGG, C., KONRAD, F., PURGSTALLER, B. & DIETZEL, M. (2018): Barium partitioning in calcite and aragonite as a function of growth rate. – *Geochimica et Cosmochimica Acta*, **237**, 65–78, New York.
- MAVROMATIS, V., GONZÁLEZ, A.G., DIETZEL, M. & SCHOTT, J. (2019): Zinc isotope fractionation during the inorganic precipitation of calcite – Towards a new pH proxy. – *Geochimica et Cosmochimica Acta*, **244**, 99–112, New York.
- MAYRHOFER, C., NIESSNER, R. & BAUMANN, T. (2014): Hydrochemistry and hydrogen sulfide generating processes in the Malm aquifer, Bavarian Molasse Basin, Germany. – *Hydrogeology Journal*, **22**, 151–162, Berlin–Heidelberg.
- MCMILLAN, E.A., FAIRCHILD, I.J., FRISIA, S., BORSATO, A. & MCDERMOTT, F. (2005): Annual trace element cycles in calcite–aragonite speleothems: evidence of drought in the western Mediterranean 1200–1100 yr BP. – *Journal of Quaternary Science*, **20**, 423–433, Chichester.
- MECHAL, A., BIRK, S., DIETZEL, M., LEIS, A., WINKLER, G., MOGESIE, A. & KEBEDE, S. (2017): Groundwater flow dynamics in the complex aquifer system of Gidabo River Basin (Ethiopian Rift): a multi-proxy approach. – *Hydrogeology Journal*, **25**, 519–538, Berlin–Heidelberg.
- MECKLER, A.N., AFFOLTER, S., DUBLYANSKY, Y.V., KRÜGER, Y., VOGEL, N., BERNASCONI, S.M., FRENZ, M., KIPFER, R., LEUENBERGER, M., SPÖTL, C., CAROLIN, S., COBB, K.M., MOERMAN, J., ADKINS, J.F. & FLEITMANN, D. (2015): Glacial-interglacial temperature change in the tropical West Pacific: A comparison of stalagmite-based paleo-thermometers. – *Quaternary Science Reviews*, **127**, 90–116, Amsterdam.
- MEYER, M.C., CLIFF, R.A., SPÖTL, C., KNIPPING, M. & MANGINI, A. (2009): Speleothems from the earliest Quaternary: Snapshots of paleoclimate and landscape evolution at the northern rim of the Alps. – *Quaternary Science Reviews*, **28**, 1374–1391, Amsterdam.
- MEYER, M.C., CLIFF, R.A. & SPÖTL, C. (2011): Speleothems and mountain uplift. – *Geology*, **39**, 447–450, Washington, D.C.
- MICHAELIS, J., USDOWSKI, E. & MENSCHL, G. (1985): Partitioning of ¹³C and ¹²C on the degassing of CO₂ and the precipitation of calcite. – Rayleigh type fractionation and a kinetic model. – *American Journal of Science*, **285**, 318–327, New Haven.
- MICKLER, P.J., BANNER, J.L., STERN, L., ASMEROM, Y., EDWARDS, R.L. & ITO, E. (2004): Stable isotope variations in modern tropical speleothems: Evaluating equilibrium vs. kinetic isotope effects. – *Geochimica et Cosmochimica Acta*, **68**, 4381–4393, New York.
- MICKLER, P.J., STERN, L.A. & BANNER, J.L. (2006): Large kinetic isotope effects in modern speleothems. – *Geological Society of America Bulletin*, **118**, 65–81, Boulder.
- MICKLER, P.J., CARLSON, P., BANNER, J.L., BREECKER, D.O., STERN, L. & GUILFOYLE, A. (2019): Quantifying carbon isotope disequilibrium during in-cave evolution of drip water along discrete flow paths. – *Geochimica et Cosmochimica Acta*, **244**, 182–196, New York.
- MILLERO, F.J., GRAHAM, T.B., HUANG, F., BUSTOS-SERRANO, H. & PIERROT, D. (2006): Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. – *Marine Chemistry*, **100**, 80–94, Miami.
- MISCHEL, S.A., SCHOLZ, D., SPÖTL, C., JOCHUM, K.P., SCHRÖDER-RITZAU, A. & FIEDLER, S. (2016): Holocene climate variability in Central Germany and a potential link to the polar North Atlantic: A replicated record from three coeval speleothems. – *The Holocene*, **27**, 509–525, Los Angeles.
- MITTERMAYR, F., BALDERMANN, A., BALDERMANN, C., GRATHOFF, G.H., KLAMMER, D., KÖHLER, S.J., LEIS, A., WARR, L.N. & DIETZEL, M. (2017): Environmental controls and reaction pathways of coupled de-dolomitization and thaumasite formation. – *Cement and Concrete Research*, **95**, 282–293, Oxford.
- MONNIN, C. & SCHOTT, J. (1984): Determination of the solubility products of sodium carbonate minerals and an application to trona deposition in Lake Magadi (Kenya). – *Geochimica et Cosmochimica Acta*, **48**, 571–581, New York.
- MOOK, W.G. (1986): ¹³C in atmospheric CO₂. – *Netherlands Journal of Sea Research*, **20**, 211–223, Amsterdam.
- MOORE, C.H. & WADE, W.J. (2013): Carbonate diagenesis: Introduction and tools. – *Developments in Sedimentology*, **67**, 67–89, Amsterdam.
- MORSE, J.W. (2004): Formation and diagenesis of carbonate sediments. – In: MACKENZIE, F.T. (Ed.): *Sediments, Diagenesis and Sedimentary Rocks*, **7**, Treatise on Geochemistry, 67–85, Oxford.
- MORSE, J.W. & ARVIDSON, R.S. (2002): The dissolution kinetics of major sedimentary carbonate minerals. – *Earth-Science Reviews*, **58**, 51–84, Amsterdam.
- MORSE, J.W. & MACKENZIE, F.T. (1990): *Geochemistry of Sedimentary Carbonates*. – *Developments in Sedimentology*, **48**, 707 pp., Amsterdam.
- MORSE, J.W., ARVIDSON, R.S. & LÜTTGE, A. (2007): Calcium carbonate formation and dissolution. – *Chemical Reviews*, **107**, 342–381, Washington, D.C.
- MOSELEY, G.E., EDWARDS, R.L., WENDT, K.A., CHENG, H., DUBLYANSKY, Y., LU, Y., BOCH, R. & SPÖTL, C. (2016): Reconciliation of the Devils Hole climate record with orbital forcing. – *Science*, **351**, 165–168, Washington, D.C.
- MPELWA, M. & TANG, S.F. (2019): State of the art of synthetic threshold scale inhibitors for mineral scaling in the petroleum industry: a review. – *Petroleum Science*, **16**/4, 830–849. <https://dx.doi.org/10.1007/s12182-019-0299-5>
- MÜHLINGHAUS, C., SCHOLZ, D. & MANGINI, A. (2007): Modelling stalagmite growth and δ¹³C as a function of drip interval and temperature. – *Geochimica et Cosmochimica Acta*, **71**, 2780–2790, New York.
- MUNDHENK, N., HUTTENLOCH, P., SANJUAN, B., KOHL, T., STEGER, H. & ZORN, R. (2013): Corrosion and scaling as interrelated phenomena in an operating geothermal power plant. – *Corrosion Science*, **70**, 17–28, Amsterdam.
- NEBEL, O. & STAMMEIER, A. (2016): Strontium Isotopes. – In: WHITE, W.M. (Ed.): *Encyclopedia of Geochemistry*, 6 p., Cham. https://dx.doi.org/10.1007/978-3-319-39193-9_137-1

- NIEDERMAYR, A., KÖHLER, S.J. & DIETZEL, M. (2013): Impacts of aqueous carbonate accumulation rate, magnesium and polyaspartic acid on calcium carbonate formation (6–40 °C). – *Chemical Geology*, **340**, 105–120, Amsterdam.
- NIELSEN, M.H. & DE YOREO, J.J. (2017): Liquid phase TEM investigations of crystal nucleation, growth, and transformation. – In: VAN DRIESSCHE, A.E.S., KELLERMEIER, M., BENNING, L.G. & GEBAUER, D. (Eds.): *New Perspectives on Mineral Nucleation and Growth. – From Solution Precursors to Solid Materials*, 353–374, Cham.
- NOAA – NATIONAL CENTERS FOR ENVIRONMENTAL INFORMATION: <https://www.ncdc.noaa.gov/data-access> (last visited: 19.08.2018).
- NOGARA, J. & ZARROUK, S.J. (2014): Evaluation of corrosion resistant alloys as construction material for acidic geothermal wells. – *Proceedings of the 36th New Zealand Geothermal Workshop*, 14 pp., Auckland.
- NOGARA, J. & ZARROUK, S.J. (2017): Corrosion in geothermal environment: Part 1: Fluids and their impact. – *Renewable and Sustainable Energy Reviews*, **82**, 1333–1346, Oxford.
- OEHLERICH, M., MAYR, C., GRIESSHABER, E., LÜCKE, A., OECKLER, O.M., OHLENDORF, C., SCHMAHL, W.W. & ZOLITSCHKA, B. (2013): Ikaite precipitation in a lacustrine environment – implications for palaeoclimatic studies using carbonates from Laguna Potrok Aike (Patagonia, Argetina). – *Quaternary Science Reviews*, **71**, 46–53, Amsterdam.
- OKRUSCH, M. & MATTHES, S. (2010): *Mineralogie – Eine Einführung in die spezielle Mineralogie, Petrologie und Lagerstättenkunde*, 8th ed., 658 pp., Berlin–Heidelberg (Springer).
- ONU, P., DIETZEL, M. & HAUZENBERGER, C.A. (2014): Formation of helictite in the cave Dragon Belly (Sardinia, Italy) – Microstructure and incorporation of Mg, Sr, and Ba. – *Chemie der Erde. – Geochemistry*, **74**, 443–452, Washington, D.C.
- OSTERMANN, M., SANDERS, D., PRAGER, C. & KRAMERS, J. (2007): Aragonite and calcite cementation in “boulder-controlled” meteoric environments on the Fern Pass rockslide (Austria): implications for radiometric age dating of catastrophic mass movements. – *Facies*, **53**, 189–208, Berlin–Heidelberg.
- OSVALD, M., MARÓTTI, G., PAP, B. & SZANYI, J. (2017): Biofilm forming bacteria during thermal water reinjection. – *Geofluids*, **2017**, 7 p., Oxford. <https://dx.doi.org/10.1155/2017/9231056>
- OTT, H., DE KLOE, K., VAN BAKEL, M., VOS, F., VAN PELT, A., LEGERSTEE, P., BAUER, A., EIDE, K., VAN DER LINDEN, A., BERG, S. & MAKURAT, A. (2012): Core-flood experiment for transport of reactive fluids in rocks. – *Review of Scientific Instruments*, **83**: 084501, New York. <https://dx.doi.org/10.1063/1.4746997>
- OTT, H., PENTLAND, C.H. & OEDAI, S. (2015): CO₂-brine displacement in heterogeneous carbonates. – *International Journal of Greenhouse Gas Control*, **33**, 135–144, New York.
- OUHENIA, S., CHATEIGNER, D., BELKHIR, M.A., GUILMEAU, E. & KRAUSS, C. (2008): Synthesis of calcium carbonate polymorphs in the presence of polyacrylic acid. – *Journal of Crystal Growth*, **310**, 2832–2841, Amsterdam.
- OWEN, R.A., DAY, C.C., HU, C.Y., LIU, Y.H., POINTING, M.D., BLÄTTLER, C.L. & HENDERSON, G.M. (2016): Calcium isotopes in caves as a proxy for aridity: Modern calibration and application to the 8.2 kyr event. – *Earth and Planetary Science Letters*, **443**, 129–138, Amsterdam.
- OZYURT, N.N., LUTZ, H.O., HUNJAK, T., MANCE, D. & ROLLER-LUTZ, Z. (2014): Characterization of the Gacka River basin karst aquifer (Croatia): Hydrochemistry, stable isotopes and tritium-based mean residence times. – *Science of the total Environment*, **487**, 245–254, Amsterdam.
- PACES, J.B., LUDWIG, K.R., PETERMAN, Z.E. & NEYMARK, L.A. (2002): ²³⁴U/²³⁸U evidence for local recharge and patterns of groundwater flow in the vicinity of Yucca Mountain, Nevada, USA. – *Applied Geochemistry*, **17**, 751–779, Amsterdam.
- PAGEL, M., BONIFACIE, M., SCHNEIDER, D.A., GAUTHERON, C., BRIGAUD, B., CALMELS, D., CROS, A., SAINT-BEZAR, B., LANDREIN, P., SUTCLIFFE, C., DAVIS, D. & CHADUTEAU, C. (2018): Improving paleo-hydrological and diagenetic reconstructions in calcite veins and breccia of a sedimentary basin by combining Δ_{47} temperature, $\delta_{18}\text{O}_{\text{water}}$ and U-Pb age. – *Chemical Geology*, **481**, 1–17, Amsterdam.
- PARKHURST, D.L. & APPELO, C.A.J. (2013): Description of input and examples for PHREEQC version 3. – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. – U.S. Geological Survey Techniques and Methods, book 6, chapter A43, 497 pp., Denver.
- PARLAKTUNA, M. & OKANDAN, E. (1989): The use of chemical inhibitors for prevention of calcium carbonate scaling. – *Geothermics*, **18**, 241–248, Amsterdam.
- PASSCHIER, C., SÜRMEIHLI, G. & SPÖTL, C. (2016a): A high-resolution palaeoenvironmental record from carbonate deposits in the Roman aqueduct of Patara, SW Turkey, from the time of Nero. – *Scientific Reports*, **6**: 28704, London. <https://dx.doi.org/10.1038/srep28704>
- PASSCHIER, C., SÜRMEIHLI, G., SPÖTL, C., MERTZ-KRAUS, R. & SCHOLZ, D. (2016b): Carbonate deposits from the ancient aqueduct of Béziers, France – A high-resolution palaeoenvironmental archive for the Roman Empire. – *Palaeogeography, Palaeoclimatology, Palaeoecology*, **461**, 328–340, Amsterdam.
- PEDERSON, C., MAVROMATIS, V., DIETZEL, M., ROLLION-BARD, C., NEHRKE, G., JÖNS, N., JOCHUM, K.P. & IMMENHAUSER, A. (2019): Diagenesis of mollusc aragonite and the role of fluid reservoirs. – *Earth and Planetary Science Letters*, **514**, 130–142, Amsterdam.
- PEDLEY, M. (2013): The morphology and function of thrombolitic calcite precipitating biofilms: A universal model derived from freshwater mesocosm experiments. – *Sedimentology*, **61**, 22–40, Amsterdam.
- PÉREZ-MEJIAS, C., MORENO, A., SANCHO, C., BARTOLOMÉ, M., STOLL, H., CACHO, I., CHENG, H. & EDWARDS, R.L. (2017): Abrupt climate changes during Termination III in Southern Europe. – *Proceedings of the National Academy of Sciences*, **114**, 10047–10052, Washington, D.C.
- PERRIN, C., PRESTIMONACO, L., SERVELLE, G., TILHAC, R., MAURY, M. & CABROL, P. (2014): Aragonite-calcite speleothems: Identifying original and diagenetic features. – *Journal of Sedimentary Research*, **84**, 245–269, Tulsa.
- PIRAJNO, F. (2009): *Hydrothermal Processes and Mineral Systems*. – 1250 pp., Berlin (Springer).
- PLAN, L., GRASEMANN, B., SPÖTL, C., DECKER, K., BOCH, R. & KRAMERS, J. (2010): Neotectonic extrusion of the Eastern Alps: Constraints from U/Th dating of tectonically damaged speleothems. – *Geology*, **38**, 483–486, Washington, D.C.
- PLAN, L., TSCHEGG, C., DE WAELE, J. & SPÖTL, C. (2012): Corrosion morphology and cave wall alteration in an Alpine sulfuric acid cave (Kraushöhle, Austria). – *Geomorphology*, **169–170**, 45–54, Amsterdam.
- PLUMMER, L.N. & BUSENBERG, E. (1982): The solubilities of calcite, aragonite and vaterite in CO₂-H₂O solutions between 0 and 90° C, and an evaluation of the aqueous model for the system CaCO₃-CO₂-H₂O. – *Geochimica et Cosmochimica Acta*, **46**, 1011–1040, New York.
- PROCHASKA, W. (2012): Siderite and magnesite mineralizations in Palaeozoic strata of the Eastern Alps (Austria). – *Journal of Alpine Geology*, **54**, 309–322, Wien.
- PROCHASKA, W. (2016): Genetic concepts on the formation of the Austrian magnesite and siderite mineralizations in the Eastern Alps of Austria. – *Geologia Croatica*, **69**, 31–38, Zagreb.

- PROKHOROV, I., KLUGE, T. & JANSSEN, C. (2019): Optical clumped isotope thermometry of carbon dioxide. – *Scientific Reports*, **9**: 4765, London. <https://dx.doi.org/10.1038/s41598-019-40750-z>
- PURGSTALLER, B., MAVROMATIS, V., IMMENHAUSER, A. & DIETZEL, M. (2016): Transformation of Mg-bearing amorphous calcium carbonate to Mg-calcite – In situ monitoring. – *Geochimica et Cosmochimica Acta*, **174**, 180–195, New York.
- PURGSTALLER, B., DIETZEL, M., BALDERMANN, A. & MAVROMATIS, V. (2017a): Control of temperature and aqueous Mg^{2+}/Ca^{2+} ratio on the (trans-)formation of ikaite. – *Geochimica et Cosmochimica Acta*, **217**, 128–143, New York.
- PURGSTALLER, B., KONRAD, F., DIETZEL, M., IMMENHAUSER, A. & MAVROMATIS, V. (2017b): Control of Mg^{2+}/Ca^{2+} activity ratio on the formation of crystalline carbonate minerals via an amorphous precursor. – *Crystal Growth and Design*, **17/3**, 1069–1078, Washington, D.C.
- R DEVELOPMENT CORE TEAM (2018): A language and environment for statistical computing. – R Foundation for Statistical Computing, Vienna, Austria. <http://www.R-project.org> (last visited: 19.08.2018).
- RANDOLPH, J.B. & SAAR, M.O. (2011): Combining geothermal energy capture with geologic carbon dioxide sequestration. – *Geophysical Research Letters*, **38**: L10401, Washington, D.C. <https://dx.doi.org/10.1029/2011GL047265>
- RAO, A. & CÖLFEN, H. (2017): Mineralization schemes in the living world: Mesocrystals. – In: VAN DRIESSCHE, A.E.S., KELLERMEIER, M., BENNING, L.G. & GEBAUER, D. (Eds.): *New Perspectives on Mineral Nucleation and Growth. – From Solution Precursors to Solid Materials*, 155–183, Cham.
- RASMUSSEN, S.O., BIGLER, M., BLOCKLEY, S.P., BLUNIER, T., BUCHARDT, S.L., CLAUSEN, H.B., CVIJANOVIC, I., DAHL-JENSEN, D., JOHNSEN, S.J., FISCHER, H., GKINIS, V., GUILLEVIC, M., HOEK, W.Z., LOWE, J.J., PEDRO, J.B., POPP, T., SEIERSTAD, I.K., STEFFENSEN, J.P., SVENSSON, A.M., VALLELONGA, P., VINTHER, B.M., WALKER, M.J.C., WHEATLEY, J.J. & WINSTRUP, M. (2014): A stratigraphic framework for abrupt climatic changes during the Last Glacial period based on three synchronized Greenland ice-core records: refining and extending the INTIMATE event stratigraphy. – *Quaternary Science Reviews*, **106**, 14–28, Amsterdam.
- REDDY, M.M. & NANCOLLAS, G.H. (1971): The crystallization of calcium carbonate: I. Isotopic exchange and kinetics. – *Journal of Colloid and Interface Science*, **36**, 166–172, Amsterdam.
- REEDER, R.J., NUGENT, M., LAMBLE, G.M., TAIT, C.D. & MORRIS, D.E. (2000): Uranyl incorporation into calcite and aragonite: XAFS and luminescence studies. – *Environmental Science and Technology*, **34**, 638–644, Washington, D.C.
- REITERER, F., JOHANNES, W. & GAMSJAGER, H. (1981): Semimicro determination of solubility constants: Copper (II) carbonate and iron (II) carbonate. – *Mikrochimica Acta*, **1**, 63–72, Wien.
- RICHARDS, D.A. & DORALE, J.A. (2003): Uranium-series chronology and environmental applications of speleothems. – *Reviews in Mineralogy and Geochemistry*, **52**, 407–460, Washington, D.C.
- RIDING, R. (2000): Microbial carbonates: the geological record of calcified bacterial-algal mats and biofilms. – *Sedimentology*, **47**, 179–214, Amsterdam.
- RIEHELMMANN, D.F.C., DEININGER, M., SCHOLZ, D., RIEHELMMANN, S., SCHRÖDER-RITZRAU, A., SPÖTL, C., RICHTER, D.K., MANGINI, A. & IMMENHAUSER, A. (2013): Disequilibrium carbon and oxygen isotope fractionation in recent cave calcite: Comparison of cave precipitates and model data. – *Geochimica et Cosmochimica Acta*, **103**, 232–244, New York.
- RIEHELMMANN, S., SCHRÖDER-RITZRAU, A., WASSENBURG, J.A., SCHREUER, J., RICHTER, D.K., RIEHELMMANN, D.F.C., TERENTE, M., CONSTANTIN, S., MANGINI, A. & IMMENHAUSER, A. (2014): Physico-chemical characteristics of drip waters: Influence on mineralogy and crystal morphology of recent cave carbonate precipitates. – *Geochimica et Cosmochimica Acta*, **145**, 13–29, New York.
- RINDER, T., DIETZEL, M. & LEIS, A. (2013): Calcium carbonate scaling under alkaline conditions – Case studies and hydrochemical modelling. – *Applied Geochemistry*, **35**, 132–141, Amsterdam.
- RIOTTE, J. & CHABAUX, F. (1999): ($^{234}U/^{238}U$) activity ratios in freshwaters as tracers of hydrological processes: the Strengbach watershed (Vosges, France). – *Geochimica et Cosmochimica Acta*, **63**, 1263–1275, New York.
- RIPKEN, M., GALLIEN, F., SCHLOTTERBACH, T. & LENGAUER, C.L. (2018): Structural and physicochemical characterization of basic calcium carbonate (BCC), $Ca_3(CO_3)_2(OH)_2 \cdot H_2O$. – *European Journal of Mineralogy*, **30**, 85–96, Stuttgart.
- RIVERA DIAZ, A., KAYA, E. & ZARROUK, S.J. (2016): Reinjection in geothermal fields. – A worldwide review update. – *Renewable and Sustainable Energy Reviews*, **53**, 105–162, Oxford.
- RODRIGUEZ-NAVARRO, C. & BENNING, L.G. (2013): Control of crystal nucleation and growth by additives. – *Elements*, **9**, 203–209, Québec.
- RODRÍGUEZ-RUIZ, I., VEESLER, S., GÓMEZ-MORALES, J., DELGADO-LÓPEZ, J.M., GRAUBY, O., HAMMADI, Z., CANDONI, N. & GARCÍA-RUIZ, J.M. (2014): Transient calcium carbonate hexahydrate (ikaite) nucleated and stabilized in confined nano- and picovolumes. – *Crystal Growth and Design*, **14**, 792–802, Washington, D.C.
- ROGERSON, M., PEDLEY, H.M., WADHAWAN, J.D. & MIDDLETON, R. (2008): New insights into biological influence on the geochemistry of freshwater carbonate deposits. – *Geochimica et Cosmochimica Acta*, **72**, 4976–4987, New York.
- ROSSI, C. & LOZANO, R.P. (2016): Hydrochemical controls on aragonite versus calcite precipitation in cave dripwaters. – *Geochimica et Cosmochimica Acta*, **192**, 70–96, New York.
- SAENGER, C. & WANG, Z. (2014): Magnesium isotope fractionation in biogenic and abiogenic carbonates: implications for paleoenvironmental proxies. – *Quaternary Science Reviews*, **90**, 1–21, Amsterdam.
- SAKOPARNIG, M., BOCH, R., WANG, X., LIN, K., SPÖTL, C., LEIS, A., GOLLOWITSCH, A. & DIETZEL, M. (2016): Calcite precipitation on glass substrates and active stalagmites in Katerloch Cave (Austria): Constraints from environmental monitoring. – *Geophysical Research Abstracts*, **18**, EGU2016-17458, Katlenburg-Lindau.
- SAND, K.K., RODRIGUEZ-BLANCO, J.D., MAKOVICKY, E., BENNING, L.G. & STIPP, S.L.S. (2012): Crystallization of $CaCO_3$ in water-alcohol mixtures: Spherulitic growth, polymorph stabilization, and morphology change. – *Crystal Growth and Design*, **12**, 842–853, Washington, D.C.
- SANNA, A., UIBU, M., CARAMANNA, G., KUUSIK, R. & MAROTO-VALER, M.M. (2014): A review of mineral carbonation technologies to sequester CO_2 . – *Chemical Society Reviews*, **43**, 8049–8080, London.
- SARKAR, A., DUTTA, K. & MAHAPATRA, S. (2013): Polymorph control of calcium carbonate using insoluble layered double hydroxide. – *Crystal Growth and Design*, **13**, 204–211, Washington, D.C.
- SARNTHEIN, M., BARTOLI, G., PRANGE, M., SCHMITTNER, A., SCHNEIDER, B., WEINELT, M., ANDERSEN, N. & GARBE-SCHÖNBERG, D. (2009): Mid-Pliocene shifts in ocean overturning circulation and the onset of Quaternary-style climates. – *Climate of the Past*, **5**, 269–283, Göttingen.
- SAUNDERS, P., ROGERSON, M., WADHAWAN, J.D., GREENWAY, G. & PEDLEY, H.M. (2014): Mg/Ca ratios in freshwater microbial carbonates: Thermodynamic, kinetic and vital effects. – *Geochimica et Cosmochimica Acta*, **147**, 107–118, New York.

- SCHAUBLE, E.A., GHOSH, P. & EILER, J.M. (2006): Preferential formation of ^{13}C - ^{18}O bonds in carbonate minerals, estimated using first-principles lattice dynamics. – *Geochimica et Cosmochimica Acta*, **70**, 2510–2529, New York.
- SCHMID, S.M., FÜGENSCHUH, B., KISSLING, E. & SCHUSTER, R. (2004): Tectonic map and overall architecture of the Alpine orogeny. – *Eclogae Geologicae Helveticae*, **97**, 93–117, Basel.
- SCHOLZ, D. & HOFFMANN, D.L. (2011): StalAge – An algorithm designed for construction of speleothem age models. – *Quaternary Geochronology*, **6**, 369–382, Amsterdam.
- SCHOLZ, D., MÜHLINGHAUS, C. & MANGINI, A. (2009): Modelling $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the solution layer on stalagmite surfaces. – *Geochimica et Cosmochimica Acta*, **73**, 2592–2602, New York.
- SCHOLZ, D., HOFFMANN, D.L., HELLSTROM, J. & BRONK RAMSEY, C. (2012): A comparison of different methods for speleothem age modelling. – *Quaternary Geochronology*, **14**, 94–104, Amsterdam.
- SCHULZ, O., VAVTAR, F. & DIEBER, K. (1997): Die Siderit-Erzlagerstätte Steirischer Erzberg: Eine geowissenschaftliche Studie, mit wirtschaftlicher und geschichtlicher Betrachtung. – *Archiv für Lagerstättenforschung der Geologischen Bundesanstalt*, **20**, 65–178, Wien.
- SEATON, N.C.A., WHITNEY, D.L., TEYSSIER, C., TORAMAN, E. & HEIZLER, M.T. (2009): Recrystallization of high-pressure marble (Sivrihisar, Turkey). – *Tectonophysics*, **479**, 241–253, Amsterdam.
- SEVILGEN, D.S., VENN, A.A., HU, M.Y., TAMBUTTÉ, E., DE BEER, D., PLANAS-BIELSA, V. & TAMBUTTÉ, S. (2019): Full in vivo characterization of carbonate chemistry at the site of calcification in corals. – *Science Advances*, **5**, eaau7447, Washington, D.C.
- SHEN, C.-C., WU, C.-C., CHENG, H., LAWRENCE EDWARDS, R., HSIEH, Y.-T., GALLET, S., CHANG, C.-C., LI, T.-Y., LAM, D.D., KANO, A., HORI, M. & SPÖTL, C. (2012): High-precision and high-resolution carbonate ^{230}Th dating by MC-ICP-MS with SEM protocols. – *Geochimica et Cosmochimica Acta*, **99**, 71–86, New York.
- SHENTON, B.J., GROSSMAN, E.L., PASSEY, B.H., HENKES, G.A., BECKER, T.P., LAYA, J.C., PEREZ-HUERTA, A., BECKER, S.P. & LAWSON, M. (2015): Clumped isotope thermometry in deeply buried sedimentary carbonates: The effects of bond reordering and recrystallization. – *Geological Society of America Bulletin*, **127**, 1036–1051, Boulder.
- SIDDALL, M., ROHLING, E.J., ALMOGI-LABIN, A., HEMLEBEN, C., MEISCHNER, D., SCHMELZER, I. & SMEED, D.A. (2003): Sea-level fluctuations during the last glacial cycle. – *Nature*, **423**, 853–858, London.
- SMART, P.L. & FRIEDERICH, H. (1986): Water movement and storage in the unsaturated zone of a maturely karstified carbonate aquifer, Mendip Hills, England. – *Proceedings of the Conference on Environmental Problems in Karst Terrains and their Solutions*, National Water Well Association, Ohio, 59–87, Columbus.
- SMITH, C.J.M. (2014): Laser ablation: A new approach to U-Pb speleothem dating. – *Talk at 25th BCRA Cave Science Symposium 2014*, Birmingham.
- SNOW, E. & YUND, R.A. (1987): The effect of ductile deformation on the kinetics and mechanisms of the aragonite-calcite transformation. – *Journal of Metamorphic Geology*, **5**, 141–153, Oxford.
- SPANOS, N. & KOUTSOUKOS, P.G. (1998): Kinetics of precipitation of calcium carbonate in alkaline pH at constant supersaturation. Spontaneous and seeded growth. – *The Journal of Physical Chemistry B*, **102**, 6679–6684, Washington, D.C.
- SPÖTL, C. & BOCH, R. (2012): Uranium Series Dating of Speleothems. – In: WHITE, W.B. & CULVER, D.C. (Eds.): *Encyclopedia of Caves*, 2nd ed., 838–844, Amsterdam.
- SPÖTL, C. & MANGINI, A. (2002): Stalagmite from the Austrian Alps reveals Dansgaard-Oeschger events during isotope stage 3: Implications for the absolute chronology of Greenland ice cores. – *Earth and Planetary Science Letters*, **203**, 507–518, Amsterdam.
- SPÖTL, C. & MANGINI, A. (2007): Speleothems and paleoglaciers. – *Earth and Planetary Science Letters*, **254**, 323–331, Amsterdam.
- SPÖTL, C. & MATTEY, D. (2006): Stable isotope microsampling of speleothems for palaeoenvironmental studies: A comparison of microdrill, micromill and laser ablation techniques. – *Chemical Geology*, **235**, 48–58, Amsterdam.
- SPÖTL, C., FAIRCHILD, I.J. & TOOTH, A.F. (2005): Cave air control on dripwater geochemistry, Obir Caves (Austria): Implications for speleothem deposition in dynamically ventilated caves. – *Geochimica et Cosmochimica Acta*, **69**, 2451–2468, New York.
- SPÖTL, C., MANGINI, A. & RICHARDS, D.A. (2006): Chronology and paleoenvironment of Marine Isotope Stage 3 from two high-elevation speleothems, Austrian Alps. – *Quaternary Science Reviews*, **25**, 1127–1136, Amsterdam.
- SPÖTL, C., BOCH, R. & WOLF, A. (2011): Eiszeitliche Klimadynamik im Spiegel eines Stalagmiten aus dem Hölloch (Bayern/Vorarlberg). – *Die Höhle*, **62**, 46–53, Wien.
- SPÖTL, C., FOHLMEISTER, J., CHENG, H. & BOCH, R. (2016): Modern aragonite formation at near-freezing conditions in an alpine cave, Carnic Alps, Austria. – *Chemical Geology*, **435**, 60–70, Amsterdam.
- STÄHL, G., PÁTZAY, G., WEISER, L. & KÁLMÁN, E. (2000): Study of calcite scaling and corrosion processes in geothermal systems. – *Geothermics*, **29**, 105–119, Amsterdam.
- STRAUHAL, T., PRAGER, C., MILLEN, B., SPÖTL, C., ZANGERL, C. & BRANDNER, R. (2016): Aquifer geochemistry of crystalline rocks and Quaternary deposits in a high altitude alpine environment (Kauner Valley, Austria). – *Austrian Journal of Earth Sciences*, **109**, 29–44, Wien.
- SU, M., HAN, J., LI, Y., CHEN, J., ZHAO, Y. & CHADWICK, K. (2015): Ultrasonic crystallization of calcium carbonate in presence of seawater ions. – *Desalination*, **369**, 85–90, Amsterdam.
- SUHARSO, BUHANI, BAHRI, S. & ENDARYANTO, T. (2011): Gambier extracts as an inhibitor of calcium carbonate (CaCO_3) scale formation. – *Desalination*, **265**, 102–106, Amsterdam.
- SÜRMELEHINDI, G., PASSCHIER, C.W., BAYKAN, O.N., SPÖTL, C. & KESENER, P. (2013): Environmental and depositional controls on laminated freshwater carbonates: An example from the Roman aqueduct of Patara, Turkey. – *Palaeogeography, Palaeoclimatology, Palaeoecology*, **386**, 321–335, Amsterdam.
- SWAINSON, I.P. & HAMMOND, R.P. (2001): Ikaite, $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$: Cold comfort for glendonites as paleothermometers. – *American Mineralogist*, **86**, 1530–1533, Washington, D.C.
- TAKAI, K., NAKAMURA, K., TOKI, T., TSUNOGAI, U., MIYAZAKI, M., MIYAZAKI, J., HIRAYAMA, H., NAKAGAWA, S., NUNOURA, T. & HORIKOSHII, K. (2008): Cell proliferation at 122° C and isotopically heavy CH_4 production by a hyperthermophilic methanogen under high-pressure cultivation. – *Proceedings of the National Academy of Sciences*, **105**, 10949–10954, Washington, D.C.
- TANG, C.C., THOMPSON, S.P., PARKER, J.E., LENNIE, A.R., AZOUGH, F. & KATO, K. (2009): The ikaite-to-vaterite transformation: new evidence from diffraction and imaging. – *Journal of Applied Crystallography*, **42**, 225–233, Oxford.
- TANG, J., KÖHLER, S.J. & DIETZEL, M. (2008a): $\text{Sr}^{2+}/\text{Ca}^{2+}$ and $^{44}\text{Ca}/^{40}\text{Ca}$ fractionation during inorganic calcite formation: I. Sr incorporation. – *Geochimica et Cosmochimica Acta*, **72**, 3718–3732, New York.
- TANG, J., DIETZEL, M., BÖHM, F., KÖHLER, S.J. & EISENHAEUER, A. (2008b): $\text{Sr}^{2+}/\text{Ca}^{2+}$ and $^{44}\text{Ca}/^{40}\text{Ca}$ fractionation during inorganic calcite formation: II. Ca isotopes. – *Geochimica et Cosmochimica Acta*, **72**, 3733–3745, New York.

- TANG, J., NIEDERMAYER, A., KÖHLER, S.J., BÖHM, F., KISAKÜREK, B., EISENHAUER, A. & DIETZEL, M. (2012): Sr²⁺/Ca²⁺ and ⁴⁴Ca/⁴⁰Ca fractionation during inorganic calcite formation: III. Impact of salinity/ionic strength. – *Geochimica et Cosmochimica Acta*, **77**, 432–443, New York.
- TANG, J., DIETZEL, M., FERNANDEZ, A., TRIPATI, A.K. & ROSENHEIM, B.E. (2014): Evaluation of kinetic effects on clumped isotope fractionation (Δ_{47}) during inorganic calcite precipitation. – *Geochimica et Cosmochimica Acta*, **134**, 120–136, New York.
- TEMPLETON, A. & BENZERARA, K. (2015): Emerging frontiers in geomicrobiology. – *Elements*, **11**, 423–429, Québec.
- TENG, H.H. (2013): How ions and molecules organize to form crystals. – *Elements*, **9**, 189–194, Québec.
- TESORIERO, A.J. & PANKOW, J.F. (1996): Solid solution partitioning of Sr²⁺, Ba²⁺, and Cd²⁺ to calcite. – *Geochimica et Cosmochimica Acta*, **60**, 1053–1063, New York.
- THALMANN, F. (1979): Zur Eisenspatvererzung in der nördlichen Grauwackenzone am Beispiel des Erzberges bei Eisenerz und Radmer/Bucheck. – *Verhandlungen der Geologischen Bundesanstalt*, **1978/3**, 479–489, Wien.
- TÖCHTERLE, P., DUBLYANSKY, Y., STÖBENER, N., MANDIĆ, M. & SPÖTL, C. (2017): High-resolution isotopic monitoring of cave air CO₂. – *Rapid Communications in Mass Spectrometry*, **31**, 895–900, Chichester.
- TOKER, E., KAYSERI-ÖZER, M.S., ÖZKUL, M. & KELE, S. (2015): Depositional system and palaeoclimatic interpretations of Middle to Late Pleistocene travertines: Kocabas, Denizli, south-west Turkey. – *Sedimentology*, **62**, 1360–1383, Amsterdam.
- TREMAINE, D.M. & FROELICH, P.N. (2013): Speleothem trace element signatures: A hydrologic geochemical study of modern cave dripwaters and farmed calcite. – *Geochimica et Cosmochimica Acta*, **121**, 522–545, New York.
- TREMAINE, D.M., FROELICH, P.N. & WANG, Y. (2011): Speleothem calcite farmed in situ: Modern calibration of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ paleoclimate proxies in a continuously-monitored natural cave system. – *Geochimica et Cosmochimica Acta*, **75**, 4929–4950, New York.
- TRIPATI, A.K., HILL, P.S., EAGLE, R.A., MOSENFELDER, J.L., TANG, J., SCHAUBLE, E.A., EILER, J.M., ZEEBE, R.E., UCHIKAWA, J., COPLIN, T.B., RIES, J.B. & HENRY, D. (2015): Beyond temperature: Clumped isotope signatures in dissolved inorganic carbon species and the influence of solution chemistry on carbonate mineral composition. – *Geochimica et Cosmochimica Acta*, **166**, 344–371, New York.
- TRUCHE, L., BAZARKINA, E.F., BERGER, G., CAUMON, M.-C., BESSAQUE, G. & DUBESSY, J. (2016): Direct measurement of CO₂ solubility and pH in NaCl hydrothermal solutions by combining in-situ potentiometry and Raman spectroscopy up to 280 °C and 150 bar. – *Geochimica et Cosmochimica Acta*, **177**, 238–253, New York.
- TUTOLO, B.M., LUHMANN, A.J., KONG, X.-Z., SAAR, M.O. & SEYFRIED JR, W.E. (2015): CO₂ sequestration in feldspar-rich sandstone: Coupled evolution of fluid chemistry, mineral reaction rates, and hydrogeochemical properties. – *Geochimica et Cosmochimica Acta*, **160**, 132–154, New York.
- VAKS, A., BAR-MATTHEWS, M., AYALON, A., MATTHEWS, A., FRUMKIN, A., DAYAN, U., HALICZ, L., ALMOGI-LABIN, A. & SCHILMAN, B. (2006): Paleoclimate and location of the border between Mediterranean climate region and the Saharo-Arabian Desert as revealed by speleothems from the northern Negev Desert, Israel. – *Earth and Planetary Science Letters*, **249**, 384–399, Amsterdam.
- VALDEZ, B., SCHORR, M., QUINTERO, M., CARRILLO, M., ZLATEV, R., STOYTCHIEVA, M. & DE DIOS OCAMPO, J. (2009): Corrosion and scaling at Cerro Prieto geothermal field. – *Anti-Corrosion Methods and Materials*, **56**, 28–34, Bradford.
- VALLEY, J.W., EILER, J.M., GRAHAM, C.M., GIBSON, E.K., ROMANEK, C.S. & STOLPER, E.M. (1997): Low-temperature carbonate concretions in the Martian meteorite ALH84001: Evidence from stable isotopes and mineralogy. – *Science*, **275**, 1633–1638, Washington, D.C.
- VAN DRIESSCHE, A.E.S., KELLERMEIER, M., BENNING, L.G. & GEBAUER, D. (2017): *New Perspectives on Mineral Nucleation and Growth – From Solution Precursors to Solid Materials*. – 380 pp., Switzerland (Springer International Publishing).
- VAN HUSEN, D. (2009): Zusammenfassender Überblick über die quartäre Entwicklung um das westliche Hochschwabmassiv (Blatt 101 Eisenerz). – *Tagungsband zur Arbeitstagung der Geologischen Bundesanstalt 2009*, Leoben, 106–117, Wien.
- VAN HUSEN, D. & FRITSCH, A. (2007): Der Bergsturz von Wildalpen (Steiermark). – *Jahrbuch der Geologischen Bundesanstalt*, **147**, 201–213, Wien.
- VAN ZUILEN, K., MÜLLER, T., NÄGLER, T.F., DIETZEL, M. & KÜSTERS, T. (2016): Experimental determination of barium isotope fractionation during diffusion and adsorption processes at low temperatures. – *Geochimica et Cosmochimica Acta*, **186**, 226–241, New York.
- VARSÁNYI, I. & KOVÁCS, L.Ó. (2006): Arsenic, iron and organic matter in sediments and groundwater in the Pannonian Basin, Hungary. – *Applied Geochemistry*, **21**, 949–963, Amsterdam.
- VARSÁNYI, I., MATRAY, J.-M. & KOVÁCS, L.Ó. (1997): Geochemistry of formation waters in the Pannonian Basin (southeast Hungary). – *Chemical Geology*, **140**, 89–106, Amsterdam.
- VASYLIEV, G., VASYLIEVA, S., NOVOSAD, A. & GERASYMENKO, Y. (2018): Ultrasonic modification of carbonate scale electrochemically deposited in tap water. – *Ultrasonics Sonochemistry*, **48**, 57–63, Amsterdam.
- VIETEN, R., WINTER, A., WARKEN, S.F., SCHRÖDER-RITZRAU, A., MILLER, T.E. & SCHOLZ, D. (2016): Seasonal temperature variations controlling cave ventilation processes in Cueva Larga, Puerto Rico. – *International Journal of Speleology*, **45**, 259–273, Tampa.
- WANG, H., ALFREDSSON, V., TROPSCH, J., ETTL, R. & NYLANDER, T. (2013): Formation of CaCO₃ deposits on hard surfaces – Effect of bulk solution conditions and surface properties. – *ACS Applied Materials and Interfaces*, **5**, 4035–4045, Washington, D.C.
- WANG, X., EDWARDS, R.L., AULER, A.S., CHENG, H., KONG, X., WANG, Y., CRUZ, F.W., DORALE, J.A. & CHIANG, H.-W. (2017): Hydroclimate changes across the Amazon lowlands over the past 45,000 years. – *Nature*, **541**, 204–207, London.
- WANNER, C., EICHINGER, F., JAHRFELD, T. & DIAMOND, L.W. (2017): Causes of abundant calcite scaling in geothermal wells in the Bavarian Molasse Basin, Southern Germany. – *Geothermics*, **70**, 324–338, Amsterdam.
- WARSINGER, D.M., SWAMINATHAN, J., GUILLEN-BURRIEZA, E., ARAFAT, H.A. & LIENHARD, J.H. (2015): Scaling and fouling in membrane distillation for desalination applications: A review. – *Desalination*, **356**, 294–313, Amsterdam.
- WASSENBURG, J.A., SCHOLZ, D., JOCHUM, K.P., CHENG, H., OSTER, J., IMMENHAUSER, A., RICHTER, D.K., HÄGER, T., JAMIESON, R.A., BALDINI, J.U.L., HOFFMANN, D. & BREITENBACH, S.F.M. (2016): Determination of aragonite trace element distribution coefficients from speleothem calcite-aragonite transitions. – *Geochimica et Cosmochimica Acta*, **190**, 347–367, New York.
- WEDENIG, M., DIETZEL, M., BOCH, R. & HIPPLER, D. (2016): Experiments on different materials (polyamide, stainless & galvanized steel) influencing geothermal CaCO₃ scaling formation: Polymorphs & elemental incorporation. – *Geophysical Research Abstracts*, **18**, EGU2016-10056, Katlenburg-Lindau.
- WEIDENDORFER, D., SCHMIDT, M.W. & MATTSSON, H.B. (2017): A common origin of carbonatite magmas. – *Geology*, **45**, 507–510, Washington, D.C.

- WESTPHAL, A., EICHINGER, F., EICHINGER, L. & WÜRDEMANN, H. (2019): Change in the microbial community of saline geothermal fluids amended with a scaling inhibitor: effects of heat extraction and nitrate dosage. – *Extremophiles*, **23/3**, 283–304, Tokyo. <https://dx.doi.org/10.1007/s00792-019-01080-0>
- WIEDERHOLD, J.G. (2015): Metal stable isotope signatures as tracers in environmental geochemistry. – *Environmental Science and Technology*, **49**, 2606–2624, Washington, D.C.
- WHITE, W.B. & CULVER, D.C. (2012): *Encyclopedia of Caves*. – 2nd ed., 945 pp., Amsterdam (Chennai Academic Press).
- WOLFGRAMM, M., RAUPPACH, K. & THORWART, K. (2011): New mineral formations and transport of particles in the thermal water loop of geothermal plants in Germany. – *Zeitschrift für Geologische Wissenschaften*, **39**, 213–239, Berlin.
- WOLTERS, M., NEHRKE, G., GUSTAFSSON, J.P. & VAN CAPPELLEN, P. (2012): Calcite growth kinetics: Modeling the effect of solution stoichiometry. – *Geochimica et Cosmochimica Acta*, **77**, 121–134, New York.
- WOODHEAD, J., HELLSTROM, J., MAAS, R., DRYSDALE, R., ZANCHETTA, G., DEVINE, P. & TAYLOR, E. (2006): U-Pb geochronology of speleothems by MC-ICPMS. – *Quaternary Geochronology*, **1**, 208–221, Amsterdam.
- WUNSCH, C. (2006): Abrupt climate change: An alternative view. – *Quaternary Research*, **65**, 191–203, Amsterdam.
- WÜRDEMANN, H., WESTPHAL, A., LERM, S., KLEYBÖCKER, A., TEITZ, S., KASINA, M., MIETHLING-GRAFF, R., SEIBT, A. & WOLFGRAMM, M. (2014): Influence of microbial processes on the operational reliability in a geothermal heat store – Results of long-term monitoring at a full scale plant and first studies in a bypass system. – *Energy Procedia*, **59**, 412–417, Amsterdam.
- WÜRDEMANN, H., WESTPHAL, A., KLEYBÖCKER, A., MIETHLING-GRAFF, R., TEITZ, S., KASINA, M., SEIBT, A., WOLFGRAMM, M., EICHINGER, F. & LERM, S. (2016): Microbial metabolic processes affect the operation of geothermal plants and the success of countermeasures. – *Grundwasser*, **21**, 93–106, Berlin–Heidelberg.
- YAN, H., LIU, Z. & SUN, H. (2017): Effect of in-stream physicochemical processes on the seasonal variations in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in laminated travertine deposits in a mountain stream channel. – *Geochimica et Cosmochimica Acta*, **202**, 179–189, New York.
- YANG, Q., SCHOLZ, D., JOCHUM, K.P., HOFFMANN, D.L., STOLL, B., WEIS, U., SCHWAGER, B. & ANDREAE, M.O. (2015): Lead isotope variability in speleothems – A promising new proxy for hydrological change? First results from a stalagmite from western Germany. – *Chemical Geology*, **396**, 143–151, Amsterdam.
- YARDLEY, B.W.D., EWING, R.C. & WHITTLESTON, R.A. (2016): Deep-mined geological disposal of radioactive waste. – *Elements*, **12**, 225–296, Québec.
- YOSHIOKA, S., OHDE, S., KITANO, Y. & KANAMORI, N. (1986): Behaviour of magnesium and strontium during the transformation of coral aragonite to calcite in aquatic environments. – *Marine Chemistry*, **18**, 35–48.
- ZAMMIT, C.M., SHUSTER, J.P., GAGEN, E.J. & SOUTHAM, G. (2015): The geomicrobiology of supergene metal deposits. – *Elements*, **11**, 337–342, Québec.
- ZARROUK, S.J. & MOON, H. (2014): Efficiency of geothermal power plants: A worldwide review. – *Geothermics*, **51**, 142–153, Amsterdam.
- ZHANG, Z., XIE, Y., XU, X., PAN, H. & TANG, R. (2012): Transformation of amorphous calcium carbonate into aragonite. – *Journal of Crystal Growth*, **343**, 62–67, Amsterdam.
- ZHOU, J., LUNDSTROM, C.C., FOUKE, B., PANNO, S., HACKLEY, K. & CURRY, B. (2005): Geochemistry of speleothem records from southern Illinois: Development of $(^{234}\text{U})/(^{238}\text{U})$ as a proxy for paleo-precipitation. – *Chemical Geology*, **221**, 1–20, Amsterdam.
- ZOU, Z., HABRAKEN, W.J.E.M., MATVEEVA, G., JENSEN, A.C.S., BERTINETTI, L., HOOD, M.A., SUN, C.-Y., GILBERT, P.U.P.A., POLISHCHUK, I., POKROY, B., MAHAMID, J., POLITI, Y., WEINER, S., WERNER, P., BETTE, S., DINNEBIER, R., KOLB, U., ZOLOTAYABKO, E. & FRATZL, P. (2019): A hydrated crystalline calcium carbonate phase: Calcium carbonate hemihydrate. – *Science*, **363**, 396–400, Washington, D.C.