

# Microbially induced mineral formation in extreme environments

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Prokaryotic microorganisms of the domains Bacteria and Archaea have the potential to dissolve and to precipitate minerals (KONHAUSER 2007). During early diagenesis the microbially driven remineralization of organic matter is shaping the chemical environment of sediments, which in turn is governing secondary mineral formation. The resultant authigenic minerals like calcite, apatite, pyrite, glauconite and countless others inherit geochemical signatures that allow the reconstruction of the biogeochemical processes that favored their formation. Stable isotope patterns of elements like carbon, oxygen, and sulfur have been used extensively to characterize modes of mineral formation during early diagenesis. The great potential of molecular fossils, deriving from microorganisms involved in mineral formation, however, is only beginning to be utilized. These so-called lipid biomarkers mostly derive from prokaryotic cell membranes and are of variable specificity and stability. Such molecular fossils allow the identification of microorganisms even in very old rocks, fostering the study of the deep time evolution of life and biogeochemical processes. The major constraint of the applicability of lipid biomarkers is the thermal maturity of the rocks under study.

Extreme environments have attracted much interest in recent years. This interest stems from the observation that many extreme environments are inhabited by deeply-branching (i.e., particular ancient forms of life) microorganisms and the desire to better understand the early evolution of the first ecosystems on Earth. Moreover, improving our understanding of the function and the limits of life in extreme environments will help identifying celestial bodies that may provide favorable conditions for the presence of life. The latter is one of the main targets of the rapidly growing field of astrobiology. A much more down-to-earth benefit of studying extreme environments is the circumstance that these systems tend to be dominated by fewer processes, making the recognition of biogeochemical pathways and their key players much easier. Life that is found in extreme environments like hydrothermal vents, ocean-floor hard rocks, or the deep crustal biosphere relies on chemosynthesis. Unlike photosynthesis, this mode of primary production gains energy for the synthesis of biomass by the oxidation of chemical compounds. Early life on Earth was chemosynthetic and life on other astronomical bodies is much more likely to be chemosynthesis-based than

photosynthesis-based.

Here, I look into some examples of secondary mineral formation in environments that are typified by the presence of reducing compounds like methane or crude oil. These compounds are the basis for life in such environments that seem to be harsh or even hostile from a metazoan perspective. Yet, the products of this style of life are ubiquitously encountered by geologists, forming ore deposits and other geological bodies.

## Mineral formation at methane seeps

Ecosystems with high abundance but low diversity metazoan communities flourishing at marine methane seeps along continental margins were first recognized about 25 years ago. Bivalve mollusks and tube worms occur in fantastic abundance at these sites on an otherwise almost barren seafloor. The so-called chemosymbiotic metazoans are dependent on bacteria harbored in their tissues, which oxidize reducing compounds like methane and hydrogen sulfide. The other striking feature of methane seeps is the formation of secondary carbonate minerals. Carbonate authigenesis is driven by the key biogeochemical process at seeps, the anaerobic oxidation of methane (AOM). In this process, ascending methane is oxidized by a consortium of archaea and sulfate-reducing bacteria (BOETIUS et al. 2000, BIRGEL et al. 2008, PECKMANN et al. 2009). As a consequence of this microbially mediated process, alkalinity increases and carbonate minerals precipitate (RITGER et al. 1987, PECKMANN et al. 2001). Because methane is the natural compound most depleted in the <sup>13</sup>C isotope, the secondary carbonates inherit this <sup>13</sup>C depletion, allowing the identification of methane-derived carbonates also in the rock record (PECKMANN & THIEL 2004). Many of the carbonates forming at seeps reveal microbial fabrics (e.g., clotted micrite) that agree with their microbial origin. Ancient seep limestones have now been recognized through most of the Phanerozoic (CAMPBELL 2006), but no methane seep deposits older than Middle Devonian are known to date (PECKMANN et al. 1999a).

Although carbonates are the by far most abundant minerals at seeps, sulfate minerals can also be rock forming, whereas sulfides are usually only an accessory phase. The volumetrically dominant carbonate phases of seep limestones are (1) microcrystalline calcite or aragonite and

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(2) fibrous aragonite cement, forming isopachous rims or botryoidal crystal aggregates. The microcrystalline phases usually contain abundant framboidal pyrite. This pyrite is a by-product of sulfate-dependent AOM, which produces sulfide ions that react with sedimentary iron phases to form iron monosulfides. These monosulfides subsequently transform into pyrite. Pyrite enclosed in modern seep carbonates is typified by low  $\delta^{34}\text{S}$  values (as low as -41‰), reflecting bacterial sulfate reduction and a wide spread of  $\delta^{34}\text{S}$  values even within individual pyrite grains of as much as 36‰ (Kohn et al. 1998). The small scale variability of  $\delta^{34}\text{S}$  values, which is also apparent for pyrite enclosed in ancient seep limestones (Peckmann & Thiel 2004), reflects bacterial sulfate reduction in microenvironments under closed system conditions, where small, residual pools of seawater-sulfate are utilized.

Fluids expelled at methane seeps often contain high amounts of dissolved barium. This barium derives from the dissolution of barite dispersed in the sediments below the depth of sulfate depletion. When seepage fluids enriched in barium get into contact with sulfate-rich seawater, barite precipitates. Such precipitates may form barite towers of more than 20 m in height on the seafloor (Aloisi et al. 2004). Structural, paleontological, and geochemical evidence indicates that some Paleozoic stratiform barite deposits formed by this mechanism at methane seeps (Torres et al. 2003). In summary, authigenic  $^{13}\text{C}$ -depleted carbonate minerals, pyrite, and barite represent a long-lasting archive of biogeochemical processes at ancient methane seeps.

### **Authigenesis of carbonate minerals in serpentinites**

When peridotites are exposed to seawater along slow- and ultraslow spreading oceanic ridges, these ultramafic rocks of the upper mantle are affected by the process of serpentization. The reactions between ultramafic rocks and seawater result in the development of high calcium concentrations and high pH values in the interacting fluids, favoring carbonate precipitation despite of low dissolved inorganic carbon contents. Zones of active serpentization are also characterized by hydrogen and methane anomalies. These reducing compounds are readily utilized by microorganisms, if suitable electron acceptors are available. Metabolisms favored under these conditions including autotrophic methanogenesis using hydrogen or methanotrophy may induce carbonate precipitation. Although carbonate formation seems to be mostly physico-chemically-driven due to high pH values and high calcium concentrations developing during serpentization, an additional biological impact on the carbonate system cannot be excluded. Probably the most well-known and most spectacular carbonate deposits associated with a serpentization setting are those of the so-called Lost City Field that is situated more than 15 km away from the spreading axis of the Mid-Atlantic Ridge. In this field, carbonate chimneys forming at the hydrothermal vents reach heights of 60 m or more (Kelley et al. 2005). Molecular fossils extracted from these chimneys indicate

that archaeal methanogenesis is indeed the dominant metabolism (Bradley et al. 2009).

Carbon, oxygen, and strontium isotope as well as rare earth element patterns of authigenic carbonate minerals recovered from different sites along the Mid-Atlantic Ridge reveal that the environmental conditions during carbonate formation in ocean-floor hard rocks vary substantially (Eickmann et al. 2009a, b). Few carbonate phases have been found showing signatures that agree with a biogenic origin from methanogenesis. The origin of secondary carbonates in ancient serpentinites is more difficult to constrain. Interestingly, many ultramafic complexes in nappes of the Alps are covered by serpentinite breccias, known as ophiocalcites (Bernoulli & Weissert 1985). Sedimentary and diagenetic fabrics as well as composition of these ophiocalcites are similar to modern analogues from ocean basins where ultramafic rocks are exposed. The  $^{13}\text{C}$  content of ophiocalcites from the Alps agrees with seawater-derived dissolved inorganic carbon as carbon source (Weissert & Bernoulli 1984). Some of the carbonate dikes apparently represent injection of marine sediment, but it should be tested, if some of the calcite is of an authigenic origin similar to the examples from the Mid-Atlantic Ridge.

### **Carbonate mineral and native sulfur formation in hypersaline environments**

Biogenic deposits of native sulfur worldwide are enclosed in evaporite sequences. The sulfur is found in association with secondary carbonate minerals. Bacterial sulfate reduction is considered to be the key process for the precipitation of this sort of sulfur and the associated carbonates (Feely & Kulp 1957, Pierre & Rouchy 1988, Peckmann et al. 1999b). Sulfate-reducing bacteria oxidize organic compounds including crude oil and methane. The bacterial metabolism leads to the production of hydrogen sulfide and an increase of carbonate alkalinity, inducing precipitation of carbonate minerals. The sulfur is believed to result from the oxidation of hydrogen sulfide, but the exact mechanisms are still unknown and a direct production of sulfur in the course of bacterial sulfate reduction cannot be excluded.

Rocks containing biogenic sulfur are classified into bioepigenetic and biosynthetic deposits. Epigenetic deposits form after burial and subsequent uplift of the evaporitic host rocks, often hundreds of millions of years after deposition. Syngenesis occurs in a similar fashion, but during sedimentation and very early diagenesis. In Europe, biogenic sulfur deposits are particularly abundant in the Mediterranean, where they are linked to evaporites that deposited during the Messinian salinity crisis. A bacterial origin of the Sicilian sulfur deposits was already suggested about one hundred years ago and isotope data on sulfur and carbonates later on confirmed this suggestion (Dessau et al. 1962). A recent study of different Sicilian sulfur and carbonate deposits revealed that the formation of secondary minerals formed along both syngenetic and epigenetic pathways, establishing that syngenetic formation and not only epigenetic formation can yield economically significant amounts of sulfur (Ziegenbalg et al. in press).

Many of the native sulfur occurrences worldwide have not been investigated to date. Their fascinating biogeochemical genesis and their link to oil and gas reservoirs make them rewarding study objects. Although sulfur is presently not mined from these deposits – it is instead extracted from oil – the ebbing of oil reserves in the future is likely to cause a renewed interest in this source of sulfur ore.

## References

- ALOISI, G., WALLMANN, K., BOLLWERK, S.M., DERKACHEV, A., BOHRMANN, G. & SUSS, E. (2004): The effect of dissolved barium on biogeochemical processes at cold seeps. - *Geochimica et Cosmochimica Acta*, **68**: 1735-1748, Amsterdam.
- BERNOULLI, D. & WEISSERT, H. (1985): Sedimentary fabrics in marine ophiocalcites, South Pennine Arosa zone, Switzerland. - *Geology*, **13**: 755-758, Boulder.
- BIRGEL, D., HIMMLER, T., FREIWALD, A. & PECKMANN, J. (2008): A new constraint on the antiquity of anaerobic oxidation of methane: Late Pennsylvanian seep limestones from southern Namibia. - *Geology*, **36**: 543-546, Boulder.
- BOETIUS, A., RAVENSCHLAG, K., SCHUBERT, C.J., RICKERT, D., WIDDEL, F., GIESEKE, A., AMANN, R., JORGENSEN, B.B., WITTE, U. & PFANNKUCHE, O. (2000): A marine microbial consortium apparently mediating anaerobic oxidation of methane. - *Nature*, **407**: 623-626, London.
- BRADLEY, A.S., HAYES, J.M. & SUMMONS, R.E. (2009): Extraordinary  $^{13}\text{C}$  enrichment of diether lipids at the Lost City Hydrothermal Field indicates a carbon-limited ecosystem. - *Geochimica et Cosmochimica Acta*, **73**: 102-118, Amsterdam.
- CAMPBELL, K.A. (2006): Hydrocarbon seep and hydrothermal vent paleoenvironments and paleontology: Past developments and future research directions. - *Palaeogeography, Palaeoclimatology, Palaeoecology*, **232**: 362-407, Amsterdam.
- DESSAU, G., JENSEN, M.L. & NAKAI, N. (1962): Geology and isotopic studies of Sicilian sulfur deposits. - *Economic Geology*, **57**: 410-438, Littleton.
- EICKMANN, B., BACH, W. & PECKMANN, J. (2009a): Authigenesis of carbonate minerals in modern and Devonian ocean-floor hard rocks. - *Journal of Geology*, **117**: 307-323, Chicago.
- EICKMANN, B., BACH, W., ROSNER, M. & PECKMANN, J. (2009b): Geochemical constraints on the modes of carbonate precipitation in peridotites from the Logatchev Hydrothermal Vent Field and Gakkel Ridge. - *Chemical Geology*, **268**, 97-106, Amsterdam.
- FEELY, H.W. & KULP, J.L. (1957): Origin of Gulf coast salt-dome sulphur deposits. - *Bulletin of the American Association of Petroleum Geologists*, **41**: 1802-1853, Tulsa.
- KELLEY, D.S. & 25 others (2005): A serpentinite-hosted ecosystem: The Lost City Hydrothermal Field. - *Science*, **307**: 1428-1434, Washington D.C.
- KOHN, M.J., RICIPUTI, L.R., STAKES, D. & ORANGE, D.L. (1998): Sulfur isotope variability in biogenic pyrite: Reflections of heterogeneous bacterial colonization? - *American Mineralogist*, **83**: 1454-1468, Washington D.C.
- KONHAUSER, K. (2007): *Introduction to Geomicrobiology*. - Blackwell Publishing, 1-425, Oxford.
- PECKMANN, J., PAUL, J. & THIEL, V. (1999b): Bacterially mediated formation of diagenetic aragonite and native sulfur in Zechstein carbonates (Upper Permian, Central Germany). - *Sedimentary Geology*, **126**: 205-222, Amsterdam.
- PECKMANN, J., WALLISER, O.H., RIEGEL, W. & REITNER, J. (1999a): Signatures of hydrocarbon venting in a Middle Devonian carbonate mound (Holland Mound) at the Hamar Laghdad (AntiAtlas, Morocco). - *Facies*, **40**: 281-296, Erlangen.
- PECKMANN, J., REIMER, A., LUTH, U., LUTH, C., HANSEN, B.T., HEINICKE, C., HOEFS, J. & REITNER, J. (2001): Methane-derived carbonates and authigenic pyrite from the northwestern Black Sea. - *Marine Geology*, **177**: 129-150, Amsterdam.
- PECKMANN, J. & THIEL, V. (2004): Carbon cycling at ancient methane-seeps. - *Chemical Geology*, **205**, 443-467, Amsterdam.
- PECKMANN, J., BIRGEL, D. & KIEL, S. (2009): Molecular fossils reveal fluid composition and flow intensity at a Cretaceous seep. - *Geology*, **37**: 847-850, Boulder.
- PIERRE, C. & ROUCHY, J.M. (1988): Carbonate replacements after sulfate evaporites in the middle Miocene of Egypt. - *Journal of Sedimentary Petrology*, **58**: 446-456, Boulder.
- RITGER, S., CARSON, B. & SUSS, E. (1987): Methane-derived authigenic carbonates formed by subduction-induced pore-water expulsion along the Oregon/Washington margin. - *Geological Society of America Bulletin*, **98**: 147-156, Boulder.
- TORRES, M.E., BOHRMANN, G., DUBE, T.E. & POOLE, F.G. (2003): Formation of modern and Paleozoic stratiform barite at cold methane seeps on continental margins. - *Geology*, **31**: 897-900, Boulder.
- WEISSERT, H. & BERNOULLI, D. (1984): Oxygen isotope composition of calcite in Alpine ophiocarbonates: a hydrothermal or Alpine metamorphic signal? - *Eclogae Geologicae Helvetiae*, **77**: 29-43, Basel.
- ZIEGENBALG, S.B., BRUNNER, B., ROUCHY, J.M., BIRGEL, D., PIERRE, C., BÖTTCHER, M.E., CARUSO, A., IMMENHAUSER, A. & PECKMANN, J. (in press): Formation of secondary carbonates and native sulphur in sulphate-rich Messinian strata, Sicily. - *Sedimentary Geology*.