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The Permian-Triassic of the Gartnerkofel-1 Core (Carnic Alps, Austria): Dolomitization of the Permian-Triassic Sequence

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With 1 Text-Figure and 1 Plate

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Carnic Alps
Upper Permian
Lower Triassic
Diagenesis
Dolomitization

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Zusammenfassung

Nahezu die gesamte durchörterte Schichtfolge der Forschungsbohrung Gartnerkofel-1 besteht aus feinkörnigem syndiagenetischem Dolomit, in dem aber noch vereinzelt Fossilreste und Sedimentstrukturen erkennbar sind. Nach der Bildung von Stylolithen infolge Drucklösung wurde in einer zweiten Phase ein grobkörniger Dolomit gebildet, der vor allem für die Werfen Formation charakteristisch ist. Auffallenderweise ist diese späte Dolomitisierung auf die Umgebung von Störungen konzentriert. Die Dolomitisierung ist mit diagenetischem Pyrit assoziiert. Dies läßt vermuten, daß die Diagenese teilweise unter anoxischen Bedingungen erfolgte und die Reduktion des Sulfats einen Dolomitisierungseffekt auslöste.

Abstract

Nearly the whole of the Gartnerkofel-1 core section is fine-grained syndiagenetic dolomite, with relics of sedimentary structures and fossils. After formation of stylolites by pressure solution, a further stage produced coarse dolomite crystallization, particularly in the Werfen Formation. Some of this late dolomitization is concentrated near faults. Dolomitization is associated with diagenetic pyrite, suggesting that the diagenesis proceeded under anoxic conditions: the reduction of sulfate may have helped dolomite nucleation.

1. Introduction

Many of the Pre-Tertiary platform carbonate sequences are presently partly or completely dolomitized. Though for many years the argument of "increasing dolomite – with age" was accepted, recently R. K. GIVEN & B. H. WILKINSON (1987) argue that the percentage of dolomite seems to correlate better with sea level changes. They argue that dolomitization is enhanced during transgressions, which are periods of high pCO_2, thus lower calcite saturation state in shallow seas. Although the Permian is a period with relative low content of dolomite (G.V. CHILINGAR, 1956) the Permo-Triassic sequence of the Alps is to a large extent dolomitized. In many regions the dolomitization is restricted both vertically or/and horizontally. In some

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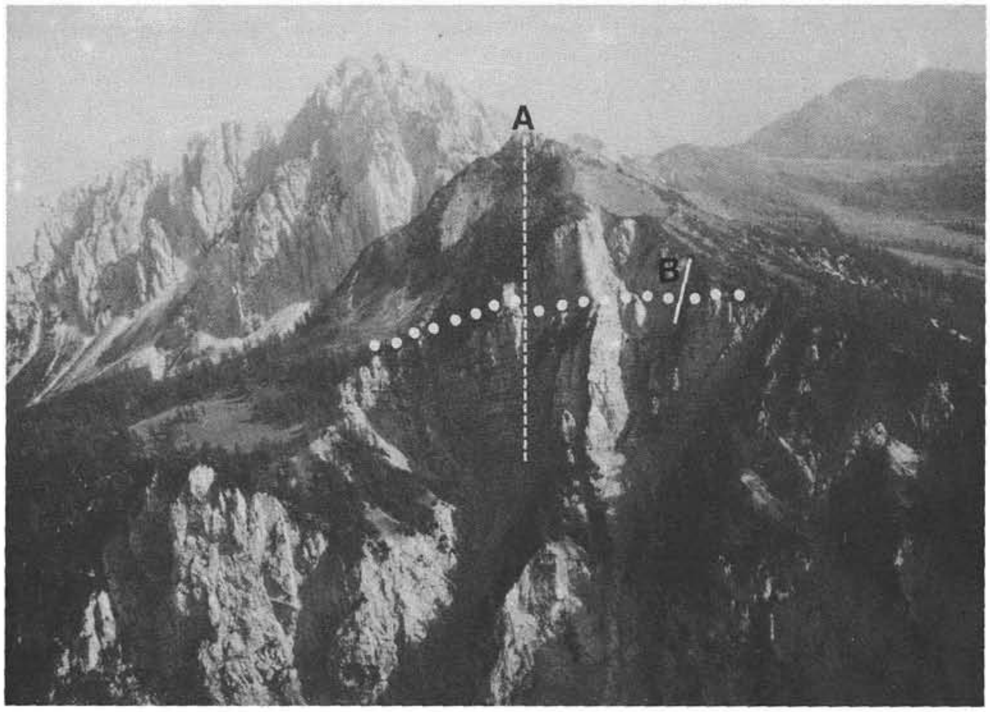


Text-Fig. 1.
Aerial photograph from the north of the Reppwand with the Gartnerkofel (2195 m) in the background.
A: Drill site on Kammleiten (1998 m);
B: Top of the outcrop section.
Dotted line indicates the Permian–Triassic boundary between the Bellerophon Formation (below) and the Werfen Formation above.
Photo: G. FLAJS, Aachen.

of the cases dolomite beds are restricted to certain horizons and in other cases to specific facies.

A wide range of models for the origin of dolomite have been suggested. They can be divided into different groups based on the salinity of the dolomitizating fluid. Models have been suggested for dolomitization by evaporite brines (J.E. ADAMS & M.C. RHODES, 1960), by hypersaline brines in a supratidal environment (G.M. FRIEDMAN & J.E. SANDERS, 1967), or by brackish groundwater (mixing zone model; B.B. HANSHAW et al., 1971). L.A. HARDIE (1987) divided the models into two groups based on the association with evaporite minerals: a hypersaline brines model, and a meteoric water model.

One of the main questions in the process of dolomitization is the source of Mg^{2+} ions. As most dolomitization models are diagenetic – meaning that it occurs after crystallization of precursor carbonate phases – the expected ratio of water to solid in such a system is rather low. In such a case one needs not only a rather high concentration of Mg^{2+} in the fluids but also a mechanism to transport large quantities of interstitial fluid through the sequence in order to remove the excess Ca^{2+} generated. Based on mass transfer of magnesium from the solution to the original calcium carbonate phases, D.W. MORROW (1982) and H. MACHEL & E.W. MOUNTJOY (1986) suggest that the only large source of Mg-rich fluid is marine water. L.S. LAND (1985) calculated that even with marine fluid at least 1000 pore volumes are needed to dolomitize one volume of carbonate sediments.

The timing of dolomitization is another aspect of the origin of platform dolomite that is not yet clearly known. The small amount of dolomitization in relatively young sediments suggests a slow process. This slow rate may explain the lack of success in dolomitization of sediments in low-temperature laboratory experiments.

Dolomite is pervasive in the marine epicontinental carbonates of the Gartnerkofel core, which therefore provided an opportunity to study the process of its formation. The origin and mode of dolomite alteration are potentially important factors in the interpretation of the analysis of trace elements, oxygen and carbon isotopes, and paleomagnetism.

2. Petrography of the Core

The bulk of the cored section is fine-grained dolostone, with occasional mm- to cm-interbeds of dolomitic marl or shale. Partial dolomitization is rare: only three of the several hundred samples are partly dolomitized.

2.1. Bellerophon Formation (Upper Permian)

(Pl. 1, Figs. 1–4, 6)

Unit 1 is completely dolomitized; nearly all samples consist of micritic and/or microsparitic dolomite (Pl. 1, Figs. 1–4). Micritic material contains fossils (Pl. 1, Figs. 2 and 4) and sedimentary structures (Fig. 6) with better preservation than coarser dolomite. Evidently conversion of micrite to microspar and fine-grained sparite (H.R. WANLESS, 1979) partially or totally destroyed primary textures. Often one can observe relics of fossiliferous micrite in slightly coarser, homogeneous and non-fossiliferous material (Pl. 1, Figs. 2 and 4). Generally the dolomite crystals are anhedral with grainsizes varying from <4 μm to 30 μm. In only a very few samples (295–293; 291; 288; 285; 313–323 m) there is a further coarsening of crystals to medium- or coarse-grained dolomite with relics of microsparite.

Carbonates from higher energy facies (dolomitic grain-/packstones) occur in the lower part of the core between samples 299 and 297 (257–327 m). Their allochems (gastropods, pelecypods, intraclasts) often cannot be identified because of strong neomorphism. These carbonates are cemented (now a medium-grained drusy cement). Previous cement generations are not preserved.

The diagenetic processes that have affected the Bellerophon Formation are: Formation of vuggy and moldic porosity; micrite conversion to microspar and sparite; dolomitization; pressure solution.

2.2. Werfen Formation (Lower Triassic)

(Pl. 1, Figs. 5, 7–10)

Units 2–4 are fine- to coarse-grained dolomite, more inhomogeneous than Unit 1. Dolomitic shaly and marly interbeds are more frequent. Nearly all the carbonates are completely dolomitized, except samples 35 (103 m), 183 and 184 (216 m) which nevertheless are partly replaced. Fine-grained dolomite is especially rich in insoluble residues (Pl. 1, Fig. 9): dark clay- and iron-rich "matrix" between dolomite crystals (Pl. 1, Fig. 8); black euhedral nuclei of dolomite crystals; concentration of clay and silt along stylolitic surfaces (Pl. 1, Fig. 7).

The fine-grained background sediment (whose precursor is micritic sediment) comprises microstylolitic, nodular, bioturbated mud-/wackestones. In these, fine-grained dolomite has mostly the grain size of microspar or fine-grained sparite (4 µm–120 µm). Crystals are anhedral to subhedral. Micrite can be found as relics in coarser material. In partly dolomitized carbonates, dolomite rhomb growth occurs preferentially along stylolitic surfaces or replaces shells of gastropods and pelecypods.

In middle- and coarse-grained calcarenites of higher energy facies (coquina tempestites or oolites), the carbonate cement has changed into anhedral to subhedral dolomite, and shells of large molluscs are completely replaced by coarse-grained dolomite (Pl. 1, Fig. 9). The grain-size ranges between 50 µm and 250 µm.

After pressure solution and solution-dolomitization (H. R. WANLESS, 1979), a further stage of dolomitization produced large euhedral or anhedral crystals (grain-size between 50 µm and 500 µm), replacing both low- and high energy sedimentary facies as well as diagenetic textures. Such dolomite often contains ghost structures of fossil material and ooids as well as of stylolites and calcitic veins. The crystals are zoned and iron-rich (stain with potassium ferrycyanide).

3. Comparison of Dolomitization among Permian-Triassic Sections in the Eastern Carnic Alps

Dolomitization in the Carnic Alps is discussed in detail by F. KAHLER & S. PREY (1963) and by K. BOECKELMANN (1988), from which the following general comparisons have been made.

Throughout this area the Bellerophon Formation is completely dolomitized, but in the Werfen Formation different degrees of dolomitization can be observed.

In the Gartnerkofel-1 core the Werfen Formation is nearly completely dolomitized. A similar situation is developed in the Garnitzen Valley, 3 km to the east. This was designated the „Plattendolomit-Fazies" of the Werfen Formation by F. KAHLER & S. PREY (1963). Both sections are characterized by vertical faults, and fault breccias. In the core the zones of tectonic movements (between 207 and 211 m; 150 and 160 m; 110 and 116 m) contain more coarse-grained dolomite, and concentrations of pyrite and hematite.

But most sections in the eastern Carnic Alps show the following, different pattern of dolomitization: The lower part of Werfen Formation (Tesero Horizon, Mazzin Member, lower Seis Member) is nearly completely dolomitized. The upper part of Seis Member has an alternating sequence of limestone, dolostone and partly dolomitized limestone. The latter consists typically of dolomitized molluscs and ooids in an unreplaced matrix. The Campil Member is completely dolomitized by early diagenesis on an arid tidal flat.

An example of such a dolomitization pattern is the Gartnerkofel outcrop section. Because there are no differences in sedimentary facies between the Gartnerkofel core and the outcrop section, differences in dolomitization are caused by some combination of tectonics and late dolomitization and are not restricted to specific facies. Alpine faults evidently facilitated the migration of Mg-rich fluids. This late tectonic-controlled dolomitization (producing coarse-grained dolomite) overprints an earlier stage of complete dolomitization of the Bellerophon Formation and partial dolomitization of the Werfen Formation. In a few restricted horizons these late replacement processes affect the geochemistry.

5. Pyrite Distribution in the Core Samples

Nearly all samples from the core contain small amounts of interstitial pyrite (Pl. 1, Figs. 1–7, 10). In most cases the crystals are small (10 µm–30 µm), their shape is anhedral, often in rounded masses and aggregates. They are seldom scattered through the beds, but more often are concentrated on surfaces that mark changes in sedimentation, e. g. at the bottom of storm layers between fine- and medium-grained dolomite (Pl. 1, Figs. 2, 4 and 6), and in fenestral fabrics between internal sediment (Pl. 1, Fig. 5) and overlying coarse-grained cement (Pl. 1, Fig. 10).

Other types of pyrite occur in fissures and veins, along stylolitic surfaces (Pl. 1, Fig. 7) and in the matrix around fossils (especially gastropods) (Pl. 1, Fig. 5). Larger amounts of pyrite occur in the intercrystalline pore space of coarse-grained dolomite (Pl. 1, Fig. 8). Cubes up to 250 µm grow together with large euhedral dolomite crystals in these open spaces (Pl. 1, Fig. 10).

Generally the crystal growth of dolomite and pyrite is similar. Fine- and medium-grained anhedral dolomite contains small irregular or rounded masses of pyrite. Coarse-grained dolomite with high porosity (euhedral crystals in open spaces) is associated with large cubes of pyrite. Samples taken from the outcrop section contain lesser amounts of pyrite than the core samples, a great number of them are free of pyrite due to surface oxidation. The evidence that pyrite oxidation is a present-day surface phenomenon can be found in the paleomagnetic record (W. ZEISSL & H. MAURITSCH, this volume). While the paleomagnetic record of Permo/Triassic was found in the core samples, this record was erased by the present day polarity in the outcrop section.

5. Dolomitization Model

The dolomite in the studied section is clearly of diagenetic origin. In most of the rocks – especially in the Upper Permian sediments – the original carbonate fabric can be clearly recognized. However, no evidence for evaporitic minerals were found in the studied part of the sequence, although to the west in South Tyrol the Permian sequence contains abundant evaporite rocks (A. BOSELLINI & L.A. HARDIE, 1973). Elsewhere in the Carnic Alps a few evaporites occur in the lowermost part of the Bellerophon Formation and in the middle and upper part of the Campil Member, respectively below and above the section cored at Gartnerkofel. Thus the main type of dolomite in the core is diagenetic non-evaporative dolomite, the most common type in marine shelf sediments. L.S. LAND (1985) and R.K. GIVEN & B.H. WILKINSON (1987) both argue that normal seawater circulation is an important mechanism for such platform dolomitization. This circulation of sea water can result from geothermal heating, or by mixing of sea water with either hypersaline or fresh water.

If the dolomitization was a late-stage overall recrystallization of the rock one might expect the isotopic composition of the sediments to be homogenized. But the fact that variations not only in $\delta^{13}C$ but also in $\delta^{18}O$ values were preserved (M. MAGARITZ and W.T. HOLSER, this volume) indicates that during dolomitization the water/rock system was dominated by the rock. This is commonly true for carbon isotopes for which a large number (500) of water volumes would have had to pass through the rock in order to shift $\delta^{13}C$ even by 1 ‰ (M. MAGARITZ, 1983). In the present case this is evidently true for the oxygen as well.

Significant evidence of the environment of dolomitization is the occurrence of intercrystalline pyrite through the whole section. In the core, almost all the rocks have minor intercrystalline pyrite (100–300 ppm S); a few are pyrite rich horizons (1–10 % S). The pyrite has wavy lamellar bedding in characteristic globular masses, and is very similar to early diagenetic "framboidal" pyrite (W.T. HOLSER, this volume) the pyrite is also diagenetic, based on the faunal record (K. BOEKELMANN, this volume), which does not indicate anoxic conditions in the water column. Oolitic sediments also are expected to be oxic when initially deposited. These observations argue that both the pyrite and the dolomite formed during an early diagenetic stage. If dolomitization was a late event, one might have expected oxidation of the pyrite that is presently found in intercrystalline spaces associated with the dolomitization.

One of the agents regarded as an inhibiter of dolomite growth in sea water is sulfate (P.A. BAKER & M. KASTNER, 1981). Evidence for association of sulfate reduction process with dolomitization was reported by K. KELTS & J.A. MCKENZIE (1982), but in their studies the amount of dolomite found was relatively small. L.S. LAND (1985) argues that as sulfate reduction is associated with production of bicarbonate ions from organic matter via the reaction

$$2\,CH_2O + SO_4^{=} \rightarrow H_2S + 2HCO_3^{-}$$

one should get $\delta^{13}C$-depleted carbonate rock. As no thick platform dolomite with $\delta^{13}C$ depleted carbonate is known he argues that this mechanism cannot be the main model for dolomitization. This seems to be the case in our section – that $\delta^{13}C$ values are not significantly ^{13}C-depleted, rather in part of the section (Permian) $\delta^{13}C$ values are enriched in ^{13}C. The relatively small amount of pyrite (few hundreds of ppm) in the rock would not have contributed sufficient bacterial derived bicarbonate to affect the $\delta^{13}C$ values. The fact that in our section we found a clear association of diagenetic pyrite and dolomite suggests that one can generate conditions of dolomitization and sulfur reduction at the same time without significantly altering the carbon isotope record.

The question is really mass balance of the sources of carbon in the system. We can turn it around and argue that only in extreme conditions when the amount of sulfate is large, we can expect to find significant carbon isotope shift, as found in gypsum replaced by calcite (A. BELLANCA et al., 1986). But if only the original sulfate of the solution is reduced, the amount of HCO_3^- ions produced will be small relative to the carbonate ions stored in the original carbonate sediments.

Thus we argue that dolomitization in the studied core was a diagenetic process under rather anoxic conditions. The source of Mg^{2+} ions for the massive dolomitization had to come from fluid circulating through the platform sediments. A possible solution is sea water. The fact that some of the sulfate was reduced may have helped dolomite nucleation.

Plate 1

Fig. 1: **Unfossiliferous micrite/microsparite.**
Fenestral fabrics are oriented parallel to bedding planes and are filled with sparite. Pyrite is enriched along these structures. Bellerophon Formation, sample 282, 313.58 m, scale: 12 mm.

Fig. 2: **Lower part: ostracod mudstone (biomicrite); upper part: unfossiliferous microsparite/fine-grained sparite with some molds of gastropods and pelecypods.**
Pyrite is enriched at the micrite/microsparite contact. Bellerophon Formation, sample 227, 255.65 m, scale: 1 mm.

Fig. 3: **Unfossiliferous mudstone (microsparite).**
Pyrite is enriched in small fissures.
Bellerophon Formation, sample 227, 255.65 m, scale: 1 mm.

Fig. 4: **Lower part: ostracod mudstone (biomicrite); upper part: unfossiliferous microsparite/fine-grained sparite.**
Contact overprinted by solution seam (black line) with some pyrite.
Bellerophon Formation, sample 246, 276.30 m, scale: 3.5 mm.

Fig. 5: **Medium-grained dolomite, rich in insoluble residues between the subhedral dolomite crystals.**
The relic of a gastropod is rich in pyrite.
Werfen Formation, sample 55, 127.55 m, scale: 0.75 mm.

Fig. 6: **Lower part: fine-grained dolomite; upper part: medium-grained dolomite.**
Generally all crystals are anhedral or subhedral. Solution seams and pyrite enrichment at the contact.
Bellerophon Formation, sample 218, 241.89 m, scale: 4 mm.

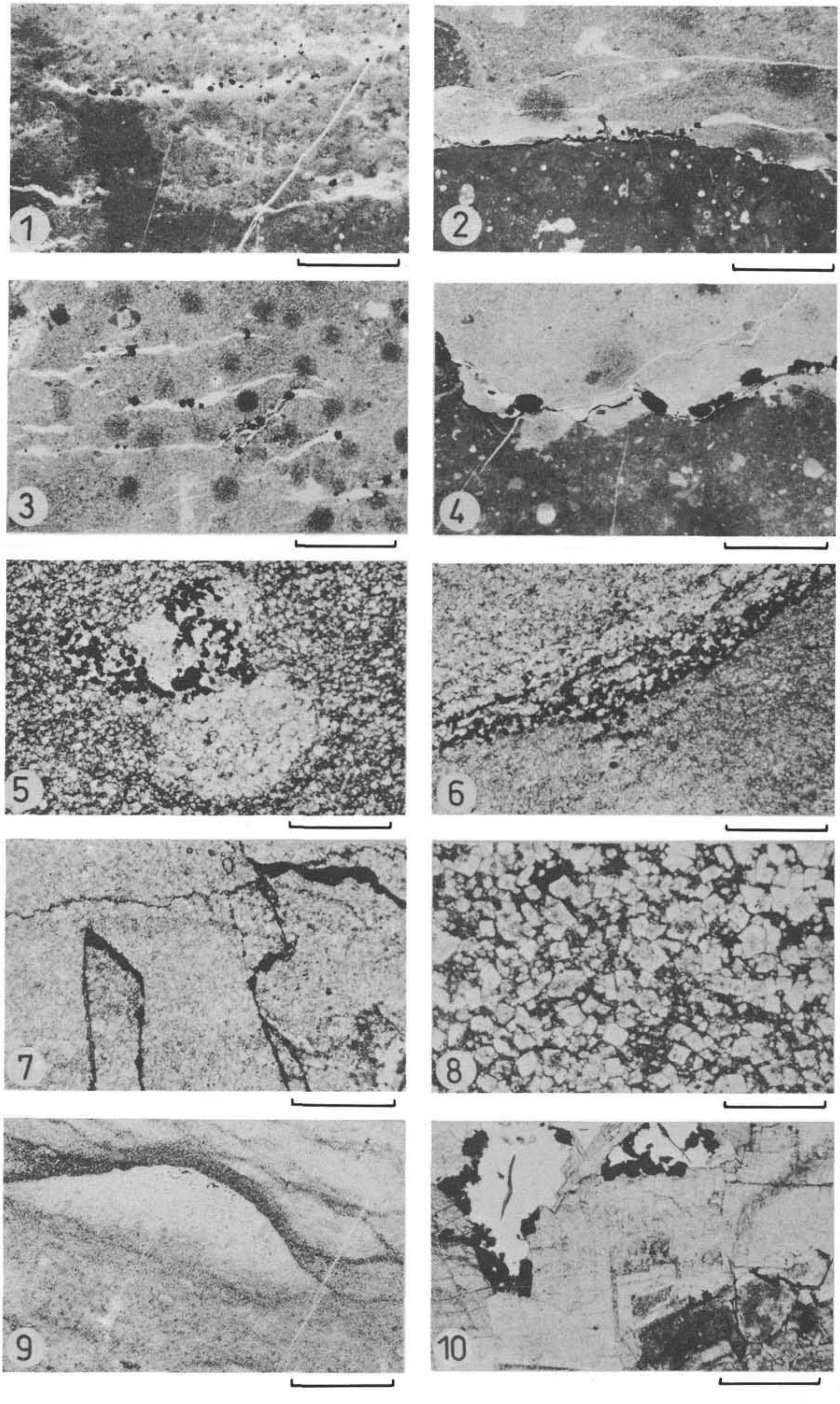
Fig. 7: **Medium-grained dolomite (even-grained anhedral crystals).**
Pyrite enrichment along stylolites.
Werfen Formation, sample 199, 227.46 m, scale: 1.3 mm.

Fig. 8: **Coarse-grained ferroan dolomite in euhedral, zoned crystals.**
Between crystals is a matrix rich in insoluble residues (especially iron oxide and pyrite).
Werfen Formation, sample 17, 79.67 m, scale: 1 mm.

Fig. 9: **Medium-grained dolomite.**
A pelecypod can be identified by the shelter porosity, filled with coarse-grained, light dolomite crystals. The shell is only preserved as a ghost structure.
Werfen Formation, Reppwand outcrop section B', sample K 30, scale: 3 mm.

Fig. 10: **Coarse-grained dolomite with large, often zoned euhedral crystals that grow into open spaces.**
Pyrite is enriched around the pore space.
Werfen Formation, sample 49, 119.27 m, scale: 2 mm.

All samples are completely dolomitized.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