### TEMPERED MICRODOLOMITES IN CRINOIDS: A NEW CRITERION FOR HIGH-GRADE DIAGENESIS

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ABSTRACT: Microdolomite inclusions in crinoids of the Middle Triassic "Trochitenkalk" stage from north and central Germany were formed during diagenesis in a closed system and normally consist of 52 - 55 mole % CaCO<sub>3</sub> (48 - 45 % MgCO<sub>3</sub>). In areas influenced by thermal activity these calcium microdolomites are tempered to stoichiometric dolomites. Thus, the microdolomite composition can be used as a new criterion for assessing the degree of diagenesis in sedimentary rocks. As an effect of the Upper Cretaceous intrusive bodies of the Bramsche-Vlotho-Solling Massifs, which influenced the overlying sediments for 1 - 10 million years, a microdolomite composition of  $d_{(104)} = 2.889$  Å (~51 mole % CaCO<sub>3</sub>) is associated with an illite crystallinity of 350 (Hb<sub>rel</sub>; <2 $\mu$ m). The composition of the microdolomites is more sensitive to short term heating (for example: ascending thermal waters near the faults of the Hessen grabens) than is illite crystallinity.

### **INTRODUCTION**

Dolomite inclusions  $5 - 20 \,\mu$ m in size occur in crystallographic continuity with the calcite hostcrystal of echinoderm fragments and early diagenetic cements in Palaeozoic and Mesozoic limestones (Richter, 1974, 1985; Davies, 1977; Lohmann and Meyers, 1977; Meyers and Lohmann, 1978; Blake et al., 1982; Leutloff and Meyers, 1984). These inclusions compose as much as 30 % by volume of these constituents. Such microdolomites are formed during the transformation of Mg-calcite to calcite and calcian dolomite via local microdissolution-reprecipitation in closed systems with nucleation of the calcian microdolomites initiated in Mg-rich domains (Lohmann

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and Meyers, 1977). The structural (and presumed compositional) ordering of such dolomites are secondary processes which take place only after the disordered calcian dolomite has formed (Blake et al., 1982). The first mechanism (Mg-calcite -> calcite and Ca-dolomite) can easily be reproduced by heating modern echinoderm fragments over a short period of time (Land, 1967; Richter, 1984; Kürmann, 1986). Experiments performed by Kürmann (1984) show that, depending on temperature, calcite with different Mg contents and dolomite with varying amounts of CaCO<sub>3</sub> are formed.

In the Middle Triassic "Trochitenkalk" (Upper Muschelkalk) the originally high-Mg calcitic crinoids and their first rims (i.e., syntaxial cements) are overlain by younger rim-cements or stable calcite/



Figure 1. Outcrop of the Muschelkalk (Middle Triassic) in north and central Germany with isolines for vitrinite reflectance (% Rm = % mean reflectance) at the Rhätic-Liassic boundary in the area of the Bramsche and Vlotho massifs (after Deutloff et al., 1980). Br: City of Bramsche;, So: Solling-Mts.; Location of crosssection A - B (after Teichmüller and Teichmüller, 1984), above. Note that the reflectance lines in the cross-section are not identical with the isoreflectance lines on the map.

Fe-calcite replacements, so that ions cannot be exchanged with (interstitial) pore waters. In areas that are not telemagmatically influenced (northern Harzvorland, Hessisches Bergland, Figures 1 and 3) the Mg-calcite was transformed into calcite and  $Ca_{52-55}$ -dolomite in closed systems during geological time (Richter, 1985). Based on this assumption, the original composition of the first Mg-calcitic rim-cements surrounding the echinoderm

fragments from the Upper Muschelkalk, between Warburg and Kassel was calculated. They contained 15 mole % MgCO<sub>3</sub> (Richter, 1984, p.79). This figure is comparable to the similarly calculated Mg<sub>13</sub> calcite cement of the Mississippian of New Mexico (Meyers and Lohmann, 1978, p. 481) and represents the typical composition of modern calcite cements formed in warm marine environments (e.g., in the Mediterranean).

Earlier results obtained along a single profile from the Egge (east of Paderborn) to the Elm (southeast of Braunschweig; Richter, 1985) showed that the  $Ca_{>50}$ microdolomite inclusions in crinoids of the Trochitenkalk (=lowest member of the Upper Muschelkalk = mo1) were tempered to stoichiometric dolomite in the telemagmatically influenced area of the Vlotho Massif (i.e., area around Vlotho, outlined by the isoreflectance lines % Rm in Figure 1). This effect could not be observed in experiments conducted over short time periods (several days; Kürmann, 1986).

The present paper deals with an areal investigation of the microdolomite pattern in the area between the cities of Osnabrück, Braunschweig and Fulda (Figure 1). Moreover this new method for classifying high-grade diagenesis was compared with classic methods, such as illite crystallinity and vitrinite reflectance. Isotopic composition and cathodoluminescence of the microdolomites were examined in random samples. Partial results were presented in Richter et al., (1986).

### **METHODS**

160 hand-size samples containing crinoid fragments (biomicrites and biosparites) were taken from exposures of the Muschelkalk stage in the area of the "Weserbergland/Harzvorland/Hessisches Bergland" (Figure 1). In additional 30 Trochitenkalk-samples were taken over from Brauckmann's (1984) collection. Microdolomites in the echinoderm fragments versus macrodolomites in the matrix were distinguished (Figure 2) because they



Figure 2. A. Thin section photograph of a crinoid with microdolomites ("mi") and matrix dolomites ("ma"), sample from 20 km southeast of Kassel (Hessische Gräben;  $d_{(104)}$  of microdolomites = 2.887 Å;  $d_{(104)}$  of matrix dolomites = 2.890 Å). B. Thin section photograph of a crinoid with microdolomites ("mi"), sample from 10 km southeast of Vlotho ( $d_{(104)}$  of microdolomites = 2.886 Å). C and D are SEM photos of microdolomites within crinoids; C. from 15 km southeast of Braunschweig ( $d_{(104)}$  of microdolomites = 2.891 Å). D same sample as B. Note space between microdolomite rhombs and calcite host crystal (probably mainly due to volume reduction during transformation of Mg-calcite to calcite and Ca-dolomite).

were formed differently (see below). Thin sections were stained with Alizarin red-s (see Füchtbauer, 1977, p. 358), in order to examine the distribution of the microdolomites in crinoids as well as the macrodolomites (=matrixdolomites) and their possible replacement by calcite. One matrix sample and two crinoids were removed from each sample. Small cleavage rhombohedrons were carefully separated from the crinoid stereoms in order to avoid mixing of microdolomite and intergranular macrodolomite crystals (Figure 2).

For X-ray diffraction analyses, the echinoderm and matrix fragments were powdered in an agate-mortar and quartz was added as an internal standard (for methods, including "mortaring-effect", see Richter, 1984, p. 15-24). Microdolomite contents of <5 % are common, so that a "Philipslong-fine-focus" tube had to be used; with 1°/min, TC (time constant) = 1, 20 mm/min and 3 diagrams for each sample, the displacement of the  $d_{(104)}$ reflection could be read with an accuracy within ± 0.001 Å (i.e. ±0.01 °2 $\Theta$ ). The mole % CaCO<sub>3</sub> can be calculated from the linear displacement of the  $d_{(104)}$ peak between 3.035 Å (calcite) and 2.886 Å (dolomite) (Richter, 1984, p. 15 - 19). This is possible for the microdolomites only, because they do not contain FeCO<sub>3</sub>, in contrast to the late-diagenetic macrodolo-



Figure 3. Composition of microdolomite inclusions in crinoids of the Middle Triassic Trochitenkalk stage from north and central Germany. Note location of cross section C - D (Figure 4). The data located within the outlined area are projected onto section C - D.

mites (Richter, 1985).

Quite a few dolomites, especially those in the matrix, were found to be composed of two or more different phases (see below). Their presence leads to a broadening of the XRD reflection peaks. To enable a comparison with other dolomites, the data used here are based on a width of 5 mm at quarter height of the  $d_{(104)}$ -peak of stoichiometric micro- to macrocrystalline dolomites (Richter, 1984, p. 21) when using an external quartz standard with a width of 3.1 mm at half height for the (100)reflection.

Illite chrystallinities were determined after Weber (1972) on oriented, ethylenglycol-solvated preparations of the unsoluble residue (<  $2\mu$ m fractions). The half-height width (Hh) of the first illite basal reflection at 10 Å on a X-ray diffractogram was measured and made less dependent on recording conditions by using quartz as a standard. The illite crystallinity Hb<sub>rel</sub> is defined as follows:

 $Hb_{rel} = Hh_{(10 \text{ \AA})}$  illite [mm]/Hh\_{(4.28 \text{ \AA})} quartz [mm]) x 100

Low Hb<sub>rel</sub>-values represent illite crystallinities typical for high-grade diagenesis.

Cathodoluminescence characteristics were examined in several samples of the limestones. Using a hot cathode instrument (acceleration voltage: 7 KeV, beam current density:  $10 \,\mu A/mm2$  (see Neuser, 1988, p. 27), magnification of objective: 10X, magnification of ocular: 12.5X, numerical aperture of objective: 0.30), calcite and dolomite with more than 20 - 40 ppm Mn show a yellow-orange-red luminescence. With decreasing Mn/Fe<sup>2+</sup> ratios, those colors are muffled to shades of brown, and finally, no luminescence can be observed (Richter and Zinkernagel, 1981). Isotopic analyses were carried out at the Derry Laboratory, Ottawa-Carleton Geosience Centre Canada, on a V. G. Sira 12 mass spectrometer.

## **DISCUSSION OF THE RESULTS**

## Regional pattern of microdolomite composition

The Upper Cretaceous intrusive bodies of the Vlotho and Bramsche Massifs are traceable in the overlying Mesozoic strata not only by increased coalification (i.e. vitrinite reflectance; Bartenstein et al., 1971; Koch and Arnemann, 1975; Deutloff et al., 1980), improved crystallisation of illite and chlorite (Brauckmann, 1984), extensive authigenesis of quartz, albite and microcline (Brauckmann, 1984; Rose and Gödecke, 1984), but also by stoichiometric microdolomites in crinoids of the Trochitenkalk (Richter, 1985 and Figure 3). The composition of the oxygen and carbon isotopes in calcite and dolomite has not changed (Table 1) during the tempering process as shown by the comparison of the northern Harzvorland figures with those of the Vlotho Massif. This similarity points to closed system transformations (Czerniakowski et al., 1984).

The main zone where stoichiometric microdolomites are found covers the regions influenced by the Vlotho, Bramsche and Solling Massifs. Because of the absence of Muschelkalk outcrops near the latter massif, samples could only be taken from neighboring areas. However, earlier observations such as increased illite crystallinities and increasing amounts of authigenic minerals (Brauckmann, 1984), and a high degree of coalification (vitrinite reflectance: 4.3 % Rm) at the surface of the Carboniferous in the Solling-Devon 1 well (Teichmüller et al., 1984) suggested an extension of the thermal anomaly towards the southeast of the Vlotho Massif.

At some distance (up to 50 km) from the Bramsche-Vlotho-Solling Massifs their tempering effect is not so distinct, but it is still reflected significantly in the composition of the microdolomites. Thus nearly stoichiometric microdolomites (=50.5 - 51.4 mole % CaCO<sub>3</sub>,  $d_{(104)} = 2.888$  Å - 2.890 Å) prevail in a 40 km broad zone, east of the area of stoichiometric (= 50.0 - 50.4 mole % CaCO<sub>3</sub>) microdolomites. But even within this zone the  $d_{(104)}$ -values, i.e. the excess CaCO<sub>3</sub>, increase with increasing distance from the thermal anomaly (Figures 3 and 4).

Beyond the central zone of the intrusive bodies, especially in the northern Harzvorland and in the Hessisches Bergland, quite a few exceptions in the regional tempering pattern can be observed (i.e. stoichiometric microdolomites) are associated with calcian microdolomites). The formation of stoichiometric dolomites in these zones can be explained by local effects:

(1) The "chimney-effect", caused by underlying salt domes, can create an increased heatflow. Thus, in the area around Salzgitter (southwest of Braunschweig) the microdolomites in four localities have been tempered to stoichiometric dolomite (Figure 3). Lewandowski (1988) observed no significant increase of illite crystalliniy in areas with underlying salt domes and areas lacking salt domes. As the heating was obviously active for only a short time, the sensitive reaction of Ca-rich microdolomites towards changing diagenetic conditions is evident, especially in one sample southwest of Braunschweig, in which stoichiometric microdolomites are accompanied by a rather poor illite crystallinity (Hb<sub>rel</sub> = 505; <2  $\mu$ m).

(2) In the east and southeast of Kassel,

Table 1: Isotopic composition (PDB) in °/∞ of carbon and oxygen isotopes in calcite and microdolomite of crinoid-fragments from untempered (northern Harzvorland) and tempered (Vlotho Massif) areas.

Northern Harzvorland		$\delta^{18}$ O	δ <sup>13</sup> C
Erk 1 - Crinoid 3	Calcite	-6.77	0.57
	Dolomite	-6.81	0.75
Erk 1 - Crinoid 8	Calcite	-5.97	1.53
	Dolomite	-4.99	1.85
Erk 1 - Crinoid 10	Calcite	-5.07	1.90
	Dolomite	-4.66	2.13
Vlotho Massif			
Le 18 - Crinoid 1	Calcite	-5.44	0.86
	Dolomite	-4.95	1.04
1			

(Figure 3) stoichiometric microdolomites occur together with calcian-microdolomites along a nearly 30 km long, intensely faulted zone that strikes NNE - SSW. This can probably be attributed to a local rise of thermal activity along deep-seated unconformities (for example, by ascending hot formation waters in combination with Tertiary volcanism like the Meissner Basalt southeast of Kassel). These thermal anomalies do not manifest themselves in the coalification map of the "Kupferschiefer" (Lower Zechstein; Kulick et al., 1984), because the data used by the authors were obtained from wells outside the graben zone.

(3) The southern accumulation of stoichiometric microdolomites around Fulda (Figure 3) can be explained by the tempering effect of the plateau basalts of the Rhön Mts. (possibly combined with faults as in samples around Fulda). The plateau basalt partially extruded directly onto sediments of the Upper Muschelkalk (Middle Triassic). Also, obviously this thermal influence was only active over a short period of time, because in one sample taken 20 km east-north-east of Fulda, stoichiometric microdolomites occur together with a rather poor illite crystallinity (Hb<sub>rel</sub> = 333; <2  $\mu$ m).

# Microdolomite composition versus illite crystallinty and vitrinite reflectance

Based on 62 illite crystallinity values and 31 vitrinite reflectance values from Brauckmann (1984), a positive correlation between the degree of stoichiometry  $(=d_{(104)}-values)$  and thermal maturity is obvious (Figures 5 and 6). Similar correlations were found by Richter et al., (1989) for Jurassic sediments of the Eastern Alps. The data used in this paper are representative for the long term



Figure 4. Mole %  $CaCO_3$  of microdolomites from locations outlined in Figure 3, along the cross-section C - D (50.0 - 50.4 mole %  $CaCO_3$  = stoichiometric; 50.5 - 51.4 mole %  $CaCO_3$  = near-stoichiometric and 51.5 - 52.7 mole %  $CaCO_3$  = non-stoichiometric).

tempering by the Bramsche-Vlotho-Solling massifs. In the Bramsche Massif, the maximum of thermal activity of the plutonic body of Upper Cretaceous age in the subsurface persisted over a period of 1-2 my (Mundry, 1971, p. 544) or 5-10 my (Stadler and Teichmüller, 1971, p. 558). In the overlying Musch-elkalk sediments of the central Vlotho Massif and the southern Bramsche Massif, maximum temperatures of 200 - 300 °C were calculated, whereas temperatures of approximately 350 °C were reached in the central Bramsche Massif (Brauckmann, 1984). The following quantitative relationships between two diagenetic parameters can be derived for long term heating / deep burial diagenesis:

(1) In Figure 5, a microdolomite composition corresponding to  $d_{(104)} = 2.889$  Å is linked with an illite crystallinity of 350 ±100 (Hb<sub>rel</sub>; non-carbonate fraction <2  $\mu$ m), which is a general deviation for this degree of crystallinity (Brauckmann, 1984). The scattering is because some of the microdolomites have undergone short period heating (e.g. by hot thermal waters, "chimney effect" near salt domes), which influenced the microdolomite composition but not the illite crystallinity. Also detrital illite might influence the measured crystallinities.

(2) As shown on Figure 6, a microdolomite composition corresponding to  $d_{(104)} = 2.889$  Å is associated with a vitrinite reflectance of 1.5 - 2.0 % Rm. In areas with a vitrinite reflectance >3 % Rm, only stoichiometric microdolomites ( $d_{(104)} = 2.886(7)$  Å) were found. On the other hand, samples from the



Figure 5: Illite crystallinity ( $Hb_{rel}$ , < 2  $\mu$ m; values from Brauckmann, 1984) and the composition of microdolomites ( $d_{(104)}$ ) within each sample. The linear-regression line has a correlation coefficent of 0.66 (least-square method). Note: (1) thermal maturity increases with decreasing Hb<sub>rel</sub>-values; (2) larger  $d_{(104)}$ -values represent less stoichiometric microdolomites (assuming stoichiometry to be 2.886 Å).

region east of Braunschweig with microdolomite compositions ranging between  $d_{(104)} = 2.890$  and 2.894 Å represent a vitrinite reflectance of 1.0 % Rm (Rhät; Lewandowski, 1988).

No comparisons between microdolomite composition and vitrinite reflectance can be made when regarding geological short term tempering, because only few vitrinite reflectance values exist from the northern Harzvorland with salt domes in the subsurface (=area with the "chimney effect"), the Hessen graben fault system and the Rhön area.

## Occurrence and distinction between microand macrodolomites

Generally, in individual hand specimens the microdolomites in the crinoids and the (usually larger) dolomite crystals in the matrix do not have the same composition (Figures 2A and 7). This fact alone



Figure 6. Vitrinite reflectance (Brauckmann, 1984) and the composition of microdolomites  $(d_{(104)})$  of corresponding samples. Note: (1) thermal maturity increases with higher reflectance values (% Rm); (2) decreasing stoichiometry of microdolomites is represented by higher  $d_{(104)}$ -values (stoichiometry = 2.886 Å).

suggests that the two types of dolomite are of different origin. The matrix dolomites (= macrodolomites) are usually less stoichiometric, (Ca, Fe richer) than the microdolomites.

The clear relationship between the  $d_{(104)}$ -values and the width at quarter height (Figure 8) suggests that the microdolomites were all formed under uniform conditions or were influenced systematically. Since such a positive correlation cannot be observed for the matrix dolomites, it must be concluded that their formation not only differs from that of the microdolomites, but it also was not uniform. As shown by their regional distribution, part of the matrix dolomites were formed in connection with the thermal activity of the Bramsche-Vlotho-Solling massifs (Figure 9), even if calcitized matrix dolomites are included. Questions concerning the time of formation of the matrix dolomites and of the dedolomite, however, remain unanswered at present.

Micro- and matrix dolomites of the Tro-



Figure 7.  $d_{(104)}$ -values of micro- and matrix-(= macro-)dolomites within the same sample. In most cases the matrix dolomites are less stoichiometric (i.e. Ca, Fe-richer) than the microdolomites.

chitenkalk (Middle Triassic) are also distinct by their cathodoluminescence. In the five samples studied the microdolomites have a red luminescence in contrast to the brown luminescence of the matrix dolomites. This brown color is similar to that of Fe-rich Triassic dolomites of the Jaggl-Plawen unit east of the Reschensee (Central Alps; Richter and Zinkernagel, 1981). The red luminescence, however depends mainly on the Mn-concentration, as the microdolomites contain no Fe<sup>2+</sup> which could cause quenching. Because the microdolomites from the Vlotho area and from the Harzvorland have an identical luminescence color, it seems that the tempering by the massif obviously did not affect the Mn-content of the microdolomites. A low Mn-content can be assumed, as modern echinoderms mostly have Mn-concentrations less than 100 ppm (Milliman, 1974). Also XRD scans show no displacement of the maximum dolomite reflection peak in stoichiometric microdolomites. On the other hand, the effective activator Mnconcentration must be higher than 20-40 ppm in both calcite and dolomite (Richter and Zinkernagel, 1981). The varying Mn-distribution in the crinoids is another striking aspect; the microdolomites have a red luminescence, whereas a blue to violetblue luminescence is observed in the surrounding calcite. The blue colors, which are caused by intrinsic luminescence, can be observed only if the calcite contains neither the quenching Fe<sup>2+</sup> ion (Amieux, 1982) nor the activating  $Mn^{2+}$  ion. This means that during the transformation of Mg-calcite to calcite and dolomite in closed systems, the Mn of the Mgcalcitic stereom and stroma cement is preferably absorbed by the dolomite lattice. This is also the case after the dolomites have been tempered. The distribution coefficient k<sup>Mn2+</sup>(calcite) of Mn into calcite equals approximately 15 for conditions under



Figure 8.  $d_{(104)}$ -values of microdolomites and matrix dolomites versus the width at quarter height (=peak sharpness) of the same reflection. Only the microdolomite  $d_{(104)}$ -values are positively correlated with the peak sharpness (linear correlation coefficien: 0.71, least-square method). This suggests that the microdolomites were all formed under uniform conditions or were influenced systematically by thermal events.

which most limestones are lithified (Pingitore, 1978, p. 801). The distribution coefficient  $k^{Mn2+}$ (dolomite) must be even higher, because Mn has the tendency to replace Mg instead of Ca if dolomite and calcite coexist (Wedepohl, 1978).

#### CONCLUSIONS

1. The microdolomites in crinoids of the Trochitenkalk normally have a mean of 52-55 mole % CaCO<sub>2</sub>.

2. In the area studied here, the Carich microdolomites were tempered to more stoichiometric compositions by the intrusive bodies of the Bramsche-Vlotho-Solling Massifs, which were thermally active over a period of 1-10 million years, in late Cretaceous time.

3. This transformation took place in a closed system, as indicated by unchanging oxygen and carbon isotopic compositions of microdolomites and calcite stereoms during heating.

4. Several local influences can also be responsible for the tempering: (1) a "chimney effect" caused by underlying salt domes and resulting in an increased heat flow, in the northern Harzvorland; (2) thermal activity in and near fault zones of the Hessen grabens and (3) Tertiary plateau basalts (e.g. in the Rhön Mts.).

5. Tempered microdolomites from the Bramsche-Vlotho-Solling area with a composition of  $d_{(104)} = 2.889$  Å are correlated with an illite crystallinity of 350 ±100 (Hb<sub>rel</sub> <2  $\mu$ m).

6. Telemagmatically influenced microdolomites with  $d_{(104)} = 2.889$  Å coincide with a vitrinite reflectance of 1.5 - 2.0 % Rm.

7. Short-time tempering (e.g. by hot thermal waters) very probably influenced the microdolomite composition but not the illite crystallinity. Thus the microdolomite composition presents a more sensitive parameter than the illite crystallinity for assessing the degree of diagenesis.

8. The microdolomites in the crinoids and the matrix dolomites have different compositions. This can be proved by both X-ray analyses and cathodoluminescence petrography. Thus, these two types of dolomites have a different origin.

9. The matrix dolomites are in part formed in connection with the thermal activity.

10. Microdolomite composition seems to be a universal tool for assessing the degree of diagenesis as it also has been successfully applied to Jurassic sediments of the Eastern Alps.

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Figure 9. Regional pattern of the distribution of matrix dolomites and dedolomite (calcitized matrix dolomite) samples. The concentration of matrix dolomite in the area influenced by the massifs suggests that they were formed in connection with the thermal activity.

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Photomicrograph of aragonite fibers in hard bottom layers of the Red Sea projecting from centers of accretion. These fibers form the cement that serves to lithify the Red Sea bottom sediment (Figure 7 on page 146 <u>in</u> Gevirtz, J.L., and Friedman, G.M., 1966, Deep-sea carbonate sediments of the Red Sea and their implications on marine diagenesis: Journal of Sedimentary Petrology, v. 36, p. 143-151).



Photomicrograph of cross section of pteropod in hard bottom layer of the Red Sea showing syntaxial and drusy fibrous aragonite. Note the pseudo-uniaxial cross under crossed nicols (Figure 9 on page 146 in Gevirtz, J.L., and Friedman, G.M., 1966, Deep-sea carbonate sediments of the Red Sea and their implications on marine diagenesis: Journal of Sedimentary Petrology, v. 36, p. 143-151).