Geologie en Mijnbouw **70**: 265–273, 1991.

Conodont color alteration and microdolomite composition – implications to the Muschelkalk limestones (Upper Triassic) overlying the Upper Cretaceous intrusive body of the Vlotho Massif (Weserbergland, Northwest Germany)

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Received 6 June 1990; accepted in revised form 21 March 1991

Abstract

The conodont color alteration index (CAI) and the microdolomite composition (MC) were used to evaluate the thermal diagenesis in the Upper Muschelkalk (Middle Triassic) limestones overlying the Cretaceous intrusive body of the Vlotho Massif in the southern part of the Lower Saxony Basin in Northwest Germany. The validity of these two methods is discussed. The CAI exhibits a greater accuracy at high levels of organic metamorphism, especially above temperatures of 180° C, whereas the microdolomite composition is an excellent indicator for differentiating low-temperature diagenesis. The good positive correlation between % Rm and CAI can probably be attributed to the fact that in both cases organic matter changes during diagenesis.

The maximum palaeotemperature range of 300–345° C ascertained by the CAI value of 5 in sediments directly over the Vlotho Massif, lies higher than the temperatures estimated with the help of other geothermometers.

Introduction

The diagenetic history of limestones can be unravelled by cement stratigraphy (Bruckschen et al. 1990a), whereas the thermal activity (here 1–10 My), caused by the Vlotho intrusion mainly results in changing mineral associations and maceral transformations. The degree of diagenesis can be deduced from various parameters, such as the mean (% Rm) and the maximum (% Rmax) vitrinite reflectance (compare Stach et al. 1982), the illite crystallinity IC (Hbrel, Weber 1972), the illite polytypism IP (% 2M-polytype, Maxwell & Hower 1967), the chlorite crystallinity CC (Ludwig 1972), the microdolomite composition MC ($d_{(104)}$ in Å; Richter 1985, Bruckschen et al. 1990b) and the conodont color alteration index CAI (Epstein et al. 1977).

This study deals with the comparison of two indicators of diagenesis, i.e. the microdolomite composition (MC) and the conodont color alteration index (CAI). Both methods were applied to limestones of the 'Trochitenkalk' Formation (Upper Muschelkalk, Middle Triassic) overlying the Cretaceous intrusive body of the Vlotho Massif.

Geological setting

The 'Trochitenkalk'-Formation of Northwest Ger-

Professor Dr. Hans Füchtbauer dedicated on the occasion of his 70th birthday

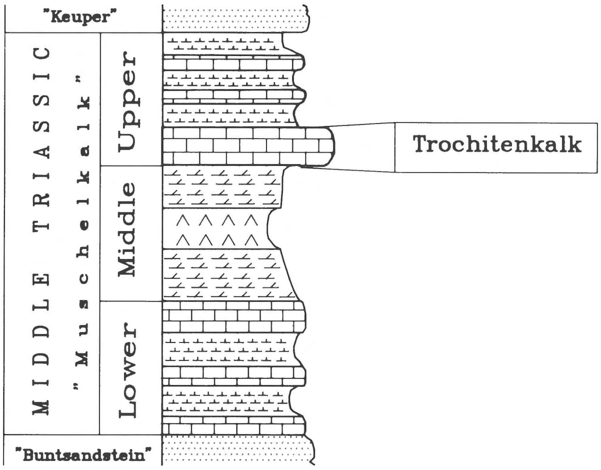

Fig. 1. Simplified stratigraphy of the Middle Triassic (Upper Muschelkalk) succession.

many, 5–15 m thick, forms the lower part of the Upper Muschelkalk (Middle Triassic). These shallow marine limestones are composed principally of skeletal calcarenites/calcirudites, with subordinate oosparites. One of the main biogenetic constituents are crinoids (in German: 'Trochiten') of *Encrinus liliiformis* (von Schlotheim).

The stratigraphic position of the 'Trochitenkalk'-Formation within the Middle Triassic succession is shown in Fig. 1.

Samples were taken from outcrops of the 'Trochitenkalk' (Fig. 2) along a WSW/ENE striking traverse (from the Egge E of Paderborn to the Elm SE of Braunschweig). The rocks had undergone burial diagenesis at a depth of 1000 to 3000 m before being telemagmatically heated by the Vlotho intrusion for a period of 1–10 My (Mundry 1971, Stadler & Teichmüller 1971). The intrusive body of the Vlotho Massif trends in a WNW-ESE direction, and probably intruded between Aptian and Upper Campanian time. Its top lies about 5 km under the present-day surface. Various diagenetic effects have been studied and the different geothermometers indicate maximum palaeotemperatures in the overlying sediments between 200–300° C (illite crystallinity data from Brauckmann (1984): 200–250° C, thermal modeling by Mundry (1971): 200–300° C).

Tools for assessing diagenesis – methods

Vitrinite reflectance (% Rm = mean or random reflectance)

As vitrinite reflectance is one of the most commonly used maturity/rank indicators of rock diagenesis, it is useful to consider reflectance data when comparing different tools for assessing diagenesis. With the help of comprehensive data already existing for coalification in sediments overlying the Vlotho Massif (Deutloff et al. 1980, Koch & Arnemann 1975, Teichmüller et al. 1984), it was possible to interpolate % Rm values for the Middle Triassic Trochitenkalk limestones.

Conodont Color Alteration Index (CAI)

Conodonts are phosphatic marine microfossils (0.1–1 mm in size) containing trace amounts of organic material and are supposed to be parts of the feeding apparatus of an extinct group of possible jawless fishes (Aldridge et al. 1986). With increasing temperature the color of conodonts changes from pale yellow to black.

Epstein et al. (1977) introduced a color alteration index (CAI), ranging from CAI 1 to CAI 5, within which conodont color changes from pale yellow to amber, light brown, dark brown, and black. The color alteration is irreversible and progressive and is directly related to depth, duration of burial and to the geothermal gradient. With the help of experimental data, Epstein et al. (1977) drew an Arrhenius-plot, from which the geologic temperatures for conodont color alteration indexes (CAI) can be read. The CAI values between 1 and 5 occur in the premetamorphic zone of thermal maturation. The color alteration below CAI 2 to 3 results from a gradual carbonization of organic matter (Epstein et al. 1977). The alteration process for higher CAI values seems to be caused by loss of organic matter, probably by oxidation and volatization of oxids (Rejebian et al. 1987). However, fluid composition and pressure (i.e. in water-bearing closed systems) tend to retard conodont color alteration (Rejebian et al. 1987).

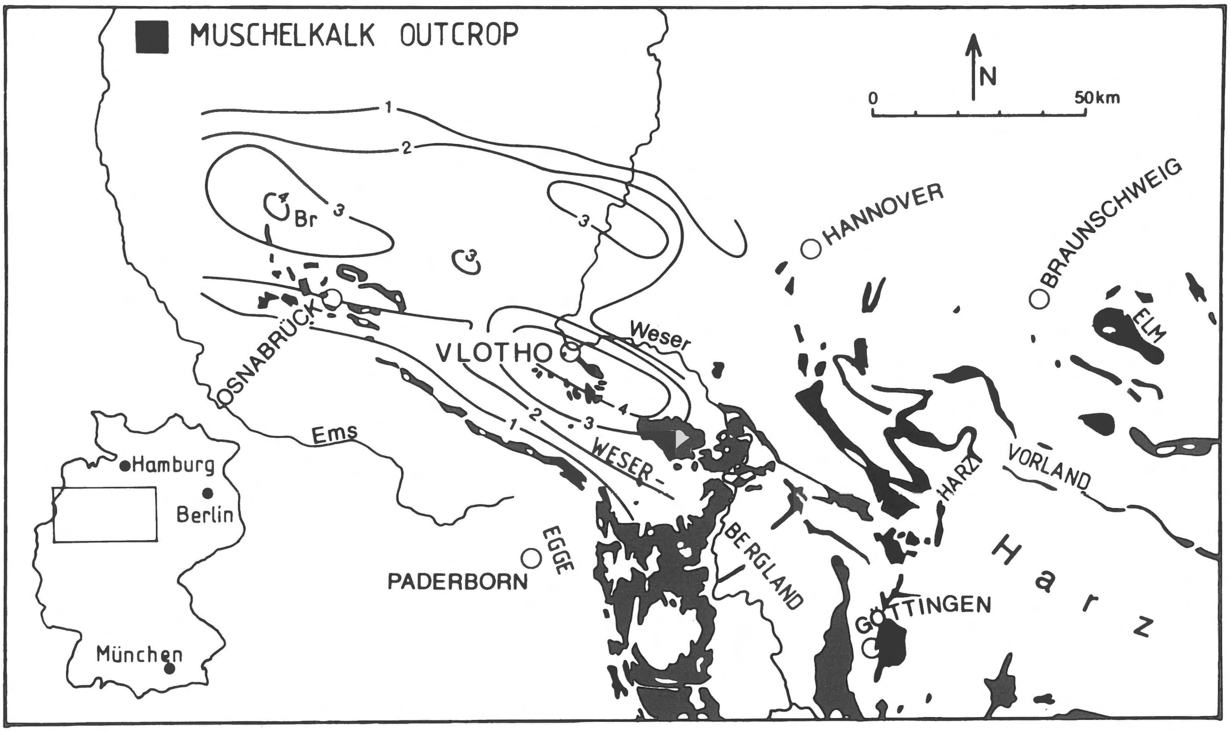

Fig. 2. Outcrop of the Muschelkalk (Middle Triassic) in north Germany with isolines for vitrinite reflectance (% Rm = % mean reflectance) at the Rhätic-Liassic boundary in the area of the Bramsche and Vlotho Massifs (after Deutloff et al. 1980). Br: City of Bramsche.

The CAI method has been applied to the conodonts (*Gondolella*) in the Trochitenkalk (Middle Triassic). The conodont color was compared under a microscope with a color standard and color charts (Epstein et al. 1977). Each CAI is distinctive enough, so that half indices were determined.

Microdolomite Composition (MC)

Subhedral to euhedral dolomite inclusions of 5–20 μm occur in echinoderm fragments and early diagenetic carbonate cements in limestones. These 'microdolomites' are in crystallographic continuity with the calcite host-crystal. They have been discussed by Richter 1974, 1985, Davies 1977, Lohmann & Meyers 1977, Meyers & Lohmann 1978, Blake et al. 1982, Leutloff & Meyers 1984. In the 'Trochitenkalk' (Upper Muschelkalk) the originally high Mg-calcitic crinoids and their first rims (i.e. syntaxial cements) are overgrown by later, stable rim-cements or the Mg-calcite rims are replaced by stable calcite/Fe-calcite, thus conserving the crinoid. In the inner part of this newly formed closed system, no interchange of ions with (interstitial) pore waters could take place. During diagenesis the 'protected' high Mg-calcite was transformed into stable low Mg-calcite and calcian dolomite (52–55 mole % $CaCO_3$) (see Fig. 3) via local microdissolution-reprecipitation in a closed system (e.g. Lohmann & Meyers 1977). In areas influenced by thermal activity or during deep burial diagenesis, these calcian microdolomites are tempered to stoichiometric dolomite (Richter 1985, Richter et al. 1986, Bruckschen et al. 1990b). Thus, the microdolomite composition can be used as a new tool for assessing diagenesis in sediments, especially in carbonate rocks.

The microdolomite composition was determined by X-ray diffraction analyses. The mole % $CaCO_3$ can be calculated from the linear displacement of the $d_{(104)}$ peak between 3.035 Å (calcite) and 2.886 Å

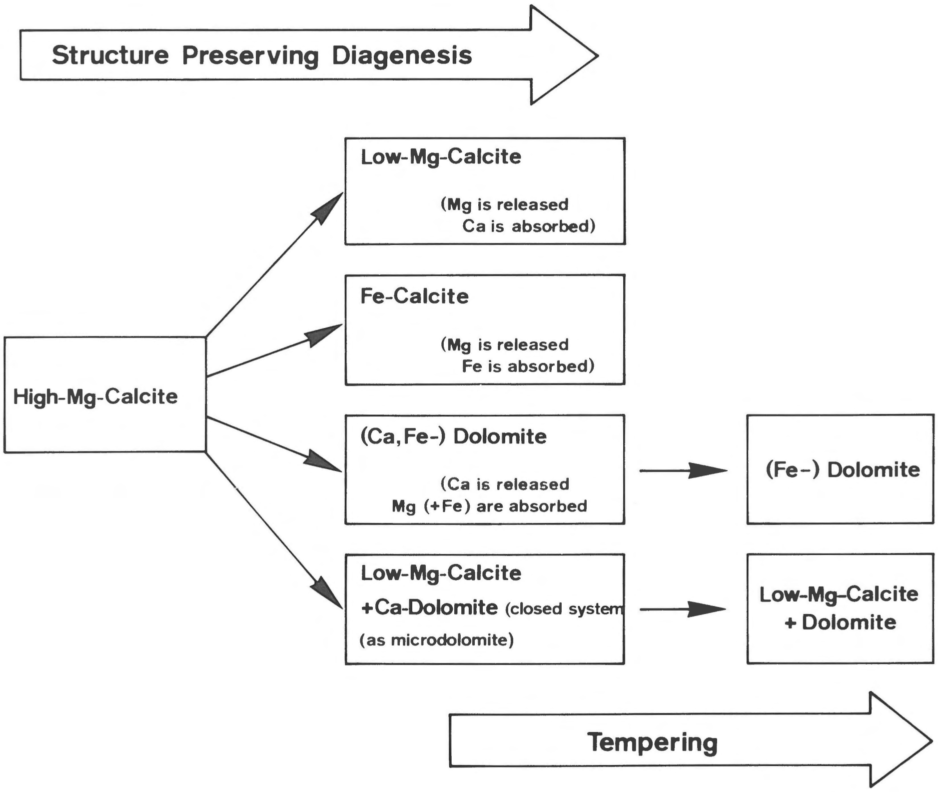

Fig. 3. Scheme showing various diagenetic processes during the transformation of high Mg-calcite into stable carbonate phases and the effect of tempering.

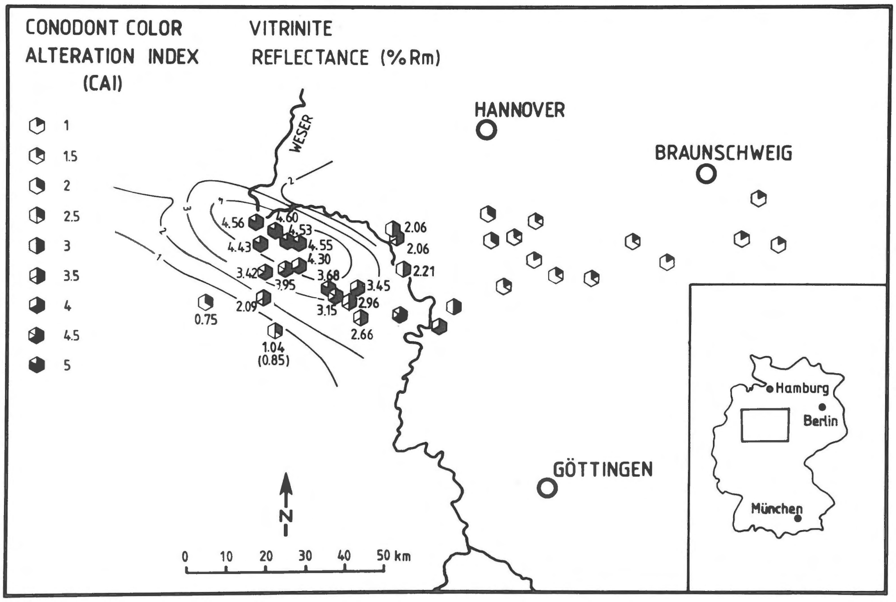

Fig. 4. Regional pattern of the conodont color alteration index (CAI) and vitrinite reflectance data for the Middle Triassic sediments in the southern part of the Lower Saxony Basin. Note: isolines for vitrinite reflectance (% Rm = mean/random reflectance) at the Rhätic-Liassic boundary in the area of the Vlotho Massif (after Deutloff et al. 1980); 3.68 etc: interpolated vitrinite reflectance values (% Rm) for the Trochitenkalk Formation; CAI values of 4.5 and 5 are typical of the central part of the Massif.

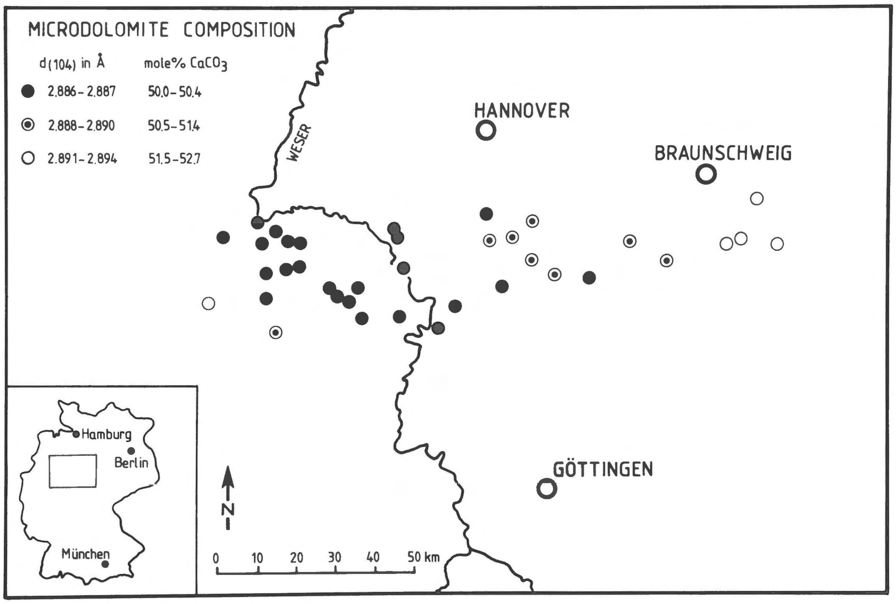

Fig. 5. Composition of microdolomite inclusions in the crinoids of the Middle Triassic Trochitenkalk stage. Filled dots: stoichiometric microdolomites with $d_{(104)}$ = 2.886–2.887 Å (50.0–50.4 mole % $CaCO_3$); open dots combined with filled dots: nearly stoichiometric microdolomites with $d_{(104)}$ = 2.888–2.890 Å (50.5–51.4 mole % $CaCO_3$); open dots: non-stoichiometric microdolomites with $d_{(104)}$ = 2.891–2.894 Å (51.5–52.7 mole % $CaCO_3$). Note: the $d_{(104)}$-values increase (excess $CaCO_3$) with increasing distance from the thermal anomaly. The $d_{(104)}$-values do not show the gradual decrease of temperature reflected by decreasing CAI values from the central part towards the eastern boundary of the intrusive body (along the Weser river; see Fig. 4).

(dolomite) with an accuracy of ± 0.001 Å (Richter 1984). This method is possible, because the microdolomites do not contain $FeCO_3$ (Richter 1985).

Results and discussion

Regional pattern

The thermally most altered sediments, directly overlying the Vlotho Massif (i.e. the area outlined by the isoreflectance lines (% Rm) in Figs 2 and 4) were telemagmatically influenced for a period of 1–10 My (Deutloff et al. 1980, Mundry 1971). In this area the $Ca_{>50}$ microdolomite inclusions in crinoids were tempered to stoichiometric dolomite ($d_{(104)}$ = 2.886–2.887 Å, Fig. 5), and in the central part, maximum CAI values of 4.5 and 5 persist, corresponding with an interpolated vitrinite reflectance value (% Rm) of 4.6 (Fig. 4). The palaeotemperature range estimated from these high CAI values lies between 245° C and 345° C. Calculations based on the geothermometer (% Rm-peak temperatures) of Barker & Goldstein (1990) show 340° C for CAI = 5. These temperatures are higher than those estimated with the help of other geothermometers. Illite crystallinity data from Brauckmann (1984) indicate 200–250° C and thermal modeling by Mundry (1971) points to 200–300° C.

The isoreflectance (% Rm) lines, as well as the CAI values reflect the gradually decreasing organic metamorphism towards the margin of the Massif. Figures 4 and 5 show that rock diagenesis/palaeotemperatures represented by CAI values 3 to 5 and by % Rm 2 to 4.6, cannot be differentiated by microdolomite composition: thus, a threshold temperature for stoichiometric microdolomites is indicated. At some distance from the Massif (east of the Weser River) the tempering effect is no longer evident. Here the nearly stoichiometric microdolomites (50.5–51.4 mole % $CaCO_3$, $d_{(104)}$ = 2.888–2.890 Å) and the CAI values of 1.5–2 are probably the result of burial diagenesis only. If a palaeogeothermal gradient of 40° C/km (Mundry 1971), a surface temperature of 20° C and a maximum of about 3000 m overburden (with local variations) in

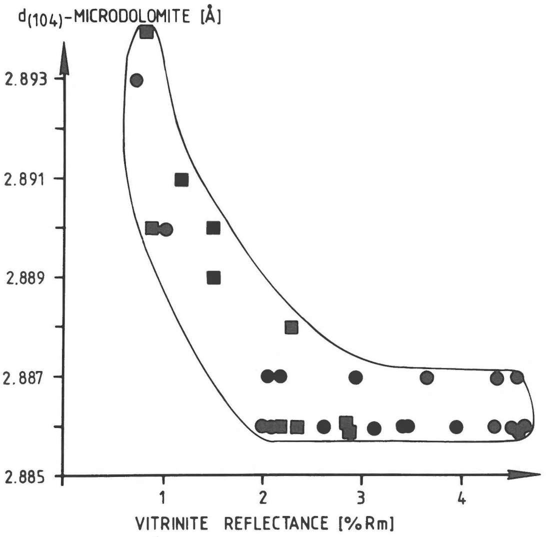

Fig. 6. Vitrinite reflectance (% Rm) and the composition of microdolomites ($d_{(104)}$) of corresponding samples. Filled squares: data from the Bramsche Massif, located NW of the Vlotho Massif (see Fig. 2, Richter et al. 1986, Brauckmann 1984). Note: For % Rm>2.5 only stoichiometric microdolomites are found.

this area are assumed, then the calculated temperature of about 140° C correlates quite well with the experimental temperature range (50–140° C for 500 My and 1 My: Epstein et al. 1977) for CAI values 1.5 to 2. East of this zone, in the area southeast of Braunschweig, CAI values of 1 and high $d_{(104)}$-values caused by excess $CaCO_3$ in microdolomites were observed. 1500 m of overburden in this region accounts for a burial temperature of 65° C, if the above mentioned assumptions are made. Thus, a CAI value of 1 can be expected here.

In the eastern part of the study area (southeast of Hannover), there are a few exceptions in the regional tempering pattern (Fig. 5). Here stoichiometric microdolomites are found near calcian microdolomites. The formation of stoichiometric microdolomites probably results from a locally increased heatflow associated with underlying salt domes in this region. The CAI data, however, do not reflect an anomalous high heat flow (CAI = 1.5). Thus it seems likely, that the microdolomite composition reacts more sensitively to temperature rises than does the CAI. On the other hand, conodont color alteration, and especially the low CAI-values in this area might be influenced by other factors, such as the chemical composition of pore fluids or the overpressure. Experimental data from Rejebian et al. (1987) indicate that color alteration can be retarded in wet closed systems.

Comparison of the different geothermometers

Based on 39 CAI and $d_{(104)}$-values and 29 vitrinite reflectance values (% Rm), a correlation between conodont color alteration (CAI) as well as the degree of stoichiometry ($d_{(104)}$) and thermal maturity is obvious (Figs 6, 7 and 8). The following quantitative relationships between the different parameters can be derived for long term heating/deep burial diagenesis.

(1) In Fig. 6 only stoichiometric dolomites ($d_{(104)}$ = 2.886(7) Å) correspond to % Rm values >2.5, indicating that no change in dolomite composition takes place above a certain temperature. According to Teichmüller & Teichmüller (1981), who correlated borehole temperatures with vitrinite reflectance data from the Upper Rhine Graben, this reflectance value can be correlated with temperatures >180° C. This temperature is in accordance with experimental data from Graf & Goldsmith (1956), which show that Ca-dolomite is completely transformed into ordered dolomite at temperatures between 190–230° C. Thus, it is obvious that microdolomite composition (MC) cannot be used to differentiate diagenesis in areas which have thermal maturities >2.5% Rm.

The degree of diagenesis, which corresponds to a thermal maturation represented by 0.5–0.85 % Rm can be correlated with microdolomite compositions between 2.891–2.893 Å (Fig. 6). Various correlations between vitrinite reflectance and temperature (Teichmüller & Teichmüller 1981, Barker & Goldsmith 1990, Kürmann & Richter 1989) indicate a temperature range of 80° C–90° C for these maturity ranks. The temperature range is in accordance with calculated temperatures based on burial depth (1500 m) and the geothermal gradient for the area southeast of Braunschweig (Fig. 5). Nearly stoichiometric dolomites ($d_{(104)}$ = 2.888–2.890 Å), however, represent vitrinite reflectance

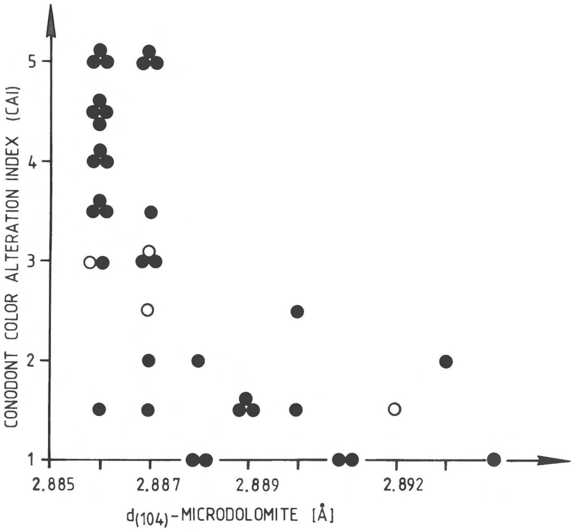

Fig. 7. Microdolomite composition ($d_{(104)}$-values in Å) versus conodont color alteration index (CAI). Open dots: data from Middle to Upper Triassic red limestones (Hallstatt type) from locations in Greece – the samples with CAI-values ≥ 2.5 were taken from Epidavros (Argolis/Greece) and the sample with $d_{(104)} = 2.892$ Å and CAI = 1.5 comes from the island of Hydra (south of Argolis). Note: (1) thermal maturity increases with higher CAI values; (2) larger $d_{(104)}$-values represent less stoichiometric microdolomites (assuming stoichiometry to be $d_{(104)} = 2.886$ Å).

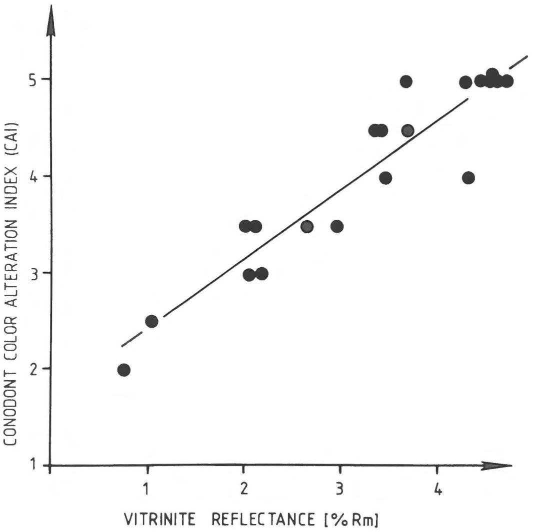

Fig. 8. Vitrinite reflectance (% Rm) versus conodont color alteration index (CAI). (Linear correlation coefficient: 0.94, least-square method.) Thermal maturity increases with higher CAI and % Rm values.

values of 2 % Rm and 1 % Rm, corresponding to a temperature range between 170° C to 100° C (for temperature: see above mentioned authors).

It seems that MC is a useful tool for differentiating low-temperature diagenesis, especially in carbonates, when no dispersed organic material for vitrinite measurements can be found. Furthermore, the rather inhomogeneous $d_{(104)}$-pattern in the region south of Hannover and Braunschweig (Fig. 5) indicates, that MC reacts sensitively to peak temperatures, e.g. to a higher heat flow in underlying salt domes in this area.

(2) In Fig. 7 the CAI-$d_{(104)}$ data plot in an 'L'-shaped trend. Such a correlation suggests that high-temperature diagenesis/low-temperature metamorphism with temperatures above 200° C (Brauckmann 1984), CAI values of 3.5–5 and stoichiometric microdolomites can be differentiated only with the help of conodont color alteration (CAI) and vitrinite reflectance (% Rm). This can also be observed in the regional pattern of microdolomite composition and CAI east of the central zone of the intrusive Vlotho Massif (Figs 4 and 5). The microdolomites in the samples taken from along the Weser river are all stoichiometric, indicating a threshold temperature for stoichiometry, whereas the CAI values and the vitrinite reflectance data suggest that the temperature decreases towards the margin of the Vlotho Massif.

Analogous to the conclusion reached from Fig. 6, the microdolomite composition (MC) enables a differentiation of low-temperature diagenesis (< 180° C).

(3) The correlation between vitrinite reflectance (% Rm) and CAI shows a good linear least-square fit (Fig. 8). The high correlation coefficient (r = 0.94) can be explained by the fact that organic matter in vitrinite and conodonts undergoes similar changes during diagenesis.

Conclusions

1. The conodont color alteration index (CAI) and the microdolomite composition (MC) were successfully used as indicators of diagenesis in the

Vlotho Massif area. Both tools were correlated with vitrinite reflectance (% Rm).

2. MC can be used for differentiating low-temperature diagenesis, especially in marine carbonate rocks, if no dispersed organic material or conodonts can be found.
3. Above a threshold temperature (> 180° C) calcian microdolomites are tempered to stoichiometric microdolomites. Thus, stoichiometric microdolomites are a good indicator of thermal highs, caused for example by deepseated intrusive bodies in the surface.
4. CAI and vitrinite reflectance (% Rm) show a very good linear correlation. This can be explained by the fact that organic matter in vitrinite and conodonts undergoes similar changes (carbonization) during diagenesis.
5. The maximum palaeotemperature range of 300–345° C, ascertained by a CAI value of 5 for sediments directly overlying the Vlotho Massif, lies higher than the temperatures estimated with the help of other geothermometers.

Acknowledgements

This research was supported by a doctoral fellowship awarded by the Alfried Krupp von Bohlen und Halbach Foundation to S. Nöth, and by the Deutsche Forschungsgemeinschaft (DFG) as project No. R 216/8 (Bruckschen, P., S. Nöth & D.K. Richter).

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