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Unique siderite occurrence in Baltic Sea: a clue to siderite-water oxygen isotope fractionation at low temperatures

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Recently formed siderite (between 1785 and 1996) at the bottom of South Baltic Sea was investigated by thin section petrography, XRD, electron microprobe (determination of major cation content) and mass spectrometry ($\delta^{13}C$ and $\delta^{18}O$ analysis). The siderite was interpreted as having formed from metallic iron partly protected from free oxygen access by wood tar with $\delta^{13}C = -24‰$ and from biogenic CO_2 produced from this organic matter. Inasmuch as the siderite has highly positive $\delta^{13}C$ values ranging from 8.05 to 15.41‰, we deduced that extremely isotopically heavy CO_2 was generated in the process of biogenic decomposition of the organic matter. It was found that the $\delta^{18}O$ values of siderite (26.58 to 27.74‰ *vs*. VSMOW) fit very well to the recalculated curve of Becker (1971)

$10^3 \ln \alpha = 3.059 \frac{10^6}{T^2} - 4.53$ and to published extrapolated experimental data.

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Key words: Baltic Sea, siderite, oxygen isotopes, isotope equilibrium, low temperatures, water.

INTRODUCTION

Natural siderite is often formed at low temperatures in the anoxic zone by bacterial methanogenesis (Curtis *et al*., 1986). This holds true especially for siderites in sedimentary or diagenetic environments. Because siderite is often one of the earliest minerals to precipitate in sediments, there has been considerable interest in using siderite geochemistry as an indicator of depositional environment (Mozley and Wersin, 1992). In this respect the oxygen isotope thermometer, is which based on the siderite-water equilibrium fractionation factor, is of great value.

It is the primary purpose of this study to test which of the calculated siderite-water fractionation factors (see Fig. 1) may be used for the interpretation of $\delta^{18}O$ values of natural siderite. The existing data from laboratory experiments (Carothers *et al*., 1988; Mortimer and Coleman, 1997; Zhang *et al*., 2001) are significantly scattered (Fig. 2). This might be due to incomplete isotope equilibrium, which cannot be attained in a short-term laboratory experiment. In this study we used siderite samples formed in very specific conditions on the bottom of the Baltic Sea, where the $\delta^{18}O$ of water and the average temperature of carbonate formation are well known. Moreover, the siderite crystallization proceeded much more slowly (over centuries) than to any laboratory experiment. The slow rate has assured isotopic equilibrium conditions for the siderite-water and siderite-CO_2 systems.

ISOTOPIC EQUILIBRIA

The oxygen isotope exchange reaction between iron carbonate and water may be written (as for other divalent metal carbonates–water systems) in the following form:

$$\frac{1}{3}\mathrm{FeC^{16}O_3} + \mathrm{H_2{}^{18}O} = \frac{1}{3}\mathrm{FeC^{18}O_3} + \mathrm{H_2{}^{16}O} \qquad [1]$$

According to the statistical-mechanical theory of isotopic equilibrium (Bigeleisen and Mayer, 1947; Urey, 1947; Bottinga, 1968; Shiro and Sakai, 1972) the equilibrium fractionation factor:

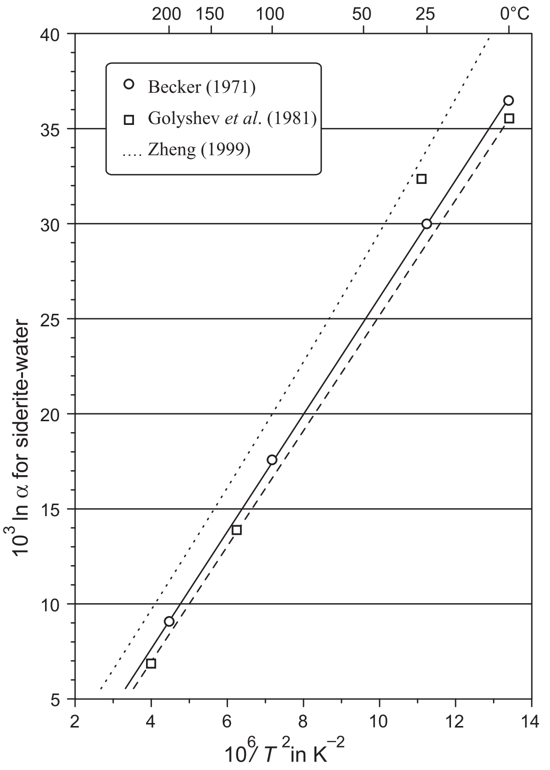

Fig. 1. Calculated oxygen isotopic fractionation factor for isotope equilibrium between siderite and water

The solid line was calculated from reduced partition functions (r.p.f.) given by Becker (1971) for siderite and the r.p.f. for water given by Hattori and Halas (1982); the broken line was calculated in a similar manner, but the point for 27°C was rejected

$$\alpha = \frac{\left(^{18}\mathrm{O}/^{16}\mathrm{O}\right)_{siderite}}{\left(^{18}\mathrm{O}/^{16}\mathrm{O}\right)_{water}} \qquad [2]$$

can be expressed by the reduced partition function ratios (r.p.f.r.) of the reacting compounds as follows:

$$\alpha = \frac{f_s^{1/3}}{f_w} \qquad [3]$$

where: f_s and f_w — the r.p.f.r. of siderite and liquid water, respectively.

For simpler handling of isotope fractionation the formula [3] is rewritten in the following logarithmic form:

$$10^3 \ln\alpha = 10^3 \ln f_s^{1/3} - 10^3 \ln f_w \qquad [4]$$

The first calculation of 10^3 ln α was made by Becker (1971) on the basis of a statistical thermodynamic method, in a way similar to that published by O'Neil *et al.* (1969). We reproduce the results of this calculation in Figure 1, but with the following modification: the results of $10^3 \ln f_s^{1/3}$ were taken from Becker's Ph.D. Thesis, while the r.p.f.r. of water are based on the calculation of Richet *et al.* (1977) for water vapor and the experimental data on liquid-vapor fractionation (Horita and Wesolowski, 1994). The following equation was found by the least square fitting for siderite-water fractionation:

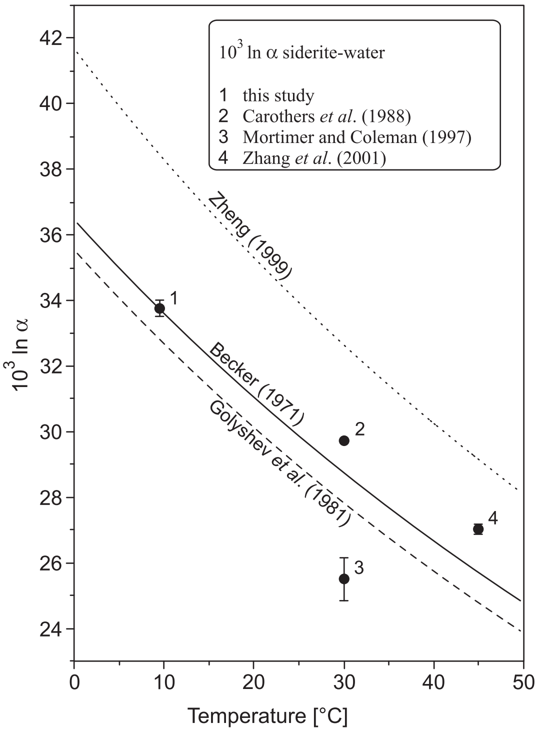

Fig. 2. Low-temperature isotope fractionation between siderite and water

Lines are theoretical plots, whereas points are experimental data

$$10^3 \ln\alpha = 3.059\frac{10^6}{T^2} - 4.53 \qquad [5]$$

where: T — the absolute temperature.

In the same way we have recalculated the data from Golyshev *et al.* (1981), which are plotted on Figure 1 as squares. It is seen that the calculated point for $T = 300$K significantly departs from the straight line, which fits to the remaining points. Hence we have rejected this point and fitted the straight line by the least squares method to the remaining points. This line is very close to that obtained from Becker's calculation. Note that the recalculated Becker's line differs somewhat from that given by Becker and Clayton (1976); it is shifted towards higher values of 10^3 ln α by about unity. Thus the straight line shown in Figure 1 is in favour of the curve (not straight line) calculated by Zheng (1999). The last curve was obtained on the basis of the siderite r.p.f.r., calculated by the modified incremental method (Zheng, 1999 and references therein), and $10^3 \ln f_w$ taken from Hattori and Halas (1982).

It should be noted that in the low-temperature range considered here, the r.p.f.r. of liquid water calculated by Hattori and Halas (1982) are nearly identical with that calculated on the basis of experimental data published by Horita and Wesolowski (1994). Therefore the three lines plotted in Figure 1 may by considered as three independent plots of equation [4] with a common $10^3 \ln f_w$ term. This approach is useful for the comparison of the siderite-water fractionation calculated by different authors. Similar plots were published by Zhang *et al*. (2001) in their figure 1, but their data were based on different values of $10^3 \ln f_w$. Moreover, their plot based on Golyshev *et al*. (1981) was not refined there as is done in our Figure 1. A large divergence between Zheng's (1999) curve and the two remaining ones is seen, particularly in the low temperature range in which the majority of siderites are formed in sedimentary and diagenetic environments.

The low temperature carbon isotope equilibrium between CO_2 and $CO_3^{=}$ is described by Halas *et al*. (1997). The precipitation of solid $FeCO_3$ shifts $\delta^{13}C$ of the precipitate towards higher values with respect to $CO_3^{=}$. For the siderite CO_2 fractionation factors the reader is referred to Jimenez-Lopez and Romanek (2004), where the experimentally determined isotope fractionation factor at $T = 25°C$ is given, in agreement with data obtained at temperatures from 30–200°C by Carothers *et al*. (1988). From the known isotope fractionation factor and $\alpha^{13}C$ of siderite one may decipher the $\delta^{13}C$ of CO_2.

DESCRIPTION OF SAMPLES

Samples of siderite selected for analyses were taken on the place of their formation from the wreck of a sunken ship, in the shallow littoral zone on the bottom of the Baltic Sea. The location of the shipwreck is shown in Figure 3. A sand layer 0.5–1.7 m thick covers the wreck of the wooden ship along with elements of the cargo and equipment lying at depths of 5–7 m, *ca*. 500 m from the shore. The cargo transported included iron plates and bars. The equipment included barrels filled with wood tar, the material used those days for protection of wooden components of ships. The catastrophe leading to the sinking of the ship, with equipment and members of the crew according to written sources, took place on the Baltic Sea during a storm on the 27th of September 1785. Spilling of the wood tar transported in barrels occurred beneath the wrecked ship, which got stuck in the sandy bottom. A culture layer comprising the sunken iron cargo, wood tar, ship equipment and bodies of the crew was formed. The spilled wood tar formed a reducing local environment in which siderite was precipitated. The rock is a sandy conglomerate with fragments of the ships equipment (e.g. the deck bell with an easily distinguishable inscription "General Carlton of Whitby, 1777"), tools, personal belongings of the crew as well as fragments of human bones and skulls, caboose equipment, chips of fossil coal, *etc*.

The conglomerate comprises a sandy gravel cemented by siderite (Chlebowski and Kowalski, 1999). Siderite is developed as two morphological varieties: with a lamellar-radial structure (Fig. 4) and with a grainy structure (Fig. 5) respectively. Microscopic and X-ray structural analyses indicated that siderite with the lamellar-radial structure represents the earlier diagenetic stage. Grainy siderite in turn represents a more mature crystallographic stage with an ordered internal structure and well-formed grain morphology, which is indicated by the well-developed walls of the crystals. The ordered internal structure of the siderite crystals (grainy variety) is linked to the removal of the isomorphic admixture of Mn, which is present in small quantities in the lamellar-radial variety. This regularity is confirmed by electron

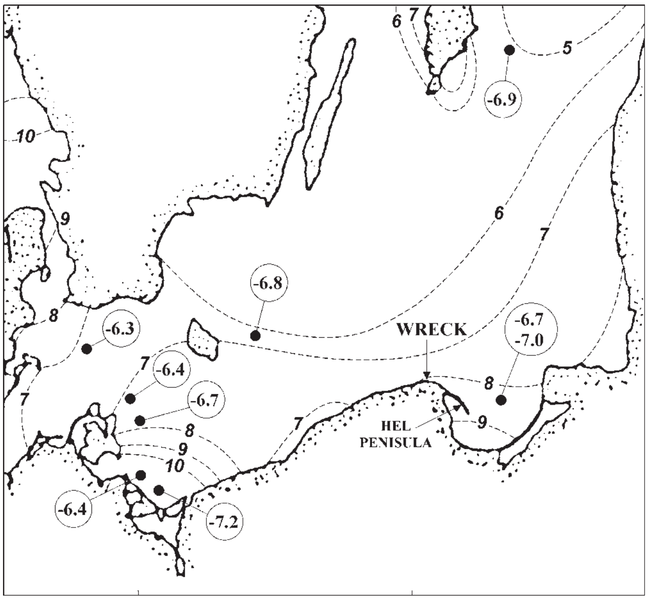

Fig. 3. Sketch map of the Baltic Sea with the position of the shipwreck

Averaged isotherms for surface water (0–10 m) are plotted for the spring season (May) according to Majewski and Lauer (1994); ^{18}O values from Fröhlich *et al*. (1988) are shown as circles

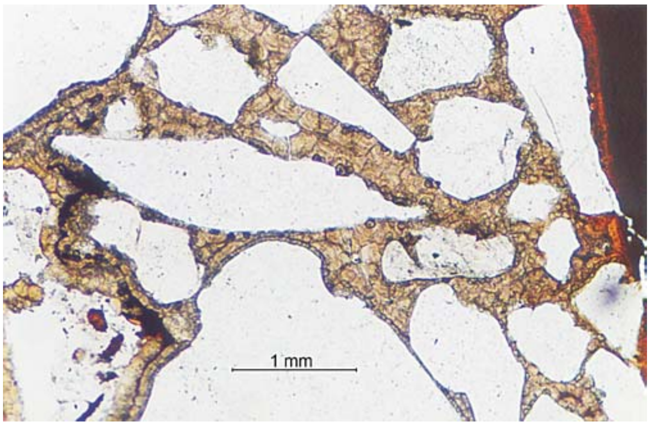

Fig. 4. Siderite with a lamellar and radial structure, binding clastic material, plane polarized light

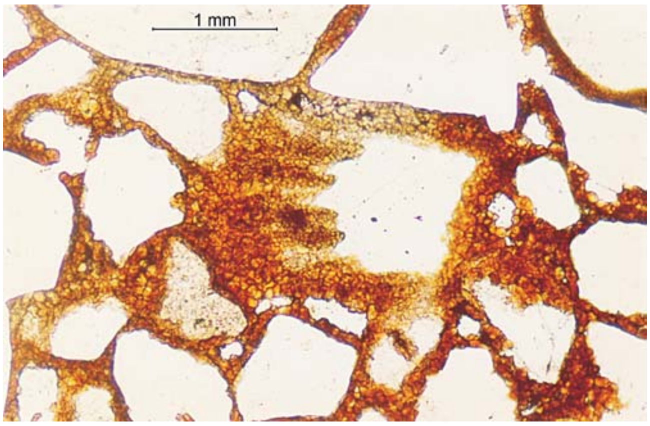

Fig. 5. Siderite with a granular structure, binding clastic material, plane polarized light

microprobe analyses of the cation content in both varieties of siderite, which indicate that the lamellar-radial siderite contains 0.002–0.006 Mn, whereas the grainy siderite contains only up to 0.002 Mn (Table 1).

Table 1

Results of quantitative chemical analyses of siderite with a lamellar and radial structure (*a*) and granular structure (*b*)

Type	Si	Mg	Ca	Mn	Fe
a	0.021	0.016	0.086	0.006	1.871
	0.001	0.007	0.110	0.002	1.880
	0.002	0.006	0.156	0.005	1.832
b	0.002	0.023	0.194	0.000	1.781
	0.001	0.019	0.129	0.000	1.851
	0.001	0.019	0.164	0.002	1.814

this table contains the number of cations based upon 6 oxygen atoms of the siderite lattice; the analysis was done by means of wavelength dispersive spectrometry (WDS)

Additionally, the content of other cations indicates an increase of Ca in relation to Mg, as is typical of shallow-littoral marine environments. The excess for this marine zone and the dominant Fe content is restricted only to the wreckage site, where its sources are the iron plates and bars beneath the deck. The contents of Fe in both structural varieties of siderite are similar, as this is the main component of siderite, contrary to the isomorphic admixtures of Mn.

Siderite crystallization still continues. The crystals still form in the rocky conglomerate on the wreck, as in laboratory experiments, in which the chemical compounds are not entirely exhausted. This is evident in those samples where a new generation of siderite crystals appears as surface coatings on the edges of older well-developed crystals (Fig. 6). The younger generation of siderite has the lamellar-radial structure.

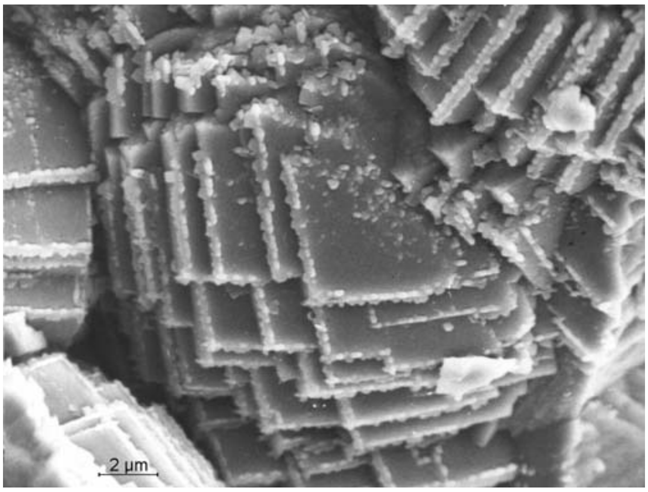

Fig. 6. Siderite developed as idiomorphic crystals with a younger-generation of lamellar siderite coating them

ANALYSIS OF δ^{18}O AND δ^{13}C

Siderites were analysed by means of a dual inlet and triple collector mass spectrometer on CO_2 prepared by 100% H_3PO_4 under vacuum at 50°C, the reaction time was 1 week. Calcite which was present at levels of a few percent (see Table 2) was removed by reaction with the phosphoric acid at 25°C within 2 hours. During this time the entire preparation line was evacuated, then the reaction temperature was rapidly (in 15 min.) increased to 50°C. The reaction time (1 week) assured a yield of CO_2 totalling 75% from the fine siderite powder (Al-Aasm *et al*., 1990). The acid fractionation factor for siderite prepared at 50°C was taken from Rosenbaum and Sheppard (1986).

The results of isotope analysis are shown in Table 2, where δ^{13}C is expressed on the VPDB scale, and δ^{18}O on the VSMOW scale. The normalization was achieved by means of analysis of CO_2 prepared from NBS-19 calcite at 25°C. The δ^{18}O *vs*. VPDB were converted to the VSMOW scale according to the formula given by Friedman and O'Neil (1977). From siderite δ^{18}O *vs*. VSMOW and δ^{18}O of water, assumed to be –7.0‰ according to Fröhlich *et al*. (1988), $10^3 \ln \alpha$ values were calculated. These values fall into a narrow range, from 33.0–34.4 (Table 2). The uncertainty of these values predominantly depends on the δ^{18}O variability of water in the study area. Judging from data obtained by Fröhlich *et al*. (1988), the δ^{18}O variability in the South Baltic is about 0.5‰. It should be noted that sea water in the study area is very well and continuously mixed due to the action of the coastal stream, which also transports sand from the western coast towards Gdańsk Bay. Therefore, including analytical uncertainties of the order of 0.1‰ (standard deviation), the mean value of $10^3 \ln \alpha$ and its uncertainty is 33.75 ± 0.6.

Table 2

Results of isotope analysis of siderite samples and estimated values of $10^3 \ln \alpha$

Sample	Type*	$\delta^{13}C_{VPDB}$ [‰]	$\delta^{18}O_{VSMOW}$ [‰]	$\delta^{18}O_{water}$ [‰]	$10^3 \ln \alpha$
Siderite 1	*a*	15.41	27.74		34.4
Siderite 2	*b*	15.26	27.65	–7.0**	34.3
Siderite 3	*a*	13.41	26.27	±0.5	33.0
Siderite 4	*a/b*	8.05	26.58		33.3
Wood tar		–24.0		mean:	33.75 ± 0.6

* — explained in Table 1
** — assigned according to Fröhlich *et al*. (1988)

Inasmuch as the equilibrium fractionation factor is solely controlled by temperature, the small spread of our results indicates a narrow temperature range in which the siderite was crystallized. This point is discussed below in detail.

DISCUSSION

The geochemical conditions under which proceeded the crystallization of siderite were predominantly anoxic, due to isolation of the iron bars and plates by the wood tar. This organic matter itself as well as wood and fossil coal, which were covered by a layer of the wood tar, underwent biochemical degradation to CO_2 and methane. The excess of these gases could easily diffuse outside the anoxic local system, but a fraction of the CO_2 could react with iron in a low temperature aqueous environment. The process of iron oxidation and the formation of iron hydroxide, which was finally converted to $FeCO_3$, was extremely slow because even now a significant fraction of the iron remains in metallic form. Thus the slow rate of siderite crystallization suggests that its $\delta^{18}O$ has recorded the temperature of the siderite-water system which remained in isotopic equilibrium.

The annual average surface temperature can be best estimated from water temperatures measured in deep wells in the study area. For example, the measured water temperatures from wells about 100 m deep on the Hel peninsula were between 9.4 and 9.8°C (Halas *et al*., 1993). However, the water temperature at the surface at the site of siderite formation varied form +2.5°C in February to +17.5°C in August (Majewski and Lauer, 1994), but the average water temperatures in the spring (May) and autumn (November) are 7.5 and 8.0°C, respectively. Thus over about half a year the surface water temperature in the study area is very close to the annual average of 9.6°C. It should be noted that the temperature oscillation cited above refers to surface water. The siderite was formed at depths of about 6 m under a 0.5–1.7 m thick cover of alluvial sand, which significantly damped the amplitude of temperature oscillation. According to the Fourier's laws, at a depth of 1 m of sand the annual temperature variation is damped by a factor of 1.7, whereas the diurnal variations are damped by a factor of 32 (Tichonow and Samarski, 1963).

Moreover, the rate of siderite crystallization seems be the highest during spring and autumn because, in these periods, water in Baltic Sea is very well mixed, promoting the escape of CO_2 from the anoxic system, which stimulates $FeCO_3$ crystallization and diffusion of some oxygen to oxidize a new fraction of the metallic iron to $Fe(OH)_2$. In summer, water is less agitated whereas the production of biogenic CO_2 is higher, which lowers the pH value of the solution and slows down the rate of siderite crystallization. Also in winter the rate of siderite crystallization may be lowered due to lower production of biogenic CO_2. Therefore the siderite under consideration has been formed in isotopic equilibrium in a narrow temperature range, close to annual mean temperature of that area.

Another source of uncertainty in this above evaluation of the $10^3 \ln \alpha$ may be some variability of the $\delta^{18}O$ of the water. The Baltic Sea water may be considered as a mixture of oceanic water ($\delta^{18}O = 0$) and water supplied from local precipitation($\delta^{18}O = -0.5‰$ in the region adjacent to the Southern Baltic (Halas *et al*., 1993). The last value depends on the mean annual surface temperature (Yurtsever, 1975) as follows:

$$\delta^{18}O = 0.521\ T\,[°C] - 14.91 \qquad [6]$$

At the beginning of the possibility of siderite formation, from 1785 to 1850, the mean annual temperature was about 1°C lower than later on (Stachlewski, 1978). This may have lowered the $\delta^{18}O$ of the precipitation by *ca*. 0.5‰, according to equation [6]. However, considering large buffering properties of the sea, these climatic variations must be limited to a small fraction of 1‰. The isotopic evolution of the Baltic Sea water in the Holocene was recorded in the $\delta^{18}O$ of carbonates formed at constant $T = 4°C$ in sediments of the Baltic Gotland deep (Jedrysek *et al*., 1999). Rodochrosite in the youngest sediments in the Gotland deep shows an increase of $\delta^{18}O$ by 1.3‰ with depth and then the $\delta^{18}O$ of rodochrosite returns to the present-day value. According to Jędrysek *et al*. (1999) these variations predominantly reflect the process of opening/closing of the Baltic Sea to the North Sea rather than a variations in the $\delta^{18}O$ of precipitation due to climate changes in this region.

In contrast to the uniform oxygen isotopic composition of the siderite investigated, carbon shows large variations of $\delta^{13}C$ (Table 2). The highest $\delta^{13}C$ values of the siderite samples fall just above the upper limit recorded for siderites from the marine environment, but much below the upper limit for siderites from continental environments (Mozley and Wersin, 1992). The $\delta^{13}C$ value of siderite can be estimated assuming that CO_2 is enriched by up to 13‰ with respect to original organic matter with $\delta^{13}C = -24‰$ (Nakai, 1961). The magnitude of $CO_3^{2-} - CO_2$ fractionation at 9.5°C is 8‰ (Halas *et al*., 1997), so the $\delta^{13}C$ of dissolved carbonate may as high as –3‰. Further fractionation during crystallization may increase the $\delta^{13}C$ of siderite by about 6‰ resulting in $\delta^{13}C = +4‰$. This value is considerably lower than that of siderite 4, whereas the remaining samples show considerably higher values. The most likely reason of these high values seems to be a larger fractionation during CO_2 generation at low temperatures than was observed in the laboratory experiments (Nakai, 1961). Another reason of higher enrichment of siderite in ^{13}C may be a faster diffusion of isotopically light CO_2 from the system.

This geochemical model of the siderite formation was recently supported by determination of the radiocarbon content in the wood tar relics and in of one siderite sample (no. 2 in Table 2). The radiocarbon content measured by accelerator mass spectrometry in both species was nearly identical (Piotrowska *et al*., 2004). The conventional dates for the siderite and the wood tar are (715 ± 25)BP and (775 ± 30)BP, respectively.

CONCLUSION

This study confirms that the oxygen isotope fractionation between siderite and water at low temperatures is best described by the r.p.f.r. originally calculated by Becker (1971) and the r.p.f.r. calculated for liquid water on the basis of the r.p.f.r. of water vapour (Richet *et al*., 1977) and liquid — vapor fractionation (Hattori and Halas, 1982; Horita and Wesolowski, 1994). Our mean result of $10^3 \ln \alpha = 33.8 \pm 0.6$ may be considered as equivalent to the experimental value obtained for the lowest temperature so far ($T = 9.6°C$). This "experimental" point closely matches the revised line of Becker (1971):

$$10^3 \ln \alpha = 3.0591 \cdot 10^6/T^2 - 4.53$$

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