Mineral. Deposita 28, 79–89 (1993)

Mineralium
Deposita

Carbon and oxygen isotopic covariations in hydrothermal calcites

Theoretical modeling on mixing processes and application to Pb-Zn deposits in the Harz Mountains, Germany

Y.-F. Zheng* and J. Hoefs

Geochemical Institute, University of Göttingen, Goldschmidtstrasse 1, W-3400 Göttingen, Germany

Received: October 23, 1991/Accepted: September 1, 1992

Abstract. Isotopic covariations of carbon and oxygen in hydrothermal calcites are quantitatively modeled in terms of the following three mixing processes: (1) mixing between two different fluids which leads to the precipitation of calcite; (2) mixing between fluid and rock: (a) calcite precipitation due to fluid/rock interaction, (b) secondary alteration of primary calcite by interaction with a subsequent fluid. The models are derived from mass balance equations. A distinction among the three mixing processes can be made on a $\delta^{13}C$ vs $\delta^{18}O$ diagram, which places important constraints on the genesis of hydrothermal mineralization. The variables which control the ultimate isotopic composition of hydrothermal calcites include the composition of the initial fluid and the wallrock, temperature, and dissolved carbon species. Owing to significant temperature-dependent fractionation effects during equilibrium precipitation of calcite from a hydrothermal fluid, the mixing processes may be distinguished by telltale patterns of isotopic data in $\delta^{13}C$ vs $\delta^{18}O$ space. In particular, caution must be exercised in postulating the fluid mixing as the cause for mineral deposition. This is demonstrated for hydrothermal Pb-Zn deposits in the western Harz Mountains, Germany. A positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values is observed for calcites from the Bad Grund deposit in the Upper Harz. Two sample profiles through calcite veins show similar correlations with the lowest δ-values at the center of the veins and the highest δ-values at the vein margins. Because the correlation array has a greater slope than for calcite precipitation at equilibrium in a closed system and because fluid mixing may not proceed perpendicular to the vein strike, it is assumed that a fluid/rock interaction is responsible for the observed correlation and thus for the precipitation of calcite. A deep-seated fluid is inferred with a $\delta^{13}C$ value of $-7‰$ and a $\delta^{18}O$ value of $+10‰$, as well as H_2CO_3 as the dominant dissolved carbon species; precipitation temperatures of the calcites are estimated to be about $280 \sim 170\,°C$. Quite different isotopic distributions are observed for calcites from the St. Andreasberg deposit in the Middle Harz. An alteration model is suggested based mainly on the isotopic distribution through a calcite vein. In addition to a primary fluid which has the same isotopic composition as that in the Bad Grund deposit and thus seems to be responsible for the precipitation of calcite associated with sulfides, an evolved, HCO_3^--dominant subsurface fluid with $\delta^{13}C$ about $-20 \sim -15‰$ and $\delta^{18}O \leq 0‰$ is deduced to alter the primary calcite at low temperatures of $70 \sim 40\,°C$.

Carbon and oxygen isotopic covariations in carbonates associated with hydrothermal mineralization have been used for obtaining information about (1) the temperature of formation of the carbonates, (2) the isotopic compositon of hydrothermal fluids involved as an indicator of their origin, and (3) the nature of dissolved carbon species (e.g. Rye and Williams 1981; Matsuhisa et al. 1985; Zheng 1990). Simultaneous variations in $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios of hydrothermal calcite during CO_2 degassing have been modeled by Zheng (1990). As an example of his theoretical modeling, carbon and oxygen isotopic data for calcites from the Kushikino gold-mining area in Japan (Matsuhisa et al. 1985) have been applied, and CO_2 degassing has been suggested as a more likely cause, instead of fluid mixing, for the precipitation of calcite and quartz.

With respect to geochemical mixing processes in hydrothermal mineralization, three types of mixing can be distinguished: (1) mixing of fluids, (2) fluid/rock interaction, and (3) secondary alteration. As is well known, the mixing of fluids is an effective mechanism of precipitating hydrothermal ore and/or gangue minerals. Several recent studies have indicated the presence of more than one type of fluid during the formation of individual ore deposits (e.g. Taylor 1974; Behr et al. 1987). Obviously, the mixing of fluids is characterized by the simultaneous presence of more than one type of fluid, whereas the occurrence of different generations of fluid is better described as secondary alteration, i.e. previously deposited minerals are overprinted by a late fluid. Additionally, chemical compositions of a fluid can be changed during its transport due to

---

* *Present address:* Institut für Mineralogie, Petrologie und Geochemie, Universität Tübingen, Wilhelmstrasse 56, W-7400 Tübingen 1, Germany

fluid/rock interaction, leading to a profound effect on the precipitation of hydrothermal minerals. The three mixing processes have significantly different implications for the genesis of hydrothermal mineral deposits and thus a distinction between them is clearly of value.

The purpose of this contribution is to develop a set of similar mass balance equations for the calculation of the simultaneous $\delta^{13}C$ and $\delta^{18}O$ changes that occur due to the mixing processes in hydrothermal mineralization. The equations are similar to those developed by Vollmer (1976) for isotopic mixing of two components, by Taylor (1977) for fluid/rock interaction, and by Sverjensky (1981) for secondary alteration of carbonates. As a case study, carbon and oxygen isotopic data for calcites from two economically significant hydrothermal Pb-Zn deposits in the Harz Mountains (i.e. the Bad Grund deposit in the Upper Harz and the St. Andreasberg deposit in the Middle Harz), Germany, are compared to calculated models. Because of very rapid rates of isotopic exchange between fluid and calcite under hydrothermal conditions (O'Neil et al. 1969), it is reasonably assumed that isotopic equilibrium has been established between different fluids or between fluid and solid (hydrothermal calcite or wallrock). Therefore, kinetic fractionation effects are not likely to have been significant in the processes of isotopic exchange, even if dissolution/precipitation of calcite could take place in the hydrothermal systems. The application of these calculations does not require that the mineral or rock phases have reached chemical equilibrium with hydrothermal fluids. In most situations, nevertheless, it is adequate to recognize that the mineral or rock compositions have advanced toward equilibrium during hydrothermal mineralization. Banner and Hanson (1990) have presented similar calculations for simultaneous isotopic and trace element variations during water-rock interaction in carbonate diagenesis.

In the following case calculations, H_2CO_3 (including dissolved CO_2) and HCO_3^- are treated as independent conservative components, as previously done by Robinson (1975), Matsuhisa et al. (1985) and Zheng (1990). Although the speciation of carbon in solution is known to be a function of temperature and fluid chemistry, it is useful in geochemistry to consider the dissolved carbon in hydrothermal fluids either as dominant H_2CO_3 or as dominant HCO_3^-. The isotopic fractionation factors for carbon among calcite, CO_2 and HCO_3^- are taken after Ohmoto and Rye (1979), for oxygen between calcite and H_2O after O'Neil et al. (1969), and for oxygen between CO_2 and H_2O after Truesdell (1974). Additionally, it is commonly assumed that isotopically H_2CO_3 behaves like CO_2, so that the fractionation involving CO_2 is applied where H_2CO_3 is involved. Moreover, isotopic ratios are represented in the conventional δ notation, and carbon isotope ratios are denoted relative to the PDB standard while oxygen isotope ratios are denoted relative to the SMOW standard.

Models for mixing processes

Mixing between two fluids

Experimental investigations have indicated that in alkaline solutions the solubility of calcite increases with temperature and that the addition of either NaCl or $CaCl_2$ increases the solubility of calcite in hydrothermal solutions (Holland and Malinin 1979). Obviously, when a fluid is $CaCO_3$-supersaturated and rich in alkali-chloride mixes with a fluid that is poor in alkali-chloride, the precipitation of calcite can result due to dilution. Suppose that two hydrothermal fluids A and B are mixed in differing proportions specified by a parameter r defined as:

$$r = A/B \tag{1}$$

where A and B are the relative weights of the two fluids in a given mixture. The isotopic compositions of carbon and oxygen in such a mixture are:

$$(1 + r)\delta^{13}C_m = r\delta^{13}C_a + \delta^{13}C_b \tag{2}$$

$$(1 + r)\delta^{18}O_m = r\delta^{18}O_a + \delta^{18}O_b \tag{3}$$

where subscripts m, a and b denote the mixture, fluids A and B respectively. Equations 2 and 3 can be combined into a single equation by eliminating the parameter r:

$$\delta^{13}C_m = \delta^{18}O_m \cdot \frac{\delta^{13}C_a - \delta^{13}C_b}{\delta^{18}O_a - \delta^{18}O_b} + \frac{\delta^{13}C_b\delta^{18}O_a - \delta^{13}C_a\delta^{18}O_b}{\delta^{18}O_a - \delta^{18}O_b} \tag{4}$$

This is the equation of a straight line in coordinates of $\delta^{18}O_m$ and $\delta^{13}C_m$. It is the locus of all points representing mixtures of fluids A and B in differing proportions, including the pure components, but in the same concentrations of carbon and oxygen. Actually, because of H_2O dominance the different fluids contain nearly equal oxygen contents ($O_b/O_a \approx {}^{16}O_b/{}^{16}O_a$) but there might exist a large difference in the carbon contents. When proportions of the carbon contents in the fluids A and B can be specified by another parameter, P, defined as:

$$P = C_b/C_a \approx {}^{12}C_b/{}^{12}C_a \tag{5}$$

Equation 2 becomes:

$$(P + r)\delta^{13}C_m = r\delta^{13}C_a + P\delta^{13}C_b \tag{6}$$

For oxygen isotopes Eq. 3 is still valid. After eliminating r from Eqs. 3 and 6, we obtain a general hydrothermal carbon–oxygen isotopic mixing equation as follows:

$$\begin{aligned}\delta^{18}O_m(\delta^{13}C_a - P\delta^{13}C_b) &+ \delta^{18}O_m\delta^{13}C_m(P - 1)\\ &+ \delta^{13}C_m(\delta^{18}O_b - P\delta^{18}O_a)\\ &+ (P\delta^{18}O_a\delta^{13}C_b\\ &- \delta^{18}O_b\delta^{13}C_a) = 0\end{aligned} \tag{7}$$

This is the equation of a hyperbola because it contains a term of $\delta^{18}O_m\delta^{13}C_m$. When $P = 1$, Eq. 7 reduces to Eq. 4. In the case of $P \neq 1$, the sense of the hyperbolic curvature (concave up or concave down) is dependent on the relative concentrations of carbon in the fluids A and B. A possible example is illustrated in Fig. 1, which shows mixing curves of fluid compositions for mixing between 'seawater' (fluid A) and 'magmatic water' (fluid B) in $\delta^{13}C$ vs $\delta^{18}O$ space. As the ratio, P, of carbon content of fluid B to fluid A becomes progressively greater or less than unity, the hyperbolic form of the function becomes more pronounced.

If a suite of cogenetic calcites is deposited during mixing of two fluids, the temperature variable must be taken into account in calculating the isotopic composi-

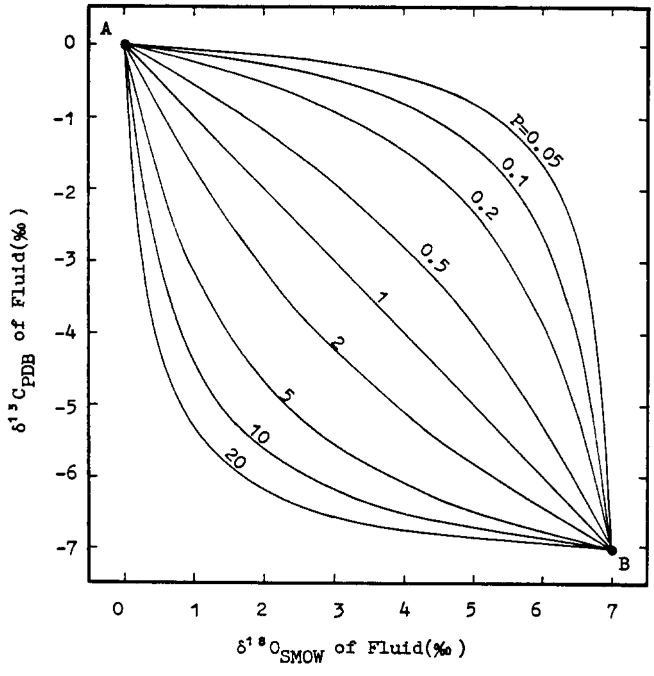

Fig. 1. Mixing curves of fluid compositions for mixing of two fluids in $\delta^{13}C$ vs $\delta^{18}O$ space. Fluid A (e.g. seawater) has $\delta^{13}C = 0‰$ (*PDB*) and $\delta^{18}O = 0‰$ (*SMOW*); fluid *B* (e.g. magmatic water) has $\delta^{13}C = -7‰$ (*PDB*) and $\delta^{18}O = +7‰$ (*SMOW*). *P* is the concentration ratio of total dissolved carbon in fluid B to in fluid A

tions of the resulting calcites because of the fractionation effect between calcite and fluid. Suppose that fluid A is dominated by HCO_3^- and has a lower temperature whereas fluid B is dominated by H_2CO_3 ($\approx CO_2$) and has a higher temperature, then carbon and oxygen isotopic ratios of calcites can be calculated by:

$$\delta^{13}C_{calcite} = \frac{X_a(\delta^{13}C_a + 10^3 \ln \alpha^{calcite}_{HCO_3^-}) + P(1 - X_a)(\delta^{13}C_b + 10^3 \ln \alpha^{calcite}_{CO_2}}{P + X_a - PX_a} \qquad (8)$$

$$\delta^{18}O_{calcite} = \delta^{18}O_b + 10^3 \ln \alpha^{calcite}_{H_2O} + X_a(\delta^{18}O_a - \delta^{18}O_b) \qquad (9)$$

where X_a represents the mole fraction of fluid A in the mixed fluid and $10^3 \ln \alpha^X_Y$ denotes the equilibrium fractionation factor between components *X* and *Y*. Fig. 2 illustrates the mixing curves of calcite compositions due to mixing between 'seawater' (fluid A, 50 °C) and 'magmatic water' (fluid B, 250 °C) in $\delta^{13}C$ vs $\delta^{18}O$ space. Obviously, the isotopic compositions of carbon and oxygen in the calcites are significantly different from those in the fluids.

Effect of fluid/rock interaction

Interaction takes place between a high-temperature hydrothermal fluid and a relatively cold wallrock as the fluid flows along open rock fractures. The interaction can involve cation ex-change, redox reactions, or both. It can thus exert a significant influence on the precipitation of gangue minerals (Holland and Malinin 1979). The loss of H^+ moves hydrothermal fluids toward saturation with respect to carbonates; gains of Ca^{2+}, Mg^{2+}, Fe^{2+} and other cations reinforce this movement. If calcite is deposited from a fluid due to fluid/rock interactions, the isotopic compositions of carbon and oxygen in the calcite are determined by the differences of isotopic ratios between the fluid and the wallrock. The isotopic compositions of the final fluid after fluid/rock interaction can be calculated by the mass balance equation (e.g. Taylor 1977):

$$W\delta^i_{fluid} + R\delta^i_{rock} = W\delta^f_{fluid} + R\delta^f_{rock} \qquad (10)$$

where superscripts *i* and *f* denote the 'initial' and 'final' composition; *W* and *R* represent the atom percentage of carbon or oxygen in fluid and rock, respectively.

In general, fluid and rock are not in isotopic equilibrium before the interaction and therefore tend to exchange their isotopes in order to approach isotopic equilibrium at the interaction temperature. At low temperatures (below 60–80 °C), meteoric groundwater will commonly maintain its oxygen isotopic composition because of very slow rates of oxygen isotope exchange between water and rock (Gat 1981), but when the water is heated up to 80 °C or more, a change in the oxygen isotope composition of the water occurs due to increasing rates of isotopic exchange. The extent of isotopic exchange depends on the relative proportions of oxygen in the fluid to that in the rock, on the initial isotope ratios of the fluid and the rock, on the fluid-rock isotopic fractionation factors (which are temperature dependent), and on the time and surface of contact. If $\delta^{18}O^f_{fluid}$ is determined by isotopic equilibration with the rock, then from Eq. 10:

$$\delta^{18}O^f_{fluid} = \delta^{18}O^i_{fluid} + \frac{R}{W}(\delta^{18}O^i_{rock} - \delta^{18}O^f_{rock}) \qquad (11)$$

A similar equation is used to calculate the isotopic composition of carbon in the final fluid:

$$\delta^{13}C^f_{fluid} = \delta^{13}C^i_{fluid} + \frac{R'}{W'}(\delta^{13}C^i_{rock} - \delta^{13}C^f_{rock}) \qquad (12)$$

Consequently, the isotopic composition of calcite which is precipitated from the final fluid is related to temperature, i.e.

$$\delta^{13}C_{calcite} = \delta^{13}C^i_{fluid} + 10^3 \ln \alpha^{calcite}_{fluid} + \frac{R'}{W'} \cdot \Delta^{13}C^i_f \qquad (13)$$

$$\delta^{18}O_{calcite} = \delta^{18}O^i_{fluid} + 10^3 \ln \alpha^{calcite}_{H_2O} + \frac{R}{W} \cdot \Delta^{18}O^i_f \qquad (14)$$

where $\Delta^i_f = \delta^i_{rock} - \delta^f_{rock}$. The isotopic composition of carbon and oxygen in the calcite can be delineated in terms of Eqs. 13 and 14, given that a relationship between $\frac{R'}{W'} \cdot \Delta^{13}C^i_f$ and $\frac{R}{W} \cdot \Delta^{18}O^i_f$ values is determined. Essentially, the change in these values represents a flux in the isotopic composition of wallrock due to the fluid/rock

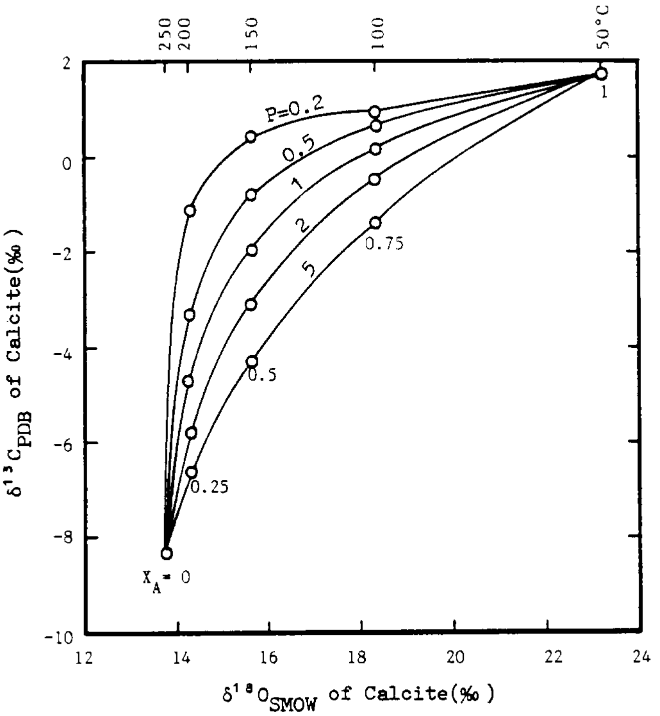

Fig. 2. Mixing curves of calcite compositions for mixing of two fluids in $\delta^{13}C$ vs $\delta^{18}O$ space. The isotopic ratios of the fluids are the same as in Fig. 1, but dissolved carbon species are different. Fluid A is dominated by HCO_3^- and has a low temperature of 50 °C, whereas fluid B is dominated by H_2CO_3 and has a high temperature of 250 °C. X_A is the mole fractionation of fluid A in the mixed solution

interaction. The change in the isotopic composition of wallrock can be quantified by direct measurement on altered and fresh wallrocks, but the atomic ratios of carbon and oxygen in the wallrock to that in the fluid are instantaneous variables and thus it is difficult to quantify them. A simplified approach, for the purpose of theoretical modeling, is to assume $R/W = R'/W'$. Then the change in the $\delta^{13}C$ and $\delta^{18}O$ values of wallrock can be used to indicate the nature of alteration.

Assuming that rock/fluid ratios (R/W) vary from 0 to 1 and temperatures decrease from 300 to 50 °C, we can calculate the theoretical curves for either H_2CO_3 or HCO_3^- as the dominant dissolved carbon species, as illustrated in Fig. 3 for an initial fluid with $\delta^{13}C = -7‰$ and $\delta^{18}O = +8‰$ in the case where the wallrock has been altered with $\Delta^{13}C^i_f > 0$ and $\Delta^{18}O^i_f > 0$. This assumed case requires that the wallrock has higher $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios than the fluid, so that the slope of correlation trends of the resulting calcite is greater than that in the closed system when H_2CO_3 acts as the dominant carbon species. Theoretically, increasing CO_2 in solution can reduce the effective oxygen isotope fractionation factor between calcite and the bulk fluid and steepen predicted $\delta^{13}C$ vs $\delta^{18}O$ trends. The increase in the dissolved CO_2 content of fluid requires an open system where carbonate in wallrock is progressively taken up by the migrated fluid. This case is substantially equivalent to the presently described effect. A similar picture can result due to changes in fluid pH, as previously demonstrated by Ohmoto (1972). Essentially, an increase in fluid pH can cause the precipitation of calcite and the resulting calcite can be progressively enriched in ^{13}C relative to that in a closed system. But a simultaneous change in the $\delta^{18}O$ values of calcite cannot result from the change in pH.

If HCO_3^- is the dominant form of dissolved carbon in hydrothermal fluids, calcite precipitated will show small variations in $\delta^{13}C$ values relative to temperature. But large variations in $\delta^{18}O$ can occur simply due to temperature effect on the $CaCO_3$–H_2O system.

Secondary alteration of hydrothermal calcite

Hydrothermal alteration of calcite at low temperatures is the other type of mixing process which does not cause original precipitation of the calcite but can systematically change the isotopic compositions of carbon and oxygen in the previously deposited calcite. The isotopic ratios of the calcite being altered by an H_2O-rich C–O–H fluid may be calculated from an integrated form of a mass balance equation (Taylor 1977). For oxygen isotope exchange, this is:

$$\frac{W}{R} = \ln\left[\frac{\delta^{18}O^i_{H_2O} + (\Delta^{18}O^{calcite}_{H_2O} - \delta^{18}O^i_{calcite})}{\delta^{18}O^i_{H_2O} - (\delta^{18}O^f_{calcite} - \Delta^{18}O^{calcite}_{H_2O})}\right] \quad (15)$$

where $\Delta^{18}O^{calcite}_{H_2O}$ is the equilibrium oxygen isotope fractionation between calcite and water. A similar equation is used to describe carbon isotope exchange, taking into account the concentration of carbon in the fluid (written here in terms of the mole fraction of HCO_3^-, $X_{HCO_3^-}$):

$$\frac{W}{R} \cdot X_{HCO_3^-} = \ln\left[\frac{\delta^{13}C^i_{HCO_3^-} + (\Delta^{13}C^{calcite}_{HCO_3^-} - \delta^{13}C^i_{calcite})}{\delta^{13}C^i_{HCO_3^-} - (\delta^{13}C^f_{calcite} - \Delta^{13}C^{calcite}_{HCO_3^-})}\right] \quad (16)$$

where $\Delta^{13}C^{calcite}_{HCO_3^-}$ indicates the equilibrium carbon isotope fractionation between calcite and HCO_3^-.

The equations given above are valid for the isotopic exchange in an open system where the fluid is replenished by fluid of the same initial isotope composition, i.e. the fluid's composition is externally controlled. Such 'open system' behavior is described by the 'single pass' exchange process (e.g. Taylor 1974). In the open system, the extent of isotopic exchange is typically larger than in a closed system.

Straightforward transformation of Eqs. 15 and 16 gives expressions for calculating the isotopic compositions of altered calcite:

$$\delta^{13}C_{calcite} = (\delta^{13}C^i_{HCO_3^-} + \Delta^{13}C^{calcite}_{HCO_3^-}) - (\delta^{13}C^i_{HCO_3^-} + \Delta^{13}C^{calcite}_{HCO_3^-} - \delta^{13}C^i_{calcite}) \cdot e^{-\frac{W}{R} X_{HCO_3^-}} \quad (17)$$

$$\delta^{18}O_{calcite} = (\delta^{18}O^i_{H_2O} + \Delta^{18}O^{calcite}_{H_2O}) - (\delta^{18}O^i_{H_2O} + \Delta^{18}O^{calcite}_{H_2O} - \delta^{18}O^i_{calcite}) \cdot e^{-\frac{W}{R}} \quad (18)$$

Closed-system exchange differs slightly from the above description in that complete and continual equilibrium is

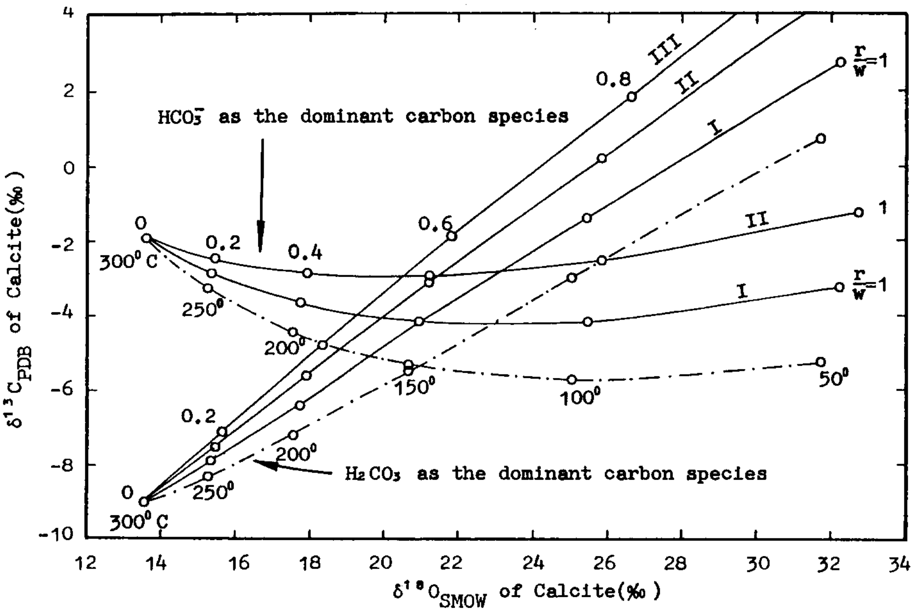

Fig. 3. Carbon vs oxygen isotope variations of calcite precipitated by fluid/rock iinteraction with progressively decreasing rock/fluid ratios (r/w) and a simultaneous change in temperature for either H_2CO_3 or HCO_3^- as the dominant dissolved carbon species. A magmatic fluid is assumed with $\delta^{13}C = -7‰$ (*PDB*) and $\delta^{18}O = +8‰$ (*SMOW*). $\Delta = \delta^{i}_{rock} - \delta^{f}_{rock}$: I—$\Delta^{13}C = 2$ and $\Delta^{18}O = 0.5$; II—$\Delta^{13}C = 4$ and $\Delta^{18}O = 1$, III—$\delta^{13}C = 6$ and $\Delta^{18}O = 2$. The precipitation of calcite under conditions of a closed system is shown by the *dot-and-dash curve*

maintained between the fluid involved and the rock. In this case, a simple form of mass balance equation (10) is used, thus:

$$\delta^{13}C_{calcite} = \frac{\delta^{13}C^{i}_{calcite} + \frac{W}{R}X_{HCO_3^-}\cdot(\delta^{13}C^{i}_{HCO_3^-} + \Delta^{13}C^{calcite}_{HCO_3^-})}{1 + \frac{W}{R}X_{HCO_3^-}} \tag{19}$$

$$\delta^{18}O_{calcite} = \frac{\delta^{18}O^{i}_{calcite} + \frac{W}{R}(\delta^{18}O^{i}_{H_2O} + \Delta^{18}O^{calcite}_{H_2O})}{1 + \frac{W}{R}} \tag{20}$$

A set of isotopic mixing curves is illustrated in Fig. 4 for exchange of a limestone with a secondary fluid at 150 and 100 °C having $X_{HCO_3^-}$values of 0.3 and 0.2, respectively. The isotopic exchange produces initially greater changes in $\delta^{18}O$ than in $\delta^{13}C$. The calculated, lower $\delta^{18}O$ end-point of the mixing curves represents the isotopic composition of calcite in equilibrium with the fluid. The form and curvature of the mixing curves depend on the $X_{HCO_3^-}$ value in the fluid, alteration temperature and the differences of isotopic ratios between the primary calcite and the secondary fluid. The similar calculations on the isotopic alteration of limestone were given by Sverjensky (1981).

From the preceding modeling it can be seen that significant correlation trends in $\delta^{13}C$ vs $\delta^{18}O$ space may be either due to the mixing of two fluids (Fig. 2), or due to a temperature effect during calcite precipitation in the case of fluid/rock interaction when H_2CO_3 acts as the dominant dissolved carbon species (Fig. 3), or due to subsequent alteration of primary calcite by interaction with a secondary fluid (Fig. 4). The shape of the mixing curves reflects the isotopic compositions of the involved fluids and wallrock (or primary calcite). Apparently, the correlation trends of any slope in $\delta^{13}C$ vs $\delta^{18}O$ space can be caused for hydrothermal calcites by the mixing of two fluids.

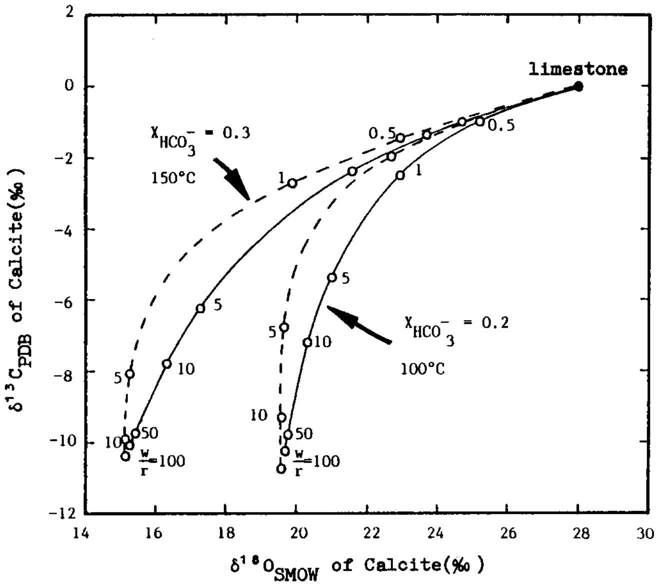

Fig. 4. Covariation of carbon vs oxygen isotopic compositions during fluid/rock interaction involving a limestone with $\delta^{13}C = 0‰$ (*PDB*) and $\delta^{18}O = +28‰$ (*SMOW*), and a fluid with $\delta^{13}C = -12‰$ (PDB) and $\delta^{18}O = +3‰$ (*SMOW*) as well as HCO_3^- as the dominant dissolved carbon, at temperatures of 150 and 100 °C respectively. $X_{HCO_3^-}$ is the mole fraction of HCO_3^- in the fluid. The *solid curves* denote the closed system and the *dashed curves* denote the open system. A progressively increasing fluid/rock ratio (w/r) is assumed for the hydrothermal alteration

With respect to the genesis of hydrothermal mineralization, the mixing between the fluids of different origins is of much more significance than the mixing between the fluids of the same origin. Geochemically, three different origins of hydrothermal fluid can be recognized in terms of carbon and oxygen isotopic compositions: (1) magmatic or deep-seated crustal fluid, which has $\delta^{13}C$ values similar to the normal mantle value (from -9 to -4‰) and $\delta^{18}O$ values from $+6$ to $+15$‰ (depending on the igneous or metamorphic rocks with which the fluid was isotopically equilibrated at high temperatures); (2) subsurface meteoric water or groundwater, which has $\delta^{13}C$ values similar to those for sedimentary organic carbon (from -30 to -20‰) and $\delta^{18}O$ values less than 0‰; (3) seawater, which has $\delta^{13}C$ and $\delta^{18}O$ values uniformly close to 0‰ (e.g. Sheppard 1986; Hoefs 1987). In modelling the genesis of hydrothermal mineralization, if fluid mixing is postulated as a cause for the precipitation of calcite, constructing the isotopic compositions of two end-member fluids permits constraints to be placed on the actual possibility of the fluid mixing. The differences in the isotopic composition and temperature of the postulated two fluids are important signatures in doing so. For example, if the postulated two fluids are to have a large difference in temperature but only a small difference in isotopic compositions which points to the same origin, it would be more reasonable to assume one fluid responsible for mineral deposition with a temperature effect than to assume the two fluids. In other words, although the fluid mixing is a possible cause for the correlation trends between the $\delta^{13}C$ and $\delta^{18}O$ values of hydrothermal calcites, it is unlikely in nature that the two fluids of different origins could have the large difference only in the temperature rather than in the isotopic compositions. Additionally, the isotopic composition of a fluid can considerably change due to fluid/rock interaction during its migration through wallrocks. But the isotopic composition of the wallrocks and temperature have to be taken into account in assuming the isotopic signature of the resultant fluid. In this context, caution must be exercised in postulating the fluid mixing as the cause for the positive correlation trends of calcite C–O isotopic ratios. Isotopic investigations of profiles across calcite veins are particularly useful for discriminating between the different mixing processes. The fit of an appropriate set of data to one of these models can be used to place limits on the origin of fluids, mineralizing temperature, and the mechanism of hydrothermal mineralization.

Application to hydrothermal Pb-Zn deposits in the western Harz Mountains

Geological setting

The Harz Mountains in Germany consist of strongly folded Silurian-Carboniferous sedimentary rocks, mainly of pelitic and psammitic compositions. In the north, their contact with Mesozoic sequences is a steeply inclined fault. To the east, south and west, they are unconformably overlain by Permian and Mesozoic rocks. Along the northern margin of the Harz Mountains the granitic Oker and Brocken plutons as well as the gabbro-norite body of Bad Harzburg are intruded into the Paleozoic sediments.

Besides the stratiform Rammelsberg ore deposit, many hydrothermal vein deposits are known in the Harz area. In some cases they extend over a length of ~ 20 km and have been mined to a depth of ~ 1000 m in a few places. The western Harz Mountains enclose two economically significant Pb-Zn ore districts, i.e. the Bad Grund deposit in the Upper Harz (Northwest in Fig. 5) and the St. Andreasberg orefield in the Middle Harz (South in Fig. 5). The detailed geological and geochemical characteristics of the two deposits have been described by Sperling (1973), Mohr (1978), Schnorrer-Köhler (1983) and Walther (1986).

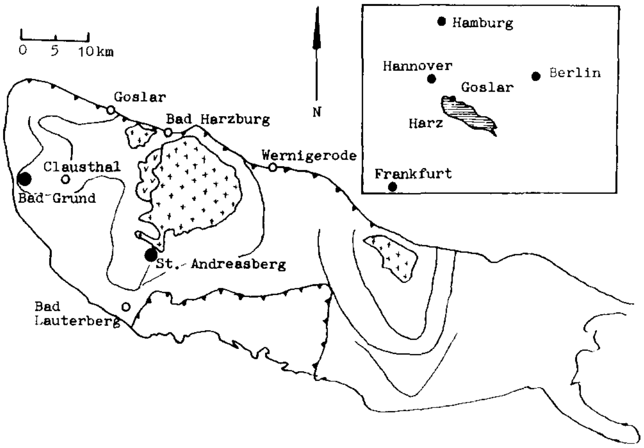

Fig. 5. Simplified geological map of the western Harz Mountains showing the location of the Bad Grund and St. Andreasberg deposits

The Bad Grund deposit is characterized by an intense vein system (Sperling 1973; Sperling and Stoppel 1979). The wallrocks of the ore veins are greywackes more than 1000 m thick and clay slates of the Lower Carboniferous Culm facies, representing the flysch of the rising Variscan mountains in the southeast. In the northern parts of the deposit, the veins occur in Devonian slate, sandstones and diabases. Four mineralization phases were distinguished according to the investigations of mineral paragenesis (Sperling 1973; Stedingk and Schnorrer-Köhler 1988). Sphalerite was predominant in phase II whereas galena was predominant in phase III. The other sulfides are small amounts of chalcopyrite and pyrrhotite. Calcites occur mainly in phase IIc, together with sphalerite (and galena) to form banded-ores, and in phase IIIa. The other gangue minerals are quartz, siderite, dolomite and barite.

The St. Andreasberg deposit is situated on the southern rim of the Brocken granitic massif (Fig. 5). The wallrock of the veins consists mainly of argillaceous schists, quartzites and cherts with flinty limestones of the Devonian along with greywackes of the Lower Carboniferous and Devonian diabases. The paragenesis is fundamentally similar to that of the Bad Grund deposit (Wilke 1952; Schnorrer-Köhler 1983). Calcites occur mostly in phase IIc, together with sulfides (galena, sphalerite, minor chalcopyrite and tetrahedrite, etc.), and in phase IIIa. The other gangue minerals are quartz and fluorite. Rejuvenation, a drusy vein structure and irregular mineralization with locally rich ore shoots are characteristic and point to remobilization subsequent to the main mineralization. Some minerals, especially various silver minerals as well as Co–Ni arsenides and antimonides, are found in much higher quantities than those in the Upper Harz districts.

Ideas concerning the age, origin and causes of the hydrothermal Pb-Zn mineralizations in the Harz Mountains have changed repeatedly. After the assumption of a connexion between the late Mesozoic-Tertiary uplift of the Harz Mountains and the ore veins orientated parallel to the northern rim of the Harz Mountains was abandoned, the concept of the Upper Carboniferous Brocken granite and its hypothetical extension to the west as the ore supplier for the ore veins in the Upper and Middle Harz prevailed (e.g. Dahlgrün 1950). However, it has been shown in recent years that a considerable amount of the vein content can be derived from underlying sediments or from more or less adjacent wallrocks (e.g. Nielsen 1968; Sperling and Nielsen 1973; Wedepohl et al. 1978). With respect to the mechanism of hydrothermal mineralization, a fluid-mixing model has been postulated by Möller et al. (1979 and 1984) who investigated the distribution of rare-earth elements (REE) in the hydrothermal calcites of the Bad Grund deposit. They concluded that the calcite of the banded-ores in the deposit crystallized from hybrid magmatic-metamorphic solutions both of which were rather rich in REE^{3+} and Fe^{3+}. Behr et al. (1987) carried out a fluid inclusion investigation of mineral parageneses from most mining districts in the Harz Mountains and recognized two types of fluid: one is a highly saline, relatively high-temperature Ca–Na (K–Mg)–Cl basinal brine; the other is a low-salinity, relatively low-temperature formation water (rich in HCO_3^- and SO_4^{2-}) or meteoric water. Thus the authors postulated a model in which the two fluids mix by seismic pumping. However, the homogenization temperatures reported by Behr et al. (1987) are somewhat too low due to the widespread presence of secondary inclusions (Lüders 1988).

Analytical results

Using the conventional phosphoric acid method (McCrea 1950), carbon and oxygen isotopic analyses were carried out for 130 calcite samples from the phases IIc to IIIa in the Bad Grund deposit and 110 calcite samples from the phases IIc and IIIa in the St. Andreasberg deposit. The results are presented in Figs. 6 and 7, respectively. All of the calcites were from fracture-filled veins, partly associated with Pb-Zn mineralizations. The minerals were separated by hand and thus appear to be pure calcite. The analytical sample set represents most of the principal occurrences of hydrothermal calcite in the two deposits. Additionally, two profiles through calcite veins in the Bad Grund deposit and a profile across a calcite vein in the St. Andreasberg deposit were sampled and the results are presented in Figs. 8 and 9, respectively. The detailed description of the samples and the complete dataset is presented in Zheng (1991) and can be delivered upon request.

As shown in Fig. 6, a significant positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values is observed for the calcites from the Bad Grund deposit, with $\delta^{13}C$ varying from − 8.8 to − 4.9‰ and $\delta^{18}O$ from + 16.4 to + 21.7‰. The calcites sampled from the banded-ores (phase IIc) all have low δ-values within a narrow variation ($\delta^{13}C$ from − 8.8 to − 7.8‰ and $\delta^{18}O$ from + 16.4 to + 17.7‰).

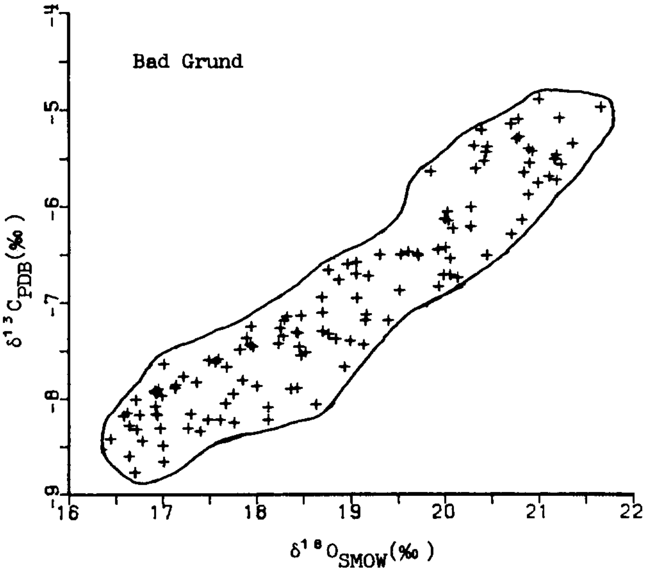

Fig. 6. The carbon and oxygen isotopic compositions of hydrothermal calcites from the Bad Grund deposit in the Upper Harz

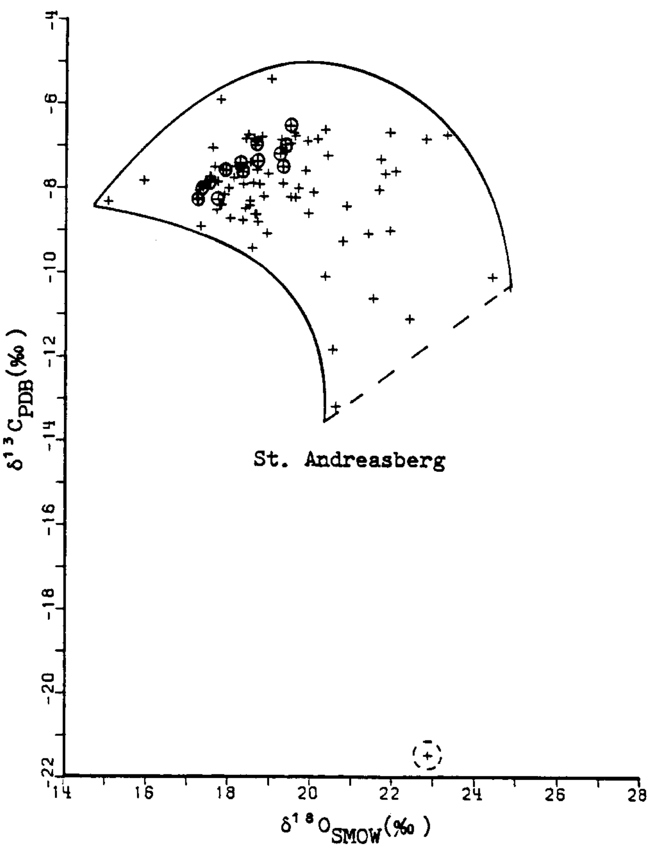

Fig. 7. The carbon and oxygen isotopic compositions of calcites from the St. Andreasberg deposit in the Middle Harz. *Circled crosses* represent the calcite samples that coexist with sulfides. Note that a sample with $\delta^{13}C \sim -21‰$ is emphasized particularly

The two profiles across 2.2 m and 3.6 m width veins show the same positive correlation on the $\delta^{13}C$ vs $\delta^{18}O$ diagram, with the lowest δ-values at the center of the veins whereas the highest δ-values identically occur at the margins of the veins (Fig. 8).

In contrast, the calcites from the St. Andreasberg deposit exhibit large variations in carbon and oxygen isotopic ratios (Fig. 7). $\delta^{13}C$ values vary from -21.5 to -5.9‰ with a mode of -13.2 to -5.9‰; $\delta^{18}O$ values range from $+15.2$ to $+24.4$‰. The samples from the profile across a 1.4-m-width vein (Fig. 9) show a similar data arrangement to that from whole of the St. Andreasberg deposit in Fig. 7, with the lowest $\delta^{18}O$ value at the vein center whereas the lowest $\delta^{13}C$ values asymmetrically occur at the vein margins. It is noteworthy that the calcites which coexist with sulfides (shown by crossed circles in Fig. 7) follow a trend similar to that found in the Bad Grund deposit, implying a similar genesis of the calcites.

Data interpretation

The observed positive correlation between the $\delta^{13}C$ and $\delta^{18}O$ values of calcites in Fig. 6 can be explained by two different processes: (1) calcite precipitation due to mixing of two fluids with different alkali-chloride concentrations, or (2) calcite precipitation from a H_2CO_3-dominant fluid due to a temperature effect coupled either with CO_2 degassing or with fluid/rock interaction.

As illustrated in Fig. 2, the mixing of two fluids can cause the precipitated calcites to have correlation trends of any slope in $\delta^{13}C$ vs $\delta^{18}O$ space, through the appropriate choice of isotopic ratios of end-member fluids, dissolved carbon species and temperatures. If fluid mixing produced the observed correlation trend in Fig. 6, there would have been two end-member fluids with distinct carbon and oxygen isotopic ratios and temperatures, and therefore different origins. This is not tenable because of the relatively narrow variations in $\delta^{13}C$ (from -8.8 to -4.9‰) and $\delta^{18}O$ (from $+16.4$ to 21.7‰) values of the calcites in Fig. 6. For the profiles in Fig. 8, furthermore, this explanation requires that one fluid is responsible for the precipitation of calcite at the center of the veins whereas the other is responsible for the precipitation of calcites at the margins of the veins. In view of fluid flow along open fractures, obviously, this explanation does not stand under close scrutiny, because the fluid mixing can only take place along the vein strike rather than perpendicular to the vein strike. Generally, calcite which fills the vein does not precipitate instantaneously; it presumably grows from the vein margins inward. The vein records a time sequence of calcite precipitation from a fluid whose temperature and/or chemical composition was changing. If the systematic change in the isotopic composition of profiled calcites corresponded to a change in the isotopic composition of a fluid mixing zone, the symmetry in the isotopic composition of vein center and margins could not be otherwise explained by the varying mixing proportions of two fluids. Additionally, differences in the isotopic ratios between vein center and margins are very small, both $\delta^{13}C$ and $\delta^{18}O$ varying within 2 ~ 3 permil (Fig. 8). This implies that the two fluids would have to have quite similar isotopic compositions, which points to needlessness in postulating the mixing of two fluids of different origins. Translation of a fluid mixing zone (or other chemical gradient) along an open fracture could be recorded in minerals progressively precipitating normal to the fracture walls. The observed positive correlations in Fig. 6 and 8 preclude the mixing between two fluids. We consider it to be a temperature-dependent trend and thus suggest that only one fluid is responsible for the precipitation of calcite.

Theoretically, calcite which is deposited from a H_2CO_3-dominant fluid at temperatures below 300 °C can have a positive correlation between $\delta^{13}C$ and $\delta^{18}O$ values simply due to a decrease in temperature, because the fractionation factors between calcite and CO_2 for carbon and between calcite and H_2O for oxygen are linearly correlated with temperature (see Ohmoto and Rye 1979; O'Neil et al. 1969). However, the solubility of calcite in a hydrothermal fluid increases with decreasing temperature (Holland and Malinin 1979). Thus calcite cannot be deposited from a fluid by simple cooling under the conditions of a closed system. Instead, an open system

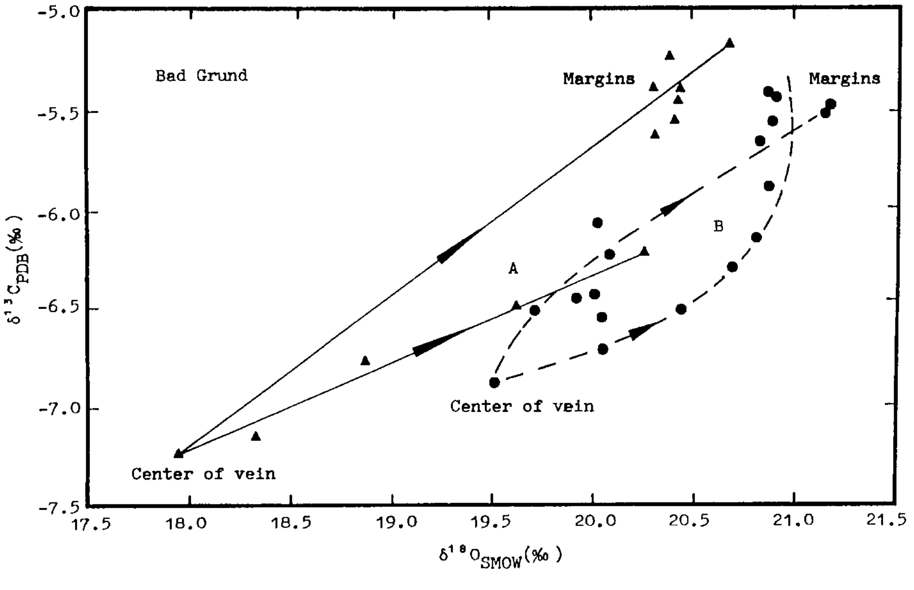

Fig. 8. The carbon and oxygen isotopic compositions of calcites from two profiles through calcite veins in the Bad Grund deposit. Profile *A* is from the Wiemannbuchter Erzmittel, No. 19, 2205E-15°, 54.2 ~ 56.4 m; profile *B* is from the Westfelderzmittel I, No. 20, 1479W-32°, 68.6 ~ 72.2 m. Note the symmetry in the isotopic composition of vein center and margins

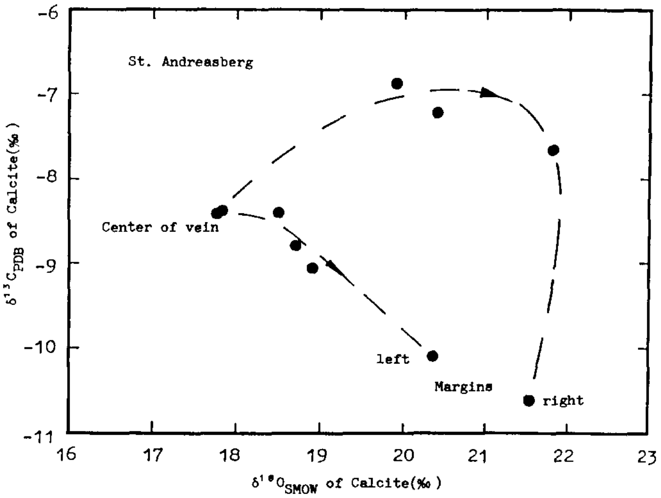

Fig. 9. The carbon and oxygen isotopic compositions of calcites from a profile across a calcite vein of about 1.4 m width (5 Bücher Mosis Gang) in the St. Andreasberg deposit. Note the asymmetric distribution of isotopic ratios across this profile with respect to the profiles from the Bad Grund deposit in Fig. 8

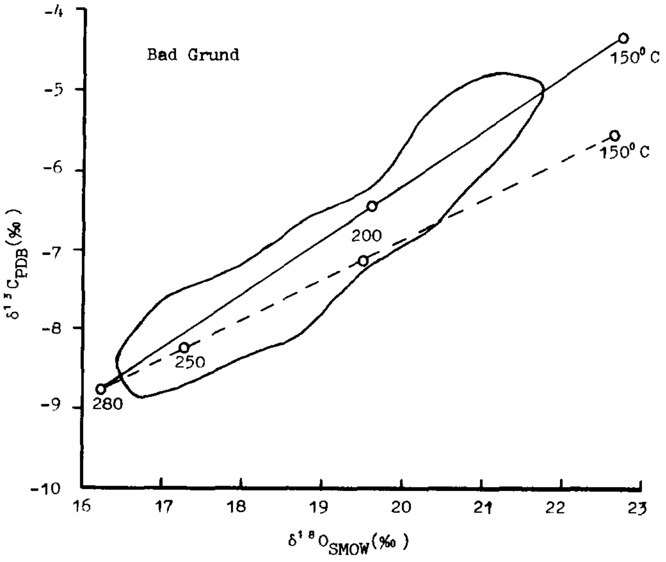

Fig. 10. A fluid/rock interaction model for the covariation of the carbon and oxygen isotopic compositions of calcites from the Bad Grund deposit as a function of temperature (*solid line*). Precipitation of calcite under closed system conditions is shown in the *dashed line*. The fluid is assumed to have $\delta^{13}C = -7‰$ (*PDB*) and $\delta^{18}O = +10‰$ (*SMOW*), H_2CO_3 as the dissolved carbon

has to be assumed in which either CO_2 degassing or fluid/rock interaction can be responsible for the deposition of calcite. A thermodynamic model of boiling of hydrothermal solutions indicates that metals complexed by chloride can be deposited largely as a result of CO_2 exsolution during boiling (Drummond and Ohmoto 1985). If calcite is deposited from a H_2CO_3-dominant fluid due to CO_2 degassing accompanied by a progressive change in temperature, the resulting calcite has a positive $\delta^{13}C$–$\delta^{18}O$-correlation whose slope is smaller than in a closed system, i.e. the $\delta^{13}C$ values of the resulting calcite are lower than those in the closed system because the degassed CO_2 is enriched in ^{13}C relative to the precipitated calcite (Zheng 1990). As shown in Fig. 10, the slope of the observed correlation is greater than for the closed system, excluding the possibility of CO_2 degassing. This relationship then leaves only one process – fluid/rock interaction – as the most likely cause for the precipitation of calcite and thus for the positive correlation in Fig. 6. This implies that the chemical and isotopic compositions of the ore-bearing fluids have progressively changed during their flow through wallrocks. Correspondingly, the wallrocks are subjected to interaction with fluid, producing hydrothermal alteration. Indeed, Sperling (1973) and Boness (1987) observed newly formed and recrystallized phyllosilicates (mostly illite) in wallrocks close to the calcite veins, although these were weak.

As demonstrated in Fig. 10, the observed positive correlation can be explained as the precipitation of calcite by a temperature decrease from 280 to 170 °C out of a large and homogeneous fluid reservoir with $\delta^{13}C \sim -7‰$ and $\delta^{18}O \sim +10‰$, in which H_2CO_3 was the dominant dissolved carbon species. The lower δ-values of calcites associated with the banded ores point to higher formation temperatures (280 ~ 250 °C) relative to the other calcites and imply an identical isotope signature of carbon and oxygen in the fluid reservoir(s) with respect to different ore bands. The observed variations in the $\delta^{13}C$ and $\delta^{18}O$ values of calcites from two profiles (Fig. 8) can be readily explained by a temperature effect, i.e. calcite at the center of the veins was precipitated at higher temperatures and calcite at the vein margins at lower temperatures. The temperature difference is about 50 °C. The modeling requires that the wallrocks have higher $\delta^{13}C$ and $\delta^{18}O$ values than the fluid. This prerequisite is fulfilled because sandstones and clay slates constitute the wallrocks in the Bad Grund deposit. Additionally, the wallrocks do not contain significant amounts of reduced carbon. The assumed Δ-values [ref. Eqs. 13 and 14] are very small, i.e. $\Delta^{13}C^{i}_{f} = 1$ and $\Delta^{18}O^{i}_{f} = 0.5$. Such small Δ-values demand not only small amounts of carbonate in the wall rocks but also small degrees of hydrothermal alteration, which is consistent with the observation of Sperling (1973). Therefore, the observed variations in the isotopic compositions of hydrothermal calcites were caused by temperature-dependent isotopic fractionations, with minor isotopic variations being caused by fluid/rock interaction (which were vital as a precipitation mechanism).

The obtained model-temperatures of 280 ~ 170 °C are comparable with (1) the temperature obtained from sulfur isotope distribution between sphalerite and galena (400 ~ 140 °C: Zheng 1991) and (2) the temperature obtained by Ga/Ge partition in sphalerite associated with calcites (≥ 240 ~ 260 °C: Möller and Stedingk 1990, personal communication). As shown before, the calcites associated with the banded-ores formed at higher temperatures than the other calcites. This also agrees with the results from sulfur isotopic geothermometry (Zheng 1991). From the profile studies on the calcite veins in Fig. 8 it appears that the calcites at the vein margins were crystallized earlier at lower temperatures with respect to the calcites at the vein centers. It is probably appropriate to extrapolate the precipitation sequence from the microscale studies on the vein profiles to the macroscale situation on the same phase.

The assumed isotopic ratios of the fluid-$\delta^{13}C \sim -7‰$ and $\delta^{18}O \sim +10‰$-apparently compare with magmatic fluids, but can also be interpreted as deep-seated crustal fluids. However, it must be pointed out that the assumed isotopic ratios of the fluid are not independent of the model temperatures. Essentially, the principal uncertainties encountered in the interpretation of carbon and oxygen isotope data for hydrothermal calcites are the temperatures of precipitation of the calcites and the $\delta^{13}C$ and $\delta^{18}O$ values of the fluid from which the calcites precipitated. It can be illustrated that the obtained model-temperatures would be 190 ~ 110 °C for the Bad Grund calcites if the isotopic ratios of the fluid are taken to be $\delta^{13}C = -9‰$ and $\delta^{18}O = +6‰$. Nevertheless, the previously given model-temperatures of 280 ~ 170 °C match the results of the other geothermometers better. This confirms the validity of the assumption of $\delta^{13}C \sim -7‰$ and $\delta^{18}O \sim +10‰$ for the fluid. Apparently, the model-temperatures of calcite precipitation and the isotopic compositions of the assumed fluid are not independent of each other. In any case, a single and homogeneous fluid reservoir is required and therefore a temperature-dependent trend is a reasonable interpretation for the observed positive correlation between the $\delta^{13}C$ and $\delta^{18}O$ values of calcites from the Bad Grund deposit. Consequently, we reason that the calcites precipitated from the deep-seated crustal fluid and did not experience kinetic fractionation effects. Additionally, we have good constraints on precipitation temperatures.

In contrast to the Bad Grund deposit, two different fluids seem to be responsible for the observed variations in the $\delta^{13}C$ and $\delta^{18}O$ values of calcites from the St. Andreasberg deposit. One fluid may be identical to that in the Bad Grund deposit and thus responsible for the precipitation of the calcites which are associated with sulfides; the other fluid must have lower temperatures, with HCO_3^- as the dominant dissolved carbon species, and have $\delta^{13}C$ from about -20 to $-15‰$ and $\delta^{18}O$ about 0‰. The isotopic and temperature features of the two fluids are comparable with the results of Behr et al. (1987) from fluid inclusion investigations, although the absolute values of their homogenization temperatures are somewhat too low due to the widespread presence of secondary inclusions (Lüders 1988). Mixing between the two fluids can be ruled out, because again the profile investigation in Fig. 9 cannot be explained by the precipitation of calcite at the vein center from one fluid whereas those at the vein margins formed from the other fluids. Instead, an alteration of primary calcite by interaction with a second fluid is a more likely process responsible for the observed isotopic variations, as modeled in Fig. 11. In this context, the two fluids are temporally separated and thus do not mix with each other. The calcites which are associated with the sulfides would be precipitated from the deep-seated fluid at temperatures of 300 ~ 150 °C. The second fluid would have low temperatures of 70 ~ 40°C and can be considered as an evolved subsurface solution. It may be responsible for the remobilisation of calcite in the St. Andreasberg deposit.

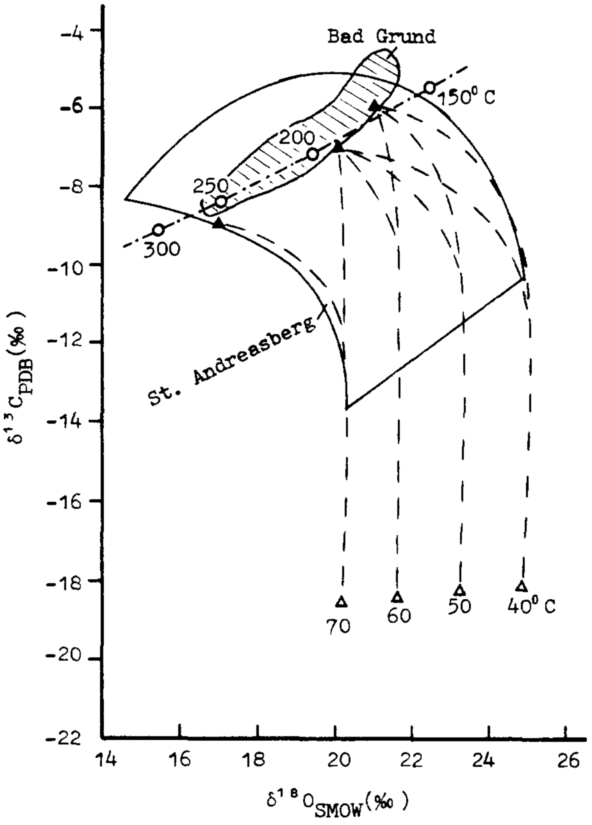

Fig. 11. An alteration model for the variation of the carbon and oxygen isotopic compositions of calcites from the St. Andreasberg deposit. The isotopic compositions of calcites from the Bad Grund deposit are shown for comparison. Two fluids are assumed: I – 300 ~ 150 °C, $\delta^{13}C \approx -70‰$ (*PDB*) and $\delta^{18}O \approx +10‰$ (*SMOW*), H_2CO_3 as the dissolved carbon; II – 70 ~ 40 °C, $\delta^{13}C \approx -20$; (*PDB*) and $\delta^{18}O \approx 0‰$ (*SMOW*), HCO_3^- as the dissolved carbon. The precipitation of primary calcite from fluid I under conditions of a closed system is shown by the *dot-and-dash line*

Conclusions

Covariations in the isotopic ratios of carbon and oxygen are modeled for hydrothermal calcites related to the following mixing processes: (1) mixing of fluids, (2) fluid/rock interaction, and (3) secondary alteration. Choosing the appropriate variables (e.g. the isotopic ratios of fluids, temperature, etc.) permits the construction of mixing trends in $\delta^{13}C$ vs $\delta^{18}O$ space for the resulting calcites. Processes such as the mixing of fluids vs fluid/rock interaction or secondary alteration may be distinguished by the specific arrangements of isotopic ratios on a $\delta^{13}C$ vs $\delta^{18}O$ diagram because of the temperature effect during equilibrium precipitation of calcite from a hydrothermal fluid. Furthermore, the profile investigation of carbon and oxygen isotopic compositions across calcite veins provides the best means of distinction between the three mixing processes.

Calcites from the hydrothermal Pb-Zn deposits in the western Harz Mountains demonstrate the applicability of the theoretical models. Investigations of profiles through calcite veins and model constraints rule out fluid mixing as the cause of the precipitation of calcites. A positive correlation between the $\delta^{13}C$ and $\delta^{18}O$ values of calcites from the Bad Grund deposit is interpreted as a temperature-dependent trend accompanied by a progressively increasing fluid/rock interaction. A deep-seated fluid is inferred with H_2CO_3 as the dominant dissolved carbon species, having a $\delta^{13}C$ value of -7‰ and a $\delta^{18}O$ value of $+10$‰; precipitation temperatures of the calcites are estimated to be about $280 \sim 170\,^{\circ}C$. Fluid/rock interaction is interpreted to play a significant role in causing the precipitation of hydrothermal calcites in the Bad Grund deposit. Conversely, the large variation in the $\delta^{13}C$ and $\delta^{18}O$ values of calcites from the St. Andreasberg deposit is explained by an alteration model. An evolved, HCO_3^--dominant subsurface fluid with $\delta^{13}C$ about $-20 \sim -15$‰ and $\delta^{18}O \leq 0$‰ has overprinted the primary calcite, which was deposited from the deep-seated fluid, at low temperatures of $70 \sim 40\,^{\circ}C$. Consequently, two temporally separated fluids were involved in the hydrothermal mineralizations in the western Harz Mountains.

Acknowledgments. This study has greatly benefited from the support by the German Science Foundation (DFG) within the framework of the project 'Intraformational Mineralizations'. We are indebted to Drs. K. Stedingk and V. Lüders for providing some samples from the deposits in the Harz Mountains. Helpful comments and suggestions by Drs. R. E. Criss and A. Searl, as well as one anonymous referee of *Mineralium Deposita* on this manuscript are gratefully acknowledged.

References

Banner, J.L., Hanson, G.N. (1990) Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. Geochim. Cosmochim. Acta 54:3123–3137

Behr, H.-J., Horn, E.E., Frentzel-Beyme, K., Reutel, C. (1987) Fluid inclusion characteristics of the Variscan and post-Variscan fluids in the Federal Republic of Germany. Chem. Geol. 61:273–285

Boness, M. (1987) Die radiometrische Altersbestimmung der Pb-Zn Lagerstätte Grund (Harz) mit der Rb/Sr-Methode. Dissertation of Göttingen University, 169 pp.

Dahlgrün, F. (1950) Die zonale Verbreitung der Gangformation des Brockenplutons im Harz. Erzmetall 3:150–153

Drummond, S.E., Ohmoto, H. (1985) Chemical evolution and mineral deposition in boiling hydrothermal systems. Econ. Geol. 80:126–147

Gat, J.R. (1981) Grundwater. In: (eds.) Gat, J.R., Gonfiantini, R. Stable isotope hydrology – Deuterium and oxygen-18 in the water cycle. IAEC, Vienna, Technical Report Series 210:223–240

Hoefs, J. (1987) Stable isotope geochemistry. 3rd edn. Springer, Berlin Heidelberg New York, 241 pp.

Holland, H.D., Malinin, S.D. (1979) The solubility and occurrence of non-ore minerals. In: (ed.) Barnes, H.L. Geochemistry of hydrothermal ore deposits, 2nd edn. Wiley, New York, pp. 461–508

Lüders, V. (1988) Geochemische Untersuchungen an Erz- und Gangartmineralen des Harzes. Berliner Geowiss. Abh. A93:1–74

Matsuhisa, Y., Morishita, Y., Sato, T. (1985) Oxygen and carbon isotope variations in gold-bearing hydrothermal veins in the Kushikino mining area, southern Kynshu, Japan. Econ. Geol. 80:283–293

McCrea, J.M. (1950) On the isotopic chemistry of carbonates and a paleo-temperature scale. J. Chem. Phys. 18:849–857

Mohr, K. (1978) Geologie und Minerallagerstätten des Harzes. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 387 pp

Möller, P., Morteani, G., Hoefs, J., Parekh, P.P. (1979) The origin of the ore-bearing solution in the Pb-Zn veins of the western Harz, Germany, as deduced from rare-earth element and isotopic distributions in calcites. Chem. Geol. 26:197–215

Möller, P., Morteani, G., Dulski, P. (1984) The origin of the calcites from Pb-Zn veins in the Harz Mountains, Federal Republic of Germany. Chem. Geol. 45:91–112

Nielsen, H. (1968) Schwefel-Isotopenverhältnisse aus St. Andreasberg und anderen Erzvorkommen des Harzes. Neues Jahrb. Mineral. Abh. 109:289–321

Ohmoto, H. (1972) Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. Econ. Geol. 67:551–578

Ohmoto, H., Rye, R.O. (1979) Isotopes of sulfur and carbon. In: (ed.) Barnes, H.L. Geochemistry of hydrothermal ore deposits, 2nd edn. Wiley, New York, pp. 509–567

O'Neil, J.R., Clayton, R.N., Meyeda, T.K. (1969) Oxygen isotope fractionation in divalent metal carbonates. J. Chem. Phys. 51:5547–5558

Robinson, B.W. (1975) Carbon and oxygen isotopic equilibria in hydrothermal calcites. Geochem. J. 9:43–46

Rye, D.M., Williams, N. (1981) Studies of the base metal sulfide deposits at McArthur River, Northern Territory, Australia: III. The stable isotope geochemistry of the H.Y.C. Ridge, and Cooley deposits. Econ. Geol. 76:1–26

Schnorrer-Köhler, G. (1983) Die Silbererzrevier St. Andreasberg im Harz, 1 Teil. Aufschlusse 34:153–175

Sheppard, S.M.F. (1986) Characterization and isotopic variations in natural waters. In: (eds.) Valley, J.W., Taylor, H.P., Jr., O'Neil, J.R., Stable isotopes in high temperature geological processes. Rev. Mineral. 16:165–183

Sperling, H. (1973) Die Erzgänge des Erzbergwerks Grund. Geol. Jb. D2:1–205

Sperling, H., Nielsen, H. (1973) Schwefel–Isotopenuntersuchungen an der Blei-Zink Erzlagerstätte Grund (Westharz, BRD). Mineral. Deposita 8:64–72

Sperling, H., Stoppel, D. (1979) Die Blei-Zink Erzgänge des Oberharzes. Geol. Jb. D34:1–252

Stedingk, K., Schnorrer-Köhler, G. (1988) Ein neues Vorkommen von rotem Glaskopf, Antimonit und Stibiconit am Erzbergwerk Grund (Oberharz). Aufschlusse 39:282–288

Sverjensky, D.A. (1981) Isotopic alteration of carbonate host rocks as a function of water to rock ratio – An example from the Upper Mississippi Valley zinc-lead district. Econ. Geol. 76:154–157

Taylor, H.P. Jr. (1974) The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. Econ. Geol. 69:843–883

Taylor, H.P. Jr. (1977) Water/rock interactions and the origin of H_2O in granitic batholiths. J. Geol. Soc. London 133:509–558

Truesdell, A.H. (1974) Oxygen isotope activities and concentrations in aqueous salt solutions at elevated temperatures – Consequences for isotope geochemistry. Earth Planet. Sci. Lett. 23:387–396

Vollmer, R. (1976) Rb-Sr and U-Th-Pb systematics of alkaline rocks: the alkaline rocks from Italy. Geochim. Cosmochim. Acta 40:283–295

Walther, H.W. (1986) Mineral deposits in the Federal Republic of Germany. In: (eds.) Dunning, F.W., Evans, A.M. Mineral deposits of Europe, Vol. 3: Central Europe. The Institution of Mining and Metallurgy & The Mineralogical Society, London, pp. 230–237

Wedepohl, K.H., Delevaux, M.H., Doe, B.R. (1978) The potential source of lead in the Permian Kupferschiefer Bed of Europe and some selected Paleozoic mineral deposits in the Federal Republic of Germany. Contrib. Mineral. Petrol. 65:273–281

Wilke, A. (1952) Die Erzgänge von St. Andreasberg im Rahmen des Mittelharz-Ganggebietes. Geol. Jb. 7:1–228

Zheng, Y.-F. (1990) Carbon–oxygen isotopic covariation in hydrothermal calcite during degassing of CO_2: a quantitative evaluation and application to the Kushikino gold mining area in Japan. Mineral. Deposita 25:246–250

Zheng, Y.-F. (1991) C–, O– und S-Isotopengeochemische Untersuchungen an hydrothermalen Lagerstätten des Harzes. Dissertation of Göttingen University, 130 pp

Editorial handling: D. Rickard