



Article Hydrothermal Calcite Precipitation in Veins: Inspired by Experiments for Oxygen Isotope Fractionation between CO₂ and Calcite from 1 °C to 150 °C

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Abstract: The oxygen isotope ratios of minerals are important for estimating the formation temperature of hydrothermal deposits. Calcite is generally found in most mining districts. The oxygen isotope ratio of hydrothermal calcite in isotopic equilibrium with a fluid depends on that of the fluid as well as the formation temperature. The isotope ratios of calcite are generally determined to measure the isotope ratios of CO₂ generated via reaction with 100% phosphoric acid at 25 °C. This is why the oxygen isotope fractionation between CO₂ and calcite at 25 °C is required to conduct the procedure. When using other carbonate minerals such as dolomite, ankerite, and siderite, the reaction requires higher temperatures. Therefore, the oxygen isotope fractionation between CO₂ and calcite at higher temperatures should be known because the laboratory standard sample of carbonates is usually calcite. Here, the oxygen isotope fractionation in CO₂ during the reaction of calcite with phosphoric acid at temperatures between 1 °C and 150 °C was thoroughly determined in the first half, and the value can be represented by the following equation: 1000 ln α = 0.494 (10⁶/T²) + 4.64. The experiments raised questions such as the equilibrium vs. kinetics issue in isotopic reactions in the formation of hydrothermal ore deposits. The raised issue is discussed in the second half based on the findings of previous isotope studies in deposits.

Keywords: hydrothermal fluid; oxygen isotope fractionation; CO₂; calcite; carbonates; hydrothermal ore deposit; isotope ratio mass spectrometry

1. Introduction

The oxygen isotope ratios of minerals are important for estimating the formation temperature of hydrothermal deposits. The isotope ratios of carbonate are measured by extracting CO_2 from the carbonate and employing isotope ratio mass spectrometry (IRMS) to examine the carbon and oxygen isotope ratios of the carbonate.

Calcite is generally found in most mining districts. Considering that the solubility of calcite increases with decreasing temperature, it cannot be precipitated from a hydrothermal fluid by simple cooling in a closed system. Thus, calcite can form as a result of the conductive heating of CO₂-rich fluid or by degassing CO₂ from the CO₂-rich fluid. Fertile calcite may also exist in the same location as barren calcite (e.g., [1]). It can be distinguished from barren calcite using the carbon and oxygen isotope ratios of calcite. The carbon and oxygen isotope ratios of calcite that are precipitated in an isotopic equilibrium with a fluid depend on the carbon and oxygen isotope ratios of the fluid, the formation temperature, and the relative proportions of dissolved carbon species (H₂CO₃ and HCO₃⁻) (e.g., [1]). Carbonate minerals other than calcite (dolomite, ankerite, rhodochrosite, siderite, etc.) are also used for mineral exploration.



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Copyright: © 2023 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). To determine the isotope ratios of calcite, CO_2 is generated from the calcite, and its carbon and oxygen isotope ratios are measured via IRMS. CO_2 is directly liberated from calcite via treatment with 100% phosphoric acid in an evacuated reaction tube in a water bath at 25 °C [2]. To calculate the oxygen isotope ratio of calcite from CO_2 analysis, the oxygen isotope fractionation between CO_2 and calcite should be known. The oxygen isotope fractionation between CO_2 and calcite depends on the temperature of the CO_2 formation, and it has been obtained at 25 °C (e.g., [3,4]). For carbonate minerals other than calcite, higher temperatures and more time are required to complete the CO_2 generation reaction.

Only two-thirds of carbonate oxygen converts into CO_2 during the reaction, and one-third of it remains in the reactant fluid. This may cause an isotope fractionation, which is a function of temperature and differences in carbonate minerals. Therefore, the reaction should be kept at a certain temperature that is determined for each carbonate mineral to ensure that the fractionation factor between CO_2 and the carbonate remains unchanged. Additionally, a laboratory working standard of calcite is used to calibrate the oxygen isotope ratio of various carbonates at various experimental temperatures. A possible temperature error in the reaction is almost canceled if an unknown carbonate sample and the working standard calcite are at the same temperature in the same reaction bath. Thus, the oxygen isotope acid fractionation factor (AFF) of the working standard calcite is experimentally obtained by measuring the oxygen isotope ratio of the CO_2 that is produced using phosphoric acid at various temperatures. When using calcite as a working standard for the isotope ratio measurements of carbonate, the oxygen isotope AFF between CO_2 and calcite at the reaction temperature should be known.

Here, the oxygen isotope ratio of CO_2 produced using phosphoric acid with a calcite working standard was experimentally measured between 1 °C and 150 °C to determine the oxygen isotope AFF between CO_2 and calcite at the reaction temperature.

Since the AFF is controlled by kinetics, the AFF is not exactly equal to the equilibrium fractionation factor (EFF). The purpose of this study is an attempt to bridge the gap between equilibrium and kinetics with practical examples. The first half of the study compared the temperature dependence of the experimentally determined AFFs with those of previous theoretical EFFs. The equilibrium versus kinetics issue of mineral formation in nature is inspired by the experiments. The second half of the study discusses the connection between equilibrium and kinetics from the previous oxygen isotopic studies at geothermal power plants and the practical equilibrium evidence in hydrothermal ore deposits.

2. Materials and Methods

2.1. Materials

The calcite sample used was CaCO₃-1, which is a laboratory working standard, at the stable isotope laboratory of the Geological Survey of Japan (GSJ). The CaCO₃-1 was made of special-grade reagent calcium carbonate powder. It was held at 300 °C for 2 h and ground to a grain size of approximately 3 µm using an agate mortar. Afterward, it was stored in a desiccator [5]. Its purity was confirmed via X-ray diffraction, and no other phases were identified. The δ^{13} C and δ^{18} O values of CaCO₃-1 and several reference materials, including NBS-18, NBS-19, and NBS-20, were repeatedly measured, and the δ^{13} C_{PDB} and δ^{18} O_{SMOW} values of CaCO₃-1 were determined to be +2.59‰ and +15.45‰ (modified after [6]), respectively. The δ^{18} O_{SMOW} value of CaCO₃-1 has been reported [5] based on the oxygen isotope fractionation factor between CO₂ and H₂O at 25 °C as 1.0407. Considering that the value was internationally modified to 1.0412 (e.g., [6]), the δ^{18} O_{SMOW} value of CaCO₃-1 was modified to +15.45‰ accordingly.

Here, 100% phosphoric acid (H_3PO_4) that reacts with calcite to produce CO_2 was synthesized as follows. A stoichiometric amount of phosphoric anhydride (P_2O_5) or more was added to the reagent, 85% phosphoric acid, with heating. The 100% phosphoric acid was confirmed by its specific gravity of ~1.9.

2.2. Analytical Methods

2.2.1. Reaction Vessel and Vacuum Line

The CaCO₃-1 was placed at the bottom of a reaction vessel made of Pyrex glass, and 1 mL of 100% H₃PO₄ was placed in the bottom of a branch arm (Figure 1). The sample size of the $CaCO_3$ -1 used for the reaction was approximately 20 mg, which corresponds to 0.0002 mol of evolved CO₂. H₃PO₄ corresponding to 20 mg of calcite in stoichiometry is 0.02 mL; however, excess H₃PO₄ is necessary because of its sticky nature. A ground glass joint of a Pyrex glass-made stopcock was attached to the reactor body with grease, and the reaction vessel was attached to a vacuum line with an interchangeable ground joint. The spherical bottom of the stopcock was first evacuated, followed by the reaction vessel. The reaction vessel with CaCO₃-1 and H_3PO_4 was evacuated to a vacuum of <0.5 Pa using a two-stage rotary vane pump. After evacuation, the vessel was removed from the line and placed in a water or oil bath, and the bottom 10 cm of the reaction vessel, which was supported by a stand, was submerged. The water bath, equipped with cooling and heating systems, was used in the experiments for temperatures between 1 °C and 40 °C. The oil bath, filled with silicone oil, was used in the experiments above 40 °C. The temperature of the water/oil was precisely controlled to a preset temperature between 1 °C and 150 °C. Thereafter, the reaction vessel was tilted for the phosphoric acid to drop to the bottom. The reaction time of the experiments for temperatures between 25 $^\circ$ C and 150 $^\circ$ C was 1 h. However, the time for temperatures below 25 °C was >15 h. After the reaction, the reaction vessel was reattached to the vacuum line and evacuated. The CO₂ gas from the reaction vessel was frozen in a liquid nitrogen trap of the vacuum line, and the impurity gas was evacuated. Then, the liquid nitrogen trap was replaced with a dry ice-ethanol trap, and vaporized pure CO₂ was collected in another liquid nitrogen trap, leaving water in the dry ice-ethanol trap.



Figure 1. Reaction vessel (capacity, ca. 50 mL) with a branch arm made of Pyrex glass (Reproduced from [5] with permission from Bull. Geol. Surv. Jpn; published by the Geological Survey of Japan) A two-way stopcock was used to maintain the vacuum for at least 1 day.

2.2.2. Carbon and Oxygen Isotope Ratios of Calcite

The carbon and oxygen isotope ratios of the evolved CO_2 were determined, following the pioneering procedure of MaCrea [2]. CO_2 gas was analyzed using a Finnigan MAT 251 mass spectrometer (Thermo Finnigan, Bremen, Germany) at the GSJ. The isotope ratios are reported in standard δ notation in per mil (‰) relative to the Vienna standard mean ocean water (SMOW) for δ^{18} O and relative to the Vienna Pee Dee Belemnite (PDB) for δ^{13} C. The reproducibility was approximately $\pm 0.03\%$ (2 σ) for the $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ values of calcite [5]. The reproducibility was quite good because of the large amount of the sample (20 mg). The obtained isotope ratios were normalized to SMOW and PDB scales using measurements of the laboratory working standard (CaCO₃-1) and a calibration standard NBS-19 [5]. The accuracy of the normalized values was $\pm 0.1\%$ (2 σ) for the $\delta^{13}C_{PDB}$ and $\delta^{18}O_{SMOW}$ values.

3. Results

Table 1 lists the results of 41 analyses, which are the δ^{13} C and δ^{18} O values of the CO₂ evolved from the CaCO₃-1 between 1 °C and 150 °C. The δ^{18} O value of CO₂ ranged from 23.03‰ to 27.04‰. The δ^{13} C value of CO₂ ranged from 2.49‰ to 2.63‰, which was approximately constant regardless of the reaction temperature. Although the accuracy was $\pm 0.1\%$ (2σ), the reproducibility of the measurements was $\pm 0.03\%$ (2σ). Therefore, it is considered that the internal consistency was maintained at $\pm 0.03\%$, and Table 1 shows the obtained data up to two decimal places. The errors in the δ^{18} O values that exceed the statistical error may reflect a slight heterogeneity in the reaction temperature. Figure 2 shows the temperature dependence of the δ^{18} O values of CO₂.

Table 1. Carbon and oxygen isotope ratios of CO₂ evolved from CaCO₃-1.

Run No.	T (°C)	Reaction Time	$\delta^{13}C_{PDB}$ (‰)	$\delta^{18} O_{\mathrm{SMOW}}$ (‰)
31094	1	>15 h	2.54	26.94
31095	1	>15 h	2.59	27.04
31086	10	>15 h	2.56	26.66
31087	10	>15 h	2.59	26.59
31055	15	>15 h	2.58	26.24
31056	15	>15 h	2.60	26.19
31049	20	>15 h	2.60	26.09
31050	20	>15 h	2.59	26.10
31046	25	1 h	2.59	25.86
31061	25	1 h	2.59	25.86
31062	25	1 h	2.58	25.81
31069	25	1 h	2.59	25.86
31076	25	1 h	2.59	25.86
31093	25	1 h	2.59	25.86
31098	25	1 h	2.59	25.86
31099	25	1 h	2.63	25.84
31106	25	1 h	2.59	25.86
31107	25	1 h	2.59	25.85
31067	30	1 h	2.59	25.63
31068	30	1 h	2.49	25.62
31063	40	1 h	2.56	25.26
31064	40	1 h	2.58	25.30
31047	50	1 h	2.61	24.94
31048	50	1 h	2.59	24.94
31052	60	1 h	2.59	24.64
31081	60	1 h	2.57	24.81
31053	70	1 h	2.58	24.35
31082	70	1 h	2.56	24.60
31070	75	1 h	2.55	24.34
31071	75	1 h	2.58	24.37
31057	80	1 h	2.55	24.24
31058	80	1 h	2.57	24.18
31059	90	1 h	2.56	24.00
31060	90	1 h	2.54	23.93
31084	100	1 h	2.52	23.87
31088	100	1 h	2.54	23.91

Run No.	T (°C)	Reaction Time	$\delta^{13}C_{PDB}$ (‰)	δ ¹⁸ O _{SMOW} (‰)
31089	100	1 h	2.51	23.71
31072	120	1 h	2.57	23.44
31091	120	1 h	2.52	23.50
31074	150	1 h	2.56	23.03
31075	150	1 h	2.55	23.10

Table 1. Cont.





4. Discussion

4.1. Oxygen Isotope Fractionation between CO₂ and Carbonate Minerals

The oxygen isotope acid fractionation factors (AFFs) between CO₂ and carbonate minerals have been experimentally determined. For example, calcite ([7] modified after [8]; [3,4,9,10]), dolomite [11], ankerite [11], and siderite [11] were reacted at 25 °C, 50 °C, 75 °C, 100 °C, and 150 °C (Table 2).

Table 2. Experimentally determined oxygen isotope acid fractionation factors (AFFs) between CO₂ and carbonate minerals.

Carbonate	Temperature	AFF (α)	Reference
Calcite	25 °C	1.01025	[7]
Calcite	25 °C	1.01025	[3]
Calcite	25 °C	1.01025	[4]
Calcite	25 °C	1.01025	[9]
Calcite	25 °C	1.01030	[10]
Calcite	50 °C	1.00924	[9]
Calcite	50 °C	1.00937	[10]
Calcite	75 °C	1.00853	[9]
Calcite	75 °C	1.00856	[10]
Dolomite	100 °C	1.00913	[11]
Ankerite	100 °C	1.00901	[11]
Siderite	100 °C	1.00881	[11]
Siderite	150 °C	1.00771	[11]

The oxygen isotope fractionation factors between the CO_2 and carbonate minerals were theoretically determined (Figure 3). The magnitude of the fractionation factor appeared to

be ordered depending on the type of carbonate minerals over a wide temperature range. A maximum value was commonly found in each CO₂–carbonate dataset at low temperatures.

Comparing several carbonate minerals in Figure 3, the fractionation factors appear to depend on the size of the carbonate crystal lattice. The isotope fractionations were primarily attributed to the effect of differences in the cation radius of the parent carbonate during bond fission [12]. The carbonates of intermediate chemical composition, particularly dolomite (CaCO₃–MgCO₃ group minerals), can be considered to behave, to a first approximation, as ideal mixtures of calcite and magnetite [12]. Chacko and Deines [13] concluded that the oxygen isotope-reduced partition function ratios correlate well with the ionic radius of the cation in the carbonate and the reduced mass of the carbonate molecule. However, neither parameter by itself can be used as a precise predictor of the fractionation factors [13].



Figure 3. Temperature dependence of the theoretically determined oxygen isotope fractionation factors between CO₂ and carbonate minerals between 0 °C and 600 °C (drawn using data from [13–15]). Chacko (2008) [13] and Chacko (1991) [14] are for the fractionation factors between CO₂ and calcite. Calcite through to siderite in the legend are the fractionation factors between CO₂ and each carbonate [15].

4.2. Oxygen Isotope Acid Fractionation between CO₂ *and Calcite at Low-to-Intermediate Temperatures*

The oxygen isotope acid fractionation factors (AFFs) between CO_2 and calcite between 1 °C and 150 °C obtained in this study are listed in Table 3. No intense experimental isotope fractionation factors have been obtained between 1 °C and 150 °C to date. Notably, the fractionation factor at each temperature was calculated using the $\delta^{18}O$ value of CO_2 (Table 3) and the $\delta^{18}O$ value of $CaCO_3$ -1 calcite (15.45‰). As the reaction temperature increased, the oxygen isotope fractionation (1000 ln α) decreased from 11.30 at 1 °C to 7.47 at 150 °C. The temperature dependence of the fractionation factor was expressed over the temperature range of 1–150 °C using the following equation:

$$1000 \ln \alpha = 0.494 \left(\frac{10^6}{T^2} + 4.64 \right), \tag{1}$$

where α is the AFF between CO₂ and calcite, and T is in kelvin.

Run No.	T (°C)	$10^{6}/T^{2}$ (K ⁻²)	δ ¹⁸ O _{SMOW} (‰)	AFF (α)	1000 lna
31094	1	13.32	26.94	1.01131	11.251
31095	1	13.32	27.04	1.01141	11.349
31086	10	12.49	26.66	1.01104	10.976
31087	10	12.49	26.59	1.01097	10.907
31055	15	12.06	26.24	1.01063	10.572
31056	15	12.06	26.19	1.01058	10.523
31049	20	11.65	26.09	1.01048	10.424
31050	20	11.65	26.10	1.01049	10.434
31046	25	11.26	25.86	1.01025	10.198
31061	25	11.26	25.86	1.01025	10.198
31062	25	11.26	25.81	1.01020	10.149
31069	25	11.26	25.86	1.01025	10.198
31076	25	11.26	25.86	1.01025	10.198
31093	25	11.26	25.86	1.01025	10.198
31098	25	11.26	25.86	1.01025	10.198
31099	25	11.26	25.84	1.01023	10.178
31106	25	11.26	25.86	1.01025	10.198
31107	25	11.26	25.85	1.01024	10.188
31067	30	10.89	25.63	1.01002	9.971
31068	30	10.89	25.62	1.01001	9.961
31063	40	10.21	25.26	1.00966	9.617
31064	40	10.21	25.30	1.00970	9.656
31047	50	9.59	24.94	1.00934	9.301
31048	50	9.59	24.94	1.00934	9.301
31052	60	9.02	24.64	1.00905	9.006
31081	60	9.02	24.81	1.00922	9.173
31053	70	8.50	24.35	1.00877	8.729
31082	70	8.50	24.60	1.00901	8.966
31070	75	8.26	24.34	1.00876	8.720
31071	75	8.26	24.37	1.00879	8.749
31057	80	8.03	24.24	1.00866	8.621
31058	80	8.03	24.18	1.00860	8.562
31059	90	7.59	24.00	1.00842	8.384
31060	90	7.59	23.93	1.00835	8.315
31084	100	7.19	23.87	1.00829	8.256
31088	100	7.19	23.91	1.00833	8.295
31089	100	7.19	23.71	1.00813	8.098
31072	120	6.47	23.44	1.00787	7.841
31091	120	6.47	23.50	1.00793	7.901
31074	150	5.59	23.03	1.00746	7.437
31075	150	5.59	23.10	1.00753	7.506

Table 3. Oxygen isotope acid fractionation factor (AFF) α between CO₂ and calcite.

Figure 4 shows the temperature dependence of the oxygen isotope AFF (α) between CO₂ and calcite and a least-squares straight line through the experimental data, which fitted the data well (R² = 0.996). The 1000 ln α values are plotted against T⁻² in Figure 4. The use of T⁻² rather than T⁻¹ has been justified by theoretical considerations (e.g., [16,17]). The reproducibility and temperature dependence were rather good, suggesting that each reaction accurately occurred at the intended temperature.

Figure 5 shows the comparison of this study and previous theoretical studies [13–15] at low-to-intermediate temperatures. A maximum value is found in the theoretically determined fractionation factors at low temperatures between 50 °C and 100 °C. Figure 5 shows the 1000 ln α values from several experimental studies. The experimental AFFs are expressed in a linear function of reciprocal squared temperature, and no maximum value is found at low temperatures, dissimilar to the theoretical data. There is a big difference in the theoretically and experimentally determined fractionation factors, though the latter is

not the equilibrium fractionation. Swart et al. [9] and the present study did not conduct total oxygen isotope determination using the BrF_5 technique. Instead, the oxygen isotope fractionation factor between CO₂ and calcite of 1.01025 at 25 °C was assumed. Although this value is internationally recognized as trustworthy [3,4,7], this might fix the fractionation factor at 1.01025 at 25 °C. Kim et al. [10] conducted the total oxygen isotope determination via the thermal decomposition of calcite, followed by the fluorination of the residual CaO using BrF_5 . Their results are similar to those of Swart et al. [9] and the present study (Figure 5), confirming that all the experimental AFFs are reliable.



Figure 4. The 1000 ln α values calculated from the oxygen isotope AFFs (α) between CO₂ and calcite are plotted against $10^6/T^2$. The temperature (°C) is shown on the upper axis. The regression line and R² (coefficient of determination) are also shown.



Figure 5. Comparison of the 1000 ln α values of the experimentally and theoretically determined fractionation factors. Note that experimentally determined AFFs are not exactly the same as EFFs. The theoretical studies are Chacko 2008 [13], Chacko 1991 [14], and Zheng 1999 [15] in the legend. Kim [10], Swart [9], and 'This study' in the legend are experimental studies. Swart et al. [9] determined the fractionation of oxygen and carbon isotopes between CO₂ and CaCO₃ using a sealed vessel method that was similar to that of the present study and also determined the value using a common acid bath method. Figure 5 shows only the results of the sealed vessel method experiments because the method is orthodox and reliable.

For the discrepancy between the theoretical and experimental fractionation factors, a question arises if the theoretical factors are EFFs. The following chapters consider the equilibrium vs. kinetics issue in isotope reactions and test how close to equilibrium the hydrothermal ore formation that is basically governed by kinetics is.

4.3. Equilibrium vs. Kinetics

$$CaCO_3 + H_3PO_4 \Rightarrow CaHPO_4 + CO_2 + H_2O.$$
 (2)

In the above reaction to obtain CO₂ from calcite, only two-thirds of the calcite oxygen converts into CO₂, and one-third of it remains in the reactant fluid. This may cause a kinetic isotope fractionation. Morishita and Matsuhisa [5] conducted CO₂ generation experiments by changing the amount of calcite with respect to the amount of phosphoric acid and observed that a nonnegligible amount of CO₂ remained in the phosphoric acid after the reaction. This phenomenon can cause oxygen isotope exchange between CO₂ and phosphoric acid; however, variations in the oxygen isotope ratios of evolved CO₂ with CO₂ yields (amount recovered as CO₂ for reactant calcite) were within 0.1‰ in the range of 83–100% yield [5]. In addition to this, no reaction was observed between CO₂ and phosphoric acid in Equation (2) [11] because no measurable shift in the δ^{18} O of the CO₂ was observed [18]. These findings may suggest the working hypothesis that the AFF is apparently close to EFF between CO₂ and calcite at the same temperature. Next, the following inferences are made.

Oxygen isotope fractionation experiments at low temperatures are extremely difficult because it is difficult to attain isotopic equilibrium between minerals and water at low temperatures. The experimentally determined apparent oxygen isotope fractionation factors between amorphous silica and water in the temperature range of 34-93 °C were obtained by measuring the oxygen isotope ratios of amorphous silica precipitated from the geothermal waters of power plants [19]. The temperature dependence of the fractionation factor (α) between amorphous silica and water at 34-93 °C is given [19] by

$$10^3 \ln \alpha = 3.52 \ (10^6 \mathrm{T}^{-2}) - 4.35. \tag{3}$$

The fractionation factor in Equation (3) is on the low-temperature extrapolation line of the oxygen isotope equilibrium fractionation between quartz and water obtained experimentally [20] at high temperatures (>250 °C). When quartz is precipitated from water, the initial formation of "absorbed silica," which is a reaction intermediate between dissolved and amorphous silica in the process of the particle growth of amorphous silica, is followed by rearrangement and interlinkage to form quartz [21]. Although there is a large structural difference between quartz and amorphous silica, there is no significant oxygen isotope fractionation between quartz and amorphous silica [19]. Therefore, the oxygen isotope fractionation between amorphous silica and water would be the rearrangement and interlinkage of "absorbed silica," which is the same as the fractionation between quartz and water [21]. The mineral precipitation environments in many epithermal vein-type deposits, including silica precipitation in geothermal environments, would be close to the isotopic equilibrium with the coexistent hydrothermal fluid.

The experimentally determined AFFs obtained in this study look like they were based on a certain principle because of the data consistency (\mathbb{R}^2 , the coefficient of determination, is near unity in Figure 4). To ensure that the fractionation factors in this study were reliable, several experimental fractionation factors at low-to-intermediate temperatures are shown in Figure 5. There appears to be high consistency among the experimental data. Although experiments under equilibrium conditions are not possible at low temperatures, the AFF at low temperatures would be similar to that under equilibrium conditions.

4.4. Equilibrium and Nonequilibrium among Minerals and Coexisting Fluid

Equilibrium between minerals A and B, or among minerals with mineral-forming fluids, is important in the ore formation environment. Equilibrium and nonequilibrium in mineral formations were studied on the epithermal quartz–calcite veins at the epithermal Kushikino deposit in Kyushu, Japan [22]. Assuming that quartz and calcite precipitate from a fluid in equilibrium, they are supposed to have the texture of the assemblage of finegrained crowded quartz and calcite grains under the microscope as a working hypothesis. In contrast, when quartz and calcite precipitate from a fluid not in equilibrium, they are supposed to have the assemblage of unevenly distributed coarse-grained quartz and/or calcite under the microscope, in which it is common to lack one mineral. Let us denote the former, "equilibrium assemblage," and the latter, "nonequilibrium assemblage." Figure 6 shows a set of δ^{18} O values for quartz and/or calcite bearing small pieces from a hand specimen. In the equilibrium assemblage (solid circles in Figure 6), both quartz and calcite precipitated in equilibrium with the coexisting fluid. The equilibrium assemblage is on the isotopic equilibrium line (broken line in Figure 6). The broken line denotes the temperature dependence of the equilibrium fractionation of oxygen isotope for quartz and calcite. The δ^{18} O value of the Kushikino hydrothermal fluid was -7.0% [22], which is stable throughout the fluid evolution, and it was assumed that the fluid was of meteoric water origin. The temperature on the broken line denotes the oxygen isotope equilibrium temperature for the quartz-calcite pair calculated using a corresponding calibration equation (either quartzwater [20] or calcite–water [23]).



Figure 6. Plot of the δ^{18} O values of quartz vs. the δ^{18} O values of calcite from the veins of the Kushikino deposit (produced from the data in [22]). The solid and open circles refer to the equilibrium and nonequilibrium assemblages, respectively. The open squares represent quartz or calcite in a small piece from the hand specimen, resulting in only one δ^{18} O value in the analyzed sample (W222V-1 has only quartz, but W222V-2 has quartz and calcite, both in the same hand specimen). The data points from the same hand specimen are connected by a tie line, implying that there are two mineralization stages in a hand specimen. The δ^{18} O values of quartz that precipitates from the fluid having -7.0% are calculated as a function of temperature using the experimentally determined equilibrium fractionation factors between quartz and water [20]. Similarly, the δ^{18} O values of calcite that precipitates from the fluid having -7.0% are calculated as a function factors between calcite and water [23]. Then, the two calculations are merged into the broken line. When a sample containing quartz and calcite is on the broken line, the quartz and calcite are considered to be in equilibrium with the fluid.

A set of δ^{18} O values for the equilibrium assemblage of quartz and calcite moves toward the upper right on the isotopic equilibrium line with decreasing temperature. Conversely, the δ^{18} O values of quartz and/or calcite are plotted off the line for the nonequilibrium assemblage (open symbols in Figure 6). They precipitated separately at different stages; thus, it was considered that the temperature or forming fluid for quartz and calcite differed. Thus, the isotopic measurements confirmed that it is possible to distinguish the equilibrium assemblage from the nonequilibrium assemblage via the microscopic observation of veins (Figure 6), which proves the working hypothesis.

4.5. Hydrothermal Deposit

As above, the equilibrium and nonequilibrium assemblages can be mineralogically determined if the mineral composition and texture of veins can be clearly distinguished. When we distinguish equilibrium assemblage from nonequilibrium assemblage via the microscopic observation of veins, the oxygen isotope equilibrium temperature of mineral formation can be calculated using the mineral δ^{18} O values. The δ^{18} O values of the quartz and calcite of the equilibrium assemblage, E1020V-2 (Figure 6), from a vein of the Kushikino deposit are 6.6‰ and 4.7‰, respectively, and the oxygen isotope equilibrium temperature is calculated to be 173 °C using the experimentally determined fractionation factors of quartzwater [20] and calcite–water [23]. The equilibrium temperature of 144 °C is calculated for the equilibrium assemblage, W222V-2 (Figure 6), in the same way. The δ^{18} O value of the coexisting hydrothermal fluid is then calculated to be -7% using the δ^{18} O value of quartz or calcite and the fractionation factor of quartz–water or calcite–water, respectively [22].

The following estimations of the oxygen isotope equilibrium temperatures of the mineral–pair formation were used as an oxygen isotope thermometer based on the isotopic equilibrium for the mineral–pair: a quartz–muscovite thermometer for tungsten–quartz vein deposits (Ohtani and Kaneuchi deposits [24]), quartz–wolframite and quartz–cassiterite thermometers for tungsten–quartz vein deposits (Takatori deposit [25]), and a quartz–calcite thermometer for gold-bearing quartz–calcite veins (Noya deposit [26]).

The study on the Kamioka skarn-type Pb–Zn deposits is a good example to consider the kinetics-to-equilibrium transition in isotopes for the genesis and evolution of the oreforming hydrothermal fluid [27]. The crystalline limestone in the mining area suffered from the ore-forming hydrothermal fluid. The δ^{13} C and δ^{18} O values of the limestone had changed from the original to varying values depending on the degree of the water/rock ratio, reaction time, and temperature. Oppositely, the direct precipitation of calcite into veins from the hydrothermal fluid also occurred. The calcite was supposed to be equilibrated with the hydrothermal fluid, and the δ^{13} C and δ^{18} O values of the isotopically reacted limestone are distributed in a wide range of isotope ratios between the original limestone and precipitated veins in a δ^{13} C – δ^{18} O graph [27]. This confirms that the isotope exchange kinetics in the limestone changed the δ^{13} C and δ^{18} O values of the veins. This most reacted limestone can be considered to be near equilibrium with the hydrothermal fluid.

We observed that the δ^{18} O values of amorphous silica precipitated from low-temperature hydrothermal fluids were on the low-temperature side extrapolation line of the isotopic equilibrium fractionation between quartz and water obtained at high temperatures (Section 4.3). The isotope exchange reaction is slow for vein-type hydrothermal deposits at low temperatures, and minerals are taken away from the hydrothermal fluid because of subsequent mineral precipitation on the previously precipitated mineral layer. Nevertheless, minerals in many epithermal vein-type deposits have been shown to be in isotopic equilibrium with coexisting hydrothermal fluid (e.g., Figure 6).

Minerals do not crystallize from fluid in perfect equilibrium. Therefore, crystal growth is essentially governed by kinetics; however, the precipitation in the vein-type deposit is extremely slow. The duration for the 1-mm growth of the Hosen-1 vein of the Hishikari gold deposit is about 10,000 years according to the ⁴⁰Ar/³⁹Ar ages of adularia [28]. Since

mineral precipitation in hydrothermal ore deposits is extremely slow, as in this example, the kinetic mineral growth in hydrothermal ore deposits can be considered to be very close to equilibrium.

5. Concluding Remarks

Carbonate minerals including calcite are used for mineral exploration. The δ^{13} C and δ^{18} O values of calcite are generally determined to measure the isotope ratios of CO₂ generated via reaction with 100% phosphoric acid at 25 °C. When using other carbonate minerals such as dolomite, ankerite, and siderite, the reaction requires high temperatures. Therefore, the oxygen isotope fractionation between CO₂ and calcite at high temperatures should be known because the laboratory standard sample of carbonates is usually calcite. The oxygen isotope AFF (α) between CO₂ and calcite between 1 °C and 150 °C was determined in this study, and the value can be represented by the following equation: 1000 ln α = 0.494 (10⁶/T²) + 4.64.

The consideration of the equilibrium versus kinetics issue of mineral formation in nature is inspired by the experiments of the first half. The relationships between equilibrium and kinetics from the previous oxygen isotopic studies on hydrothermal ore deposits are discussed in the second half. Several isotopic studies (Kushikino deposit [22,29], Ohtani and Kaneuchi deposits [24], Takatori deposit [25], and Noya deposit [26]) were introduced, assuming that the mineral assemblages were close to equilibrium. We observed varying degrees of kinetic reactions and equilibrium goals in the $\delta^{13}C-\delta^{18}O$ relationship of limestone at the Kamioka deposit [27]. These previous findings in several hydrothermal ore deposits suggest that actual isotope fractionations in nature, even at low-to-intermediate temperatures, are similar to equilibrium fractionations among minerals with coexisting fluid.

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