

Evidence of Crustal Fluid Flow Conduit (Mizu-michi) in Rocks by Stable Isotopic Zonation of Minerals

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Abstract

The crustal fluid conduit (Mizu-michi) contains large displacements of brittle rocks caused by faults and fractures during crustal movements. Mizu-michi is confirmed as veins, altered zones on a macro-scale, and grain-boundaries on a micro-scale.

Macro- and micro-scale stable isotope studies are carried out from outcrops to grain-boundary scale in different types of crustal rock. The combination of carbon and oxygen isotopic analyses provided important constrains on the origin and the transportation mechanism of crustal fluid, mainly composed of carbon(C)-hydrogen (H)-oxygen (O) fluid during crustal movements. Isotopic data also provide evidence of the evolution of the crustal fluids on a molecular scale, accompanying an isotope-exchange mechanism involving fluids and minerals, and have major implications for micro fracture-controlled fluid-flow processes in the deep Earth's crust.

Key words; carbon isotope, oxygen isotope, isotopic zonation, Mizu-michi, crustal fluid

Introduction

Earthquakes result from an abrupt movement of the brittle crust, which results in many faults and fracture zones at tectonically active regions. Upon the formation of fracture zones, probably along active faults, meteoric water will penetrate the deep crust and squeeze deep-seated water out through active faults zones. The stable isotopic characterization of deep-seated and meteoric water and exchange processes of water-rock reactions have been examined for decades, achieving considerable progress. Evidence of water-rock interaction is normally recorded in minerals as chemical zonation or isotopic zonation. Crustal fluid conduit (Mizu-michi), which is normally filled with quartz and carbonate, is considered to be a fossil fluid conduit that flowed through fractures formed by crustal dislocations including earthquakes. Understanding Mizu-michi will give us important knowledge of crustal rock fracturing in the deep crust, on the basis of which to develop deep underground applications, such as the disposal of high-level nuclear wastes.

In geochemistry, stable isotopes of hydrogen(H),

carbon(C), nitrogen(N), oxygen(O), and sulfur(S) are powerful tools for studying behavior in water and circulation of such light elements. These elements are mainly constituents of geologically important fluids such as meteoric, oceanic, connate water, and metamorphic fluid, thus they provide a means of directly studying the effects of fluid-rock interaction. In addition, stable isotopes are used as tracers to determine the source of an element, as palaeothermometers, and for inferring diffusion and reaction mechanisms in geological processes.

Understanding the behavior of carbon and oxygen isotopes in metamorphic fluids is essential to elucidate the processes of fluid-rock interaction, because of the predominance of C-H-O fluid species in metamorphic environments (Crawford and Hollister, 1986). The heterogeneity of carbon and oxygen isotopes in carbonate minerals in crystalline limestone may result from exchange reactions with the chemical species in the metamorphic fluid generated by decarbonation reactions, and/or infiltration with exotic source fluids. The moderately slow kinetics of carbon and oxygen isotope exchanges among

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coexisting minerals and intergranular fluid may result in isotopic zonation of minerals in response to time-integrated fluid processes. Isotope and chemical zonation in minerals may, thus, provide important constraints on mechanism of metamorphic fluid flow from macro-scales (e.g. Cartwright and Oliver, 1994; Cartwright *et al.*, 1995; Cartwright and Buick, 1995) to micro-meter scales (e.g. Wada, 1988; Arita and Wada, 1990; Valley and Graham, 1996, Wada *et al.*, 1998, Graham *et al.*, 1998). The study of isotopic zonation in minerals is one of the most powerful methods for elucidating fluid kinetic processes, especially the behavior of water.

At any scale, stable isotopic variations would be caused by the results of complete or incomplete water-rock interactions during the crustal evolution of the Earth.

Here, I would like to review current research, especially at the micro-scale, on stable isotopic aspects of fracture-filled carbonates in a brittle state of sedimentary and metamorphic rocks.

Notation of carbon and oxygen stable isotopic ratios

Stable isotopic ratios are measured relative to a standard and are expressed in parts per thousand (‰). Isotopic ratios are expressed as a value δ . Using oxygen isotopes, δ value is calculated as follows,

$$\delta^{18}\text{O}(\text{‰}) = \left\{ \frac{(^{18}\text{O}/^{16}\text{O})_{\text{(sample)}}}{(^{18}\text{O}/^{16}\text{O})_{\text{(standard)}}} - 1 \right\} \times 1,000$$

For carbon isotopes, $^{18}\text{O}/^{16}\text{O}$ ratio is substituted by $^{13}\text{C}/^{12}\text{C}$ ratio.

There are currently two standards used for oxygen isotopes. Low-temperature carbonates measurements are made relative to PDB-Belemnite from the Cretaceous Peedee Formation, South Carolina, U.S.A. All other measurements are calculated relative to concentrations in Vienna Standard Mean Ocean Water (V-SMOW). V-SMOW and PDB values are related by the expressions as follows, (Rollinson, 1993)

$$\delta^{18}\text{O}_{\text{V-SMOW}} = 1.03091 \delta^{18}\text{O}_{\text{PDB}} + 30.01$$

δ -notation for carbon isotopes is made relative to the PDB-standard, which is similar to oxygen isotopes. The PDB standard is used because its $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are close to that of an average marine limestone.

Analytical procedure and sample preparations

CO_2 was extracted from pulverized carbonates by a reaction with concentrated phosphoric acid (pyrophosphoric acid) in vacuo at a constant temperature when the sample size is sufficient to yield much more than $1\mu\text{mol}$. Oxygen isotope ratios of silicates and oxide samples were analyzed using BrF_5 for fluorination to release free oxygen gas. The oxygen gas released was reacted with hot carbon to convert it quantitatively into carbon dioxide. Fluorination reaction was carried out using Laser-based reaction apparatus (Sharp, 1990, 1992) for micro-scale analyses. Although these micro-scale techniques were developed during the last decade, the precision of carbon and oxygen isotopic ratios using a conventional preparation of carbonates is still high for investigating of micro-scale fluid-rock interaction processes. The highly sophisticated analytical procedure for micro-scale isotope determination of carbonates is described as follows.

For carbon and oxygen isotope ratios in micro-scale sampling of grain boundaries, a prism with a cross-section of about 1mm^2 taken out from the polished surface using a dental diamond saw was placed on a flat surface of a water-ice block of electric freezing microtome (Wada, 1988). The grain boundary surface of the prism was oriented in parallel to the blade of the microtome and mounted with water ice. The calcite crystals were shaved together with the ice block at intervals of 20–50 micrometers. A pulverized calcite sample was instantaneously obtained along with melt water on the heavy microtome blade, then dried and collected in a small stainless steel cup. The pulverized sample in the cup was dropped into a reaction vessel, which containing concentrated phosphoric acid at 60.00°C in vacuo, and the CO_2 evolved was purified using a normal-pentane freezing trap (Wada *et al.*, 1982; 1984; 1991; 1996).

Isotopic analyses of CO_2 were carried out on a conventional dynamic gas-flow and dual inlet with a mass spectrometer installed. The reference standard gas was normally calibrated with respect to a NBS-20 calcite standard from Solnhofen, Bavaria, Germany. The standard deviation (σ) of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements of calcite are normally less than 0.03‰ and 0.05‰, respectively, for small amounts of CO_2 more than $0.1\mu\text{mol}$. (Wada *et al.*, 1982; 1984).

Onset of fractures in semi-consolidated sedimentary rocks

During diagenetic processes, semi-consolidated sediments are commonly cemented by minerals in authigenic phases such as carbonate and/or silica. These authigenic minerals are formed from pore water solutes and their chemical and isotopic compositions should reflect the compositions of pore water. A study of such minerals will provide an understanding of the geochemical and biogeochemical processes in post-depositional environments. These processes in sedimentary sequences may strongly affect the carbon and oxygen isotopic compositions of the carbonates formed. Wada and Okada (1990) reported isotopic analyses of carbonate cement in drill core samples collected from the CIROS-1 drill core (Robinson, 1987) retrieved in the Ross Sea, Antarctica. The CIROS-1 drill core was recovered from the continental shelf of Ross Sea at a water depth about 200 meters and continuous sedimentary sequences down to 702.14 meters beneath the sea floor. The sedimentary sequences were overlies of the Antarctic glacier, fractured in some depths, with carbonate minerals filling the fractures.

Carbonate is a common constituent of the CIROS-1 drill-core. Calcite occurs only as cemented micrites, and aragonite as sparry crystals. As shown in Fig. 1, sparry aragonite crystals filling a vein and large sparry crystals are found in the central part of the vein. Sandstones were composed mostly of carbonate-quartzose arenite and partly of calcareous feldspathic arenite and quartzose wacke. A thin section of carbonate vein and cements along the quartz grains are also shown in Fig. 2. Sand grains are generally sorted and subrounded to a well-rounded shape. Fig. 2 shows the characteristic aragonite vein filled with about 0.5 mm in width and aragonite filled on both sides of quartz grain within a few millimeteres along the vein. Aragonite filled the gaps at both sides of all quartz grains, developing perpendicular to the veins, indicating that the Glacial overburden produces the pressure gaps around these quartz grains under an environment of sub-consolidated sediments, as well as forming brittle fractures.

The aragonite vein of ANT-7 filled the fracture of about 7 mm in width, and was collected from 261.01

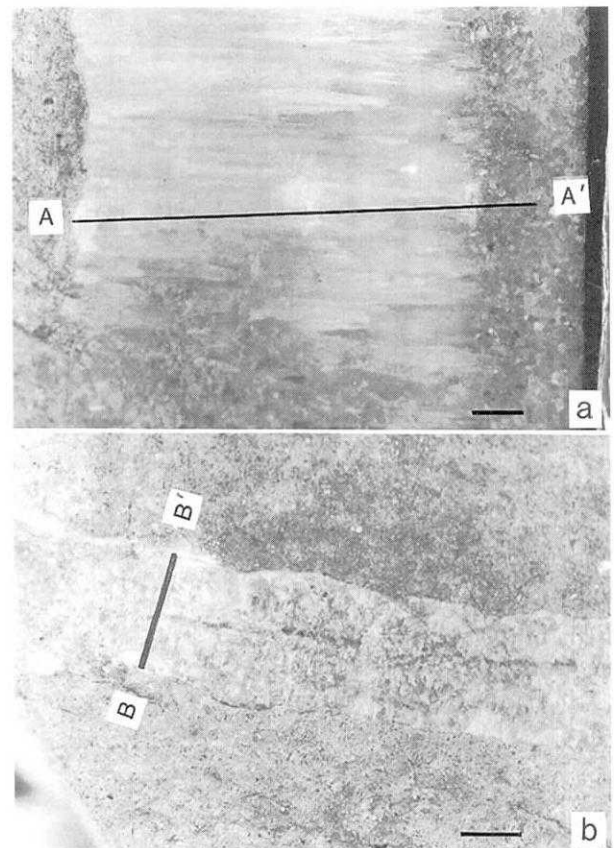


Fig. 1. a; ANT-7, 264.01 m subbottom. Fibrous sparry aragonite crystal growing perpendicular to the vein. Semi-micro scale isotopic analyses (Fig. 3A) were carried out along traverse A-A'. b; ANT-12, 599.46-53 m subbottom. Aragonite vein-filled and cemented well-sorted quartzose arenite. Semi-micro scale isotopic analyses (Fig. 3B) were carried out along the traverse B-B'. (Wada and Okada, 1990)

-meters subdepth CIROS-1 drilled core, from +3 to +6‰ in $\delta^{13}\text{C}$ (PDB) and from -8 to -12‰ in $\delta^{18}\text{O}$ (V-SMOW) with variations showing M-shape and W-shape distributions, respectively (Fig. 3). On the other hand, for samples of ANT-12 collected from 599.46-53 -meter depth CIROS-1 drilled core, $\delta^{13}\text{C}$ values of -2 to -7‰ variation show a U-shaped isotopic distribution; a constant $\delta^{18}\text{O}$ value of about -10‰ in PDB scale was observed through the vein. These results are interpreted as the mixing of sources of fluids for the precipitation of carbonates containing different carbon and oxygen isotopic ratios. Semi micro-scale analyses of the $\delta^{18}\text{O}$ values of ANT-7 (264.01-meter subdepth) revealed that there may be a large change of $\delta^{18}\text{O}$ values in fluids resulting from a change of mixing ratio of seawater (0‰) and glacier ice-water (-14--23‰ in V-SMOW scale of snow precipitation

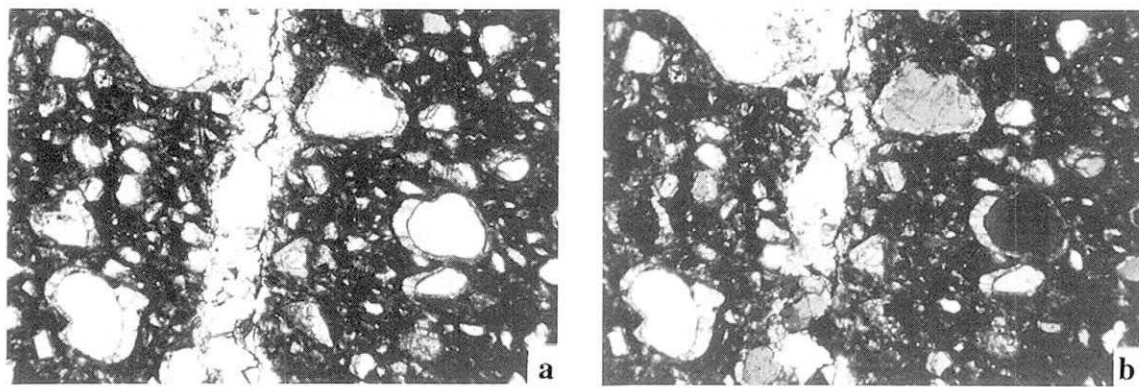


Fig. 2. Aragonite vein-filled and developed at the both sides of quartz grains of drilled core from the CIROS-1 drillhole, Ross Sea, Antarctica. Poorly sorted, round quartzose wacke (a—plain polarized light; b—crossed nicols) scale bar=1 mm. (Wada and Okada, 1990)

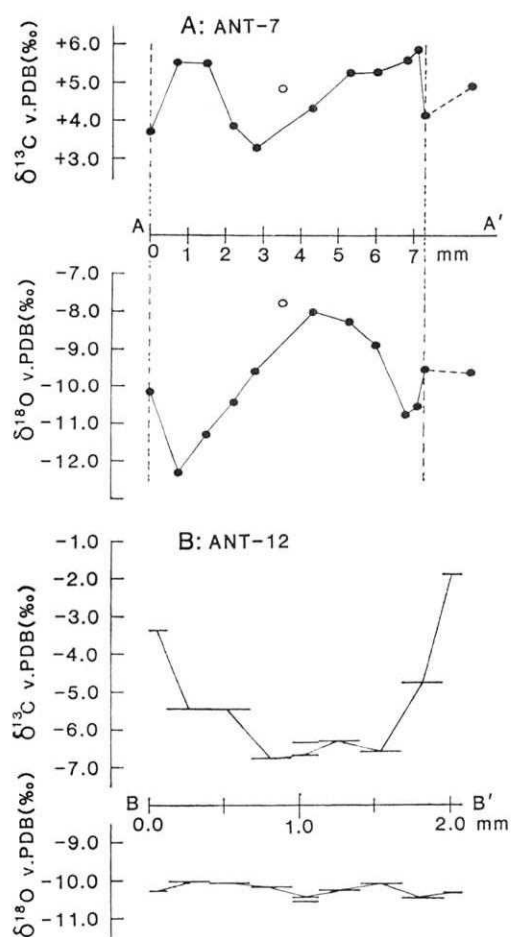


Fig. 3. Semi-micro scale carbon and oxygen isotopic compositions of vein-filled aragonites of ANT-7, and ANT-12. The traverses A-A' and B-B' are shown in Fig. 1. (Wada and Okada, 1990)

at McMurd Sound area and -40% in V-SMOW scale of glacier ice-water at the Dry Valley area, by Matsubaya *et al.*, 1979). Using the paleotemperature scale

for aragonite-water (Grossman and Ku, 1981), the low $\delta^{18}\text{O}$ values of fluid equilibrated with the aragonite precipitation in ANT-7 and 12 calculated on the assumption that precipitation took place at 0°C , the estimated $\delta^{18}\text{O}$ values of fluid composition are in the range of -7 to -12% in V-SMOW scale. Because the $\delta^{18}\text{O}$ values of seawater are normally 0% in V-SMOW scale, this means that the fluid is strongly diluted by glacial ice water in any cases.

The origin of the carbon in aragonite precipitation is due to the different sources of carbon dioxide in fluid. The $\delta^{13}\text{C}$ values of marine carbonates are normally around 0% , whereas those for plankton and detrital organic material from the Ross Sea are around -27% (Sackett, 1986). It has been well established that ^{13}C -enriched carbonate up to $+15\%$ is precipitated in a closed system of the fermentation zone under anaerobic conditions deeper than about 10 m (Irwin *et al.*, 1977). In contrast, highly ^{13}C -depleted carbonate of less than -25% is precipitated at relatively shallow depths where there is a methane oxidizing zone or a sulfate reduction zone caused by microbacterial activity. At further depths (more than 1000 m ?), the ^{13}C value of carbon dioxide is expected to be more negative (-10 to -25%) due to abiotic decarbonation reactions. Although we could not identify the causes of formations of such fractures; e.g., due to Earthquake displacement or glacier overburden, and the age and depth of carbonate precipitation, these $\delta^{13}\text{C}$ values of precipitated aragonites could be characterized by the mixing ratios of sources of carbon dioxide in the fluid for aragonite precipitation during diagenesis. According to analyses of interstitial water recovered from the Deep Sea

Drilling Project core, the $\delta^{18}\text{O}$ value of the interstitial water increased with an increase of subdepth (Matsuhisa and Matsumoto, 1985), because the temperature increases with the subdepth and the interstitial water isotopically reacted with sediments including clay minerals. The W and M shape distributions of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of ANT-7 aragonite vein, respectively, indicate the change of mixing ratio of the two sources of water such as Glacier predominant water with positive $\delta^{13}\text{C}$ values and water similar to sea water, rather than temperature change. Further, a constant $\delta^{18}\text{O}$ value of ANT-12 may indicate that the $\delta^{18}\text{O}$ value of fluid is equilibrated or close to being equilibrated with sediment at a deeper part of the sedimentary sequences at a constant temperature relative to the precipitation depth of ANT-7.

Thus, precise stable isotopic analyses will give an important constrain to investigate the origin and the evolutionary process of the invaded diagenetic fluid sources for fracture-filled carbonates.

Isotopic evidence of the onset of fracture in crystalline marble in regional metamorphism.

During the formation of fracture or displacement of ductile rocks by earthquakes, the fracture zone is filled with crustal fluids, even in the deep crust, because we can observe many carbonate or silicate veins as being ductile and plastic deformed in metamorphic rocks. Such carbonate or silicate veins were considered to be precipitated from migmatitic silicate melts in the higher metamorphic terrains and hydrothermal water invaded these crystalline rocks. Stable isotope characterization and isotopic zonation in minerals may provide important constrains on the formation of such silicate and carbonate veins.

Recent advances in micro-analytical techniques have enabled the detection of intracrystalline isotope variations (Crowe *et al.*, 1990; Elsenheimer and Valley, 1993; Sharp, 1990, 1992; Wada, 1988) and have led to the discovery of micro-scale isotope zonation in metamorphic minerals, resulting from either inter-crystalline diffusion during cooling from peak metamorphic temperatures or interaction with grain-boundary fluids (Arita and Wada, 1990; Chamberlain and Conrad, 1991; Eiler *et al.*, 1992, 1995; Kohn *et al.*, 1993). Large-scale oxygen isotopic heterogeneity within single crystals was observed in metamorphic magnetite and hydrothermal quartz, indicating fluid

flow in micro-fractures, as reported by Valley and Graham (1991, 1993, 1996). The isotope profiles and zonation patterns in minerals, thus, yield valuable insights into time-integrated fluid-flow processes in the crustal evolution.

Satish-Kumar *et al.*, (1998) present major-oxygen isotope zonation, with a scale of millimeters, in a calcite crystal from a marble sample from East Antarctica. They offered their deductions about the mechanism involved in the isotope exchange between the fluids and calcite.

The marble sample in their study is from the granulite-facies terrain of Lutzow Holm Bay, where peak granulite-facies metamorphism occurred at temperatures of $750 \pm 50^\circ\text{C}$ and pressures of 7 ± 1 kbar (Yoshida, 1978; Santosh and Yoshida, 1992). The marble crops out in the lower calcareous formation, which is interlayered with orthopyroxene-bearing charnockites and pelitic aluminous gneisses (Yoshida, 1979). The immediate contact lithologies of the marble band are orthopyroxene granulites, which structurally overlie the layer, and pelitic garnet gneiss occurs beneath the layer. The marble band has a width of about 100 meters. Stable isotopic study on the marble horizon across the strike analyzed carbon and oxygen isotopes, and the results indicate homogeneous carbon and oxygen isotope distribution ($\delta^{18}\text{O}$; $17 \pm 1\%$ and $\delta^{13}\text{C}$; $0 \pm 1\%$). This is indicative of lack of a large-scale fluid infiltration events and peak metamorphic isotope homogenization through a regional prograde devolatilization reaction (Valley, 1986). The marble hand specimen with an anomalous isotope heterogeneity observed was collected from the marginal portion of the band in contact with the garnet gneiss. The sample is composed of a granoblastic mineral assemblage of calcite + forsterite (serpentinized) + phlogopite + spinel + graphite.

On the other hand, across a 1.2-mm-wide domain, a calcite crystal from a granulite facies marble from East Antarctica exhibits micro-scale oxygen isotope heterogeneity, been enhanced by a channelized fluid flow. As shown in Figs. 4 and 5, the oxygen isotope compositions range over 21‰ — a major zonation. Calcite along a boundary in contact with phlogopite has an average $\delta^{18}\text{O}$ value of -5% ; the oxygen isotope composition remains constant, along a profile that extends about $700\mu\text{m}$ into the grain

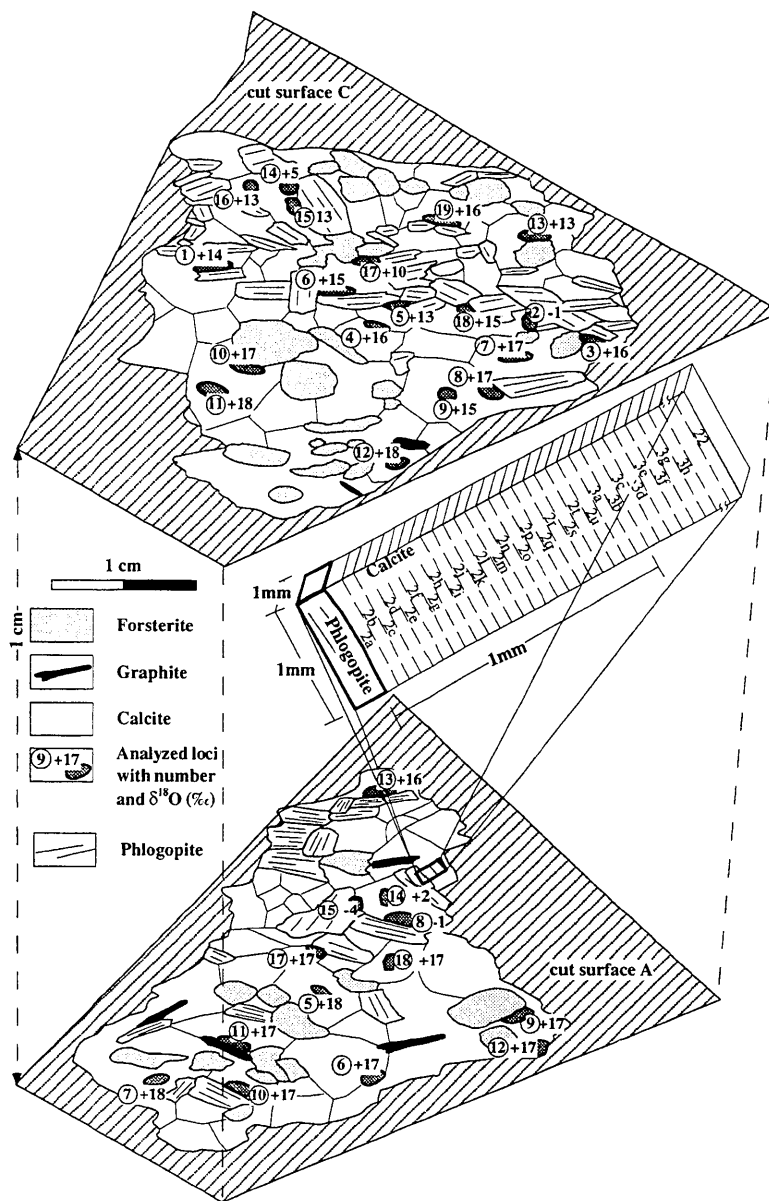


Fig. 4. Sketches of two cut surfaces through an Antarctic marble specimen ~ 1 cm apart showing normally analyzed spots with sample numbers (within circles) and $\delta^{18}\text{O}$ values in SMOW scale. The area where micro-scale traverse (isotopic profiles in Fig. 5) was carried out is on the cut surface A. Cut surface C shows a phlogopite-enriched zone that has reduced oxygen isotope values; they are typically about $+13\text{‰}$, but the lowest is -1‰ . This zone can be traced to the lower surface A, as similar reduction can be seen in the same zone 1 cm below. A fracture-controlled hydrothermal-fluid influx along this zone has been interpreted to be the cause of this heterogeneity. (Satish-Kumar *et al.*, 1998)

indicating equilibrium with source fluids of a meteoric origin. Continued measurements inward along the profile show the $\delta^{18}\text{O}$ values rise to reach $+16\text{‰}$. The corresponding carbon isotope variation is only about 0.6‰ . Isotope heterogeneity is observed mainly in a phlogopite rich zone where the $\delta^{18}\text{O}$ values are lower ($13 \pm 5\text{‰}$) than those away from the zone ($17 \pm 1\text{‰}$). It is inferred from the distribution of

^{18}O depletion that preferential micro-fracturing and hydrothermal fluid flow resulted. The constant $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values from the grain boundary inward for similar distances ($700\ \mu\text{m}$) suggest a solution-reprecipitation mechanism, whereas the smoothly increasing $\delta^{18}\text{O}$ and decreasing $\delta^{13}\text{C}$ values afterwards along the profile indicate a diffusion-controlled isotope exchange between the later precipitated calcite and the

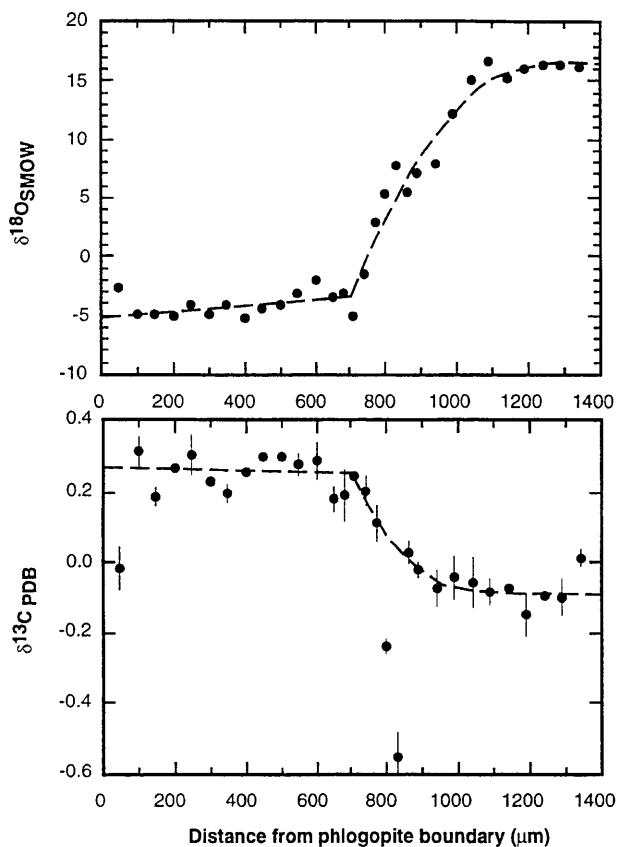


Fig. 5. Micro-scale $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles across calcite crystal from its contact with phlogopite inward (analytical location is shown in Fig. 4). The sample was collected from Lutzow Holm Bay, East Antarctica. Notice that as far as $700\mu\text{m}$ in from the boundary, both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values are more or less the same and then show a sharp but smooth decrease and increase, respectively. The constant nature of both carbon and oxygen isotopes indicates a solution-precipitation mechanism for isotope exchange between dissolved calcite and fluids of a probable meteoric origin, and smooth curve deeper in the calcite grain may indicate volume diffusion between original calcite and later-precipitated calcite. (Satish-Kumar *et al.*, 1998)

original grain (core). The results of Satish-Kumar *et al.*, (1998) provide important evidence of the isotope-exchange mechanism involving fluids and minerals, and have major implications for micro-fracture-controlled fluid-flow processes in the Earth's crust.

The infiltrating fluids and the calcite in grain-boundary contact with phlogopite can be assumed to be in complete isotopic equilibrium, because the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of the calcite does not show any significant variation as far as $700\mu\text{m}$ into the grain from the boundary. Because they do not have tight con-

straints on the actual temperature of infiltration, the $\delta^{18}\text{O}$ value of the infiltrated hydrothermal fluid is difficult to obtain. These data indicate that the infiltrating fluids had $\delta^{18}\text{O}$ values less than -5% . These results place the source of fluids as meteoric (Shepard, 1986).

These results shown by Satish-Kumar *et al.* (1998) provide the first direct evidence of major isotopic alterations on a micro-scale resulting from late-stage hydrothermal and channeled meteoric-fluid infiltration along hydro-fractures developed in preferential high-strain grain boundaries. The evidence provides an exotic fluid invasion mechanism into the crystalline marble of stained ductile rocks prior to the formation of fractures or micro-fractures. A solution-precipitation mechanism combined with later diffusion is interpreted as the cause of such micro-scale isotopic heterogeneity.

Fracture formations of a contact metamorphic event by granitic intrusions.

During the intrusion of granitic rocks, fractures or displacements of fracture zone of country rocks around the intrusive rocks may be filled with metamorphic fluids emanating from the granite and released by devolatilization or decarbonation reactions with igneous rocks.

Wada (1988) first reported isotopic zonation in calcite and graphite crystals, and clarified the features of a metamorphic fluid flow along grain boundaries and its relation to the time-integrated reaction between calcite and the fluid in the Hida metamorphic terrain in Japan. Arita and Wada (1990) reported oxygen isotopic troughs at the rims of calcite from a contact aureole at the same metamorphic terrain. They showed that only oxygen isotopes in grain boundaries were preferentially exchanged with a metamorphic fluid. The observed oxygen isotopic trough and the lack of a similar trough in carbon was explained by appealing to infiltration by a water rich metamorphic fluid, generated from the surrounding biotite gneiss (Arita and Wada, 1990).

According to Wada *et al.* (1998), a hand specimen of crystalline limestone in contact with a wollastonite vein (sketch figure in Fig.6) was collected a few meters from the granite contact near the location of UTS-1 reported by Arita and Wada (1990). The calcite marble consisted of mono-mineralic, large grains

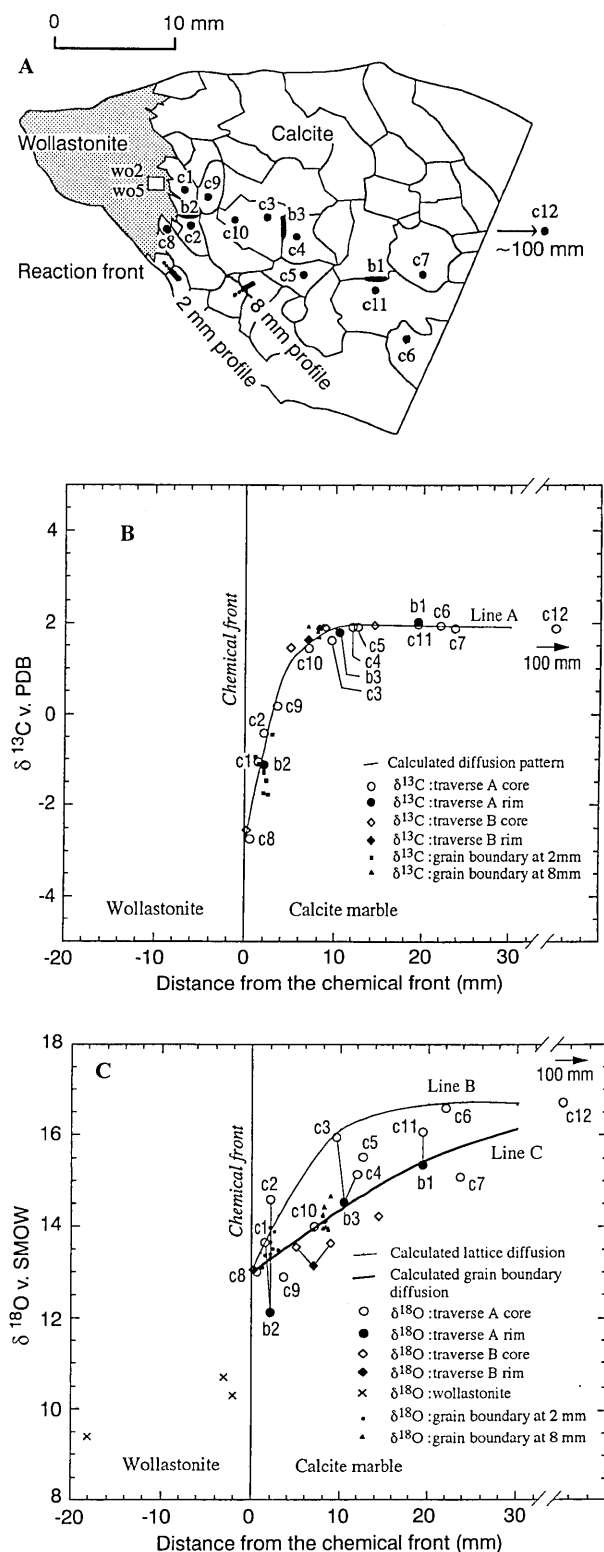


Fig. 6A-C. Carbon and oxygen isotopic profiles along a traverse perpendicular to the reaction front of calcite marble collected from Hida metamorphic terrain, central Japan where wollastonite formed during contact metamorphism. A; Sampling localities for cores (denoted c), rims (denoted b) and micro-scale zonation around the grain boundary of

calcite crystals at 2 and 8 mm from the reaction front. B; carbon isotopic profile along the Traverse, C; oxygen isotopic profile along the Traverse. Numbers refer to those in Fig. 6A. The fitting curves (lines A, B, and C) are calculated based on semi-finite diffusion model by Crank (1975). (Wada *et al.* 1998)

with an equigranular texture. Wollastonite veins filled the fracture and reacted with silica in the metamorphic fluid which emanated from the Utsubo granite (Inazuki, 1982). To clarify the behavior of carbon and oxygen isotopes of metamorphic fluid at micrometer to millimeter scales at the reaction front of the wollastonite vein samples, nearly perpendicular to the wollastonite reaction front were selected for isotopic analyses.

The $\delta^{18}\text{O}$ values of calcite along a traverse shown in Fig. 6 showed a steep isotopic gradient with scattering deep in the calcite marble. Four data of calcite rims denoted by solid marks in Fig. 6 are tied with adjacent grain core of the calcite marble. It is noteworthy that $\delta^{18}\text{O}$ values from the grain boundary were always lower than those of the adjacent grain cores. On the other hand, all $\delta^{13}\text{C}$ data of cores, rims and immediate contacts of calcite to wollastonite in the traverse, basically fall on a unique fitting curve. Three $\delta^{18}\text{O}$ values of wollastonite also are plotted in Fig. 6 and seemed to show an isotopic gradient of about 10.5‰ near the reaction front and 9.5‰ at 20 mm from the chemical front.

These results show that oxygen-containing chemical species could have more easily penetrated the grain boundary of the calcite. On the other hand, for the carbon isotopic compositions in a traverse of the marble, one could not recognize a special role of the grain boundary during the carbon isotopic exchange reaction around the wollastonite vein. When we simplify the homogeneous metamorphic fluid flow in the wollastonite vein, an isotopic transportation might occur in the direction perpendicular to the wollastonite reaction front accompanying the isotopic exchange between calcite and metamorphic fluid. To explain the carbon and oxygen isotopic depth profiles shown in Fig. 6, the fitting curves calculated using a simple semi-infinite one dimensional diffusion model (Crank, 1975) are applicable, and can be expressed by the following equation.

$$(C_x - C_1) / (C_0 - C_1) = \text{erf} \{ X / 2(Dt)^{1/2} \}.$$

where C_x is the concentration at some depth X , C_0 is

the initial concentration of the calcite, C_1 is the concentration at the wollastonite vein, D is the diffusion constant, t is the duration, and erf is the error function. The diffusion constant is normally dependent on temperature. The peak contact metamorphic temperature was estimated to be about 600°C, on the basis of oxygen isotopic fractionation between calcite and wollastonite (Wada *et al.*, 1998).

Assuming the oxygen self-diffusion constant for calcite by Farver (1994), at the temperature of 600°C, the duration for the lattice-diffusion for the profile shown by line B in Fig. 6, can be calculated to be in the order of 0.76×10^6 years. According to the depth profile in the calcite grain boundary reported by Wada (1988) and Arita and Wada (1990), to form a 300 μm oxygen profile the duration can be calculated to be in the order of 10^3 years.

As noted by Heinrich and Gottschalk (1994), the CO_2 produced by decarbonation reactions probably escaped through a semipermeable membrane of meta-argillite-marble boundary as an immiscible low-density $\text{H}_2\text{O}-\text{CO}_2$ fluid into overlying marble through grain-edge migration. These oxygen isotopic results around the wollastonite vein suggest migration of the metamorphic fluid was small and probably not perpendicular to but parallel to the aquifer, including the vein itself, which is similar to the fluid flow of high-density brine obtained by Heinrich and Gottschalk (1994). According to Holness and Graham (1991), during the infiltration of metamorphic fluid migration, the X_{CO_2} in the fluid was restricted in the medium around a temperature of 650°C. Our isotopic data suggest that metamorphic marble normally has an impermeable property and there was no infiltration and advective evidence around the wollastonite vein. Thus, carbon chemical species such as CO_2 or CO_3 ions in metamorphic fluid should migrate into crystalline marble mainly through body or lattice diffusion. On the other hand, water molecules can penetrate into the grain through grain boundary diffusion, as well as lattice diffusion. Thus the mass transfer in the marble around the wollastonite vein is mostly controlled by diffusion, specifically for carbon, and the observed profile represents a diffusion transport.

These estimations of the behavior of fluids that invaded the contact metamorphic aureole will provide information on the duration of fracture action

using isotopic micro-scale zonation at the fluid-rock isotopic front. These different behaviors of carbon and oxygen isotopic and chemical species will give the actual role of fluid chemistry in the fracture and the grain boundaries in marbles during deep crustal evolution.

Summary

Here I have presented a method for detecting "Mizu-michi" in sedimentary rocks and crystalline marbles in different situations based on studies carried out by our group on stable isotopes. As shown in this report, macro-scale and micro-scale stable isotopic studies on vein-filled minerals in the fractures formed by earthquakes and deformation processes will provide a powerful tool to identify the origins of crustal fluids and reaction processes in the fluid-country rock interactions. The micro-scale isotopic study on metamorphic marbles was started using secondary ion mass spectrometry (SIMS) techniques as shown in Graham *et al.*, (1998). The precision of the stable isotopic analyses using SIMS is still poor, and there is no zonation of carbon isotopes in marble, which was distinctly detected by conventional mass-spectrometric analyses. Furthermore, an age determination of such vein-filled fracturing events of the ductile rocks is essential. We should further develop the age determination only for mono-mineralic carbonate and quartz veins.

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