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Carbon and oxygen isotope measurement of carbonate molecule in spurrite [$Ca_5Si_2O_8(CO_3)$]

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Abstract Spurrite [$Ca_5Si_2O_8(CO_3)$], a calc-silicate mineral with a carbonate molecule, is a product of high-temperature contact metamorphism, a typical example of which is found at the Fuka contact aureole, Okayama Prefecture, Japan. We report here carbon and oxygen isotope composition of CO_2 released from the reaction of spurrite with phosphoric acid in the temperature range of 25℃ to 100℃. While reacting with the acid carbon isotopes did not fractionate, while oxygen isotope shows considerable isotope fractionation with varying reaction temperature, similar to other carbonate minerals. This suggests that the carbon and oxygen isotope measurements can be carried out using acid extraction method. In the Fuka contact aureole, carbon isotope fractionation of about 3‰ is observed between coexisting spurrite and coarse-grained calcite. If in equilibrium the carbon isotope fractionation between carbonate molecule in spurrite and calcite has the potential application as an isotope geothermometer. However, oxygen isotope distribution between calcite and spurrite could not be critically evaluated because of the uncertainties of source oxygen isotopes values of infiltrating fluids during the skarn formation and the fractionation of it between silicate and carbonate phases.

Key words: spurrite, skarn, contact metamorphism, carbon and oxygen isotopes, Fuka

Introduction

High-temperature skarn formation during the contact metamorphism of limestone results in the formation of a variety of skarn minerals in the $CaO - SiO_2 - CO_2$ system. Spurrite [$Ca_5Si_2O_8(CO_3)$] is one among them. However, the occurrence of spurrite is very limited in nature, due to the necessity of extraordinary high-temperature (~1000℃), specific silica activity and fluid composition during skarn formation (Joesten, 1974; Satish-Kumar *et al.*, 2004). Notable occurrences of spurrite skarn has been reported from Kilchoan (Agrell, 1965), and Christmas Mountains (Joesten, 1974, 1976) and Fuka, Okayama (Kusachi, 1975; Kusachi *et al.*, 1978). Skarn formation at Fuka has been studied principally for understanding its mineralogy and geochemistry, which subsequently resulted in the finding of several new minerals (*e.g.*, Henmi *et al.*, 1973, 1977). Element mobility and mechanism of skarn formation were the focus of earlier studies by Kusachi (1975) and Kusachi *et al.* (1978), where they concluded that lattice diffusion of elements was the prominent skarn forming mechanism. Although, mineralogical and geochemical studies have progressed, the role of fluids in the formation of spurrite skarn is unclear yet.

Studies on skarn formation elsewhere, have proved that high temperature reactive fluid is mostly $H_2O - CO_2$ in composition (Bowman *et al.*, 1985). H_2O is considered to be originally derived from the magma, whereas CO_2 is derived from the decarbonation reactions associated with skarn formation. In contrast with the widely reported low- to medium-temperature skarn (*e.g.*, wollastonite skarn) formation, the high-temperature skarns are associated with the formation of carbonate-bearing silicate minerals such as spurrite and tilleyite. In this case, a more complex situation arises because CO_2 is partly released from the system and partly retained in spurrite. The present study, the first of its kind, aims at the carbon and oxygen isotope measurement of the carbonate molecule in spurrite, and discusses the isotope systematics during high-temperature skarn formation.

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Occurrence and mineralogy

Fuka limestone mine is located 30 km west-northwest of Okayama city. Unaltered samples of spurrite skarn were collected from the third level of the mine, where clear contact relation between igneous rock, the skarn and the marble is observed. The skarn has two zones, yellow and gray zone. The yellow zone, named as wollastonite zone hereafter, is few centimeters in thickness and consists of wollastonite and garnet, whereas the gray zone, called spurrite zone hereafter, has few meters of width and composed mainly of spurrite.

Petrographic studies revealed that the wollastonite zone has a mineral assemblage of wollastonite + grossular + vesuvianite, whereas the spurrite zone has a mineral assemblage of spurrite ± vesuvianite ± tilleyite ± gehlenite ± schorlomite ± foshagite ± hillebrandite ± calcite. Tilleyite is mainly found near the boundary of the spurrite zone with marble, formed between spurrite and calcite and the grain size is smaller than spurrite. Foshagite and hillebrandite, which are secondary alteration products of spurrite and tilleyite, are found as thin veins. Gehlenite is mostly altered to vesuvianite or other opaque minerals. Vesuvianite and schorlomite are found sporadically in the skarn. Two types of calcite are observed in the spurrite zone. First type has coarse-grain size, similar to those found in the marble zone, whereas the second type is very fine-grained (few micrometers in size), which is observed in the cleavage and fractures of other minerals. Optical properties of spurrite and tilleyite are similar; however cathodoluminescence is a useful mean to distinguish between them. Spurrite shows green luminescence, tilleyite displays orange-red and calcite shows dark red luminescence under same intensity (Satish-Kumar *et al.*, 2006).

Representative chemical composition of spurrite and tilleyite were analyzed using an electron microprobe (JEOL-JXA733 at the Centre for Instrumental Analysis, Shizuoka University) are shown in Table 1. The results are consistent with the ideal composition reported in Deer *et al.* (1992) for both minerals.

Table 1 Representative mineral chemical analysis of spurrite and tilleyite (Sample No. 0109113F 4-3). Cation numbers were calculated on the basis of 9 oxygen atoms. CO_2 content was calculated stoichiometrically.

	Spurrite	Tilleyite
SiO_2	26.77	24.50
TiO_2	0.01	0.00
Al_2O_3	0.00	0.00
Fe_2O_3	0.00	0.03
MnO	0.05	0.00
MgO	0.00	0.01
CaO	62.72	56.75
Na_2O	0.10	0.00
CO_2^*	9.79	17.97
Total	99.45	99.26
Cations based on 9 oxygen atoms		
Si	1.99	2.01
Ti	0.00	0.00
Al	0.00	0.00
Fe^{3+}	0.00	0.00
Mn	0.00	0.00
Mg	0.00	0.00
Ca	5.00	4.98
Na	0.01	0.00
CO_2	0.99	2.01

*calculated

Experiments and results

Analytical method

Carbon and oxygen isotopic composition of calcite were measured using the method described in Wada *et al.* (1982, 1984). Calcite from specific sampling points, such as grain core or grain boundary were sampled from a cut and polished slab using a cutter knife. The powder was collected in steel thimble and dropped into phosphoric acid at 60℃ in an online reaction chamber, under vacuum conditions, which is connected to the inlet system of Finnigan MAT 250 mass spectrometer. Evolved gas was cryogenically purified to retain CO_2.

The measurement of carbon and oxygen isotopes of spurrite was carried out based on the procedure similar to dolomite/ankerite, as described in Nagai & Wada (1993). Aliquots of spurrite powder from same specimen were weighed and kept in a steel thimble at the bottom of glass tube having a small bulge, where phosphoric acid was stored. The glass tube was then evacuated and encapsulated. Since the relationship between reaction temperature, yield and fractionation for isotope measurements of spurrite is unknown, aliquots of same sample were reacted with phosphoric acid at varying temperature conditions of 25℃, 40℃, 60℃, 80℃ and 100℃. The released CO_2 was cryogenically purified and the volume measured using Hg-manometer in the inlet system of MAT-250 mass spectrometer. Purified gas was used for carbon and oxygen isotope measurements.

Results

Results of carbon and oxygen isotope compositions are summarized in Table 2 and Figure 1. Yield was calculated as the percentage of CO_2 gas produced during the reaction,

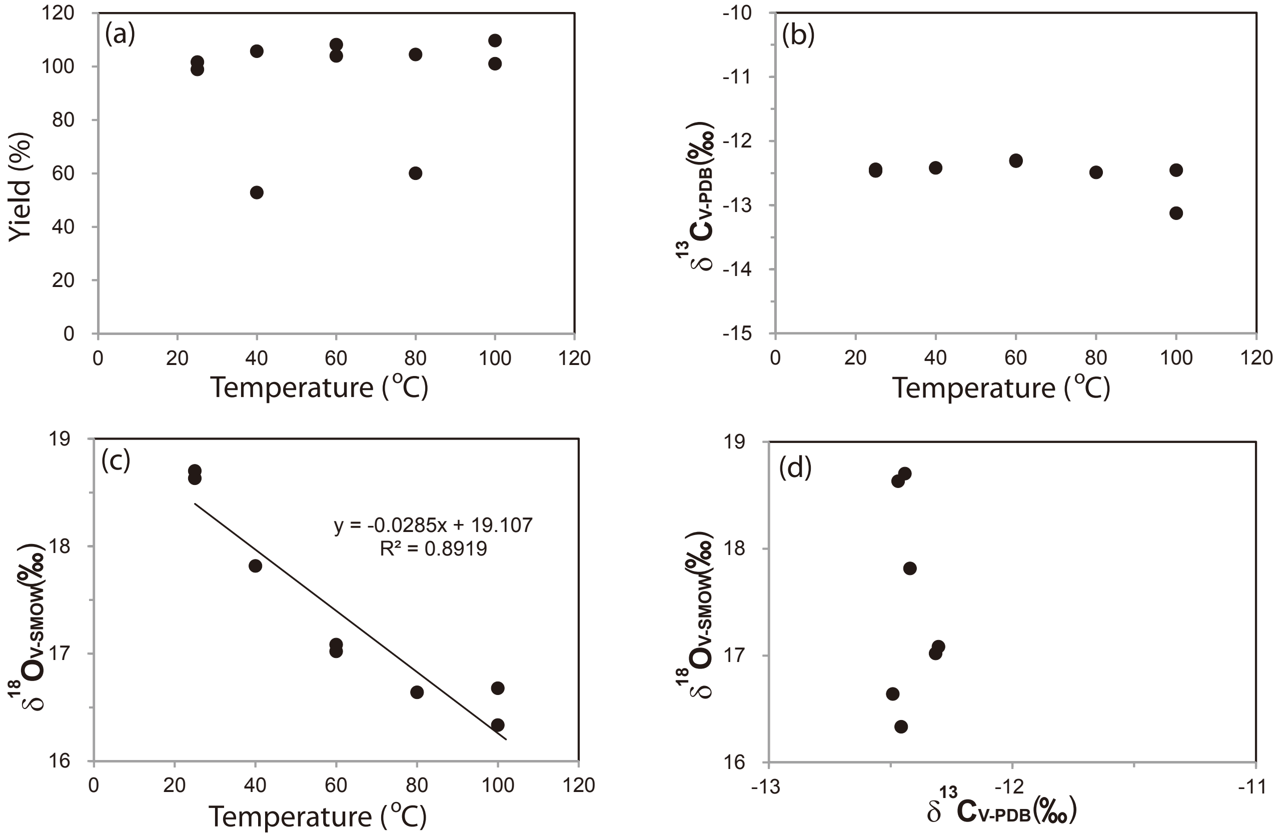

Fig. 1 Experimental results on the extraction of CO_2 from spurrite at varying temperature conditions. (a) Yield versus reaction temperature. Note that two of the experiments show very low yields possibly caused by the presence of other silicate mineral phases. (b) Variation of $\delta^{13}C_{V\text{-}PDB}$ values with reaction temperature. (c) Variation of $\delta^{18}O_{V\text{-}SMOW}$ values with reaction temperature. Similar to other carbonate minerals the oxygen isotopes show clear fractionation with lowering of $\delta^{18}O_{V\text{-}SMOW}$ values with increasing temperature of reaction. (d) Carbon versus oxygen isotope cross plot of all experimental results.

Table 2 Experimental results of spurrite under varying reaction temperatures. Yield relates to the percentage of generated CO_2 gas to that of the stoichiometrically calculated content.

Temperature (℃)	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}SMOW}$ (‰)	Yield (%)
25	–12.47	18.63	101.6
25	–12.44	18.70	98.9
40	–11.66	19.71	52.8
40	–12.42	17.82	105.7
60	–12.32	17.02	103.9
60	–12.30	17.08	108.1
80	–12.63	17.23	60.0
80	–12.49	16.64	104.4
100	–13.13	16.68	101.0
100	–12.46	16.33	109.7

with the stoichiometrically estimated CO_2 in spurrite. The yield of some samples exceeded 100% because of the possible presence of calcite inclusions, which should generate about five times larger volume of CO_2 gas than for spurrite. Also, in some experiments the yield was lower than 100% (Fig. 1a). We suspect that this was due to the presence of other silicate impurities such as schorlomite or vesuvianite.

The results obtained for extraction experiments under varying temperature shows that the $\delta^{13}C$ values (-12.52 ± 0.06‰) are similar irrespective of reaction temperature (Fig. 1b), with the exception one result at 40℃ showing anomalous yield (Fig. 1a) and isotope values (Table 2). However, the $\delta^{18}O$ values vary widely (16.33~19.71‰) suggesting a temperature dependent oxygen isotope fractionation during CO_2 extraction from spurrite (Fig. 1c). Considering the reaction rate, yield, reproducibility and convenience for direct comparison with the isotopic composition of calcite the reaction temperature for spurrite was chosen to be 60℃.

Carbon and oxygen isotope results of spurrite and calcite in the spurrite zone and calcite in the marble are given in Table 3. The $\delta^{13}C$ value of coarse calcite in the spurrite zone is –8.78 ± 0.24‰, and that of marble is +3.96‰ and

Table 3 Stable isotopic results of carbonate molecule in spurrite and calcite from Fuka contact aureole (Sample No. 0109113F 4-3).

Zone	Spurrite			Calcite	
	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}SMOW}$ (‰)	Yield (%)	$\delta^{13}C_{V\text{-}PDB}$ (‰)	$\delta^{18}O_{V\text{-}SMOW}$ (‰)
spurrite	–12.51	15.35	92	–8.43	11.68
spurrite	–12.12	15.41	99	–8.98	10.21
spurrite	–13.14	16.86	93	–8.73	11.40
spurrite	–13.36	16.31	104	–9.47	12.84
spurrite	–11.90	16.63	117	–8.06	12.31
spurrite	–12.10	16.79	89	–9.00	13.96
marble				3.96	24.03
marble				4.08	24.25

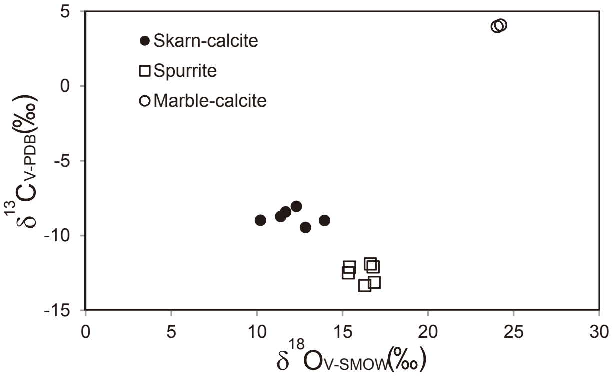

Fig. 2 The relationship of $\delta^{13}C_{V\text{-}PDB}$ and $\delta^{18}O_{V\text{-}SMOW}$ of carbonate molecule in spurrite (open square), coarse calcite within the skarn (filled circle) and calcite in the marble (open circle).

+4.08‰. The $\delta^{13}C$ values of spurrite were further lower than the calcite within the skarn, with an average of –12.51 ± 0.36‰.

The average $\delta^{18}O$ value of calcite in the spurrite zone is +12.07 ± 1.65‰ ($n = 6$), whereas the $\delta^{18}O$ value of spurrite is +16.23 ± 0.47‰ ($n = 6$). In the spurrite zone the $\delta^{18}O$ value of spurrite increases with an increase in $\delta^{18}O$ value of calcite.

The relationship between $\delta^{13}C$ and $\delta^{18}O$ values of spurrite and calcite in all zones are shown in Figure 2.

Discussion

Carbon and oxygen isotope measurement in spurrite

The yields of CO_2 gas from spurrite in most of our experiments were constant around 100%, regardless of reaction temperature. The relationship between reaction temperature and $\delta^{13}C$ values suggests that no carbon isotope fractionation occur during the reaction between acid and spurrite, similar to other carbonate minerals. This also implies that all CO_2 in the carbonate molecule of spurrite is released during the reaction with phosphoric acid. In the case of oxygen isotopes, the $\delta^{18}O$ values decreases with increasing reaction temperature, which is similar to other carbonate minerals such as siderite, ankerite or dolomite as reported in Sharma & Clayton (1965). However, the scatter of our results is much larger, which restricts us from a quantitative evaluation of oxygen isotope fractionation. The possible reasons for this large scatter might be the presence of microscopic calcite inclusions in spurrite and the fractionation of oxygen isotopes between oxygen in the carbonate molecule and the silicate molecule within the spurrite, which needs further experiments to solve.

Decarbonation induced carbon isotope fractionation in spurrite

We consider that coarse calcite crystals in the spurrite zone are possibly in equilibrium with co-existing spurrite during contact metamorphism. For the repeated measurements of the co-existing calcite and spurrite in the same sample, a consistent carbon isotope fractionation of about 3 to 4‰ was observed. Spurrite is formed by the decarbonation reaction between calcite and aqueous silica, during which 4 molecules of CO_2 are released and one is retained in spurrite, *i.e.*, 5calcite + $2SiO_2(aq)$ = spurrite + $4CO_2$. Our results show that the $\delta^{13}C$ value of spurrite is lower than that of calcite. A possible reason for this could be the difference in bonding strengths of carbonate molecule in spurrite and those in calcite. A simple decarbonation type isotope evolution model does not work in this case, since carbon is partitioned between the carbonate molecule in spurrite, the released CO_2 and those retained in the unreacted calcite. Carbon isotope fractionation between CO_2 and calcite, as reported in Chacko *et al.* (1991), is 3.17‰ at 1025K. Although the fractionation between calcite – CO_2 – spurrite is not known, as a first approximation we could assume that the $\delta^{13}C$ values we have obtained for spurrite and calcite in the spurrite zone represent equilibrium fractionation between spurrite, calcite and CO_2. If this is true and given that there is no other source of carbon than primary calcite, then spurrite retains more ^{12}C than the released CO_2.

Yoshino & Satish-Kumar (2001) observed a similar trend between scapolite and calcite in a calc-silicate rock, where carbon δ isotopic composition of scapolite is lower than the co-existing calcite, whereas oxygen isotopic composition of scapolite is slightly higher than that of calcite, as observed in the present study (Fig. 2). It is therefore plausible that measurable equilibrium carbon isotope fractionation exist between carbonate molecule in a carbonate-bearing silicate mineral and co-existing calcite, which has a potential to be developed as an isotope geothermometer.

The carbon isotope fractionation observed during decarbonation should also have an effect on the $\delta^{18}O$ values. However, in the case of oxygen, in addition to decarbonation, infiltration of H_2O fluid from the magma also causes oxygen isotope exchange. Furthermore, the CO_3 molecule in spurrite can partition oxygen between calcite ($CaCO_3$) and aqueous silica (SiO_2). In this study we have only measured the oxygen generated from the CO_3 component in spurrite, whereas the oxygen in the silicate molecule could not be measured. Studies on oxygen isotopic distribution between carbonate and silicate molecule in same silicate mineral has never been attempted before and hence difficult to ascertain. However, it is clear that the calcite has lower $\delta^{18}O$ value than carbonate molecule in spurrite. It's still unclear that which one or more of the processes, decarbonation or fluid infiltration or oxygen isotope partitioning between silicate and carbonate molecule, plays the dominant role in the distribution of oxygen isotopes during high-temperature skarn formation.

Conclusion

The $\delta^{13}C$ value of spurrite was measured successfully in the present study. Temperature dependence of fractionation in oxygen isotope during the reaction of spurrite with phosphoric acid was observed, but could not be evaluated because of large variations of isotopic values. Decarbonation reactions play an important role in the distribution of carbon isotopes during spurrite skarn formation, where spurrite has δ lower $\delta^{13}C$ values than associated calcite, implying a fractionation between these two phases. Regarding $\delta^{18}O$ values of spurrite, several factors need to be constrained such as decarbonation, fluid infiltration, oxygen isotope partitioning between silicate and carbonate molecule to evaluate the oxygen isotope distribution in skarn environments.

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References

Agrell S. O. (1965), Polythermal metamorphism of limestones at Kilchoan, Ardnamurchan. *Mineralogical Magazine*, **34**, 1–15.

Bowman J. R., O'Neil J. R. & Essene E. J. (1985), Contact skarn formation at Elkhorn, Montana. II: Origin and evolution of C-O-H skarn fluids. *American Journal of Science*, **285**, 621–660.

Chacko T., Mayeda T. K., Clayton R. N. & Goldsmith J. R. (1991), Oxygen and carbon isotopic fractionation between CO_2 and calcite. *Geochimica et Cosmochimica Acta*, **55**, 2867–2882.

Deer W. A., Howie R. A. & Zussman J. (1992), *Rock Forming Minerals 2nd edition*. Longman, London, 696p.

Henmi C., Kusachi I., Henmi K., Sabine P. A. & Young B. R. (1973), A new mineral bicchuite, the natural analogue of gehlenite hydrate, from Fuka, Okayama Prefecture, Japan and Carneal, County Antrim, Northern Ireland. *Mineralogical Journal*, **7**, 243–251.

Henmi C., Kusachi I., Kawahara A. & Henmi K. (1977), Fukalite, a new calcium carbonate silicate hydrate mineral. *Mineralogical Journal*, **8**, 374–381.

Joesten R. (1974), Local equilibrium and metasomatic growth of zoned calc-silicate nodules from a contact aureole, Christmas Mountains, Big Band region, Texas. *American Journal of Science*, **274**, 876–901.

Joesten R. (1976), High-temperature contact metamorphism of carbonate rocks in a shallow crustal environment, Christmas Mountains, Big Band region, Texas. *American Mineralogist*, **61**, 776–781.

Kusachi I. (1975), Occurrence and genesis of skarns at the Fuka North outcrop, the town of Bitchu, Okayama Prefecture. *Bulletin of School of Education, Okayama University*, **43**, 71–105.

Kusachi I., Henmi C. & Henmi K. (1978), Gehlenite-spurrite skarns at the Fuka West outcrop, the town of Bitchu, Okayama Prefecture. *Bulletin of School of Education, Okayama University*, **48**, 25–39.

Nagai Y. & Wada H. (1993), Development and applications of micro-scale isotopic analysis for metamorphic dolomites. *Geoscience reports of Shizuoka University*, **19**, 25–34.

Satish-Kumar M. Mori H. Kusachi I. & Wada H. (2006), Cathodoluminescence microscopy of high-temperature skarn minerals from Fuka contact aureole, Okayama, Japan. *Geoscience Reports of Shizuoka University*, **33**, 21–38.

Satish-Kumar M., Yoshida Y. & Kusachi I. (2004), The role of aqueous silica concentration in controlling the mineralogy during high temperature contact metamorphism: A case study from Fuka contact aureole, Okayama, Japan. *Journal of Mineralogical and Petrological Sciences*, **99**, 328–338.

Sharma T. & Clayton R. N. (1965), Measurement of O^{18}/O^{16} ratios of total oxygen of carbonates. *Geochimica et Cosmochimica Acta*, **29**, 1347–1353.

Wada H., Fujii N. & Niitsuma N. (1984), Analytical method of stable isotope for ultra-small amounts of carbon dioxide with MAT-250 mass spectrometer. *Geoscience Reports of Shizuoka University*, **10**, 103–112.

Wada H., Niitsuma N. & Saito T. (1982), Carbon and oxygen isotopic measurement of ultra-small samples. *Geoscience Reports of Shizuoka University*, **7**, 35–50.

Yoshino T. & Satish-Kumar M. (2001), Origin of scapolite in deep-seated metagabbros of the Kohistan Arc, NW Himalayas. *Contributions to Mineralogy and Petrology*, **140**, 511–531.