NOTE

A reconnaissance oxygen isotope study of clinopyroxenes from four Japanese skarn deposits

HIDEHIKO SHIMAZAKI¹ and MINORU KUSAKABE²

Geological Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo 113¹, and Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori-ken, 682-02², Japan

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Oxygen isotopic compositions are determined for eleven clinopyroxenes from the Kamioka (−2.4 ~ −0.4‰, SMOW), Tsumo (+5.0 ~ +7.0), Yaguki (−1.5 ~ +2.5) and Fujigatani (+10.5 ~ +10.8) skarn deposits in Japan. Oxygen isotope values of ore-forming fluids estimated from the obtained data on clinopyroxenes are generally in good agreement with those estimated from the published data on skarn calcites. Among the studied deposits, the skarns in the Kamioka and Yaguki mines were formed under the influence of fluids with considerably low oxygen isotopic ratios.

INTRODUCTION

Many recent papers have demonstrated that stable isotope studies are powerful to trace fluid sources and fluid-rock interactions in a variety of geologic environments. Since classical works by Shieh and Taylor (1969) and by Taylor and O'Neil (1977), stable isotope investigations of skarn deposits also have realized satisfactory results in interpreting skarn petrogenesis (e.g., Bowman *et al.*, 1985a, b; Brown *et al.*, 1985; Rose *et al.*, 1985).

According to these previous works, calcite crystals observed interstitially among skarn silicate minerals in deposits, called skarn calcite hereafter, have oxygen and carbon isotope values completely different from those of surrounding carbonate rocks, and in most cases have values defined by the fluids responsible for the formation of the skarn silicates. Morishita and Matsuhisa (1983) also recognized in a preliminary report on the Kamaishi Fe-Cu skarn deposits, that skarn calcites have rather constant oxygen and carbon isotope values, and are thought to have been precipitated in isotopic equilibrium with the solution and associated minerals such as magnetite and quartz in the deposits.

On the basis of these investigations, an

attempt started to estimate oxygen and carbon isotopic compositions of hydrothermal solutions responsible for major skarn deposits in Japan, using the isotopic data on skarn calcites from those deposits (Shimazaki *et al.*, 1985; Shimizu *et al.*, 1986). It is, however, not fully confirmed yet whether skarn calcites always have isotopic compositions equilibrated with fluids of main ore-forming stages in each deposit. Thus, the purpose of the present work is to know, although very preliminarily, isotopic compositions of silicate oxygen in some representative skarn deposits in Japan, and to check whether the data are concordant with those obtained in the study on skarn calcites.

EXPERIMENTAL

In order to estimate oxygen isotopic compositions of ore-forming fluids, eleven clinopyroxene samples were provided from four skarn deposits in Japan. Clinopyroxene is a main constituent of skarns in most deposits, and is noticed as a reliable recorder of the oxygen isotopic compositions of fluids prevailed (Brown *et al.*, 1985). Matthews *et al.* (1983) experimentally determined the temperature dependence of oxygen isotope fractionation factor between diopside and water, and recognized no

Table 1. Oxygen isotopic composition of clinopyroxenes from Japanese skarn deposits

Mine Name	Sample No.	$\delta^{18}\text{O}$ (‰) (SMOW)	Locality	Specimen
Kamioka	HS73051011	-0.4	Tochibora Adit, -300mL, No. 9 O.B.	Cpx sk with Zn-Pb ore
	HS83082704	-0.7	Tochibora Adit, -240mL, Sasabira O.B.	Cpx sk with Zn-Pb ore
	HS65071402	-2.4	Maruyama Adit, 200 mL, No. 1 O.B.	Cpx sk with Zn-Pb ore
Tsumo	HS75100306	+5.0	Maruyama Adit, -225 mL	Cpx sk with W ore
	HS71102504	+7.0	Maruyama Adit, -75 mL	Cpx sk with Cu ore
	HS62081101	+6.1	Maruyama Adit, -25 mL	Gar-cpx sk with Cu-Zn ore
Yaguki	HS65081709	+0.5	No. 1 O.B., 130 mL, W360	Barren cpx sk
	HS65080401	+2.5	No. 1 O.B., 250 mL, W60N2	Barren cpx sk
	HS65111801	-1.5	No. 2 O.B., 360 mL, W360	Cpx sk with Cu-W ore
Fujigatani	HS72081603	+10.8	Akemidani Adit, -100 mL, No. 2 O.B.	Cpx-gar sk with W ore
	HS72081620	+10.5	Akemidani Adit, -20 mL, No. 1 O.B.	Barren cpx-gar sk

Abbreviations – cpx: clinopyroxene, gar: garnet, L: mine level, O.B.: ore body, sk: skarn

significant difference in the fractionation data for diopside and hedenbergite.

Four skarn deposits were selected because each of them is a representative of different types of skarn deposits in Japan, that is, the Kamioka Zn-Pb, Tsumo Cu-Zn-Pb, Yaguki Cu-Fe-W and Fujigatani W deposits. Geology and mineralization of these deposits are reported in many previous papers: e.g., Okuno (1964) and Akiyama (1980) on the Kamioka, Shimazaki (1968a, b) and Sugaki *et al.* (1981) on Tsumo, Shimazaki (1969) and Ogawa and Shida (1975) on Yaguki, and Sato (1980) and Matsueda and Arai (1982) on Fujigatani deposits.

The skarn specimens were crushed, and cleavage pieces of clinopyroxene were picked up under the binocular. Oxygen in the clinopyroxene samples was extracted by the BrF_5 technique (Clayton and Mayeda, 1963). The pulverized samples of about 18mg each were placed in nickel reaction tubes, and were reacted with BrF_5 at 600°C for 11 hours. The outline of the gas preparation line used in the present study was given by Matsuhisa *et al.* (1971). Oxygen isotope ratios of obtained CO_2 gas were measured with a Nier-McKinney type mass spectrometer, and the results are given relative to the standard SMOW in terms of a conventional δ expression in per mil unit. The total uncertainty in $\delta^{18}\text{O}$ values in the present measurements, is estimated to be $\pm 0.2\text{‰}$ or better. Some samples were measured twice, and the results were identical within this error range.

Fig. 1. Oxygen isotopic compositions of clinopyroxenes from four Japanese skarn deposits, with those of fluids estimated from the data on clinopyroxenes and skarn calcites. Solid circle represents clinopyroxene (this study), and open circle skarn calcite (Shimazaki *et al.*, 1985; Shimizu *et al.*, 1986). Bar and dash lines show the ranges of oxygen isotopic compositions of fluids estimated from clinopyroxene and skarn calcite, respectively.

RESULTS AND DISCUSSION

Oxygen isotope data obtained are summarized in Table 1 with some comments on the occurrence of the specimens, and are plotted in Fig. 1 as solid circles. Although the whole range of isotopic values of clinopyroxenes is from -2.4 to $+10.8\text{‰}$, those from the same mine show relatively small variation of 2 to 4‰ , and seem to represent a range peculiar to each mining area.

As stated before, oxygen isotope data have been accumulated on skarn calcites from these

deposits (Shimazaki *et al.*, 1985; Shimizu *et al.*, 1986). Figure 1 includes comparison of oxygen isotopic compositions of fluids estimated from the clinopyroxenes and skarn calcites. The fractionation between clinopyroxene and water is taken as -1‰ (Matthews *et al.*, 1983) on the assumption that the skarns were formed at about 500°C . The fractionation between calcite and water is taken as 3‰ (O'Neil *et al.*, 1969) on the assumption that the skarn calcites were precipitated at about 400°C . Although no temperature estimation has yet been carried out on the studied clinopyroxene and calcite samples, approximate formation temperatures of $500^{\circ} \pm 50^{\circ}\text{C}$ for anhydrous skarn silicate assemblages, and of 400° – 300°C for quartz-calcite-hydrous mineral assemblages, are confirmed in various skarn deposits (e.g., Bowman *et al.*, 1985b; Brown *et al.*, 1985). The temperature dependence of oxygen isotope fractionation factor between clinopyroxene and water is so small that temperature estimation error, say $\pm 100^{\circ}\text{C}$, gives almost negligible effect on the estimated $\delta^{18}\text{O}$ values of fluids. The temperature dependence of fractionation factor between calcite and water is relatively large, especially in the lower temperature range. The fractionation between calcite and water is 5.5‰ at about 300°C . If skarn calcites, however, were precipitated above 300°C it could be concluded that oxygen isotopic compositions of fluids are not much different for the skarn silicates and skarn calcite stages in each mine. The fact gives a sound base for estimating oxygen isotopic compositions of ore-forming fluids from the data on skarn calcites.

There is, however, an exception such as the Tsumo mine where about 5‰ discrepancy in fluid compositions was obtained between those estimated from clinopyroxene and calcite. The discrepancy could not be explained by uncertainty in the estimation of formation temperatures of two minerals. Oxygen isotopic composition of fluids was most likely lowered when the skarn calcite stage was reached. In the deposits, hydrothermal fluids of diverse origins are supposed to have contributed to the forma-

tion and later modification of the ore deposits. Thus, oxygen isotopic compositions of fluids can be estimated from the isotopic data on skarn calcites, but an independent confirmation through analyses of skarn silicates is recommended.

Another remarkable feature shown in Fig. 1 is the prevalence of fluids with relatively low oxygen isotopic ratios for some deposits such as in the Kamioka and Yaguki mines. In fact, Wada (1978) has reported that $\delta^{19}\text{O}$ values for calcites in the Kamioka deposits distribute in the range of several per mil around zero. The Kamioka is one of the most productive mines in Japan, and the origin of the deposits has long been debated with a large spectrum of interpretations from modified Precambrian syngenetic deposits (Akiyama, 1980) to skarn deposits genetically related to latest Cretaceous to early Tertiary felsic igneous activity (Okuno, 1964). The fact that fluids with low $\delta^{18}\text{O}$ values prevailed not only at later stages but also at the skarn-forming stage, suggests continuous participation of meteoric water in the formation of the Kamioka deposits.

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