HYDROGEN ISOTOPE DETERMINATION OF FLUID INCLUSION WATER FROM EPITHERMAL VEIN QUARTZ : DO VALUES ACCURATELY REFLECT WATER OF DEPOSITION

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SUMMARY – Fine-grained quartz and adularia in the Hishikari (Japan) crustiform epithermal veins, contain up to –1 wt.%, excluding adsorbed and fluid inclusion water. Water extracted from the veins is predominantly from sub-micron size fluid inclusions in quartz which are the remnants of water from precursor hydrous silica polymorphs. Quartz-rich parts of veins have total water contents >0.5 wt.%, and constant 6D values (-75‰). These 6D values are lower than present day meteoric water (-50‰). Hydrogen isotope analyses of amorphous silica and water from geothermal power plants and natural springs suggest that a 20 to 0‰ fractionation occurs between the precursor silica polymorphs and water at epithermal temperatures (150°C to 200°C). Extraction of water from he-grained epithermal quartz is not considered to be a suitable technique for determining the δD_{H_2O} values of palaeo-geothermal waters.

1 INTRODUCTION

In ore deposits which lack suitable hydrous minerals, the hydrogen isotope composition of water extracted from fluid inclusions has frequently been used to characterize the δD value of palaeo-hydrothermal water (e.g., Sheets et al., 1996). However, anomalous δD values of fluid inclusion water in quartz, which cannot be easily explained by any plausible fluid source or interaction processes have been reported in several studies (Kelly and Rye, 1979; Charef and Sheppard, 1987; Gleeson et al., 1999). This technique assumes that the isotope values of water extracted from fluid inclusions reflect the unfractionated isotope value of the liquid from which the minerals precipitated, but just how reliable is this method for estimating δD_{H_2O} values?

In an earlier study of epithermal veins from the Hishikari Au-Ag deposit, Japan, Faure et al. (1998) demonstrated that the quartz and adularia, which are deficient in fluid inclusions, contain anomalous high concentrations of water (up to 1 wt.%), but the source of the water was unknown. Fournier (1985) suggested that many epithermal veins precipitated from hydrothermal solutions that were supersaturated with respect to quartz. This resulted in the deposition of amorphous silica which subsequently crystallized to quartz or an intermediate crystalline form such as opal CT chalcedony. Quartz textures such as mosaic, colloform, pseudoacicular, etc., have been interpreted to reflect crystallization, or recrystallization, from amorphous silica or other intermediate, unstable phases of silica (Sander and Black, 1988; Saunders, 1990, 1994; Dong et al., 1995). An underlying assumption in measurement of δD values of fluid inclusion water is that there is no fractionation between quartz and water (merely trapped), but does this assumption hold if the quartz was initially deposited as silica?

Here we present the results of degassing, FTIR and D/H analyses of water-rich quartz-adularia from the Hishikari epithermal deposit, Kyushu, Japan. Also, we report the magnitude of hydrogen isotope fractionation empirically determined for pairs of amorphous silica and coexisting thermal water at known temperatures taken from natural hot springs and geothermal power plants. We discuss the source of the water in Hishikari vein samples and possible mechanisms of hydrogen isotope fractionation in the course of the epithermal quartz formation, and the suitability of fine-grained, epithermal quartz for δD_{H_2O} value determination.

2 HISHIKARI EPITHERMAL AU-AG DEPOSIT

The Hishikari gold-silver deposit is classified as a low-sulfidation (Hedenquist, 1986) epithermal type and has an age extending between 1.25 and 0.6 Ma (Izawa et al., 1993). Previous studies on the deposit reported that there were no suitable hydrous minerals to obtain hydrogen isotope data to compliment the oxygen data measured from the silicate minerals (Matsuhisa and Aoki, 1994). In trying to resolve this we discovered that quartz and adularia contain an order of magnitude more water than would be expected for non-hydrous minerals (Faure et al., 1998). The source of the water was enigmatic, because quartz and adularia in the Hishikari epithermal veins typically have very few, small fluid inclusions. We have attempted to establish the source of this water and whether it could be used to accurately reflect the isotope composition of the water from which the quartz precipitated.

2.1 Mineralogy

Vein samples were collected from the mono-axial Ryosen **5** vein system at **4,** 10, 37 and 70 m levels in the Honko Deposit of the Hishikari mine. Minerals in the veins were identified by thin-section observations and X-ray diffractometry (XRD).

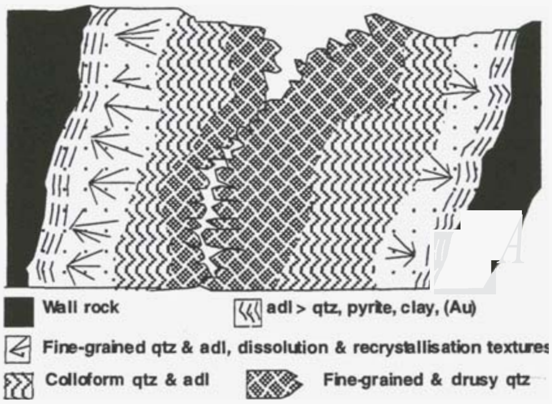

Figure 1. Sketch of a mono-axial vein (Keisen **40** m Level) from the Hishikari epithermal Au-Ag deposits. Vein width **14** cm. qtz = quartz; adl = adularia

Primary gangue minerals in the crustiform Hishikari veins consist predominantly of quartz and adularia, and rare calcite, truscottite, smectite and kaolinite. The principal ore minerals are pyrite, marcasite, chalcopyrite, argentite, electrum (average 70 wt. % Au) and naumannite-aguilarite (Izawa et al., 1990). Sulphide-, gold- and silver-rich bands ("ginguro") typically occur in the outer (early) parts of simple vein systems, parallel to the contact with the wall rock. Adularia:quartz usually decreases from the outer portions (1 to 0.8) of a vein towards a center of clear, drusy quartz (Fig. 1).

Excluding the central drusy quartz, adularia and quartz are usually very fine *grained* (1 µm to ~ 200 µm, usually c 50 µm), milky, typically colloform, and exhibit a range of textures. The quartz and adularia grains are typically randomly orientated and equant grains, showing no indications of earlier euhedral growth. Common textures are mosaic (penetrating grain boundaries), feathery, lattice-bladed, ghost-bladed pseudo-acicular and saccaroidal textures which have been interpreted as reflecting precursor amorphous silica, or an intermediate silica polymorph, and replacement of previous minerals (Dong et al., 1995). Mamillary surface textures, similar to those described from the Sleeper epithermal deposit, are also prevalent and also reflect a precursor amorphous silica (Saunders, 1990). **XRD** traces show that the quartz from Hishikari veins have *peak* positions and relative *peak* heights indistinguishable from pure and well crystallized quartz.

2.2 Water in Vein Samples

Incremental heating of Hishikari vein samples releases a significant amount of volatiles over a wide temperature range (Fig. 2). Cryogenic purification and manometric measurements of the volatiles, on a vacuum extraction line, reveal that they consist essentially of water. Hishikari quartz-adularia granules (**20** to **40#** size) contain up to about 1.5 wt.% water and samples crushed to < 80 µm (to minimize water from fluid inclusions) contain up to about 0.8 wt.% H_2O. These values are distinctly anomalous compared to granules of typical quartz or feldspar that have between 0.01 and 0.1 wt.% H_2O, depending on the size and number of fluid inclusions. Typically, fluid inclusions decrepitate at about the same or slightly higher temperatures as their temperature of homogenization. However, in the case of the Hishikari powder samples more than 70 % of the water is released **at** temperatures well above those typical of epithermal conditions (180°C to 250°C).

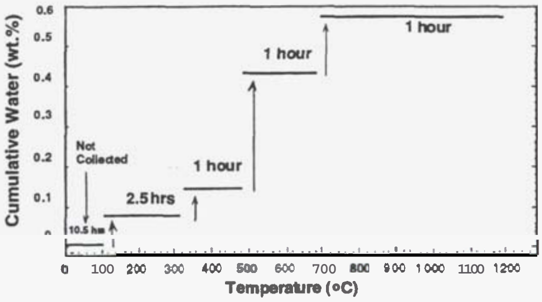

Figure 2. Cumulative amount of water extracted from **a** quartz-adularia sample crushed to a powder (<80 µm).

The release of large amounts of water particularly at about the α/β transition temperatures (570°C), indicates the importance of crystallographic displacement and reconstructive transformations in the release of the water. Quartz-rich portions of the Ryosen vein from Hishikari tend to have higher amounts of total water (~ 0.5 to 0.8 wt.%) and adularia dominant parts have relatively lesser amounts of water (~ 0.2 to **0.6** wt.%; Fig. **3).** A small proportion of hydrogen (<5 wt.% of the total water), not as H_2O, is released at temperatures greater than 600°C.

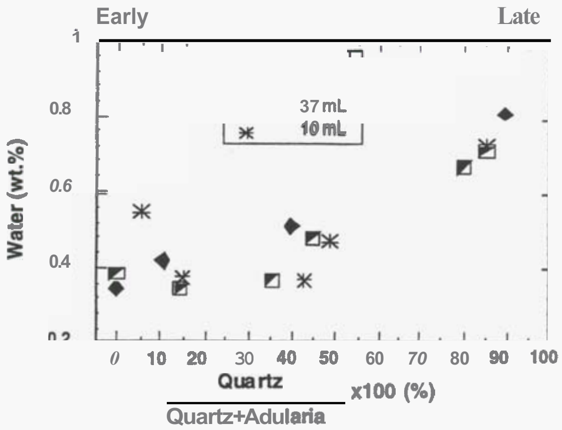

Figure 3. Weight percent water extracted after 2 hours of outgassing at 120°C from powdered Hishikari vein samples, related to quartz content.

2.3 Fourier Transformation Infrared Analyses

Fourier transformation infrared (FTIR) analysis in the IR wavelength region (2500 cm^{-1} to 4000 cm^{-1}) reveals a broad peak at about 3400 cm^{-1}, consisting of several overlapping peaks associated with molecular water (Fig. 4A). Freezing the samples in a N_2 atmosphere to progressively lower temperatures (down to -190°C) shifts the molecular water peak (3400 cm^{-1}) gradually toward the ice peak (3220 cm^{-1}; Fig. 4B), again showing the presence of molecular water, in spite of the fact that no fluid inclusions *are* visible using a standard light transmitting microscope.

Unlike FTIR scans at IR wavelengths, scans at near-IR wavelengths have the advantage that they can distinguish between hydrogen in molecular water (5200 cm^{-1}; O-H vibrations) and silanol type hydrogen (4500 cm^{-1}; Si-O-H and/or Al-O-H vibrations). Analysis at near-IR wavelengths of Hishikari samples again identifies the presence of large amounts of water, and shows that hydrogen is predominantly in the form of molecular water rather than silanol group hydrogen (Fig. 5).

We believe that the excess water in the veins is probably in sub-micron size inclusions. The water was trapped during the crystallization of the precursor hydrous silica which was subsequently crystallized to quartz. Textural evidence from the quartz supports a silica polymorph precursor.

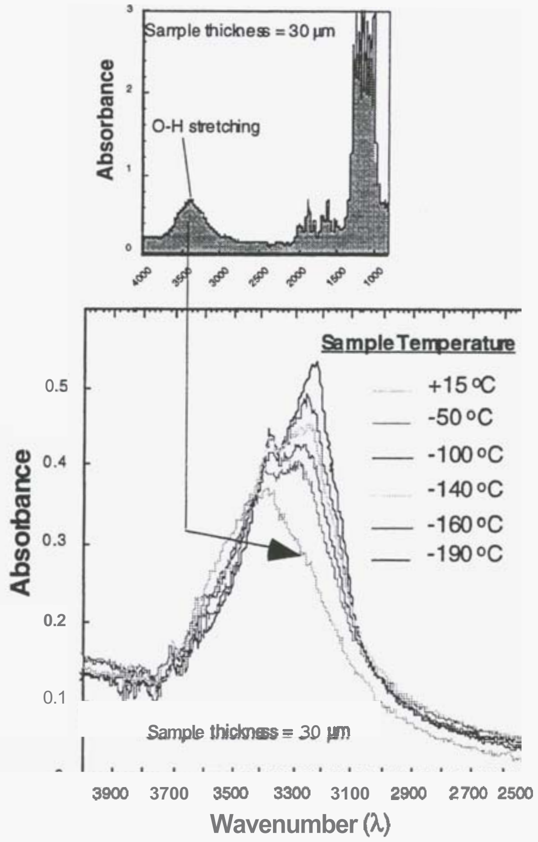

Figure 4. FTIR analysis in the IR wavelength region (2500 cm^{-1} to 4000 cm^{-1}). **A** Full spectrum. **B** Freezing sample gradually shifts water peak (3400 cm^{-1}) toward the ice peak (3220 cm^{-1}).

2.4 D/H of Water Extracted from Quartz and Adularia

Water was extracted from quartz-adularia samples after outgassing for at least 5 hours at 120°C. The reproducibility of hydrogen isotope results is improved markedly by crushing the samples to a fine powder less than 80 μm (Faure et al., 1998), hence removing larger fluid inclusions. Volatiles are released from the sample by heating up to 1200°C until extraction is complete. The D/H ratios of hydrogen gas produced from water (see Hedenquist et al., 1998 for method) are reported in the familiar δ-notation in per mil (‰) relative to V-SMOW (Fig. 6).

Waters extracted from later stage quartz-rich samples have higher and more consistent δD values (-75‰) as compared to early, adularia-rich samples (-115 to –95‰) (Fig. 6). The variation of δD values may indicate that hydrothermal fluids at the early vein forming stage were isotopically depleted relative to that of the later, barren stages of the veins, or that the variation reflects the change in the proportion of

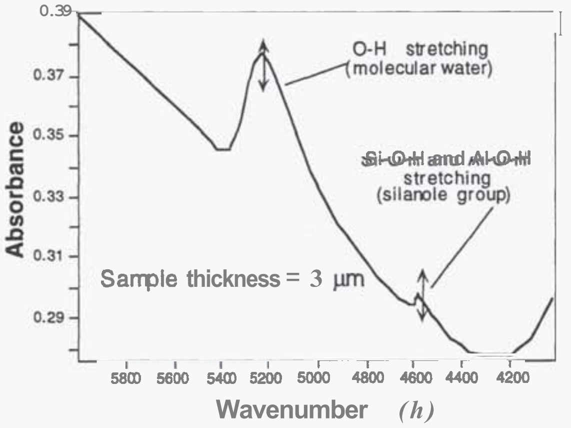

Figure 5. FTIR spectrum at near-IR wavelengths for Hishikari quartz-adularia. Arrows indicate range of variation of peak heights from eighteen samples.

the different sources of the water; micro-inclusions, hydrous mineral inclusions and minor hydrous minerals (Faure et al., 1998). Although the exact cause of this variation is not certain at present, we prefer the latter explanation, mainly because the total water extracted is considerably less in the adularia-rich samples (Fig. 3).

If the δD values of water extracted from the vein samples accurately reflect values of palaeo-geothemal waters, then the hydrothermal waters may have isotopically exchanged with the host sediments (Shimanto Supergroup; δD values ~ -140‰) or the ore-forming fluid (or a part of it) may have originated from water released from the basement sedimentary rock at the onset of formation of the epithermal deposit (Imai et al., 1998). Alternatively it is possible that the low D/H ratios are a result of isotope fractionation during multiple processes of initial deposition of water-rich amorphous silica from the mineralizing fluid, and partial water loss by later crystallization of the amorphous silica to quartz. If the latter is the case, we need to evaluate hydrogen isotope fractionation associated with these processes for estimating the original isotopic composition and the origin of the mineralizing fluid. Water dissolved in amorphous silica is loosely bound to the silicate structure and the hydrogen could have isotopically fractionated with respect to the surrounding free water.

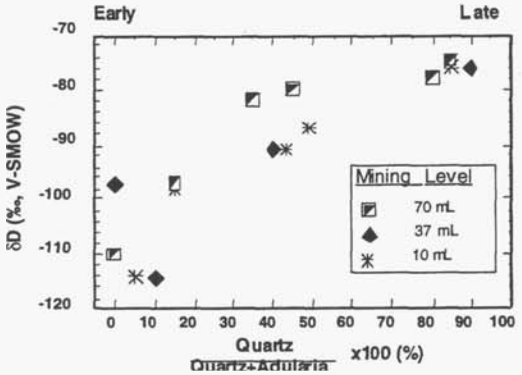

Figure 6. δD values of water extracted from quartz-adularia samples as, shown in Figure 3.

3 ISOTOPE FRACTIONATION BETWEEN SILICA & HYDROTHERMAL WATER

Nine pairs of amorphous silica (silica scale) and water samples coexisting at known temperatures between 85°C to 155°C were collected from geothermal power plants and natural hot springs in Japan and New Zealand. The sample descriptions and temperature data are as follows:

(1) A hot spring at Osorezan, northern Honshu, Japan - amorphous silica, precipitated onto a plastic plate over one year (1996-1997), was collected from the outflow of a near neutral pH, boiling spring with a water temperature of 95°C;
(2) An aging tank at the Otake geothermal power plant in Kyushu, Japan - water temperatures at the sampling points were 95°C and 85°C;
(3) A wellhead steam separator and a pipe leading to a reinjection well at the Hatchobaru geothermal power plant in Kyushu, Japan - the temperature of the water precipitating the silica after phase separation was estimated to be about 150°C, and water before reinjection had a temperature of 93°C;
(4) A pipe after the wellhead steam separator and a drainage pipe at the Mori geothermal power plant in northern Japan - the temperature of the water in the drainage pipe was 95°C and the water after steam separation was estimated to be 155°C;
(5) A drainage pipe at the Onikobe geothermal power station, northern Japan - the water temperature was 95°C, and
(6) The Rotokawa geothermal field, New Zealand - the temperature of the water was 89°C.

3.1 D/H Measurement of Water from Hydrothermal Silica

Air-dried silica samples were crushed to a fine powder using a mortar and pestle and checked for purity by X-ray diffraction spectrometry prior to isotopic analysis. For hydrogen isotope analyses, powdered samples were heated for at least 5 hours at 120°C in a vacuum line, and volatiles released during this procedure were pumped away to remove adsorbed or loosely bound water. Water was extracted from the silica in the same method as the Hishikari quartz-adularia. All analyses were done in duplicate, or repeatedly until replicates were better than ± 3‰, and results are reported as averages.

The analytical results suggest that a fractionation of about 20 to 70‰ does occur at temperatures of 85°C to 155°C (Fig. 7). The fractionation factors (α) between amorphous silica and geothermal water are given by

$$\alpha = (1+10^{-3}\delta D_{silica})/(1+10^{-3}\delta D_{water}) \qquad (1).$$

The relationship of ln a to temperature appears to be linear and inversely proportional (Fig. 7). XRD analysis of the Hatchobaru 93°C sample showed trace amounts of kaolinite, hence the data for this sample is not included in the calculation for the linear regression. The temperature of water from the well head separators at Hatchobaru (about 150°C) is only an estimate, and may be a cause of small errors in the calculation of the fractionation factor. Assuming that the fractionation between the silica and water is linearly extrapolated to higher temperatures and that fractionation between silica polymorphs is minimal, the expected fractionation at about 200°C would be about W‰.

4 DISCUSSION

As shown above, the 6D value of water extracted from the Ryosen 5 vein dominated by fine-grained quartz, is consistently –75‰. Assuming that silica precipitated between temperatures of about 200°C and 150°C, a maximum fraction of about 20‰ is expected between the silica and water. A δD value of about –55‰ is calculated for the coexisting thermal water at about 150°C. This value is approximately the same as the present day local meteoric water (-50‰). However, if the silica was in isotopic equilibrium with thermal water at about 200°C, the D/H fractionation between silica and the thermal water would be zero, then the δD value of the thermal water is calculated to be –75‰, which is too low as compared with present-day local meteoric water, suggesting that other fractionation processes may have occurred. Amorphous silica from geothermalpower stations has about 6 wt.% water, whereas the Hishikari quartz has about 1 wt.%. It is conceivable that during the crystallisation of silica polymorphs loss of water resulted in a fractionation of D/H ratio, with D-depletion of the remaining water.

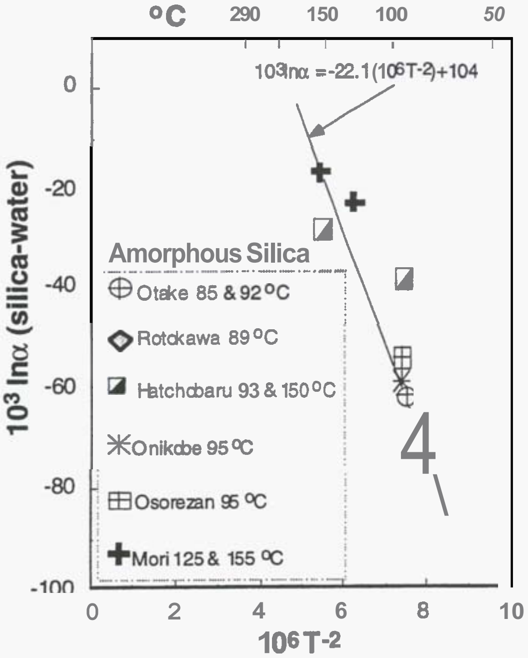

Figure 7. Near linear relationship between hydrogen isotope fractionation (ln α) of water extracted from amorphous silica and water from which silica precipitated at temperatures between 85 and 155°C.

5 CONCLUSIONS

We propose that the water extracted from the Hishikari epithermal quartz-adularia is present predominantly in quartz within sub-micron size inclusions as molecular H_2O that was trapped during rapid growth of the starting silica or polymorph of silica, which later crystallized to quartz. The 6D values of bulk water extracted from the Ryosen 5 vein samples are consistently less than –75‰.

Measurements of D/H of water extracted from amorphous silica that precipitated in hot natural springs and geothermal power plants suggest that a D/H fractionation of 20 to 0‰ could occur between the precursor silica polymorphs and water at epithermal temperatures (150°C to 200°C). Based on the D/H isotopic fractionation between silica and water determined empirically in this study, the δD values of water in isotopic equilibrium with the Hishikari precursor silica at 150°C is calculated to be –55‰, which is very close to that of the present-day local meteoric water (-50‰). However, if temperatures of about 200°C is assumed, very little D/H isotopic fractionation occurred between the primary silica polymorphs and water and the mineralizing fluid might have been significantly lower in 6D value than present-day local meteoric water. Fractionation could also have occurred as a consequence of partial dehydration during the crystallisation of the silica polymorph to quartz, which modified the initial δD value of water trapped in the minerals.

Evidence from Hishikari epithermal veins indicate that they have incorporated large quantities of fractionated water, because the veins were primarily deposited as hydrous silica polymorphs which were crystallized to quartz. Empirical evidence indicates that hydrogen isotope fractionation does occur between silica and water at temperatures < 200°C. Water extracted from fine-grained epithermal quartz is, therefore, not consided a reliable technique for determining the δD_{H_2O} values of palaeo-geothermal waters.

6 ACKNOWLEDGMENTS

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