Lithium–strontium isotope and heavy metal content of fluid inclusions and origin of ore-forming fluid responsible for tungsten mineralization at Takatori mine, Japan

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Ore-forming fluid trapped in vein quartz as fluid inclusions from tungsten ore at the Takatori mine was extracted by a crush-leach technique. The trace metal content and isotopic composition ($\delta^7\text{Li}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio) of inclusion fluids were measured. Although quartz single crystals can host fluid inclusions associated with different generations, careful selection of analytical samples made it possible to separate the temporal mineralization stages. We succeeded in reconstructing the evolution of the ore-forming fluid from the results of chemical analyses. $\delta^7\text{Li}$ values of the ore-forming fluid were between -2.6 and $+7.9\text{‰}$, gradually increasing in the later stages. The early-stage fluid characterized by low $\delta^7\text{Li}$ values was derived from magma with a meta-sedimentary source (S-type granite). During precipitation of Li-bearing minerals, the $\delta^7\text{Li}$ value of the ore-forming fluid became larger. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of early-stage ore-forming fluid was 0.7202 to 0.7276 , suggesting that the fluid responsible for tungsten mineralization was derived from S-type magma, and this magma had a different origin from the granitic rocks widely distributed in the mining area.

Keywords: fluid inclusion, lithium isotope, initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, Takatori mine, tungsten mineralization

INTRODUCTION

Tungsten, one of the most important strategic materials in present-day industries, has been recovered from a variety of ore deposits. They are grouped into seven types: vein/stockwork, skarn, porphyry, strata-bound, disseminated, placer and brine/evaporate deposits. Among them, skarn and vein/stockwork deposits host 40 and 34% of known world tungsten ore reserves, respectively (Werner *et al.*, 1998). Because most skarn and vein type tungsten deposits are associated with granitic intrusive rocks, magmatic fluid is the most probable source for tungsten and related ore metals. However, the contribution of the magmatic component to the ore-forming fluid responsible for tungsten mineralization, its temporal importance, and its relation to the source of ore metals are largely controversial (e.g., Breiter *et al.*, 1999; Dolníček *et al.*, 2012). In the present study, one of the most typical Japanese vein-type tungsten deposits at the Takatori mine was selected,

and ore-forming fluid was extracted from fluid inclusions hosted in quartz crystals. Isotopic data for Li and Sr, in addition to the heavy metal content of the ore-forming fluid, were determined in order to elucidate the origin and temporal changes of the fluid. To our knowledge, this is the first such study that has been applied to hydrothermal tungsten deposits.

There have been several pioneering studies to determine the isotopic composition of ore-forming fluid trapped as fluid inclusions. Banks *et al.* (2000) measured Cl isotopes in fluid inclusions and discussed the magmatic nature of the ore-forming fluid. Analysis of hydrogen isotopes from vein quartz in epithermal gold deposits at the Hishikari mine suggested a meteoric origin for the fluid (Imai *et al.*, 1998). On the basis of Rb/Sr isochrons, geochronological research was carried out for fluid inclusions (Shepherd and Darbyshire, 1981). Teng *et al.* (2006) measured $\delta^7\text{Li}$ for fluid inclusions in pegmatite quartz crystals. Although all of these studies demonstrated that isotopic analysis of fluid inclusions is convincing method to apply to hydrothermal ore deposits, a consistent methodology has not yet been fully established. Because the amount of inclusion fluid that is extracted is very small, problems related to contamination are a concern. In the present study, we examined the

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Fig. 1. Location and geological map of the Takatori mining area (modified after MITI, 1987).

validity of crush-leach extraction of inclusion fluid for application to the study of hydrothermal ore deposits.

GEOLOGICAL BACKGROUND

Regional geology

The tungsten deposit of the Takatori mine is located at Shirosato Town, Ibaraki prefecture. The Jurassic Yamizo Group, composed of alternating beds of shale and sandstone, siliceous shale and bedded chert is exposed in this area (Fig. 1). The Yamizo Group has a general strike of N45°E and a dip of 45°NW, and comprises the Kunimiyama, Takatori and Ayuta formations. The Takatori formation which hosts the tungsten deposits contains three sections: a chert-dominated lower section, a sandstone-dominated middle section and a chert-dominated upper section. The ore deposit at the Takatori mine is mainly contained within the middle section (Ikeda *et al.*, 1983).

There are two types of intrusive rocks in the Yamizo Group. The first is the Iwafune granodiorite, which is exposed in a region about 4 km northeast of the mine (Fig. 1). The second is Inada type granite, which is widely exposed in a region about 13 km south of the mine. Although no igneous rock has previously been reported in the vicinity of the mine, Ogasawara *et al.* (1994) suggested that a hidden leucocratic granitic body lies to the south of the deposit. This is based on the fact that aplite veins that have undergone greisenization were found in drilling cores at the south of the deposit. They also suggested that the low-gravity anomaly observed 3 km southwest of the mine is due to the presence of leucocratic granite (MITI, 1987).

Ore deposit

The ore deposit at the mine is composed of several

veins distributed within the area of 900 m (E-W) × 500 m (N-S). Two groups of veins exist, one steeply dipping with a strike of N45°W and the other gently dipping to N10°-55°W; the former veins are more fertile.

The No. 7 vein, where the samples used in the present study were obtained, is the most important vein in the mine, and extends about 900 m along the strike and about 300 m along the dip, respectively. The width of the vein is variable, with a maximum of about 2 m. Ore minerals observed in the No. 7 vein are wolframite, pyrite, arsenopyrite and chalcopyrite, with accessory amounts of sphalerite, galena, stannite, pyrrhotite and cassiterite. Quartz is the dominant gangue mineral and is accompanied by small amounts of lepidolite, fluorite, topaz, rhodochrosite, calcite, sericite and kaoline minerals. The nature of the veins has been described by Kikuchi and Tokukura (1951), Otsuka *et al.* (1963) and Sakamoto (1985). These studies have revealed that tungsten mineralization (wolframite precipitation) occurred during the early stage of vein formation. Ikeda *et al.* (1983) classified the vein quartz into semitransparent and milky white categories, noting that the anhedral semitransparent quartz is closely associated with wolframite. Wolframite is the most significant ore mineral in the mine, becoming more abundant toward the wall-rock side of the vein (Fig. 2) and the crystals are sometimes partly exposed in the form of druse.

The history of mineralization in the No. 7 vein is characterized by an early wolframite-topaz-fluorite-muscovite stage (Stage-1), an intermediate sulfide-fluorite stage (Stage-2), a late cassiterite stage (Stage-3), and a final rhodochrosite-calcite-clay stage (Stage-4). Throughout all of these stages, quartz remains the dominant gangue mineral. The occurrence of these stages and the paragenesis of the vein are schematically shown in

Fig. 2. Paragenesis of the No. 7 vein, Takatori mine. A) Schematic sketch of the vein (modified after Ikeda et al., 1983). B) Paragenetic diagram for samples of this study.

Fig. 2. The age of the mineralization is estimated at 68.7 Ma on the basis of K/Ar dating of muscovite in the No. 7 vein (Shibata and Ishihara, 1974).

SAMPLES

Samples for this study were taken from a collection possessed by the University of Tsukuba. These samples were obtained from the No. 7 vein at levels between -4 (60 m above sea level) and -6 (sea level). In order to extract the inclusion fluid, quartz sample from Stages-1 to -4 were carefully selected. The minerals associated with the quartz are shown in the paragenetic diagram in Fig. 2.

Stage-1 quartz crystals are anhedral with sizes of <1 cm, and are usually associated with wolframite. Most of this quartz is milky, and transparent parts are rarely found. Stage-2 and -3 quartz crystals were separated from middle part of the vein and some of them are euhedral prismatic crystals of several cm in size, and occur in druse. The drusy quartz associated with Stage-4 is euhedral and

is covered by clay minerals that precipitated during the final stage of the mineralization.

The quartz contains several generations of fluid inclusions. The primary Stage-1 inclusion is a liquid-vapor 2-phase type with dimensions of 10–25 μm . Liquid CO_2 -containing 3-phase inclusions are rarely observed. Stage-2 and -3 fluid inclusions are 2-phase types, with shapes varying from ellipsoid to indeterminate, with dimensions of 20–150 μm . Stage-4 inclusions are 2-phase liquid-vapor type. The number of inclusions in the vein quartz increases in the later stages. The milky nature of Stage-1 quartz makes it difficult to observe fluid inclusions in polished thin sections, while Stage-2, -3 and -4 quartz is clear, so that inclusions can be easily observed. No daughter minerals were observed in inclusions from any of the stages. The homogenization temperature and salinity of fluid inclusions obtained from microthermometric analyses are as follows; 327°–349°C and 4.8–6.3 wt% NaCl eq. for Stage-1, 316°–341°C and 2.4–5.8 wt% NaCl eq., and 298°–322°C and 1.9–2.9 wt% NaCl eq. for Stages-3 and -4, respectively (Masukawa and Hayashi, 2008).

Table 1. Crush-leached metal weight (μg) represented as those from 1 g quartz

Sample No.	Li	Al	Cr	Mn	Ni	Cu	Zn	Rb	Sr	Cs	Ba	Nd	W	Pb
Stage-1														
M7	7.87	365	2.54	127	0.904	2.20	7.07	9.83	40.2	2.65	3.40	5.54	403	0.340
M10	21.8	1000	4.01	298	0.084	2.54	27.3	35.5	1.18	2.96	11.5	0.01	481	0.412
M11	43.5	1660	9.62	541	4.35	31.1	26.9	83.2	184	5.48	30.6	18.2	771	0.710
M18	2.22	280	0.072	326	0.036	3.48	2.88	4.41	0.29	0.463	1.56	0.01	457	1.63
M19	8.72	805	0.419	117	0.163	16.5	10.8	11.5	6.25	2.99	3.17	0.317	64.0	0.725
M21	86.5	5530	0.427	769	2.27	70.1	27.0	213	95.0	5.77	89.4	11.4	100	2.20
Stage-2														
M4	3.06	274	8.46	35.0	0.065	1.32	7.97	5.10	1.29	3.04	3.10	0.005	36.3	0.357
M5	4.75	776	5.24	75.2	0.220	2.01	11.7	7.01	11.0	3.42	1.85	0.169	7.71	0.404
M12	1.84	122	0.565	25.1	0.017	0.413	3.06	3.70	0.070	0.174	1.24	—	12.0	0.026
M13	6.88	202	0.608	12.5	0.087	1.03	10.2	2.80	2.87	4.32	0.788	0.082	9.24	0.659
M16	9.44	449	0.553	316	0.124	5.11	17.4	18.1	1.09	3.03	5.83	0.017	48.6	0.842
M17	5.41	463	0.215	61.1	0.096	1.39	6.98	2.38	1.77	3.41	1.01	—	1.89	0.630
Stage-3														
M3	2.88	82.1	3.34	4.59	0.061	1.58	1.03	3.60	0.267	1.22	1.24	—	1.20	0.697
M8	2.26	66.4	0.653	1.86	0.005	0.068	4.51	1.60	0.221	0.194	0.992	0.031	3.57	0.031
M14	3.20	65.1	0.484	1.82	0.033	0.377	3.78	3.28	0.500	0.355	1.40	—	0.432	0.031
M20	3.84	96.3	0.284	3.55	0.019	0.525	2.32	2.72	0.284	0.446	1.17	—	7.04	0.138
Stage-4														
M6	1.55	54.8	1.45	1.53	0.126	0.458	6.39	3.07	0.179	0.330	0.901	—	0.156	0.114
M15	6.07	47.5	0.660	1.85	0.041	0.902	8.83	5.79	0.078	0.947	0.430	—	—	0.072

ANALYTICAL METHODS

Crush-leach method to extract ore-forming fluid

All quartz samples analyzed in this study were in the form of thin sections (1 mm thickness) that were first subjected to microscopic observations. Following double-sided polishing, the quartz grain sizes were observed to be 0.5–1 mm. Contaminant minerals were removed by picking under a binocular microscope. After microscopic observations, the quartz samples were washed ultrasonically using 2% ultrapure 100-grade (hereafter, UP100-grade) HNO_3 (Kanto Chemical Co.) and 18.2 M Ω -grade water prepared by a Millipore purification system (hereafter, Milli-Q water). Subsequent procedures such as column separation were undertaken under a filtered airflow (cleanliness level better than class 1000). The clean laboratory and all analytical equipment used in this study were located at the Kochi Core Center.

After drying, about 0.1 g of the quartz grain sample was crushed to a fine powder using an agate mortar. Subsequently, 0.2 ml 2% ultrapure-grade (hereafter, UP-grade) HNO_3 (Kanto Chemical Co.) was added into the agate mortar. We assumed that the elements recovered during the crush-leach process represent ore-forming fluid that is preserved in fluid inclusions and/or at grain boundaries. The recovered solution was filtered through 0.2 μm PTFE syringe filters to remove any particulates. All equip-

ment used for the crush-leach process, including the agate mortar, pestle and filtered syringe, were washed repeatedly using 15% electronic-grade (EL-grade) HNO_3 and 18.2 M Ω Milli-Q water.

After evaporation of the recovered fluid, the sample was dissolved in 3.1 ml 5% UP-grade HNO_3 . Most of recovered solution was used for Li and Sr isotopic measurements, while a portion (about 1/30) was used for determination of chemical compositions. The weights of the recovered Li, Mn, Rb, Sr, W, Pb and Ba were determined using a quadrupole inductively coupled plasma mass spectrometer (ELAN-DRC II, PerkinElmer) with diluted sample solutions containing an internal indium standard. The uncertainties for all measurements are better than $\pm 3\%$, as estimated from the reproducibility (2RSD) of standard solutions whose salt contents are higher than those of the analyzed samples.

Li and Sr isotopic measurements

Lithium and strontium isotope ratios were measured using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS; Neptune, Thermo Sci. Co.) and a thermal ionization mass spectrometer (TIMS; Triton, Thermo Sci. Co.), respectively, after two-step column separation. Most of the analytical protocols have been documented previously in Nishio *et al.* (2010). The first-stage separation for Li and Sr was carried out using a

Table 2. Delta ^7Li values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios

Sample No.	$\delta^7\text{Li}$ (‰)	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}_0^{\text{a}}$	Li (ng) ^b	Sr (ng) ^c
Stage-1					
M7	1.08	0.726437	0.725763	54	275
M10	1.19	—	—	72	—
M11	-1.31	0.728337	0.727089	90	378
M18	-2.54	—	—	31	—
M19	0.73	0.730584	0.725540	35	25
M21	-2.65	0.733779	0.727592	75	82
Stage-2					
M5	-1.61	0.726668	0.724914	13	31
M13	7.85	0.727480	0.724796	53	22
M16	0.59	—	—	34	—
M17	1.68	0.723874	0.720170	42	14
Stage-3					
M3	5.22	—	—	40	—
Stage-4					
M15	4.53	—	—	13	—
JB-2	4.55	0.7036786	—	6	130

a) Calculated on the basis of mineralization age of 68.7 Ma.

b) The Li quantities recovered for Li isotopic analyses.

c) The Sr quantities recovered for Sr isotopic analyses.

quartz glass column filled with 6 ml Bio-Rad AG50W X8 (200–400 mesh) cation-exchange resin. The second Li purification was carried out using a quartz glass column filled with 0.8 ml Bio-Rad AG50W X12 (200–400 mesh) cation-exchange resin, while the second Sr purification was carried out using a polypropylene column that was filled with 1 ml Eichrom Sr resin (50–100 μm).

The $^7\text{Li}/^6\text{Li}$ ratios were measured using the MC-ICP-MS, which was equipped with a high-sensitivity skimmer cone, “x-cones”. The purified Li solution was diluted in 2% ultrapure HNO_3 to about 10 ng g^{-1} Li and was introduced into the MC-ICP-MS through an Aridus desolvating system (Cetac Technologies) with a microconcentric PTEE nebulizer (100 $\mu\text{l min}^{-1}$). Before measurements were carried out on each sample and the standard, the beam intensities at an m/e value of 6 and 7 for 2% HNO_3 were measured as the background for 30 s. Subsequently, the beam intensity ratios at m/e values of 6 and 7 were measured 30 times in succession (4 s per ratio) after 1 min of initial uptake of the sample solution. A sample injection time of less than 4 min requires 0.4 ml of sample solution, equivalent to 4 ng Li. The Li standard solution (NIST L-SVEC) was measured before and after sample analysis to correct for instrumental mass bias. The typical ^7Li intensity of the 10 ng g^{-1} Li standard solution was 20 pA (a 2 V signal with a $10^{11} \Omega$ resistor), which is much higher than the background level of 0.2 pA. The measured $^7\text{Li}/^6\text{Li}$ ratios were expressed as permil deviations from the NIST L-SVEC standard: $\delta^7\text{Li} = [({}^7\text{Li}/$

$^6\text{Li})_{\text{sample}}/({}^7\text{Li}/^6\text{Li})_{\text{L-SVEC standard}} - 1] \times 1000$. The uncertainty in the $\delta^7\text{Li}$ value was better than $\pm 0.3\text{‰}$, as estimated from the long-term reproducibility of $+8.29 \pm 0.27\text{‰}$ (2 SD, $n = 22$), during a period from May 2007 to August 2008, for our 10 ng g^{-1} in-house Li standard (Kanto Chemical Co.).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured using the Triton TIMS after purified 10–300 ng Sr samples were loaded on single tungsten filaments together with a tantalum activator solution (Birck, 1986). The long-term reproducibility of the 80 ng Sr and 8 ng Sr was 0.7102507 ± 0.0000066 (2 SD, $n = 36$) and 0.7102577 ± 0.0000114 (2 SD, $n = 7$), during a period from May 2007 to May 2009, with respect to the NIST SRM 987 standard, respectively.

RESULTS

Table 1 lists the trace element amounts determined by crush-leach analysis, which are represented as elemental weights per 1 g of quartz. The concentrations of trace metals are not absolute values, since inclusion fluids were extracted from a cluster of quartz grains with an unknown mass of the total inclusion fluid. The metallic ratios for each sample rather than metal concentration are effective values, and the metal concentrations are normalized by that of Cs in the plots shown in Fig. 4. Cs is believed to be an incompatible element, and thus a good index for the evolution of the ore-forming fluid (Audétat and Pettke, 2003).

Table 2 lists the $\delta^7\text{Li}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The Li quantities recovered for the Li isotopic analysis are also listed in Table 2, and range from 13 to 90 ng Li, which are sufficient to determine $\delta^7\text{Li}$ values to within $\pm 0.3\text{‰}$, as previously mentioned. We also analyzed the $\delta^7\text{Li}$ value of a small amount of Li (6 ng Li) after 2-step column chromatography. This was a portion of a solution (180 ng Li) decomposed from abundant JB-2 rock (0.023 g). The $\delta^7\text{Li}$ value for rock standard JB-2 has been reported in many papers, and the average value was given by Rosner *et al.* (2007) as $+4.78\text{‰}$ ($n = 12$), which agrees with the value of $+4.55\text{‰}$ we obtained for the 6 ng Li sample, within the $\delta^7\text{Li}$ uncertainty of $\pm 0.3\text{‰}$.

The Sr quantities recovered for Sr isotopic analyses are listed in Table 2, and range from 14 to 378 ng Sr. Our $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for 130 ng Sr from rock standard JB-2 was 0.7036786 (Table 2).

In order to evaluate the contamination introduced during the elemental abundance measurements, procedural blanks, which are the elemental weights recovered in the crush-leach process in the absence of a sample, were determined. Figure 3 shows the procedural blanks of trace elements, together with the weights recovered during actual sample analyses. As can be seen, the procedural blanks of the elements plotted in Fig. 3 are significantly

Fig. 3. Results of blank test. Note that blank values are 1–2 orders of magnitude lower than those of samples.

less than those recovered during sample analyses.

The Li and Sr blanks obtained by crush-leaching are 160 pg Li and 100 pg Sr, respectively. The Li and Sr blanks obtained by 2-step column chromatography are 7 pg Li and 50 pg Sr, respectively. Thus, the Li and Sr procedural blanks for the overall isotopic analysis procedure are 167 pg Li and 150 pg Sr, respectively. The amounts of Li and Sr recovered from the samples are 13–90 ng Li and 14–378 ng Sr, respectively, which are significantly higher than the procedural blanks.

DISCUSSION

Chemical composition of inclusion fluids

Selected metal/Cs ratios with respect to the Ba/Cs ratio are plotted in Fig. 4. The Li/Cs, Al/Cs and Rb/Cs ratios correlate well with the Ba/Cs ratio with correlation factors of $R^2 = 0.736$, 0.777 and 0.949 , respectively. The good correlations among these metals suggest that they have the same origin and undergo similar behavior during the evolution of the ore-forming fluid. Since Li, Rb and Ba are selectively captured in feldspar, plagioclase would be expected to host these trace elements, and Al is the major constituent of plagioclase. Our data suggests that the ore-forming fluids were in equilibrium with plagioclase throughout the entire mineralization process. On the other hand, the heavy metals, Mn, Cu and W, do not show any correlation with the Ba/Cs ratio. In addition, no significant correlation between a pair of any heavy metal/Cs ratios was observed.

Based on the results of experimental studies to determine the partition coefficients of metals, $D_{\text{fluid/melt}}^{\text{metal}}$, between a coexisting peraluminous melt and a supercritical fluid, the partition coefficients were found to decrease in the order of $\text{Cu} > \text{Mn} > \text{W} > \text{Ba}$ (Candela and Piccoli, 1995). These experiments were carried out using natural haplogranite, synthetic quartz–albite granite or quartz–albite–orthoclase systems as starting materials at temperatures of 750–880°C and pressures of 1–2 kb (Carron and Lagache, 1980; Holland, 1972; Candela and Holland, 1984; Manning and Henderson, 1984). The value of $D_{\text{fluid/melt}}^{\text{Cu}}$ varies from ~1 for low-salinity fluids, up to ~50 at high salinities, and is determined by the relationship $D_{\text{fluid/melt}}^{\text{Cu}} = 9.1 \times m_{\text{Cl}^-}$ (where m_{Cl^-} indicates molality of Cl^-) (Candela and Holland, 1984). The fluid/melt partitioning behavior of W is not as well constrained as that of Cu, although experiments suggests its partition coefficient is low, $D_{\text{fluid/melt}}^{\text{W}} = \sim 1$, and is independent from m_{Cl^-} (Manning and Henderson, 1984; Keppler and Wyllie, 1991). The salinity of the fluid inclusions during Stages-1 to -4 is moderate at 6 to 2 wt% NaCl equivalent (Masukawa and Hayashi, 2008), and gradually decreases in the later stages. Concentrations of heavy metals in fluid inclusions obtained in this study are in the order of $\text{Mn} > \text{W} > \text{Cu} > \text{Ba}$ (Table 1), with no apparent systematic variations (Fig. 4). The erroneously high values of the Mn/Cs (1700) and W/Cs (713) ratios for the Stage-1 fluid (see Figs. 4D and 4F) are probably due to contamination from fine inclusions of wolframite crystals; values for other heavy metals for this sample are in a similar range to those for other samples. The irregular relation among heavy metals suggests that the concentration of metals in the ore-forming fluid is not controlled by the partition coefficient between the fluid and melt, nor has the initial fluid composition been changed during its separation from the magma and transportation to the ore-deposition site. Since real magmatic fluid has a high salinity and commonly contains NaCl daughter crystals, the moderate salinity measured in previous studies (Masukawa and Hayashi, 2008; Enjoji, 1972; Takenouchi and Ichikuni, 1982) suggests a possibility that the ore-forming fluid of the Takatori deposit is not a pure magmatic fluid directly separated from magma.

According to a synchrotron X-ray fluorescence (SXRF) analysis of a single fluid inclusion hosted in quartz carried out by Masukawa and Hayashi (2008), the concentration of heavy metals in the inclusion fluid was very high during Stage-1, at >1000 ppm for Fe, Mn, Cu, Zn and W. The heavy metal concentration suddenly drops during Stage-2 and gradually decreases during the later stages. This excursion of the heavy metal content suggests that the contribution of magmatic fluid to the ore-forming fluid was large during Stage-1, but declined sud-

Fig. 4. Correlations between Ba/Cs and heavy metals/Cs atomic ratios. A) Li/Cs, B) Al/Cs, C) Pb/Cs, D) Mn/Cs, E) Cu/Cs, F) W/Cs, G) Sr/Cs, H) $\delta^7\text{Li}$ and I) initial $^{87}\text{Sr}/^{86}\text{Sr}$.

denly during Stage-2 and later stages. Masukawa and Hayashi (2008) suggested that the ore-forming fluid during Stage-1 and those during the later stages have different origins.

Li isotope of inclusion fluids

The $\delta^7\text{Li}$ values shown in Fig. 5 lead to a similar conclusion as above. For the Stage-1 fluid, $\delta^7\text{Li}$ is between -2.6 and $+1.2\text{‰}$, for the Stage-2 fluid between -1.6 and $+7.9\text{‰}$, and for the Stage-3 and -4 fluids between 5.2 and 4.5‰ . A number of granitic and rhyolitic rocks have been analyzed, and they showed generally light but variable isotopic compositions: $\delta^7\text{Li} = -1.2$ to $+3.9\text{‰}$ for international rock standards (G-2, JG-2 and JR-2) (James and Palmer, 2000; Chan and Frey, 2003; Pistiner and Henderson, 2003). Granitic rocks in eastern Australia have

also been analyzed, and the data showed a wide range of $\delta^7\text{Li}$ values from -1.4 to $+8.0\text{‰}$ (Bryant *et al.*, 2003; Teng *et al.*, 2004). Among these granitic rocks, those derived from meta-sedimentary source rocks exhibit lighter average compositions (S-type granites; $\delta^7\text{Li} = -1.4$ to $+2.1\text{‰}$) than I-type granites ($+1.9$ to $+8.0\text{‰}$).

The behavior of Li isotopes during the generation of magmatic fluid exsolved from hydrous granitic magma is not fully understood. Theoretical and experimental studies on Li isotope fractionation factor between supercritical fluids and melt at magmatic temperatures are scarce. Recent experimental studies (Wunder *et al.*, 2007, 2011) and *ab initio* calculations (Kowalski and Jahn, 2011) suggest that isotopically heavy fluid ($\delta^7\text{Li} > \sim 2\text{‰}$ with respect to coexisting solid) is formed during reaction with spodumene, however fluid becomes light ($\delta^7\text{Li} < \sim 1.5\text{‰}$)

Fig. 5. Change of $\delta^7\text{Li}$ values of ore-forming fluids through Stages-1 to -4. Note that $\delta^7\text{Li}$ values become larger toward later stages.

with respect to coexisting solid) in the case reaction with staurolite at temperatures $>700^\circ\text{C}$. Although there remains significant uncertainty, these experimental studies probably suggest that the degree of Li isotopic fractionation between the fluid and melt is not very large. Recently, Teng *et al.* (2006) measured the $\delta^7\text{Li}$ values of fluid inclusions leached from quartz in Tin Mountain pegmatite from South Dakota. The $\delta^7\text{Li}$ values of the fluid inclusions were found to be $\sim 4\text{‰}$ higher than that of the bulk rock, and they suggested a fractionation factor of $\sim 4\text{‰}$ between the fluid and melt. They also calculated Li isotopic fractionation modeled by Rayleigh distillation during fluid exsolution from granitic melt, and suggest generation of $\delta^7\text{Li} = \sim 4\text{‰}$ heavier fluids from H_2O saturated peraluminous melt of $\sim 14\%$ H_2O content. If similar relation is applicable in this study, the $\delta^7\text{Li}$ values of -2.6 to -1.2‰ for the Stage-1 fluid probably suggest the coexistence of magma with $\delta^7\text{Li} = -6.6$ to -5.2‰ . The low $\delta^7\text{Li}$ value can be reasonably explained by the presence of magma from a meta-sedimentary source (S-type granite).

The magmatic contribution to the ore-forming fluid is also consistent with oxygen isotope data. Morishita and Matsuhisa (1982) showed oxygen isotope data for vein quartz ($\delta^{18}\text{O} = +13\text{‰}$) and Li-bearing muscovite ($\delta^{18}\text{O} = +10$ to $+11\text{‰}$). Shibue *et al.* (2005) also measured the oxygen isotopic composition of vein quartz at $\delta^{18}\text{O} = +9.7$ to $+10.5\text{‰}$. Based on $\delta^{18}\text{O}$ values for H_2O calculated using a fractionation factor between water–silicate minerals and the temperature of ore deposition, they concluded that the $\delta^{18}\text{O}_{\text{fluid}}$ values agree with those for magmatic

fluids derived from S-type granitic rock.

As seen in Fig. 5, the $\delta^7\text{Li}$ values gradually increase in the later stages, to -1.6 to $+7.9\text{‰}$ for the Stage-2 fluid and $+4.5$ to 5.2‰ for the Stage-3 and -4 fluids. In the ore-forming environment at the Takatori mine, a potential source material for relatively high $\delta^7\text{Li}$ values is country rock. The country rock of the study area is composed of meta-sedimentary rocks of the Jurassic Yamizo Group. They were derived from seafloor sediments, and such rock are known to have high Li concentration with $\delta^7\text{Li} = \sim 14\text{‰}$ (Chan *et al.*, 1992). Although an accurate $\delta^7\text{Li}$ value for the country rock is not known, lithium exchange between the fluid and the country rock and/or mixing with ground water would increase the $\delta^7\text{Li}$ value of the fluid.

Precipitation of Li-bearing minerals will also increase $\delta^7\text{Li}$ of ore-forming fluid. Although concentration of metals shown in Table 1 is not absolute values, however, concentrations of heavy metals such as W and Mn remarkably decrease in later stages. Masukawa and Hayashi (2008) revealed that concentration of heavy metals decreased in later stages from the SXRF analyses of fluid inclusion. Therefore, metal content data of Table 1 roughly agree with that of concentration of metals in ore-forming fluid. The concentration of Li in the ore-forming fluid gradually decreases in the later stages (Table 1), and this would suggest precipitation of Li-bearing minerals such as lepidolite. The degree of lithium isotope fractionation between Li-bearing minerals and an aqueous solution is controlled by intricate factors such as temperature, pressure and m_{Cl^-} . Recently, Wunder *et al.* (2007) investigated Li isotopic fractionation between synthetic Li-mica of the system $\text{K}_2\text{O}-\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ and hydrothermal fluid at temperatures between 350° and 500°C . They observed a temperature-dependent fractionation, with fluids being heavier than coexisting Li-mica by $\delta^7\text{Li} = 1.5-5.3\text{‰}$. Since Li-mica is a typical accessory mineral in the tungsten ore of this study (Fig. 2), precipitation of Li-mica might cause a shift to higher $\delta^7\text{Li}$ in the ore-forming fluids during the later stages. SXRF analyses of single fluid inclusion by Masukawa and Hayashi (2008) show concentration of heavy metals in the late-stage fluids, especially the Stages-3 and -4, are very low. Fluids of Stages-3 and -4 must be residual solution after precipitation of ore-forming minerals that includes Li.

Sr isotope of inclusion fluids

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ($^{87}\text{Sr}/^{86}\text{Sr}_0$) were calculated on the basis of a mineralization age of 68.7 Ma (Shibata and Ishihara, 1974), and are shown in Fig. 6. They vary from 0.7255 to 0.7275 for the Stage-1 fluid and from 0.7201 to 0.7249 for the Stage-2 fluid; thus, Stage-2 fluid has lower $^{87}\text{Sr}/^{86}\text{Sr}_0$ ratios than those for the Stage-1 fluid. The $^{87}\text{Sr}/^{86}\text{Sr}_0$ ratios for the Stage-1 fluid agree with the values of 0.7260 and 0.7270 obtained for fluorite (Nakano

Fig. 6. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ore-forming fluids of Stage-1 and -2. Data for fluorite and country rock (Nakano, 1990; Nakano *et al.*, 1987) are also shown.

et al., 1987) from the No. 7 vein. Because Rb content in fluorite is negligible, above $^{87}\text{Sr}/^{86}\text{Sr}$ values can be assumed as initial ones. Nakano *et al.* (1987) and Nakano (1990) also measured $^{87}\text{Sr}/^{86}\text{Sr}$ for wall-rock sandstone and reported slightly lower initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7120 to 0.7280, compared to those obtained for vein minerals.

Origin of ore-forming fluid

Our initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, especially those for the Stage-1 fluid, suggest a magmatic source for the ore-forming fluid. The Stage-1 fluid exhibits high $^{87}\text{Sr}/^{86}\text{Sr}_0$ values, low $\delta^7\text{Li}$ and high W/Cs atomic ratios (Fig. 7), all of which can be reasonably well explained by it having a magmatic source. Granitic rocks from the Yamizo Mountains, where the Takatori mine is located, have $^{87}\text{Sr}/^{86}\text{Sr}_0$ ratios of ~ 0.7102 (Shibata and Takagi, 1989), and can be classified as I-type rocks. If Sr isotope compositions have been preserved during partial melting of source rock, the difference of $^{87}\text{Sr}/^{86}\text{Sr}_0$ ratios between this study and that of granitic rocks of the Yamizo Mountain suggests different magma. Under oxidizing conditions, such as those applicable to the I-type magma, the efficiency of extracting tungsten from a source rock into magma is relatively low. Under reducing conditions, however, tungsten behaves as an incompatible element in term of its crystal-melt partitioning behavior and its concentration will increase during crystal fractionation (Candela, 1992). When magma forms from the partial melting of metasedimentary rocks, the melt will be relatively hydrous and will tend to crystallize at deep in the crust. Such a melt is also likely to be paralminous and relatively reduced since it will have equilibrated with metasedimentary material that might have contained organic matter. Because tungsten is incompatible under reduced conditions its concentration will rise in the residual melt. When the H_2O -fluid phase exsolve it will interact with a highly differentiated melt

Fig. 7. Correlations of W/Cs atomic ratio with $\delta^7\text{Li}$ (A) and $^{87}\text{Sr}/^{86}\text{Sr}_0$ (B).

that is significantly enriched in tungsten (Robb, 2005).

The results of the present study suggest that the ore-forming fluid responsible for the tungsten mineralization has a genetic relation with S-type magma, and this conclusion agrees with behavior of tungsten in magmatic-hydrothermal system. This magma responsible for tungsten mineralization at the Takatori deposit has a different origin from the granitic rocks widely distributed in the Yamizo Mountains.

SUMMARY

The results of this study can be summarized as follows.

Ore-forming fluid trapped in vein quartz as fluid in-

clusions was extracted by a crush-leach technique. The trace metal content and isotopic composition ($\delta^7\text{Li}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio) of inclusion fluids were measured. Although quartz single crystals can host fluid inclusions associated with several generations, careful selection of analytical samples made it possible to separate the temporal mineralization stages, and the evolution of the ore-forming fluid could be traced from the chemical analysis data.

The quartz-wolframite vein at the Takatori mine was formed by four stages of hydrothermal mineralization. The ore-forming fluid during the early stage (Stage-1) is characterized by low $\delta^7\text{Li}$ values and high heavy metal content. This fluid is not a pure magmatic fluid separated from hydrous magma, but is closely related with granitic magma.

The $\delta^7\text{Li}$ values for the Stage-1 fluid are between -2.6 and $+1.2\text{‰}$, those for the Stage-2 fluid between -1.6 and $+7.9\text{‰}$, and those for the Stage-3 and -4 fluids between $+4.5$ and 5.2‰ ; $\delta^7\text{Li}$ gradually increases in the later stages. The low $\delta^7\text{Li}$ values for the Stage-1 fluid can be reasonably well explained by magma with a meta-sedimentary source (S-type granite). During precipitation of Li-bearing minerals, the $\delta^7\text{Li}$ of the ore-forming fluid increased, and these fluids became trapped in the Stage-2, -3 and -4 inclusions.

The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the ore-forming fluids is 0.7255 to 0.7275 for Stage-1 and 0.7201 to 0.7249 for Stage-2; thus, the Stage-2 fluid has a lower $^{87}\text{Sr}/^{86}\text{Sr}$ value than that of Stage-1. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the Stage-1 fluid suggests that the ore-forming fluid responsible for tungsten mineralization was derived from S-type magma, and this magma had a different origin from the granitic rocks widely distributed in the mining area.

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