Experimental study on metasomatism in huebnerite – CaCl₂ solution system

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Experiments on metasomatism in a system comprising huebnerite and aqueous CaCl₂ solution were performed at 130, 150, and 170 °C. SEM observations revealed the formation of euhedral crystals of scheelite replacing huebnerite in all experiments. The replacement texture of huebnerite by scheelite was classified as rim replacement texture. Although the molar volume ratio of replacing mineral to replaced mineral was 1.12 for the present study, huebnerite was replaced by scheelite. This suggests that the influence of molar volume ratio is small on the metasomatism of huebnerite to scheelite, which has not been expected in previous studies. Our results also suggest that the metasomatism of huebnerite to scheelite can be achieved if the CaCl₂ concentration in the solution and the reaction temperature are sufficiently high. The apparent rate constant k for huebnerite dissolution in the metasomatism is approximately 10^{-9} – 10^{-6} mol l⁻¹ s⁻¹; the activation energies are 9.6, 20.7, and 31.2 kJ/mol for CaCl₂ concentrations of 0.01, 0.10, and 1.00 mol/l, respectively. The precipitation of scheelite can be the rate-determining process of the metasomatism during the initial stage when the W concentration in the solution is high.

Keywords: Metasomatism, Replacement texture, Huebnerite, Scheelite, Aqueous CaCl₂ Solution, Dissolution, Precipitation, Activation energy

INTRODUCTION

Tungsten, which is one of the most important rare metals, is mainly used to produce filaments and superhard alloys. The commercially important minerals of tungsten are divided into two groups—one is scheelite (CaWO₄) group (space group *I4₁/a*) and the other is wolframite [(Fe, Mn) WO₄] group (space group *P2₁/c*). The end members of the wolframite series are ferberite (FeWO₄) and huebnerite (MnWO₄). In wolframite, the Fe/(Fe + Mn) ratio is 0.2–0.8. The complete solid solution series between ferberite and huebnerite is known to occur in nature. The metasomatism of scheelite to the wolframite group and vice versa is also known to occur in nature (William, 1945; Baumer, 1985; Uchida et al., 1989).

An experimental study on tungstates has indicated that the metasomatism of scheelite to huebnerite is influ-

enced by pH (Baumer, 1985). Uchida et al. (1989) have reported that the metasomatism of scheelite to ferberite, huebnerite, or wolframite occurs more frequently at high temperatures (400–600 °C) than at low temperatures. In their study on the metasomatism of scheelite to huebnerite, Tamura et al. (2002) explained that metasomatism occurs at 100–150 °C, and they classified the replacement texture of scheelite by huebnerite as pseudomorphic replacement texture. The value of the apparent rate constant k for scheelite dissolution in the metasomatism of scheelite to huebnerite is found to be 10^{-6} – 10^{-4} mol l⁻¹ s⁻¹, and the activation energies are 15.3, 24.1, and 18.5 kJ/mol for MnCl₂ concentrations of 0.01, 0.10, and 1.00 mol/l, respectively (Tamura et al., 2002). In contrast, metasomatism of huebnerite to scheelite has not been reported thus far. Most of the previous researches have focused on the metasomatism of tungstates at temperatures of 400–600 °C (Baumer, 1985; Uchida et al., 1989) while the formation temperature of tungstates is reported to be between 250 and 350 °C (e.g., Tsunoda and Shimizu, 1995). Therefore, the metasomatism of tungstates is expected to occur

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at temperatures lower than 400–600 °C.

We examined the metasomatism of huebnerite to scheelite in the temperature range of 130–170 °C, which is significantly lower than the formation temperature of tungstates. The reaction solution used in this study was aqueous CaCl_2 solution. The chloride ion is the major anion in the fluid inclusion associated with W mineralization (Shibue, 1987, 1993). We have found that the metasomatism of huebnerite to scheelite is successful even at 130–170 °C within a reaction time of 72–672 h.

EXPERIMENTAL

Starting Material

We used huebnerite obtained from the Pasto Bueno mine, the Republic of Peru, as the starting material. Huebnerite is reddish-brown to reddish-black in color and typically occurs as flat prismatic crystals with a length of several centimeters. Quartz coexists with huebnerite. A large number of pores, each with a diameter of 20 μm , were observed on the polished surface vertical to the (010) plane under a reflection microscope (Fig. 1). However, no compositional zonal structure was observed in the studied samples. The chemical formula of huebnerite determined by using an electron probe microanalyzer (EPMA, JEOL JXA-733, Ocean Research Institute The University of Tokyo) was $\text{Mn}_{0.98-1.01}\text{W}_{1.02-0.99}\text{O}_4$ ($\text{O} = 4$) with an average formula of $\text{Mn}_{1.00}\text{W}_{1.00}\text{O}_4$ (number of analysis = 63). The samples used as starting materials were either powdered or chipped. Huebnerite crystals were crushed to form gravel (diameter: 2–5 mm). Each huebnerite grain was studied under a stereoscopic microscope, and the grains contaminated with impurities were discarded. The powdered sample was then pulverized in an agate mortar. Particles with diameters between 90 and 106 μm were collected and cleaned ultrasonically in ethanol. The specific surface area of the powdered sample was determined to

Figure 1. Photomicrograph showing the polished section of the starting chipped sample.

be 0.06 m^2/g with a Brunauer Emmett Teller method (BET method, Micrometrics, Flow Sorb., Taiheiyo consultant Co., Ltd.). The chipped sample was prepared by cutting the original sample along its cleavage and polishing it with a #800 emery paper. The dimensions of the sample were $1.50 \times 2.00 \times 3.00$ (± 0.01) mm.

Reaction solution

Aqueous CaCl_2 solutions with concentrations of 0.01, 0.10, and 1.00 mol/l were used as the reaction solutions. The chloride solution was chosen because chloride ion is the major anions in the fluid inclusion associated with W mineralization (Shibue, 1987, 1993), and many previous experiments on the metasomatism of tungstates were conducted using chloride solutions (Baumer, 1985; Uchida et al., 1989).

Experimental procedure

The powdered sample (100.0 ± 0.2 mg) was first dispersed in a 7 ml PFA bottle in order to prevent cohesion. The PFA bottle was then placed in a 50 ml Teflon reaction vessel containing 45 ml of aqueous CaCl_2 solution. In the experiment performed on the chipped sample, the sample was placed in a Teflon reaction vessel containing 50 ml of aqueous CaCl_2 solution. Each Teflon reaction vessel was enclosed in a stainless steel pressure container and placed in an electric furnace. The experimental temperatures were 130, 150, and 170 (± 2) °C. After the each reaction finished, the stainless steel pressure container was taken out from the electric furnace and immediately quenched in cold water. The pH of the reaction solution was measured, and the solid phase and aqueous solution were separated with a 20 μm membrane filter. Then, the pH and the Mn, Ca, and W concentrations of the aqueous solution were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Electron, ICAP-757, University of Tsukuba; Hitachi, Z-6100, AIST).

The color change in the powdered samples was observed under natural light. The occurrence of scheelite was verified under ultraviolet light since scheelite exhibits luminescence under ultraviolet light. The surfaces of the powdered samples were observed by scanning electron microscopy (SEM, Hitachi, S4100, Taiheiyo Consultant Co., Ltd.; JEOL, JSM 5800LV). After the observation, the powdered samples were further pulverized in an agate mortar and then divided into two portions. One portion (20.0 mg) of the sample was dissolved in aqua regia. After evaporation to dryness, 10 ml of 6 N aqueous HCl solution was added. The amount of scheelite in each sample was calculated from the concentrations of Mn and Ca

Figure 2. Variation in pH of aqueous CaCl_2 solution with time for the powdered samples.

Figure 3. Variation in Mn concentration of aqueous CaCl_2 solution with time for the powdered samples.

Table 1. Variation in W concentration in CaCl_2 aqueous solution with time

Aqueous CaCl_2 solution (mol/l)	0.01			0.10			1.00		
	130	150	170	130	150	170	130	150	170
Temperature ($^{\circ}\text{C}$)									
Duration (hrs)	mol%								
72	0.02	0.02	0.02	0.05	0.02	0.02	0.12	0.02	0.02
120	n.d.	0.02	0.01	0.03	0.02	0.01	0.09	n.d.	0.01
168	n.d.	0.02	n.d.	0.03	0.01	0.01	0.08	n.d.	n.d.
336	n.d.	0.01	0.01	0.01	0.01	0.01	0.08	n.d.	n.d.
504	n.d.	0.01	0.01	0.01	0.01	0.01	0.08	n.d.	n.d.
672	n.d.	0.01	0.01	0.01	0.01	0.01	0.07	n.d.	n.d.

in the solution by ICP-AES. The samples were dissolved according to the method used by Honma and Nakata (1985). The remaining portion (20.0 mg) of the pulverized sample was used for X-ray diffraction analysis (XRD, Rigaku, Rint 1200). The cracked surfaces of the chipped samples were analyzed by SEM. Further, we measured the shortest edge (1.5 mm before experiment; see "Starting material") using a digital vernier caliper before and after each run.

RESULTS

Liquid Phase

The pH values of the 0.01, 0.10, and 1.00 mol/l aqueous CaCl_2 solutions before the experiment were $5.64 (\pm 0.18)$, $6.42 (\pm 0.30)$, and $7.34 (\pm 0.23)$, respectively. The pH showed a significant decrease during the initial stage and then decreased relatively slowly with time (Fig. 2). The Mn and W concentrations in the aqueous solution changed

with time. The Mn concentrations in the powdered sample increased with time in all the runs (Fig. 3). The Mn concentration was highest in the 1.00 mol/l aqueous CaCl_2 solution at 170 $^{\circ}\text{C}$. For all the samples, the Ca concentration did not change with time. The W concentration was high during the initial stage and decreased with time (Table 1).

Solid phase

Powdered sample. The surfaces of the powdered samples were observed under natural light and ultraviolet light (Fig. 4). Under natural light, the samples were observed to be reddish-brown to reddish-black in color (Fig. 4a). On the contrary, under ultraviolet light, the reaction samples were observed to be of a pale fluorescent color. The intensity of the pale fluorescent color increased with time, thereby indicating an increase in the amount of scheelite on the sample surface with time (Fig. 4b).

The SEM images of the surfaces of the powdered

Figure 4. Photomicrograph showing the color of powdered samples. (a) Under natural light. (b) Under ultraviolet light. A, 130 °C; B, 150 °C; C, 170 °C.

samples are shown in Figure 5. The surface of the starting material is shown in Figure 5a. Fine particles of huebnerite with diameters of several hundred nanometers were observed. These particles could not be removed even after cleaning the starting material in an ultrasonic washing machine. Initially, small crystals of irregular shapes and sizes of 0.5–2 μm were obtained by precipitation (Fig. 5b). Energy dispersive spectroscopy (EDS) analysis of these crystals revealed that they were scheelite. The crystal faces of the precipitates became more distinct and the precipitates were converted to octahedral crystals with time. A large number of etch pits were observed on the surface of huebnerite (Figs. 5b–5i). The octahedral crystals of scheelite became more distinct and the size of the crystal increased with the reaction temperature. The maximum crystal size of scheelite was less than 10, 15, and 25 μm at 130, 150, and 170 °C, respectively, when the reaction time was 672 h (Figs. 5d–5f). The amount of precipitated scheelite increased with the CaCl_2 concentration in the aqueous solution (Figs. 5d, 5g, and 5h). The octahedral crystals of scheelite were not uniformly distributed on the surface of huebnerite and were more abundantly on the (010) plane than the other planes (Fig. 5i). The roughness of the (010) plane increased owing to the dissolution

at high reaction temperatures, high concentration of the reaction solution, and long reaction time.

The XRD patterns of the powdered samples are shown in Figure 6. Only peaks corresponding to huebnerite were observed in the starting material. On the other hand, peaks corresponding to huebnerite and scheelite were detected in all the experimental runs, while peaks corresponding to other minerals were not observed. The intensities of the peaks corresponding to scheelite increased with time.

The amount of scheelite increased linearly with time for the first 168 h of the reaction but the formation rates decreased after 200 h. The amount of scheelite formed increased with the reaction temperature (Fig. 7). The amount of scheelite formed also increased with the CaCl_2 concentration in the aqueous solution; the maximum amount of scheelite was formed in the 1.00 mol/l aqueous CaCl_2 solution at 170 °C. The amount of scheelite obtained after 672 h was approximately 20 mol%.

Chipped sample. The fractured surfaces of the chipped samples were observed by SEM (Fig. 8). With time, scheelite crystals grew in size and the crystal shape was converted to octahedral crystals. Huebnerite dissolved selectively in the reaction solution, and scheelite growth on the dissolution plane was observed. Pores were formed along the boundary between huebnerite and scheelite at the portion in which the reaction layer thickened. A change in the weight and thickness of the shortest edge (1.50 mm) after each run was observed (Table 2). The thickness increased by approximately 0.6% after 2016 h.

DISCUSSION

Pores are generally formed between the crystals of the product mineral in metasomatism when the molar volume ratio of replacing mineral to replaced mineral, V_2/V_1 , is less than 1. In this case, metasomatism is easily achieved because the reaction solution can penetrate the pores to reach the surface of the replaced mineral. On the contrary, metasomatism hardly proceeds when V_2/V_1 is greater than 1 because the reaction solution cannot penetrate the pores easily (Schouten, 1934; Ridge, 1949; Nakata et al., 1994; Putnis, 2002). Although the V_2/V_1 value was 1.12 for the present study, the metasomatism of huebnerite to scheelite occurred. This suggests that the influence of molar volume ratio is small on the metasomatism of huebnerite to scheelite.

In contrast to previous studies (Baumer, 1985; Uchida et al., 1989), which showed that metasomatism of huebnerite to scheelite occurs at high temperatures (400–600 °C), this study shows that the abovementioned

Figure 5. SEM images of the sample surfaces. (a) Starting material (huebnerite). (b) 150 °C, 0.10 mol/l aqueous CaCl_2 solution, 72 h. (c) 150 °C, 0.10 mol/l, 168 h. (d) 150 °C, 0.10 mol/l, 672 h. (e) 130 °C, 0.10 mol/l, 672 h. (f) 170 °C, 0.10 mol/l, 672 h. (g) 150 °C, 0.01 mol/l, 672 h. (h) 150 °C, 1.00 mol/l, 672 h. (i) 170 °C, 0.10 mol/l, 504 h.

metasomatism can occur at low temperatures (130–170 °C). However, the rate of metasomatism is slower at low temperatures than the rate of metasomatism at high temperatures. The results of this study are consistent with those reported previously, which state that the rates of dis-

solution and precipitation of minerals during metasomatism are controlled by the reaction temperature (Merino et al., 1993, 1994; Wang et al., 1995; Nahon and Merino, 1996, 1997; Merino and Dewers, 1998; Fletcher and Merino, 2001).

Figure 6. XRD patterns of powdered samples. (a) Starting material (huebnerite). (b) 170 °C, 1.00 mol/l, 168 h. (c) 170 °C, 1.00 mol/l, 336 h. (d) 170 °C, 1.00 mol/l, 504 h. (e) 170 °C, 1.00 mol/l, 672 h. Sch, scheelite.

Figure 7. Diagram showing the formation of scheelite with time for the powdered samples.

William (1945) reported narrow rims of scheelite surrounding huebnerite in the tungsten deposit near Townsville. The replacement texture of huebnerite by scheelite observed in nature and the texture of scheelite observed in this study are very similar. The thickness and roughness of the chipped sample increased with time (Table 2) because of the growth of scheelite crystals on both sides of the huebnerite surface. On the basis of SEM observations (Figs. 5 and 8) and the variation in the thickness of the chipped sample (Table 2), the replacement

Figure 8. Photomicrograph showing a broken section of the cracked surface for the chipped samples (150 °C, 0.10 mol/l aqueous CaCl_2 solution, 4032 h). Hue, huebnerite; Sch, scheelite.

texture of huebnerite by scheelite is classified as rim replacement texture. However, Tamura et al. (2002) reported the absence of a specific trend in the variation of the thickness of the chipped sample during the metasomatism of scheelite to huebnerite. They classified this replacement texture as pseudomorphic replacement texture.

The decrease in the amount of huebnerite is calculated from the variation in the Mn content of the powdered samples with time. Figure 9 shows the variation in the amount of Mn with time. The plot of Mn concentration against time on a semilog graph indicates that the Mn concentration of the powdered sample decreases linearly with time. However, this does not necessarily indicate that the Mn concentration decreases exponentially; this is because the range of the concentration is so narrow that we cannot eliminate other possibilities. The values of k for

Table 2. Weight and thickness of chipped samples

Duration (hrs)	Number	Weight			Thickness		
		Start (mg)	End (mg)	Rate of increase (%)	Start (mm)	End (mm)	Rate of increase (%)
672	1	59.3	59.1	-0.3	1.498	1.501	0.2
672	2	56.5	56.3	-0.4	1.503	1.505	0.1
1344	1	54.8	54.5	-0.5	1.497	1.503	0.4
1344	2	57.3	57.0	-0.5	1.505	1.509	0.3
2016	1	57.2	56.6	-1.0	1.503	1.512	0.6
2016	2	57.4	56.7	-1.2	1.499	1.508	0.6

Figure 9. Difference in huebnerite and aqueous CaCl_2 solutions for the powdered samples with respect to reduction in the amount of huebnerite as a function of time.

dissolution of huebnerite are estimated from the slope of the straight line which was obtained from the experimental data plotted on the concentration versus time diagram. The values of k in this study are approximately 10^{-9} – 10^{-6} $\text{mol l}^{-1} \text{s}^{-1}$ (Table 3). The values of k for dissolution of scheelite in the metasomatism of scheelite to huebnerite are approximately 10^{-6} – 10^{-4} $\text{mol l}^{-1} \text{s}^{-1}$ (Table 3). The value of k obtained in this study is 10^{-2} times smaller than the metasomatism of scheelite to huebnerite (Tamura et al., 2002). This distinct difference is considered to be due to differences in the solubility between huebnerite and scheelite. In general, dissolution rates of minerals (e.g., silicate, oxides, etc.) are related to their solubilities (e.g., Lasaga, 1981). The solubility products of scheelite and huebnerite are $10^{-7.68}$ (Khodakovskii and Mishin, 1971) and $10^{-11.57}$ (Naumov et al., 1974) at 300 °C, respectively. Although the solubility product data for the temperature

Table 3. Estimated values of k and activation energy E for dissolution of huebnerite and that of scheelite*

System		Apparent reaction	Activation
Concentration of solute (mol/l)	Temp. (°C)	rate constant k ($\text{mol l}^{-1} \text{s}^{-1}$)	energy E (kJ mol^{-1})
0.01 CaCl_2	130	7.3×10^{-8}	9.6
	150	8.6×10^{-8}	
	170	1.5×10^{-7}	
0.10 CaCl_2	130	1.9×10^{-7}	20.7
	150	3.3×10^{-7}	
	170	7.0×10^{-7}	
1.00 CaCl_2	130	4.4×10^{-7}	31.2
	150	7.8×10^{-7}	
	170	3.1×10^{-6}	
0.01 MnCl_2	100	1.3×10^{-5}	15.3
	125	3.1×10^{-5}	
	150	4.9×10^{-5}	
0.10 MnCl_2	100	1.9×10^{-5}	24.1
	125	7.5×10^{-5}	
	150	1.6×10^{-4}	
1.00 MnCl_2	100	4.0×10^{-5}	18.5
	125	1.2×10^{-4}	
	150	2.1×10^{-4}	

* Corrected version of Tamura et al. (2002).

range in which the present study is carried out (130–170 °C) is not available, it is likely that within this range, the solubility product of scheelite is significantly higher than that of huebnerite.

The temperature dependency of k is determined by the Arrhenius equation $k = A \cdot \exp(-E/RT)$, where A is the Arrhenius frequency factor; E , the activation energy (kJ/mol); R , the gas constant ($8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$), and T , the absolute temperature (K). The value of k for each system is calculated and plotted against the reciprocal of the absolute temperature (Fig. 10). The plots of the values of $\ln k$ for all the systems are approximately linear. The value of E is obtained by multiplying the gradient of the straight line with $-R$ (Tominaga and Komoto, 1994). The values of E obtained in this study are 9.6, 20.7, and 31.2 kJ/mol

Figure 10. Relationship between T and k of huebnerite and aqueous CaCl_2 solutions for the powdered samples.

for CaCl_2 concentrations of 0.01, 0.10, and 1.00 mol/l, respectively (Table 3). In our previous experimental study in which a CaWO_4 -aqueous MnCl_2 solution was used for studying the metasomatism of scheelite to huebnerite, the E values were 15.3, 24.1, and 18.5 kJ/mol for MnCl_2 concentrations of 0.01, 0.10, and 1.00 mol/l, respectively (Table 3).

The possible rate-limiting factors of the metasomatism of huebnerite to scheelite can be: (a) dissolution of huebnerite, (b) precipitation of scheelite from solution, and (c) diffusion of Mn^{2+} and Ca^{2+} near the surface of huebnerite. The diffusion of Mn^{2+} and Ca^{2+} does not appear to limit the rate of the metasomatism because of plenty of pores near the surface (Figs. 5 and 8). The W concentration in the solution is high during the initial stage of the metasomatism and decreases with time (Table 1), indicating a relatively high dissolution rate of huebnerite. In fact, the dissolution rate of huebnerite during the initial stage is higher than the precipitation rate of scheelite. Therefore, the precipitation of scheelite is thought to determine the rate of the metasomatism during the initial stage, when the W concentration in the solution is high.

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