Experimental investigation of the simultaneous partitioning of divalent cations between löllingite or safflorite and 2 mol/L aqueous chloride solutions under supercritical conditions

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In order to elucidate partition behavior of divalent cations between minerals and aqueous chloride solutions under supercritical conditions of fluid phase, we conducted experiments of the simultaneous partitioning of Ni\(^{2+}\), Mg\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\), Fe\(^{2+}\), and Mn\(^{2+}\) between löllingite (FeAs\(_2\)) or safflorite (CoAs\(_2\)) and 2 mol/L aqueous chloride solutions under the conditions of 500 and 600 °C, 100 MPa. Natural löllingite and safflorite were used as starting materials. The bulk partition coefficient (\(K_{PB}\)) for the cation partition reactions can be expressed as follows:

\[
K_{PB} = \frac{x_{MeAs2}}{x_{FeAs2} \text{ or } CoAs2} \cdot \frac{m_{FeAs2} \text{ or CoAs2}}{m_{MeAs2}}
\]

where \(x_{MeAs2}\) indicates the molar fraction of each end-member in the solid phase. \(m_{MeAs2}\) is the total molar concentration of Me-bearing aqueous species in aqueous chloride solution. For the experiments using löllingite, the order of partition coefficients of divalent cations was:

\[
\text{Co}^{2+} > \text{Fe}^{2+} > \text{Ni}^{2+} >> \text{Mg}^{2+} = \text{Zn}^{2+} \geq \text{Mn}^{2+},
\]

ranging from \(-4\) to 2.3 in logarithm. The order of partition coefficients for safflorite was:

\[
\text{Co}^{2+} > \text{Ni}^{2+} >> \text{Fe}^{2+} > \text{Mg}^{2+} > \text{Zn}^{2+} \geq \text{Mn}^{2+},
\]

ranging from \(-6\) to 0.6 in logarithm. The partition coefficient–ionic radius (PC–IR) curves of löllingite and safflorite showed almost no difference between 500 and 600 °C. The PC–IR curves of löllingite and safflorite have a steeper slope than multiple oxide minerals. Mg\(^{2+}\), Co\(^{2+}\), Fe\(^{2+}\), and Mn\(^{2+}\) exhibit partition behavior according to ionic radius. On the other hand, Ni\(^{2+}\) shows a positive partition anomaly in both löllingite and safflorite, whereas Zn\(^{2+}\) shows a large negative partition anomaly that increases with increasing As concentration in the order of pyrite < arsenopyrite < löllingite. Minerals with high ionic bond properties (e.g., ilmenite, magnetite) that have the same 6-fold coordinated sites have a wider PC–IR curve than sulfide, arsenic sulfide, and arsenide minerals with high covalent bond properties. This observation suggests that the selectivity of cations is strong in sulfide, arsenic sulfide, and arsenide minerals with covalent bonds compared with that of multiple oxide minerals with ionic bonds. However, because the electronegativity of arsenic is slightly smaller than that of sulfur, the width of the PC–IR curve seems to slightly narrow in the order of sulfide minerals (pyrite) > arsenic sulfide minerals (arsenopyrite) > arsenide minerals (löllingite).

Keywords: Löllingite, Safflorite, Aqueous chloride solution, Partition coefficient, Supercritical condition

INTRODUCTION

We have conducted experiments under supercritical conditions of the fluid phase under 500-800 °C, 100 MPa to determine the simultaneous partitioning behavior of divalent cations between various silicate, multiple oxide, and sulfide minerals (e.g., Uchida et al., 2004a, 2004b; Uchida and Maruo, 2007; Uchida et al., 2019) and aqueous chloride solutions. Similar researches have not been performed by other researchers. In this study, we conducted simultaneous divalent metal cation partition experiments using löllingite (FeAs\(_2\)) and safflorite (CoAs\(_2\)), which are arsenide minerals that have never been tested. Previous
partition experiments have been reported involving sulfide minerals, pyrite (FeS2) and pyrrhotite (Fe1–xS) (Uchida et al., 2017), which frequently occur in hydrothermal deposits in addition to arsenic sulfide minerals, arsenopyrite (FeAsS) and cobaltite (CoAsS) (Uchida et al., 2019). The partition coefficient versus ionic radius (PC–IR) curves (Matsui et al., 1977) for pyrite, pyrrhotite, arsenopyrite, and cobaltite show the similar tendency. In particular, Ni2+ shows a positive partition anomaly and Zn2+ shows a negative partition anomaly, which is the same as that reported for multiple oxide minerals such as ilmenite (Uchida et al., 2000) and magnetite (Uchida et al., 2004b). However, the widths of the PC–IR curves drawn from the partitioning of Mg2+, Co2+, Fe2+, and Mn2+ differ substantially. The widths for sulfide and arsenic sulfide minerals are much narrower than those of multiple oxide minerals, which indicates that minerals in these groups have strong selectivity for divalent metal cations.

**MATERIALS AND METHODS**

**Solid starting materials**

In this study, divalent cation exchange experiments were conducted using löllingite (FeAs2) or safflorite (CoAs2) and (Ni, Mg, Co, Zn, Fe, Mn)Cl2 aqueous solutions. Löllingite has an ideal chemical composition of FeAs2, belongs to the orthorhombic crystal system, and is classified as a pyrite group mineral (Gaines et al., 1997). Fe occupies 6-fold coordinated sites surrounded by six As atoms. In natural löllingite, Co tends to replace Fe, and S also exchanges for As (Gaines et al., 1997). According to Scott (1983), löllingite is stable up to temperatures of ~ 700 °C. In this study, we use löllingite from the Kobushi mine, Nagano Prefecture, Japan (Fig. 1a) as starting material. The löllingite sample was crushed to a particle size of 0.5–1.0 mm, and then impurities were removed using tweezers under a stereomicroscope. Chemical analysis using an energy dispersive X-ray microanalyzer reveals that löllingite contain 30.01 ± 0.15 mol% Fe, 0.75 ± 0.09 mol% Co, 0.06 ± 0.07 mol% Ni, 0.15 ± 0.21 mol% Mg, 0.02 ± 0.06 mol% Mn, 0.00 ± 0.07 mol% Zn, 2.34 ± 0.06 mol% S, and 66.67 ± 0.15 mol% As. Minerals other than löllingite were not detected from powder X-ray diffraction analysis (Fig. 2a).

The ideal chemical formula for safflorite is CoAs2. Safflorite belongs to the orthorhombic crystal system the same as löllingite, but is classified as member of the marcasite group (Gaines et al., 1997). Co occupies 6-fold coordinated sites surrounded by six As atoms. In natural safflorite, a significant amount of Fe replaces Co (Gaines et al., 1997). In this study, safflorite from Timiskaming District, Ontario, Canada was used as starting material.

(Fig. 1b). Because the safflorite ore contains substantial amounts of calcite, it was crushed to a particle size of 0.5–1.0 mm and treated with 0.1 mol/L hydrochloric acid for 2 h to decompose the calcite. Safflorite obtained by the above treatment was used as starting material. Chemical analysis using an energy dispersive X-ray microanalyzer show that safflorite contained 25.56 ± 0.08 mol% Co, 2.93 ± 0.04 mol% Fe, 2.18 ± 0.06 mol% Ni, 0.46 ± 0.11 mol% Mg, 0.48 ± 0.07 mol% Zn, 0.17 ± 0.03 mol% Mn, 2.67 ± 0.06 mol% S, and 65.55 ± 0.15 mol% As. Some peaks of cobaltite, kaolinite, and unidentified minerals were confirmed from powder X-ray diffraction analysis (Fig. 2c). Löllingite and safflorite form a complete solid solution in nature (Radeliffe and Berry, 1968).

**Liquid starting materials**

A mixture of 2 mol/L aqueous chloride solutions was used as the liquid starting material for reaction with the solid starting materials (löllingite and safflorite). The chemicals used are as follows: reagent grade of NiCl2·6H2O, MgCl2·6H2O, CoCl2·6H2O, ZnCl2, FeCl2·4H2O, and MnCl2·4H2O (Junsei Chemical Co. Ltd.). In the löllingite experiments, an aqueous chloride solution was used by preparing a mixture of 1 mol/L ZnCl2, CoCl2, NiCl2, MnCl2, and MgCl2 solutions at a volume ratio of 5:2:1:20:20. In the safflorite experiments, an aqueous chloride solution was used by preparing a mixture of 1 mol/L ZnCl2, FeCl2, NiCl2, MnCl2, and MgCl2 solutions at a volume ratio of 5:1:1:20:20. Mn and Mg concentrations were increased in the starting aqueous chloride solutions in both experiment sets to exceed the lower quantification limit of these elements in löllingite and safflorite after experiments.

**Experimental procedure**

We combined 30 mg of solid starting material (löllingite or safflorite) that had been well ground using an agate mortar, 30 µl of the reaction solution described above, and less than 1 mg of anthracene (C14H10), which is a reducing agent to keep Fe and Mn in a divalent state in a

![Figure 1. Solid starting materials. (a) Löllingite from the Kobushi mine, Nagano Prefecture, Japan. (b) Safflorite from Timiskaming District, Ontario, Canada.](image)
gold pipe with an outer diameter of 3.0 mm, inner diameter of 2.7 mm, and a length of ~ 35 mm that was electrically welded on one side. The opposite side of the gold pipe was then sealed by electric welding (Tables 1 and 2) and stored in an oven at 105 °C overnight. The weight was then measured to check whether sealing was complete without leakage. A gold pipe containing the reactants was placed in a cold–seal type high–pressure reaction vessel made of stellite 25 (HP Technos, HP–MRA–114S with 5.5 cm³ volume) with a stainless steel filler rod of 150 mm in length and 5.0 mm in diameter to reduce the temperature gradient. The temperature was then raised to a predetermined target temperature in a horizontal electric furnace. The temperature was measured using a chromel–alumel thermocouple attached to the outer wall of the reaction vessel. The electric furnace temperature was controlled using a digital temperature controller (Shimaden Co Ltd., DSS83 series). Water was used as the pressure medium. The pressure was measured using a pressure gauge (Yamazaki Keiki Co. Ltd., 200 MPa) connected to the reaction vessel using a capillary tube. The pressure

Table 1. Experimental conditions in the FeAs₂–(Ni²⁺, Mg²⁺, Co²⁺, Zn²⁺, Mn²⁺)Cl₂–H₂O system

| Run No. | Duration Days | Temperature (°C) | Pressure (kb) | Solid (mg) | Fluid (µL) |
|---------|----------------|------------------|--------------|------------|------------|
| Lo501  | 7              | 500              | 1            | 20.2       | 30°        |
| Lo502  | 7              | 500              | 1            | 20.6       | 30°        |
| Lo503  | 7              | 500              | 1            | 20.2       | 30°        |
| Lo504  | 7              | 500              | 1            | 20.5       | 30°        |
| Lo601  | 5              | 600              | 1            | 20.0       | 30°        |
| Lo602  | 5              | 600              | 1            | 20.3       | 30°        |
| Lo603  | 5              | 600              | 1            | 19.9       | 30°        |
| Lo604  | 5              | 600              | 1            | 20.2       | 30°        |

*ZnCl₂:NiCl₂:CoCl₂:MnCl₂:MgCl₂ = 5:1:2:20:20 (1 mol/L in total)

Table 2. Experimental conditions in the CoAs₂–(Ni²⁺, Mg²⁺, Zn²⁺, Fe²⁺, Mn²⁺)Cl₂–H₂O system

| Run No. | Duration Days | Temperature (°C) | Pressure (kb) | Solid (mg) | Fluid (µL) |
|---------|----------------|------------------|--------------|------------|------------|
| Sa501  | 7              | 500              | 1            | 20.5       | 30°        |
| Sa502  | 7              | 500              | 1            | 20.0       | 30°        |
| Sa503  | 7              | 500              | 1            | 21.1       | 30°        |
| Sa504  | 7              | 500              | 1            | 20.5       | 30°        |
| Sa505  | 7              | 500              | 1            | 19.9       | 30°        |
| Sa506  | 7              | 500              | 1            | 20.4       | 30°        |
| Sa601  | 5              | 600              | 1            | 20.3       | 30°        |
| Sa602  | 5              | 600              | 1            | 21.1       | 30°        |
| Sa604  | 5              | 600              | 1            | 20.6       | 30°        |
| Sa605  | 5              | 600              | 1            | 20.0       | 30°        |
| Sa606  | 5              | 600              | 1            | 20.9       | 30°        |

*NiCl₂:FeCl₂:ZnCl₂:MnCl₂:MgCl₂ = 1:1:5:20:20 (1 mol/L in total)

Figure 2. Powder X-ray diffraction patterns of solid starting materials and solid run products. (a) Starting materials of löllingite, (b) solid run products (run no. Lo601) at 600 °C and 100 MPa using löllingite. (c) Starting materials of safflorite. (d) Solid run products (run no. Sa601) at 600 °C and 100 MPa using safflorite.
was adjusted manually using a hand pump connected by a capillary tube. The experimental temperatures were 500 and 600 °C for both löllingite and safflorite and the pressure was held at 100 MPa. Our preliminary experiments showed that portions of the löllingite decompose at 700 °C and magnetite begins to form. The entire solid phase becomes magnetite at 800 °C. Safflorite also begins to decompose above 700 °C and in addition to safflorite, the formation of cobaltite and magnetite was also confirmed. The experimental duration was 7 days at 500 °C and 5 days at 600 °C (Tables 1 and 2).

After each experiment was completed, the high-pressure reaction vessel was removed from the electric furnace, put into a stainless steel bucket filled with water, and rapidly quenched. After cooling, the gold pipe was removed from the high-pressure reaction vessel and weighed to confirm that there was no leakage. The gold pipe was then opened, the run products were washed in a beaker using a syringe filled with pure water, and the solid and liquid phases were separated using a membrane filter (Millipore: 25 mmØ, 0.45 µm). The liquid phases were diluted to 50 cm$^3$ with a distilled water.

**Analytical method**

The high-temperature and high-pressure treated solid phase was identified using powder X-ray diffractometer (XRD: RIGAKU RINT-ULTIMA3). A copper X-ray tube was used over the range of 2θ = 2–80°. For the solid phase, the observation and chemical analysis were performed using a scanning electron microscope (SEM: JEOL JSM–6360) equipped with an energy dispersive detector (EDS: Oxford Instruments INCA ENERGY). The sample was dispersed on carbon tape and then subjected to carbon coating. Chemical analysis was conducted on mineral surfaces, performed on Ni, Mg, Co, Zn, Fe, Mn, As, and S for 1000 s per point and at least 3 points per sample, and the average value was obtained.

The liquid phase was quantitatively analyzed for divalent cations (Ni, Mg, Co, Zn, Fe, and Mn) using an inductively coupled plasma atomic emission spectrometer (ICP-AES: Thermo Fisher Scientific iCAP 6300). The measurement was performed 3 times for 10 s, and the average value was obtained.

**RESULTS**

**Experimental results for löllingite**

As a result of observing löllingite after experiments using SEM, no recrystallization or decomposition was detected (Fig. 3a). Only löllingite was detected from both the 500 and 600 °C experiments by XRD measurements (Fig. 2b). A halo peak was observed around 2θ = 20–30°. In the XRD measurements, a small amount of sample (~ 10 mg) was ground in an agate mortar, dissolved in water, applied to a glass plate for rock thin section, and dried. This peak was therefore considered to be a halo peak derived from glass.

The chemical analysis results by SEM–EDS are summarized in Table 3 with the chemical composition of the starting material. The molar fraction of As is particularly high; 64.8 and 64.6 mol% at 500 and 600 °C, respectively. The S contents were 2.3 and 2.6 mol%, respectively, and the As + S contents were 67.1 and 67.2 mol%, respectively. For the cations, the amount of Fe was considerably high, 30.2 and 30.9 mol% at 500 and 600 °C, respectively, followed by Co, Ni, Mg, Zn, and Mn.

Table 4 shows the molar fraction of divalent cations in the solid phase (löllingite) and liquid phase. The measured molar ratio of Fe in löllingite is 89.5–95.8 mol%, Co is 3.1–5.6 mol%, Ni is 0.2–1.4 mol%, Mg is 0.1–0.7 mol%, Zn is 0.2–0.5 mol%, and Mn is 0.1–0.3 mol% at 500 and 600 °C. The analytical accuracy (1σ) for the solid phase is 0.23 mol% for Fe, 0.15 mol% for Co and Ni, 0.33 mol% for Mg, 0.20 mol% for Zn, and 0.09 mol% for Mn.

However, the measured molar ratio of Fe in the liquid phase is 3.8–20.7 mol%, that for Co is 0.0–1.4 mol%, Ni is 0.0–0.1 mol%, Mg is 23.0–29.6 mol%, Zn is 12.2–20.9 mol%, and Mn is 43.7–50.0 mol% at 500 and 600 °C. The analytical accuracy (1σ) for the liquid phase is approximately 0.5% for Mn, Mg, Zn, and Fe, and about 5% for Co and Ni.

**Experimental results for safflorite**

When safflorite is observed after experiments using SEM, there is no evidence of recrystallization or decomposition, as in the case of löllingite (Fig. 3b). XRD analysis shows that, in addition to safflorite, some cobaltite is detected at both 500 and 600 °C (Fig. 2d). A very small amount of an unidentified mineral is also detected. A halo peak is observed around 2θ = 20–30°, which is owing to
Table 3. Chemical compositions of löllingite before and after experiments by SEM–EDS

| Solid starting material | mol% | Fe   | Co   | Ni   | Mg   | Mn   | Zn   | S   | As   |
|------------------------|------|------|------|------|------|------|------|-----|------|
| Point 1                | 30.61| 0.59 | 0.01 | 0.15 | 0.01 | 0.00 | 2.72 | 65.91|
| Point 2                | 29.35| 0.72 | 0.12 | 0.13 | 0.00 | 0.00 | 2.09 | 67.60|
| Point 3                | 30.07| 0.94 | 0.05 | 0.18 | 0.05 | 0.00 | 2.21 | 66.50|
| Average                | 30.01| 0.75 | 0.06 | 0.15 | 0.02 | 0.00 | 2.34 | 66.67|

| Solid run products at 500 °C | mol% | Fe   | Co   | Ni   | Mg   | Mn   | Zn   | S   | As   |
|------------------------------|------|------|------|------|------|------|------|-----|------|
| L501                         | 31.15| 1.36 | 0.22 | 0.14 | 0.02 | 0.06 | 2.52 | 64.53|
| L502                         | 29.57| 2.70 | 0.47 | 0.18 | 0.05 | 0.08 | 1.98 | 65.02|
| L503                         | 30.12| 1.83 | 0.16 | 0.22 | 0.03 | 0.08 | 2.53 | 64.64|
| L504                         | 29.81| 2.32 | 0.44 | 0.13 | 0.02 | 0.07 | 2.28 | 64.95|
| Average                      | 30.16| 2.05 | 0.32 | 0.17 | 0.03 | 0.07 | 2.33 | 64.79|

| Solid run products at 600 °C | mol% | Fe   | Co   | Ni   | Mg   | Mn   | Zn   | S   | As   |
|------------------------------|------|------|------|------|------|------|------|-----|------|
| L601                         | 31.27| 1.31 | 0.10 | 0.04 | 0.09 | 0.09 | 2.43 | 64.67|
| L602                         | 30.66| 1.65 | 0.28 | 0.21 | 0.05 | 0.17 | 2.83 | 64.17|
| L603                         | 30.93| 1.51 | 0.34 | 0.14 | 0.02 | 0.06 | 2.52 | 64.25|
| L604                         | 30.84| 1.01 | 0.08 | 0.14 | 0.05 | 0.06 | 2.40 | 65.42|
| Average                      | 30.93| 1.37 | 0.20 | 0.13 | 0.05 | 0.10 | 2.55 | 64.63|

Table 4. Chemical compositions of the starting materials and experimental results in the FeAs₂-(Ni²⁺, Mg²⁺, Co²⁺, Zn²⁺, Mn²⁺)Cl₂-H₂O system

| T (°C), P (kb) | Run No. | Mg    | Mn    | Fe    | Co    | Ni    | Zn    |
|---------------|---------|-------|-------|-------|-------|-------|-------|
| Solid starting material | Loelligite | 0.0048 | 0.0006 | 0.9684 | 0.0242 | 0.0019 | 0.0000 |
|                 | Fluid   | 0.4347 | 0.4347 | 0.0000 | 0.0435 | 0.0435 | 0.0435 |
|                | Lo501   | 0.0041 | 0.0006 | 0.9455 | 0.0413 | 0.0068 | 0.0017 |
|                 | Fluid   | 0.2301 | 0.4586 | 0.1016 | 0.0002 | 0.0004 | 0.2091 |
|                | log Kₚ₈ | -2.5712 | -3.8469 | 0.0000 | 1.3804 | 0.2729 | -3.0665 |
|                | Lo502   | 0.0053 | 0.0014 | 0.8949 | 0.0817 | 0.0141 | 0.0025 |
|                 | Fluid   | 0.2665 | 0.5025 | 0.0387 | 0.0009 | 0.0025 | 0.1888 |
|                | log Kₚ₈ | -2.8364 | -3.5698 | 0.0000 | 0.5743 | -0.5056 | -2.3350 |
| Liquid starting material | Loelligite | 0.0068 | 0.0009 | 0.9294 | 0.0556 | 0.0048 | 0.0024 |
|                | Fluid   | 0.2649 | 0.4786 | 0.0836 | 0.0003 | 0.0006 | 0.1721 |
|                | log Kₚ₈ | -2.6365 | -3.7653 | 0.0000 | 1.2642 | -0.1201 | -2.8951 |
|                | Lo503   | 0.0040 | 0.0006 | 0.9091 | 0.0708 | 0.0135 | 0.0020 |
|                | Fluid   | 0.2945 | 0.4805 | 0.0376 | 0.0011 | 0.0016 | 0.1846 |
|                | log Kₚ₈ | -3.2537 | -4.2793 | 0.0000 | 0.4123 | -0.4604 | -3.3410 |
|                | Lo601   | 0.0012 | 0.0027 | 0.9504 | 0.0399 | 0.0030 | 0.0027 |
|                | Fluid   | 0.2964 | 0.4860 | 0.0716 | 0.0003 | 0.0008 | 0.1449 |
|                | log Kₚ₈ | -3.5104 | -3.9733 | 0.0000 | 1.0010 | -0.5602 | -2.8483 |
|                | Lo602   | 0.0063 | 0.0015 | 0.9286 | 0.0499 | 0.0086 | 0.0052 |
|                | Fluid   | 0.2911 | 0.5203 | 0.0425 | 0.0017 | 0.0093 | 0.1351 |
|                | log Kₚ₈ | -2.9908 | -4.1998 | 0.0000 | -0.0590 | -1.5700 | -3.3133 |
|                | Lo603   | 0.0041 | 0.0008 | 0.9359 | 0.0456 | 0.0104 | 0.0031 |
|                | Fluid   | 0.2400 | 0.4709 | 0.1099 | 0.0146 | 0.0034 | 0.1614 |
|                | log Kₚ₈ | -2.6939 | -3.9694 | 0.0000 | -0.4343 | -0.4466 | -2.6430 |
|                | Lo604   | 0.0043 | 0.0015 | 0.9584 | 0.0314 | 0.0026 | 0.0020 |
|                | Fluid   | 0.2324 | 0.4368 | 0.2072 | 0.0009 | 0.0009 | 0.1219 |
|                | log Kₚ₈ | -2.4033 | -3.1441 | 0.0000 | 0.8828 | -0.1796 | -2.4572 |

Molar fractions of divalent cations in löllingite and aqueous chloride solutions and partition coefficients (Kₚ₈).
the same reason as in the case of löllingite.

The chemical analysis results by SEM–EDS are summarized in Table 5 with the chemical composition of the starting material. The molar fraction of As is considerably high: 65.7 and 65.0 mol% at 500 and 600 °C, respectively. The S content is 2.6 and 2.2 mol%, respectively. Co cations are abundant, 26.0 and 25.8 mol% at 500 and 600 °C, respectively, followed by Fe and Ni. Mg, Mn and Zn were less than 0.5 mol%.

Table 6 shows the molar fraction of divalent cations in the solid phase (safflorite) and liquid phase. The molar ratio of Co in safflorite is 76.6–81.1 mol%, that of Fe is 9.5–10.8 mol%, Ni is 6.2–11.4 mol%, Mg is 0.6–2.1 mol%, Zn is 0.1–0.7 mol%, and Mn is 0.1–2.0 mol% at 500 and 600 °C. The analytical accuracy (1σ) for the solid phase is 0.02 mol% for Co, 0.13 mol% for Fe, 0.17 mol% for Ni, 0.33 mol% for Mg, 0.21 mol% for Zn, and 0.09 mol% for Mn.

Table 5. Chemical compositions of safflorite before and after experiments by SEM-EDS

| Solid starting material | mol% | Fe | Co | Ni | Mg | Mn | Zn | S | As |
|------------------------|------|----|----|----|----|----|----|---|----|
| Point 1                |      | 2.39 | 25.26 | 2.46 | 0.00 | 0.46 | 1.21 | 2.94 | 65.29 |
| Point 2                |      | 3.89 | 24.83 | 2.15 | 1.38 | 0.05 | 0.00 | 1.83 | 65.86 |
| Point 3                |      | 2.52 | 26.58 | 1.92 | 0.00 | 0.01 | 0.23 | 3.25 | 65.50 |
| Average                |      | 2.93 | 25.56 | 2.18 | 0.46 | 0.17 | 0.48 | 2.67 | 65.55 |

| Solid run products at 500 °C | mol% | Fe | Co | Ni | Mg | Mn | Zn | S | As |
|------------------------------|------|----|----|----|----|----|----|---|----|
| Sa01                         |      | 3.35 | 24.72 | 2.99 | 0.44 | 0.04 | 0.15 | 2.64 | 66.61 |
| Sa02                         |      | 3.46 | 26.21 | 2.19 | 0.45 | 0.08 | 0.03 | 2.09 | 65.85 |
| Sa03                         |      | 3.55 | 26.26 | 2.29 | 0.49 | 0.11 | 0.15 | 2.79 | 64.89 |
| Sa04                         |      | 3.22 | 26.00 | 1.99 | 0.67 | 0.10 | 0.10 | 2.54 | 66.08 |
| Sa05                         |      | 3.66 | 26.30 | 2.09 | 0.30 | 0.07 | 0.24 | 2.70 | 64.64 |
| Sa06                         |      | 3.19 | 26.24 | 2.57 | 0.54 | 0.05 | 0.09 | 2.58 | 65.85 |
| Average                      |      | 3.41 | 25.96 | 2.35 | 0.48 | 0.08 | 0.13 | 2.56 | 65.65 |

| Solid run products at 600 °C | mol% | Fe | Co | Ni | Mg | Mn | Zn | S | As |
|------------------------------|------|----|----|----|----|----|----|---|----|
| Sa01                         |      | 3.41 | 26.09 | 3.05 | 0.67 | 0.16 | 0.13 | 1.82 | 65.68 |
| Sa02                         |      | 3.49 | 25.73 | 3.02 | 0.21 | 0.11 | 0.08 | 2.56 | 64.90 |
| Sa03                         |      | 3.55 | 25.97 | 3.38 | 0.36 | 0.06 | 0.05 | 2.22 | 64.63 |
| Sa04                         |      | 3.51 | 25.67 | 3.25 | 0.28 | 0.16 | 0.10 | 2.34 | 64.96 |
| Sa05                         |      | 3.14 | 25.61 | 3.05 | 0.43 | 0.06 | 0.05 | 2.17 | 64.83 |
| Sa06                         |      | 3.42 | 25.81 | 3.15 | 0.39 | 0.11 | 0.08 | 2.22 | 65.00 |
| Average                      |      | 3.41 | 25.96 | 2.35 | 0.48 | 0.08 | 0.13 | 2.56 | 65.65 |

Partitioning of divalent cations between löllingite and aqueous chloride solution

In this study, we assumed that an equilibrium achieved between the mineral surface and aqueous chloride solution. The bulk partition reaction of divalent cations between löllingite and aqueous chloride solution is expressed as follows:

\[ \text{FeAs}_2 + \text{Me}_{\text{aq}} = \text{MeAs}_2 + \text{Fe}_{\text{aq}} \]  

(1)

where Me represents Ni, Mg, Co, Zn, and Mn excluding Fe. In addition, aq indicates an aqueous species. The bulk partition coefficient \( K_{PB} \) for the above reaction is expressed as:

\[ K_{PB} = \frac{x_{\text{MeAs}_2}}{x_{\text{FeAs}_2}} \frac{m_{\text{Me}_{\text{aq}}}}{m_{\text{Fe}_{\text{aq}}}} \]  

(2)

where \( x_{\text{MeAs}_2} \) indicates the molar fraction of each end-member in the solid phase. \( m_{\text{Me}_{\text{aq}}} \) is the total molar concentration of Me–bearing aqueous species. Judging from previous studies (Uchida et al., 2000), it is inferred under the present experimental conditions that neutral aqueous species such as FeCl\(_2\) and CoCl\(_2\) are dominant. Therefore, it is considered that partition coefficients obtained from the bulk composition and from the neutral dissolved species coincide with each other. Larger partition coefficients are associated with easier incorporation of a divalent cation, \( \text{Me}^{2+} \), in löllingite over the liquid phase. Table 5 shows the partition coefficients obtained from Eq. (2). Figure 4 shows PC–IR diagrams with the logarithmic value of the partition coefficient expressed by Eq. (2) on the vertical axis, and ionic radius of 6-fold coordinated sites by Shannon and Prewitt (1970) on the horizontal axis. In the case of löllingite, the partition coefficient is...
largest for Co$^{2+}$ at both 500 and 600 °C, followed by Fe$^{2+}$ and Ni$^{2+}$, in spite of the fact that the main divalent cation component is Fe$^{2+}$. However, Mg$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$ show small values. The PC–IR curves in the figure are obtained using a least-square method with a quadratic equation on the assumption that Mg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Mn$^{2+}$ show normal partition behavior according to ionic radius. In this case, Ni$^{2+}$ clearly shows a positive partition anomaly whereas Zn$^{2+}$ shows a negative partition anomaly. The peak of the PC–IR curve is between Co$^{2+}$ and Fe$^{2+}$ at approximately 0.77 Å.

### Table 6. Chemical compositions of the starting materials and experimental results in the CoAs$_2$–(Ni$^{2+}$, Mg$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, Mn$^{2+}$)Cl$_2$–H$_2$O system

| $T$ (°C), $P$ (kb) | Run No. | Solid starting material | Liquid starting material | Mg | Mn | Fe | Co | Ni | Zn |
|-------------------|---------|------------------------|-------------------------|----|----|----|----|----|----|
| **500 °C, 1 kb**  | Sa501   | Safflorite             | Fluid                   | 0.1421 | 0.5873 | 0.1357 | 0.0015 | 0.0026 | 0.1308 |
|                   | Sa502   | Safflorite             | Fluid                   | 0.2234 | 0.5046 | 0.0954 | 0.0002 | 0.0004 | 0.1760 |
|                   | Sa503   | Safflorite             | Fluid                   | 0.2380 | 0.4870 | 0.0571 | 0.0003 | 0.0003 | 0.2173 |
| **600 °C, 1 kb**  | Sa601   | Safflorite             | Fluid                   | 0.1467 | 0.5966 | 0.1106 | 0.0020 | 0.0028 | 0.1413 |
|                   | Sa602   | Safflorite             | Fluid                   | 0.2241 | 0.4991 | 0.0904 | 0.0003 | 0.0004 | 0.1855 |
|                   | Sa604   | Safflorite             | Fluid                   | 0.2137 | 0.4829 | 0.1145 | 0.0006 | 0.0007 | 0.1877 |
|                   | Sa605   | Safflorite             | Fluid                   | 0.2121 | 0.4885 | 0.1809 | 0.0002 | 0.0005 | 0.1178 |
|                   | Sa606   | Safflorite             | Fluid                   | 0.2356 | 0.5120 | 0.1605 | 0.0002 | 0.0005 | 0.0911 |

Molar fractions of divalent cations in safflorite and aqueous chloride solutions and partition coefficients ($K_{PB}$).

**Partitioning of divalent cations between safflorite and aqueous chloride solution**

The bulk partition reaction of divalent cations between safflorite and aqueous chloride solution is expressed as follows, as in the case of safflorite:
CoAs$_2$ + Me$_{aq}$ = MeAs$_2$ + Co$_{aq}$  (3),

where Me represents Ni, Mg, Zn, Fe, and Mn excluding Co. The bulk partition coefficient ($K_{PB}$) for the above reaction is expressed as:

$$K_{PB}(\text{CoAs}_2) = \frac{x_{\text{MeAs}_2}}{x_{\text{CoAs}_2}} \cdot \frac{m_{\text{Co}_{aq}}}{m_{\text{Me}_{aq}}}$$  (4).

Table 6 summarizes the partition coefficients obtained from Eq. (4), and Figure 5 shows the PC-IR diagrams. In the case of safflorite, the partition coefficient for Co$^{2+}$, which is the main component, is the largest at both 500 and 600 °C, followed by Ni$^{2+}$. Compared with these cations, the partition coefficients of other cations are considerably smaller and are in the order of Fe$^{2+}$ > Mg$^{2+}$ > Mn$^{2+}$. The PC-IR curves were obtained on the assumption that Mg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Mn$^{2+}$ show normal partitioning behavior according to ionic radius. In this case, like löllingite, Ni$^{2+}$ shows a positive partition anomaly whereas Zn$^{2+}$ shows a negative partition anomaly. The peak of the PC-IR curves is near Co$^{2+}$ between Co$^{2+}$ and Fe$^{2+}$ at approximately 0.76 Å.

**DISCUSSION**

In this study, simultaneous partitioning experiments of Ni$^{2+}$, Mg$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Fe$^{2+}$, and Mn$^{2+}$ between löllingite or safflorite and aqueous chloride solutions were performed under conditions of 500 and 600 °C and 100 MPa. The partition coefficients for löllingite are in the order of Co$^{2+}$ > Fe$^{2+}$ > Ni$^{2+}$, and apart from these, Mg$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$ show almost the same small partition coefficients. However, in the case of safflorite, Co$^{2+}$ shows a relatively large partition coefficient, followed by Ni$^{2+}$. Apart from this, Fe$^{2+}$ shows the next largest partition coefficient. Mg$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$ show small partition coefficients as well as in löllingite. These relationships for partition coefficients are very similar to those for arsenopyrite and cobaltite, respectively (Uchida et al., 2019). The PC-IR curves obtained from the partition coefficients of Mg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, and Mn$^{2+}$ are also similar to those for arsenopyrite and cobaltite with peaks at 0.76 and 0.77 Å, respectively. Zn$^{2+}$ clearly shows a negative partition anomaly in löllingite and safflorite, whereas Ni$^{2+}$ clearly shows a positive partition anomaly. In this respect, the results are similar to those of arsenopyrite and cobaltite (i.e., arsenic sulfide minerals) and pyrite and pyrrhotite (i.e., sulfide minerals) (Fig. 6). Although the width of the PC-IR curves is different, similar results are observed for multiple oxide minerals such as ilmenite (Uchida et al., 2000, 2004b, 2017, 2019) at 600 °C and 100 MPa. In löllingite and safflorite, divalent cations occupy 6-fold coordinated sites. Zn$^{2+}$ shows a clear negative partition anomaly because Zn$^{2+}$ does not have a preference for non-4-fold coordinated sites (Matsui et al., 1977). On
The optimum ionic radius for löllingite determined from metal cations for löllingite was as follows: under conditions of 500 and 600 °C and 100 MPa.

and 2 mol/L aqueous chloride solution were conducted Co²⁺, Zn²⁺, Fe²⁺, and Mn²⁺ between löllingite or sa

of the PC bonds. Because the electronegativity of arsenic is slightly with covalent bonds compared with in minerals with ionic bonds. Ilmenite and magnetite (Fig. 6), which have high ionic bond properties (e.g., ilmenite and cobaltite) are steeper than those of multiple oxide minerals such as ilmenite and magnetite. Sulfide, arsenic sulfide, and arsenide minerals have strong covalent bonds, and the selectivity of minerals for elements is therefore stronger than in minerals with ionic bonds.

Ni²⁺ shows a positive partition anomaly in both löllingite and safflorite, whereas Zn²⁺ shows a large negative partition anomaly. The negative Zn²⁺ partition anomaly increases with increasing As concentration in the order of pyrite < arsenopyrite < löllingite.

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The optimum ionic radius for löllingite obtained from the PC–IR curve was approximately 0.76 Å, which is slightly smaller than that of löllingite.

The PC–IR curves for löllingite and safflorite as well as those for sulfide minerals (pyrite and pyrrhotite) and arsenic sulfide minerals (arsenopyrite and cobaltite) are steeper than those of multiple oxide minerals such as ilmenite and magnetite. Sulfide, arsenic sulfide, and arsenide minerals have strong covalent bonds, and the selectivity of minerals for elements is therefore stronger than in minerals with ionic bonds.

Ni²⁺ shows a positive partition anomaly in both löllingite and safflorite, whereas Zn²⁺ shows a large negative partition anomaly. The negative Zn²⁺ partition anomaly increases with increasing As concentration in the order of pyrite < arsenopyrite < löllingite.

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the other hand, Ni²⁺ has a preference for 6-fold coordinat-ed site (Matsui, 1979).

The PC–IR diagrams of Fe–bearing minerals, pyrite (FeS₂), arsenopyrite (FeAsS), and löllingite (FeAs₂) (Figs. 4 and 6) are essentially the same. However, the negative partition anomaly of Zn²⁺ tends to increase in the order of pyrite < arsenopyrite < löllingite. As mentioned above, the negative partition anomaly of Zn²⁺ is not observed in minerals with 4-fold coordinated sites such as spinel (Uchida et al., 2004b) and sphalerite (Uchida et al., 2004a), but is observed in 6-fold and 8-fold coordinated sites (Uchida et al., 2004a, 2004b). Thus, the negative partition anomaly of Zn²⁺ is owing to the fact that Zn²⁺ prefers 4-fold coordinated sites. Uchida et al. (2019) discussed the effect of electronegativity on element partitioning in sulfide and arsenic sulfide minerals. The electronegativities of oxygen, sulfur, and arsenic are 3.44, 2.58, and 2.18, respectively (Pauling, 1960). The electronegativities of sulfur and arsenic are smaller than that of oxygen, and therefore covalent bonds dominate in sulfide, arsenic sulfide, and arsenide minerals. It is thus speculated that the negative partition anomaly of Zn²⁺ is also related to electronegativity. PC–IR diagrams for sulfide, arsenic sulfide, and arsenide minerals are essentially the same as those for ilmenite and magnetite (Fig. 6), which have high ionic bond properties. However, in addition to the difference in the observed Zn²⁺ anomaly, a difference in the width of the PC–IR curves is also noted. In other words, minerals with high ionic bond properties (e.g., ilmenite and magnetite) that have the same 6-fold coordinated sites have a wider PC–IR curve than sulfide, arsenic sulfide, and arsenide minerals with high covalent bond properties. This observation suggests that the selectivity of cations is strong in sulfide, arsenic sulfide, and arsenide minerals with covalent bonds compared with in minerals with ionic bonds. Because the electronegativity of arsenic is slightly smaller than that of sulfur, the width of the PC–IR curve seems to slightly narrow in the order of sulfide minerals > arsenic sulfide minerals > arsenide minerals.

CONCLUSIONS

Simultaneous partitioning experiments of Ni²⁺, Mg²⁺, Co²⁺, Zn²⁺, Fe²⁺, and Mn²⁺ between löllingite or safflorite and 2 mol/L aqueous chloride solution were conducted under conditions of 500 and 600 °C and 100 MPa.

The order of partition coefficients of the divalent metal cations for löllingite was as follows:

Co²⁺ > Fe²⁺ > Ni²⁺ >> Mg²⁺ = Zn²⁺ ≥ Mn²⁺.

The optimum ionic radius for löllingite determined from the PC–IR curve was approximately 0.77 Å. The order of partition coefficients for safflorite was as follows:

Co²⁺ > Ni²⁺ >> Fe²⁺ > Mg²⁺ > Zn²⁺ > Mn²⁺.

The optimum ionic radius for safflorite obtained from the PC–IR curve was approximately 0.76 Å, which is slightly smaller than that of löllingite.

The PC–IR curves for löllingite and safflorite as well as those for sulfide minerals (pyrite and pyrrhotite) and arsenic sulfide minerals (arsenopyrite and cobaltite) are steeper than those of multiple oxide minerals such as ilmenite and magnetite. Sulfide, arsenic sulfide, and arsenide minerals have strong covalent bonds, and the selectivity of minerals for elements is therefore stronger than in minerals with ionic bonds.

Ni²⁺ shows a positive partition anomaly in both löllingite and safflorite, whereas Zn²⁺ shows a large negative partition anomaly. The negative Zn²⁺ partition anomaly increases with increasing As concentration in the order of pyrite < arsenopyrite < löllingite.

The optimum ionic radius for löllingite determined from the PC–IR curve was as follows:

Co²⁺ > Ni²⁺ >> Fe²⁺ > Mg²⁺ > Zn²⁺ > Mn²⁺.

The optimum ionic radius for safflorite obtained from the PC–IR curve was approximately 0.76 Å, which is slightly smaller than that of löllingite.
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