Halogen fractionation during vapor-brine phase separation revealed by in situ Cl, Br, and I analysis of scapolite from the Yixingzhai gold deposit, North China Craton

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ABSTRACT

Halogens (Cl, Br, and I) are major complexing agents for metal ions, and their ratios (Br/Cl and I/Cl) have been used to determine the source and evolution of hydrothermal fluid. Halogen fractionation during hydrothermal fluid evolution, however, has been inferred from several studies, which poses problems in using halogen ratios as a fluid tracer. The Br/Cl and I/Cl ratios of scapolite are consistent with those ratios present in the coexisting fluid during the mineral’s formation, making scapolite particularly useful for understanding hydrothermal fluid evolution. In this paper, we present fluid inclusion microthermometry, major elements, and in situ halogens and Sr isotope analysis of scapolite formed from a high salinity hydrothermal fluid during the vapor-brine phase separation at the Yixingzhai gold deposit, North China Craton, to better understand halogen fractionation during vapor-brine phase separation. The studied scapolite has 1.84–3.41 wt% Cl, 389–806 ppm Br, 8.4–24.4 ppm I, and significantly high Br/Cl (6.1–14.7 × 10^-3) and I/Cl (91–302 × 10^-6) molar ratios that likely result from the preferential incorporation of Br and I into the brine phase compared to Cl entering the vapor phase during fluid phase separation. Based on fluid inclusion microthermometry results, the Rayleigh fractionation simulation shows that the Br/Cl and I/Cl ratios of the brine are estimated to be up to 18 × 10^-3 and 500 × 10^-6 during the formation of scapolite. These results reveal halogen fractionation during the vapor-brine phase separation of hydrothermal fluids. This view has implications for interpreting the halogen systematics of scapolite and other minerals formed in similar environments, particularly when they are used as a fluid tracer.

Keywords: Scapolite; Halogen fractionation; Phase separation; Hydrothermal fluid
INTRODUCTION

Halogens (Cl, Br, and I) are important agents for complexation and transportation of metals in hydrothermal fluid systems (Webster and Holloway 1988; Webster et al. 2004). The Br/Cl and I/Cl ratios in hydrothermal fluids are commonly preserved during fluid migration (fluid buffered), and thus have been used as a fingerprint of the source and evolution of hydrothermal fluids (Böhlke and Irwin 1992; Heinrich et al. 1993; Irwin and Roedder 1995; Kendrick et al. 2002, 2013). Nonetheless, several studies have revealed halogen fractionation during hydrothermal fluid evolution processes, posing a big challenge in using halogen geochemistry to constrain fluid sources (Berndt and Seyfried 1997; Lüders et al. 2002; Kurosawa et al. 2016). Possible factors or processes that cause halogen fractionation include low-pressure segregation of hydrothermal fluid from magma (Bureau et al. 2000, 2010, 2016; Kurosawa et al. 2016), precipitation of Cl-bearing minerals (e.g., biotite, amphibole, and halite; Markl and Bucher 1998; Svensen et al. 1999; Kusebauch et al. 2015), and vapor-brine phase separation of hydrothermal fluids (Ishibashi et al. 1994; Oosting and Von Damm 1996; Berndt and Seyfried 1997; Lüders et al. 2002). Experimental studies suggest that Br preferentially partitions into the vapor phase compared to Cl during phase separation of a hydrothermal fluid system (Foustoukos and Seyfried 2007; Seo and Zajacz 2016). In contrast, other studies indicate that the Br/Cl ratios in the vapor phase are lower than those in the brine phase (Oosting and Von Damm 1996; Liebscher et al. 2006). Seo and Zajacz (2016) proposed that the degree of Br/Cl fractionation between brine and vapor phases depends on the types of alkali-halide and alkali-OH complexes in the hydrothermal system. These discrepancies highlight that the mechanisms of halogen fractionation during vapor-brine
phase separation remain to be understood.  

Scapolite group minerals are volatile-rich and have a diverse range of compositions $[(Ca,Na)_4Al_6Si_6O_{24}(SO_4,CO_3)–Na_4Al_3Si_9O_{24}Cl]$. They can form in magmatic, metamorphic, and hydrothermal environments and are stable over a wide range of temperature and pressure (Shaw 1960; Evans et al. 1969; Goldsmith and Newton 1977; Dong 2005; Filiberto et al. 2014; Almeida and Jenkins 2017). Previous studies suggest that the Br/Cl and I/Cl ratios of scapolite are equivalent to those ratios of the coexisting fluids during the scapolite formation (Pan and Dong 2003; Kendrick and Phillips 2009). In addition, the chlorine contents of scapolite are correlated with the salinity of coexisting hydrothermal fluids (Ellis 1978; Oliver et al. 1992, Zhu et al. 2015). Thus, halogen chemistry of scapolite has been widely applied to understand the genesis of ore deposits and associated fluid evolution. For instance, the composition and Br/Cl ratios of scapolite have been used to quantify the assimilation of evaporites during iron skarn mineralization in the Daye district, South China (Zhu et al. 2015; Zeng et al. 2019) and to identify the mixing of metamorphic and magmatic fluids in the genesis of IOCG deposits in the Norrbotten district, Northern Sweden (Bernal et al. 2017).

Skarn minerals in breccia pipes formed by the replacement of carbonate-bearing rocks are mainly related to fluid buffered metasomatic processes involving magmatic-hydrothermal fluids (Einaudi et al. 1981; Matthews et al. 1996). Geochemical and fluid inclusion features of skarn minerals provide important information on the evolution of hydrothermal fluids (Kwak 1986; Jamtveit et al. 1993; Baker et al. 2004). The Tietangdong Fe-Au skarn breccia pipe is located at the Yixingzhai gold deposit in the Taihangshan district, North China Craton (Zhang et al. 2019). Scapolite commonly
occurs in this breccia pipe and coexists with other skarn minerals. They contain heterogeneous fluid inclusions assemblages, which consist of vapor-rich and daughter crystal-bearing fluid inclusions (Zhang et al. 2020). This indicates that the scapolite formed from a hydrothermal fluid that underwent phase separation. Thus, scapolite from the Tietangdong breccia pipe can record the Br/Cl and I/Cl variation of the coexisting hydrothermal fluids. This provides an excellent opportunity to elucidate the halogen fractionation behavior during fluid phase separation. In this study, we conducted fluid inclusion microthermometry, halogen geochemistry (Cl, Br, and I), and Sr isotope analysis of scapolite to provide insights into the mechanisms of halogen fractionation during the phase separation of hydrothermal fluid.

GEOLOGICAL BACKGROUND

The Yixingzai gold deposit is one of the largest gold deposits in the Taihangshan district, North China Craton (Fig. 1a). It includes four breccia pipes and several NW-/NNW-trend auriferous quartz veins hosted in Archean tonalite-trondhjemite-granodiorite (TTG) and amphibolite rocks (Fig. 1b). The Tietangdong Fe-Au skarn breccia pipe (250 × 150 m at the surface) is roughly controlled by two sets of parallel NW- and NE-trend faults with steep boundaries and extends more than 1400 m in depth (Fig. 1c). The breccia clasts include numerous sub-angular to rounded polymictic clasts, with diameters ranging from a few millimeters to several meters. They are composed of prograde skarn (garnet, diopside, and scapolite), retrograde skarn (actinolite, tremolite, epidote, and chlorite), TTG, amphibolite, diabase, diorite porphyry, and felsite. The interstitial matrix and cement include debris, calc-silicate minerals, calcite, and quartz,
indicating a physical brecciation of the rocks followed by subsequent hydrothermal alteration. Some NS-trending quartz porphyry dikes cut the breccia pipe (Fig. 1b) with a zircon U-Pb age of 141 ± 1 Ma, indistinguishable from the skarn garnet U-Pb age (140 ± 2 Ma; Zhang et al. 2020).

Three hydrothermal alteration and mineralization stages in the Tietangdong breccia pipe have been recognized by detailed field and petrographic observations. These include the prograde skarn, retrograde skarn, and quartz-sulfide-calcite stages. The prograde skarn stage is characterized by the formation of garnet, diopside, scapolite, and minor magnetite (Figs. 2a-d). The retrograde skarn stage is represented by epidote, actinolite, magnetite, and sulfide minerals, with minor electrum and late-stage scapolite (Figs. 2e-g). They commonly replace or cement the prograde skarn minerals (Fig. 2a). Finally, the quartz-sulfide-calcite stage is characterized by pervasive quartz, sulfides, calcite, and adularia, which frequently occur in the open vugs of the breccia pipe. The mineral paragenesis sequences of Tietangdong are summarized in Fig. 3, showing that the scapolite coexisted with other skarn minerals in the prograde and retrograde skarn stages.

SAMPLES AND METHODS

Sample description

Ten scapolite-rich samples were collected for petrographical, microthermometrical, geochemical, and Sr isotopic studies (Fig. 1c). Detailed sample descriptions are listed in Table S1, Supplementary Materials and are briefly described here. Samples TTD18, 18Scp-3, and 18Scp-1 were taken from the open pit, with mineral associations of garnet, scapolite, and diopside. Samples 830Scp-5, 830Scp-13, 830Scp-15, 830Scp-18, and
T510-6 were taken from the 830 m and 510 m underground adits. Samples T601-152 and T601-181.3 were taken from drill core T510ZK601, with mineral associations of garnet, scapolite, diopside, epidote, actinolite, calcite, and quartz. Double-polished thin sections were examined under an optical microscope to investigate the mineralogy and textural features. Subsequently, scapolite grains with different mineral associations were extracted, handpicked, and mounted in 25 mm-diameter epoxy mounts. Then, carbon-coated sections and mounts were observed by back-scattered electron (BSE) and cathodoluminescence (CL) imaging on scanning electron microscopes.

**Fluid inclusion microthermometry**

Fluid inclusion microthermometry was performed on a Linkam 600 heating-freezing stage and a Linkam TS1400XY heating stage mounted on the Olympus BX53M microscopes at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan). The Linkam 600 stage was calibrated at -56.6 °C, 0.0 °C, and 374.1 °C using pure H₂O-CO₂ and H₂O synthetic fluid inclusion standards, and the Linkam TS1400XY stage was calibrated at 374.1 °C using a pure H₂O synthetic fluid inclusion standard. Fluid inclusion assemblages (FIAs), which represent a group of petrographically constrained and contemporaneously entrapped fluid inclusions (Goldstein and Reynolds 1994), were chosen for microthermometric measurements. A cycling technique was undertaken to obtain homogenization and ice melting temperatures (Goldstein and Reynolds 1994). Total uncertainties range from 2–3 °C for the heating stage (temperature above 100 °C) and ± 0.2 °C for the freezing stage (-56.6 to 0.0 °C). The program HokieFlincs for the NaCl-H₂O system (Steele-MacInnis et al. 2012) was used to calculate the salinity and pressure of fluid inclusions.
Electron probe microanalysis

Electron probe microanalysis (EPMA) of scapolite was conducted using a JEOL JXA-8230 Superprobe at the Center for Material Research and Analysis, Wuhan University of Technology. Analyses were performed using a 15 kV accelerating voltage and a 20 nA beam current with a 5 μm beam to avoid potential diffusion of Na and Cl (Hammerli et al. 2013). The peak counting times were 20 seconds for Sr and S, and 10 seconds for the other elements. The background was measured on both sides of the peak for half of the peak time. The Kα line was chosen for Na, Al, Si, Mg, Fe, K, Ca, Ti, Cl, F, Sr, and S. The Lα line was chosen for Mn. Natural mineral standards include albite (Na, Si, and Al), K-feldspar (K), plagioclase (Ca), tugtupite (Cl), celestite (Sr and S), pyrope (Mg), rutile (Ti), hematite (Fe), rhodonite (Mn), and fluorite (F). The USNM R6600-1 scapolite (Cl: 1.43 wt%; Jarosewich et al. 1980) was used as a secondary standard. The raw data were corrected using the internal ZAF routine. The detection limits of all the elements were approximately 0.02 wt%. The measured value of USNM R6600-1 is 1.39 ± 0.05 wt% for Cl (n = 10, 2σ; Table S2). The mineral formula was calculated based on Si + Al = 12 atom per formula unit and Cl + S + C = 1 atom per formula unit (Evans et al. 1969; Teertstra and Sherriff 1997). The detailed analytical method for EPMA of actinolite is listed in the Supplementary Materials.

Halogen analysis of scapolite

A femtosecond laser ablation (LA) instrument (J200, Applied Spectra, Inc., USA) coupled to the Thermo Element XR Sector-field ICP-MS was used to obtain halogen concentrations of scapolite at the Institute of Mineral Resource, Chinese Academy of
A laser spot size of 50 µm was used throughout these measurements. A repetition rate of 8 Hz was used along with a carrier gas rate of helium of 0.70 L/min and the argon make-up gas rate of 1.20 L/min to introduce the ablated material into the ICP torch. The ICP-MS was tuned using a NIST SRM 610 glass to reach robust conditions and low oxide production which was monitored as ThO⁺/Th⁺ < 0.3%. For each analysis cycle, a 30 seconds background signal was collected before the laser was switched on for 20 seconds of ablation of the sample material. Then a washout period of 70–100 seconds was set after measurements to ensure low and stable halogen backgrounds. Only ²⁹Si, ³⁵Cl, ⁷⁹Br, ⁸¹Br, and ¹²⁷I were determined to provide optimal counting time for halogen concentrations. Furthermore, the reference materials (see below) were repeatedly analyzed every 10 analyses of the studied scapolite and monitored throughout the session for drift. Raw data were reduced via the software package ICPMSDataCal (Liu et al. 2010). Silicon concentrations quantified by EPMA were used as the internal standard for data reduction. The scapolite standards ON70 (1.94 wt% Cl, 1877 ppm Br; Evans et al. 1969; Teertstra and Sherriff 1997; Zhang et al. 2017a) and AF8 (7.16 wt% Cl, 148 ppm Br, and 28.4 ppm I determined by bulk analysis) were used as the external standard for Cl, Br, and I data reduction. AF5 (7.12 wt% Cl, 661 ppm Br, and 106 ppm I, bulk analysis) was used as a secondary standard. The measured values of AF5 are 7.11 ± 0.59 wt% for Cl, 658 ± 56 ppm for Br, and 102 ± 10 ppm for I (n = 12, 2σ; Table S3). The scapolite Cl contents detected by LA-ICPMS are consistent with the Cl concentrations obtained from EPMA within 2σ uncertainty (Fig. S1c). The details on the LA-ICPMS and bulk halogen analyses on the reference materials are listed in the Supplementary Materials.
Strontium isotope analysis of scapolite

Sr isotopes of scapolite were measured by a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Bremen, Germany) in combination with a Geolas HD excimer ArF laser ablation system (Coherent, Göttingen, Germany) at the Wuhan Sample Solution Analytical Technology Co., Ltd, Hubei, China. The Neptune Plus was equipped with nine Faraday cups fitted with $10^{11}$ Ω resistors. The Faraday collector configuration of the mass system was composed of an array from L4 to H3 to monitor Kr, Rb, Er, Yb and Sr. The combination of the high-sensitivity X-skimmer cone and Jet-sample cone was employed. In the laser ablation system, helium was used as the carrier gas for the ablation cell. Laser conditions included spot diameter (120 μm), pulse frequency (8 Hz), and fluence (~8 J/cm²). A signal smoothing device (Hu et al. 2012) was used downstream from the sample cell to eliminate the short-term variation of the signal. The data reduction for LA-MC-ICPMS analysis was conducted using ICPMSDataCal (Liu et al. 2010). The interference correction strategy was the same as the one reported by Tong et al. (2016) and Zhang et al. (2018). One natural feldspar megacryst (anorthite YG4301) was used as the secondary standard to verify the accuracy of the calibration method for in situ Sr isotope analysis. Measured $^{87}\text{Sr} / {^{86}\text{Sr}}$ values of YG4301 are 0.70343 ± 0.00021 ($n = 4$, 2σ), which are consistent with the recommended $^{87}\text{Sr} / {^{86}\text{Sr}}$ values of 0.70343 ± 0.00002 (Zhang et al. 2018).
RESULTS

Textures and geochemistry of scapolite

Two different types of scapolite (Scp I and Scp II) are distinguished by their mineral associations. Scp I grains occur at 1300, 830, 510, and 328.7 m above sea level (a.s.l.) in the Tietangdong breccia pipe (Fig. 1c). They are coarse-grained and euhedral crystals (0.2–1.5 cm), which are intergrown with garnet, diopside, and magnetite at the prograde skarn stage (Figs. 2a-d, 3). Some Scp I grains have been formed by the replacement of plagioclase phenocrysts in the diorite fragments, with a grain size of 0.2–0.5 cm (Figs. 2b, c). Scp II crystals (0.5–2 cm) filling in the voids of breccia clasts are commonly associated with actinolite, epidote, and pyrite at the retrograde skarn stage (Figs. 2e-g, 3). Scp II mainly occurs at 830, 510, and 358 m a.s.l. in the Tietangdong breccia pipe (Fig. 1c).

Most scapolite grains have relatively homogeneous textures in CL and BSE images (Figs. 4a-c). A few scapolite grains have overgrowth textures, such as CL-dark irregular zoning rims and CL-bright homogeneous cores (Fig. 4d). The cores are considered as Scp I, whereas the rims are generally associated with actinolite and epidote (Figs. 2e, f) and represent Scp II.

Results of EPMA analyses on the scapolite are tabulated in Tables 1 and S2. All analyzed scapolite grains have meionite equivalent (Me) of 27.5–49.8% (n = 136), with FeO, MnO, TiO₂, MgO, and F generally being below the detection limits (Table S2). All samples follow the \([\text{Na}_4\text{Cl}]\text{Si}_2\text{[NaCa}_3\text{CO}_3]\text{Al}_2\) substitution mechanism (Fig. 5a; Hassan and Buseck 1988) and show a negative correlation between Cl and equivalent anorthite.
Scp I crystals have Me of 27.5–40.3% and Eq. An of 26.0–38.8% (Table 1, Figs. 5a-c). They contain 22.08–23.80 wt% Al₂O₃, 52.38–57.52 wt% SiO₂, 7.16–9.17 wt% Na₂O, and 6.59–9.75 wt% CaO, with minor amounts of K₂O (0.83–2.02 wt%) and SrO (0.20–0.35 wt%). The contents of Cl, SO₃, and CO₃ in Scp I range from 2.53–3.48 wt%, 0.04–0.33 wt%, and 0.82–2.36 wt%, respectively (Table 1, Fig. 5d). Scp II grains have 34.4–49.8% Me and 31.5–42.9% Eq. An (Table 1, Figs. 5a-c), and contain 22.56–24.46 wt% Al₂O₃, 51.39–54.92 wt% SiO₂, 5.76–8.16 wt% Na₂O, and 8.39–12.27 wt% CaO. The contents of Cl, SO₃, and CO₃ in Scp II crystals vary from 2.19–2.90 wt%, 0.06–0.50 wt%, and 1.52–2.85 wt%, respectively (Table 1, Fig. 5d).

**Fluid inclusions**

Three types of primary fluid inclusion are distinguished by their textural and phase proportion features at room temperature. These types include daughter mineral-bearing three phases (S-type), vapor-rich aqueous (V-type), and liquid-rich aqueous (L-type) fluid inclusions. For each type, fluid inclusions have constant phase proportions (Fig. 6b) and commonly occur in mineral growth zones (Fig. 6c). The fluid inclusions (5–15 μm diameter) often display rounded or negative crystal shapes (Figs. 6a, b), but some show irregular boundaries (Figs. 6c, d). S-type fluid inclusions are composed of liquid, vapor, halite, sylvite, and/or other unidentified daughter crystal phases at room temperature. They commonly occur in scapolite, diopside, and epidote (Figs. 6a-d). V-type fluid inclusions are dominated by a vapor phase generally higher than 65% of the total volume and typically coexist with S-type varieties (Figs. 6a-d). The coexistence of S- and V-type fluid inclusions is interpreted as boiling FIA s in the skarn minerals (Audétat 2022; Figs. 6a-d). L-type fluid inclusions are commonly present in epidote and calcite, with 15–30%
vapor phase. A few irregularly shaped fluid inclusions with inconsistent phase proportions are observed in the studied scapolite (Fig. 6d), indicating the reequilibration of fluid inclusions (Bodnar, 2003). In this case, fluid inclusion microthermometry results from scapolite are not presented. Therefore, the fluid inclusion microthermometry results from diopside and epidote which are associated with two stages scapolite, are used to determine the salinity, temperature, and pressure of hydrothermal fluids during the scapolite formation.

The microthermometry results are summarized in Table 2 and illustrated in Fig. 7. All S-type inclusions are characterized by the final disappearance of the vapor phase after the dissolution of daughter crystals. L-type inclusions homogenize into the liquid phase. S-type inclusions in diopside have a final homogenization temperature of 544–586 °C and calculated salinities of 37.0–54.8 wt% NaCl eq. (Fig. 7). Homogenization temperatures of S- and L-type inclusions in the epidote are 441–470 °C and 413–433 °C, respectively (Fig. 7). The calculated salinities of S- and L-type inclusions are 32.5–38.7 wt% NaCl eq. and 7.9–10.5 wt% NaCl eq., respectively (Fig. 7). L-type inclusions in calcite have total Homogenization temperatures of 146 to 169 °C and calculated salinity of 5.4–9.9 wt% eq. (Fig. 7). Due to the unclear boundaries of the vapor phase, the V-type fluid inclusions were not measured.

Halogen geochemistry of scapolite

Halogen contents of scapolite determined by LA-ICPMS are summarized in Table 1 and listed in Table S3. The Scp I crystals have 2.07–3.41 wt% Cl, 389–659 ppm Br, and 10.1–17.9 ppm I. The Br/Cl, I/Cl, and Br/I molar ratios range from 6.1–11.9 × 10⁻³, 91–191 × 10⁻⁶, and 49.9–75.5, respectively. The Scp II grains have 1.84–3.10 wt% Cl, 395–
806 ppm Br, and 8.4–24.4 ppm I, with Br/Cl, I/Cl, and Br/I molar ratios ranging from 7.4–14.7 × 10⁻³, 105–302 × 10⁻⁶, and 42.0–94.1 respectively. Zoned scapolite grains in sample T510-6 show variable halogen ratios between the core and rim. The CL-bright core (Scp I) has lower Br/Cl (8.6–8.9 × 10⁻³) and I/Cl (137–140 × 10⁻⁶) values, whereas the CL-dark rim (Scp II) has higher Br/Cl (11.9–14.4 × 10⁻³) and I/Cl (205–302 × 10⁻⁶) values (Fig. 4d). The Br and I contents of the studied scapolite grains show no correlation with Cl (Figs. 8a, b), whereas Br is correlates positively with I (Figs. 8c, d).

**Strontium isotopes of scapolite**

In situ Sr isotope results of five representative scapolite samples are listed in Table 3. All scapolite grains have significantly low Rb/Sr ratios (< 0.03), implying negligible radiogenic Sr. Thus, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ values can be considered as the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of scapolite. Scp I and Scp II grains have $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.7099 to 0.7112 and 0.7104 to 0.7116, respectively. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of all the scapolite increase with increasing Br/Cl and I/Cl values (Fig. 9).

**DISCUSSION**

**Formation conditions of scapolite**

In the Tietangdong Fe-Au skarn breccia pipe, Scp I grains are closely associated with the prograde skarn minerals (Figs. 2a-d, 3, Table S1), and Scp II grains are commonly intergrown with the retrograde skarn minerals (Figs. 2e-g, 3, Table S1). The mineral association and fluid inclusion features of the studied samples (Fig. 6) indicate the hydrothermal origin of scapolite. The high SO₃ contents of the scapolite (0.18 wt% on
average) imply that the sulfur species in the hydrothermal fluid include sulfate (e.g., $\text{SO}_4^{2-}$, Qiu et al. 2021), suggesting an oxidized ore-forming fluid. This view is also confirmed by the occurrence of hematite and magnetite in these samples. The relatively high Cl contents (2.19–3.48 wt%) and marialite proportions ($\text{Me} = 27.5–49.8$; Figs. 5b-d) in scapolite suggest elevated Cl and Na concentrations in the coexisting hydrothermal fluid (Ellis 1978; Oliver et al. 1994). This view is confirmed by the presence of high salinities of S-type fluid inclusions in diopside and epidote (32.5–54.8 wt% NaCl eq.; Table 2). The microthermometry results show that Scp I and II grains have formed from high temperature (544–586 °C for Scp I, 441–470 °C for Scp II; Table 2) hydrothermal fluids under low-pressure conditions (44.1–58.8 MPa for Scp I, 30.2–33.5 MPa for Scp II; Table 2). The coexisting S-type and V-type fluid inclusions in diopside, scapolite, and epidote imply that they form under fluid phase separation.

Scapolite from the Tietangdong breccia pipe has relatively high Cl and low Eq. An values (Fig. 5b). These chemical characters are similar to hydrothermal scapolite from the Tieshan iron skarn deposit in Hubei Province, China, the Nickel plate Au deposit in British Columbia, Canada (Pan and Dong 2003), the Jinshandian iron skarn deposit in Hubei Province, China (Zeng et al. 2019), and the Clarke Head metasomatic syenite in Nova Scotia, Canada (Pe-Piper et al. 2019). In contrast, they are significantly distinct from the metamorphic scapolite in amphibolite-facies calc-silicates at Mary Kathleen, Australia (Oliver et al. 1992) and Idaho, America (Rebbert and Rice 1997). The studied scapolite has relatively low $\text{CO}_3^-$/ ($\text{SO}_3^- + \text{CO}_3^- + \text{Cl}$) ratios and high Cl contents, similar to the magmatic-hydrothermal origin scapolite from the Norrbotten district, Sweden (Fig. 5d, Bernal et al. 2017). Furthermore, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of scapolite (0.7099–0.7116; Table 3)
are slightly higher than the coeval granite porphyry related to the breccia pipe (0.7091–0.7092; Zhang et al. 2017b), but they are much lower than the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the metamorphic rocks in this region (0.7130–0.7180; Jahn et al. 1999). The Sr isotope data suggest that the studied scapolite formed from a magmatic-hydrothermal fluid that interacted slightly with the Archean wall rocks (Figs. 9a, b). Taken together, we propose that the studied scapolite grains formed from an oxidized, high-salinity fluid resulting from the fluid phase separation of magmatic-hydrothermal fluid at high-temperature and low-pressure conditions. However, the Br/Cl and I/Cl values of all the studied scapolite are significantly higher than those values of the magmatic-hydrothermal fluid (Fig. 10), for reasons that will be discussed later.

**Origin of the high Br/Cl and I/Cl fluid**

The significantly high Br/Cl and I/Cl values of the scapolite from the Tietangdong breccia pipe may be explained by (1) large Br/Cl and I/Cl partition coefficients (>1) between scapolite and fluids in Cl-poor (< 0.03 wt% Cl) meionitic scapolite groups, (2) mixing of magmatic-hydrothermal fluid with external high Br/Cl and I/Cl fluids, or (3) halogen fractionation during hydrothermal fluid evolution. Previous studies have shown that Cl-poor meionitic scapolite (0.02–0.03 wt% Cl, Me = 76.7%) from Laurence-McGill Farm (LM-Q) in the Grenville Province has unusually high Br/Cl (39.1–54 × 10$^{-3}$) and I/Cl (226–284 × 10$^{-6}$) ratios (Kendrick and Phillips 2009; Fig. 10). These high halogen ratios may result from the high Br/Cl and I/Cl partition coefficients (> 1) between Cl-poor meionitic scapolite and fluids (Kendrick and Phillips 2009). However, high Br/Cl and I/Cl ratios do not occur in the scapolite (1.79–4.13 wt% Cl, Me = 7.1–48.8%) from Haliburton Highway (HAL-O), Tory Hills, Bancroft (TB-O), and Bear Lake (BL-Q) in
the Grenville Province (Kendrick and Phillips 2009; Fig. 10). In this study, all scapolite grains from the Tietangdong breccia pipe are high Cl scapolite (2.19–3.48 wt% Cl; Me = 27.5–49.8%), which precludes the first hypothesis. In the second case, magmatic-hydrothermal fluid mixing with high Br/Cl sources (marine evaporites or organic-rich sediment) may cause significantly high Br/Cl values of the scapolite, but those mixing fluids have significantly lower or higher I/Cl ratios than the studied scapolite (Zherebtsova and Volkova 1966; Polya et al. 2000; Sekimoto and Ebihara 2013; Hanley and Koga 2018; mixing trend 1 and 3, Fig. 10). This precludes the second hypothesis. We therefore suggest that these high Br/Cl and I/Cl values of the studied scapolite most likely resulted from halogen fractionation during hydrothermal fluid evolution. In this case, three processes may cause such halogen fractionation, including (1) low-pressure devolatilization of a cooling magma (Bureau et al. 2000, 2010, 2016; Kurosawa et al. 2016), (2) precipitation of Cl-bearing minerals (Markl and Bucher 1998; Svensen et al. 1999; Kusebauch et al. 2015), and (3) phase separation of hydrothermal fluid (Ishibashi et al. 1994; Oosting and Von Damm 1996; Berndt and Seyfried 1997; Lüders et al. 2002).

Halogen fractionation may result from fluid exsolution from a cooling magma at low pressure, because Br/Cl and I/Cl partition coefficients between the fluid and its parental magma are negatively related to the pressure (Bureau et al. 2000; Bureau et al. 2010; Lukanin 2015; Bureau et al. 2016; Kurosawa et al. 2016; Hsu et al. 2019). However, fluids exsolved from volcanoes under very low-pressure conditions have Br/Cl and I/Cl values of 0.17–4.15 × 10⁻³ and 0.84–703.20 × 10⁻⁶, respectively (Webster et al. 2018; Fig. 10). These halogen ratios are much lower than the Br/Cl values of the studied scapolite.
Therefore, we propose that the significantly high halogen ratios in the studied scapolite are not controlled by the segregation of hydrothermal fluids from the magma at low pressure.

Halogen fractionation in hydrothermal fluids may be attributed to the precipitation of Cl-bearing minerals (such as halite, biotite, and amphibole). Several studies propose that most Cl-bearing minerals (halite, biotite, and amphibole) preferentially incorporate Cl into their structures rather than Br and I (Svensen et al. 2001; Mark et al. 2005; Kusebauch et al. 2015). For example, the precipitation of halite possibly increases the Br/Cl and I/Cl ratios of hydrothermal fluids (Andersson 2019, Michallik et al. 2021; Fig. 10). However, S-type fluid inclusions in the studied minerals were finally homogenized by vapor disappearance after the dissolution of salt crystals (Table 2), indicating the scapolite formed from a salt unsaturated fluid (Goldstein and Reynolds 1994; Driesner and Heinrich 2007; Fig. 7). Precipitation of massive Cl-bearing actinolite (Cl: 0.01–0.12 wt%, Fig. S2, Table S4) may also elevate the Br/Cl and I/Cl ratios of the hydrothermal fluids, because Cl preferentially partitions into the actinolite than Br and I (Svensen et al. 1999, 2001; Kusebauch et al. 2015). This view is confirmed by the higher Br/Cl and I/Cl values of Scp II than Scp I (Fig. 8d). However, the Scp I grains are not intergrown with any Cl-bearing minerals and have extremely high Br/Cl and I/Cl values. Thus, we proposed that the precipitation of Cl-bearing minerals may not be the predominant factor causing halogen fractionation in the scapolite-forming fluid.

Halogen fractionation observed for the Tietangdong scapolite is most likely related to the phase separation of the hydrothermal fluids. An experimental study (Liebscher et al. 2006) shows that Br preferentially partitions into the brine phase compared to Cl (380–
404 450 °C, 22.9–41.7 MPa). Other experimental studies, however, show that Br/Cl values in
405 the vapor phase are higher than the brine (388–550 °C, 25–35 MPa, Foustoukos and
406 Seyfried 2007; 900 °C, 90–150 MPa, Seo and Zajacz 2016). These differences may be
407 attributed to the interference of different ionic compositions in various experimental
408 sequences (Seo and Zajacz 2016). Fluid inclusions in quartz from the Tsushima granite
409 system, Japan (Kurosawa et al. 2016) have higher Br/Cl values in brine compared to the
410 coexisting vapor phase. This view is consistent with the significantly high Br/Cl ratios of
411 the studied scapolite grains, which are in equilibrium with the high-salinity fluid from
412 phase separation of magmatic-hydrothermal fluid. Therefore, we propose that Br
413 preferentially partitioned into the brine phase relative to Cl during fluid phase separation.
414 In addition, I and Br may have similar behavior during the phase separation of
415 hydrothermal fluids. This conclusion is supported by (1) Br and I have similar ionic sizes
416 (0.196 Å for Br; 0.220 Å for I; Shannon 1976), (2) Br/I values are overall constant during
417 seawater evaporation (Fig. 10), and (3) Br and I contents have a positive correlation in
418 the studied scapolite (Fig. 8c). Collectively, the significantly high Br/Cl and I/Cl values
419 of the studied scapolite can be explained by the phase separation of hydrothermal fluids.
420 A halogen fractionation model associated with fluid phase separation is proposed to test
421 this hypothesis (see below and Supplementary Materials).

422 **Halogen fractionation model**

423 As summarized above, the high Br/Cl and I/Cl values of scapolite from the
424 Tietangdong breccia pipe can be interpreted in terms of halogen fractionation due to
425 phase separation of the magmatic-hydrothermal fluid. Based on Drummond and Ohmoto
426 (1985), elements partition during phase separation of hydrothermal fluids is similar to
Rayleigh distillation. Thus, the Br/Cl and I/Cl values in separated brine phases can be quantitatively described as a simple Rayleigh fractionation model:

\[
C_{\text{Br/Cl}}^{\text{Brine}} = C_{\text{Br/Cl}}^{\text{Initial}} \times (1 - F_{\text{Vapor}})^{(1/K_{D(\text{Br/Cl})}^{\text{Brine-vapor}} - 1)}
\]

(1)

\[
C_{\text{I/Cl}}^{\text{Brine}} = C_{\text{I/Cl}}^{\text{Initial}} \times (1 - F_{\text{Vapor}})^{(1/K_{D(\text{I/Cl})}^{\text{Brine-vapor}} - 1)}
\]

(2)

where \(C_{\text{Br/Cl}}^{\text{Brine}}\) and \(C_{\text{I/Cl}}^{\text{Brine}}\) represent the Br/Cl and I/Cl molar ratios of the brine, respectively; \(C_{\text{Br/Cl}}^{\text{Initial}}\) and \(C_{\text{I/Cl}}^{\text{Initial}}\) refer to the Br/Cl and I/Cl molar ratios of the initial hydrothermal fluids, respectively; \(F_{\text{Vapor}}\) is the mass ratio between vapor and initial fluids. \(K_{D(\text{Br/Cl})}^{\text{Brine-Vapor}}\) and \(K_{D(\text{I/Cl})}^{\text{Brine-Vapor}}\) represent the Br/Cl and I/Cl exchange coefficients between the brine and vapor phases. The \(C_{\text{Br/Cl}}^{\text{Initial}}\) (1.5/1.8/2.0 \(\times\) 10\(^{-3}\)) and \(C_{\text{I/Cl}}^{\text{Initial}}\) (16/30/55 \(\times\) 10\(^{-6}\)) values were estimated from hydrothermal fluids degassed from magmas (Johnson et al. 2000; Burgess et al. 2002; Burgess et al. 2009; Kendrick et al. 2017; Table S6). The \(K_{D(\text{Br/Cl})}^{\text{Brine-Vapor}}\) is calculated from the equation proposed by Liebscher et al. (2006):

\[
K_{D(\text{Br/Cl})}^{\text{Brine-Vapor}} = 0.349 \times \ln[1.697 \times (D_{\text{Cl}}^{\text{Brine-Vapor}} - 1) + e^{(1/0.394)}]
\]

(3)

Based on the temperature, pressure, and salinity conditions under which the Tietangdong scapolite precipitated (Table 2), the \(K_{D(\text{Br/Cl})}^{\text{Brine-Vapor}}\) values are calculated to be 2.26 and 2.27 at 580 °C/45 MPa and 450 °C/30 MPa respectively (Fig. S3). The \(K_{D(\text{I/Cl})}^{\text{Brine-Vapor}}\) is assumed to be the same as \(K_{D(\text{Br/Cl})}^{\text{Brine-Vapor}}\), because Br and I have similar behavior during phase separation of hydrothermal fluids.

The Br/Cl and I/Cl ratios of brines are estimated to increase gradually with the progressive vapor loss (represented by \(F_{\text{Vapor}}\)) in the Tietangdong breccia pipe during the phase separation of initial hydrothermal fluids. They can be up to 18 \(\times\) 10\(^{-3}\) of Br/Cl and
500 × 10^{-6} of I/Cl at 98% vapor loss (Fig. S3, Table S6). Based on the fluid inclusion microthermometry results and mass balance calculation, the brine inclusions in the Scp I can be formed from 90–93% vapor loss of the initial hydrothermal fluids (Table S7). This result is consistent with our simulation result that 90–95% vapor loss can cause the high halogen ratios of the studied scapolite (Fig. 10). Hence, the simulation results confirm that the significantly high Br/Cl and I/Cl values of the studied scapolite can be attributed to extensive fluid phase separation.

**IMPLICATIONS**

The integrated study of fluid inclusion microthermometry, halogen geochemistry, and Sr isotope suggests that scapolite grains from the Tietangdong breccia pipe formed from an oxidized, high-temperature (544–586 °C for Scp I and 441–470 °C for Scp II), high salinity (37.0–54.8 wt% NaCl eq. for Scp I and 32.5–38.7 wt% NaCl eq. for Scp II), and low pressure (44.1–58.8 MPa for Scp I and 30.2–33.5 Mpa for Scp II) magmatic-hydrothermal fluid at prograde and retrograde skarn stages. The studied scapolite grains have significantly high Br/Cl (6.1–14.7 × 10^{-3}) and I/Cl (91–302 × 10^{-6}) values, which can be interpreted as the phase separation of magmatic-hydrothermal fluids. The phase separation could trigger halogen fractionation characterized by the preferential partitioning of Br and I into the brine compared to Cl. This study highlights the role of fluid phase separation in causing halogen fractionation, thus providing new insights into using halogens as a fluid tracer to determine the source and evolution of hydrothermal fluids under complex geological environments.
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Seo, J.H., and Zajacz, Z. (2016) Fractionation of Cl/Br during fluid phase separation in


**FIGURE CAPTIONS**

**Figure 1.** (a) A sketch map showing the tectonic divisions of the North China craton (NCC) and the location of the Taihangshan district (modified from Li et al. 2012). Geological map (b) and A-A’ cross-section (c) of the Tietangdong breccia pipe showing the sample locations (modified from Jing 1985).

**Figure 2.** Photographs and microphotographs showing the mineralogy and texture of the scapolite samples. (a) Scp I coexisting with garnet which is cemented by actinolite and epidote. (b) Plagioclase phenocrysts in diorite breccia replaced by Scp I grains. (c) Magnetite intergrown with Scp I. (d) Euhedral Scp I intergrown with garnet. (e-f) Scp II grains intergrown with massive actinolite, epidote, and pyrite. (g) Scp II intergrown with actinolite. Act-actinolite, Ep-epidote, Grt-garnet, Di-diopside, Mag-magnetite, Py-pyrite.

**Figure 3.** Paragenetic sequence of the Tietangdong breccia pipe. The thickness of the lines represents the relative contents of minerals.

**Figure 4.** CL and BSE images showing scapolite textures (Scp I and Scp II). (a) Homogenous Scp I grain. (b) Homogenous Br/Cl and I/Cl values in Scp I grain. (c) Scp II grain. (d) Zoned Scp II grain overgrown on homogenous Scp I. The bright core has low Br/Cl and I/Cl values, whereas the dark rim displays high halogen ratios.

**Figure 5.** Distribution of major elements in Scp I and Scp II. (a) Al/ (Al + Si) vs. Me of the scapolite. The solid line showing \([\text{Na}_4\text{Cl}]\text{Si}_2[\text{NaCa}_3\text{CO}_3]\text{Al}_2\) and...
34

[NaCa₃CO₃]Si-[Ca₄CO₃]Al non-linear substitutions. Scapolite samples plot between 27.5% and 49.8% Me. (b, c) The Cl vs. Eq. An of the Scp I and Scp II. Data of hydrothermal scapolite from Pan and Dong (2003), Pe-Piper et al. (2019), and Zeng et al. (2019). Data of metamorphic scapolite are from Oliver et al. (1992) and Rebbert and Rice (1997). (d) Ternary diagram CO₃-10 × SO₃-Cl showing volatile components in the Scp I and Scp II (modified from Bernal et al. 2017 and Gajdošová et al. 2019). Apfu-atom per formula unit.

Figure 6. Microphotographs showing fluid inclusion assemblages in diopside, epidote, and scapolite from the Tietangdong breccia pipe. (a) Vapor-rich (V-type) and daughter mineral-bearing (S-type) fluid inclusions in diopside. (b) S-type fluid inclusions with constant phase proportions coexisting with V-type fluids in diopside. (c) S-type fluid inclusions coexisting with V-type fluids within the growth zone of epidote. (d) V-type fluid inclusions coexisting with S-type fluid inclusions in the Scp I grain. V-vapor phase, L-liquid phase, H-halite, S-sylvite, X-unidentified phase, Di-diopside, Ep-epidote.

Figure 7. Homogenization temperature vs. salinity diagram of fluid inclusion assemblages. Isobars and critical curves based on Atkinson (2002). Di-diopside, Ep-epidote, Cal-calcite.

Figure 8. Distribution of halogens in Scp I and Scp II. (a, b) Br and I vs. Cl diagrams showing that Br and I have no correlation with Cl. (c) Positive correlation between I vs. Br. (d) I/Cl vs. Br/Cl molar ratios of the scapolite. Note that the halogen ratios of Scp I

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and Scp II show two trends.

**Figure 9.** $^{87}\text{Sr}/^{86}\text{Sr}$ vs. molar ratios of Br/Cl (a) and I/Cl (b) diagrams. The density graph of $^{87}\text{Sr}/^{86}\text{Sr}$ values of Scp I and Scp II is illustrated in (a). $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Hewan granite porphyry and metamorphic rocks from Zhang et al. (2017b) and Jahn et al. (1999) respectively.

**Figure 10.** I/Cl vs. Br/Cl diagram (molar ratios) for scapolite in the Tietangdong breccia pipe. The blue (brine trend) and gray dotted (vapor trend) lines represent the Rayleigh fractionation modeling of halogens fractionation during hydrothermal fluid phase separation. Halogen reservoirs include seawater$^1$ (Riley and Chester 1971); seawater evaporation trajectory$^2$ (Zherebtsova and Volkova 1966); sylvite$^3$ (Holser, 1979); evaporite$^4$ and organic matter$^5$ (Kendrick and Burnard 2013); marine pore fluids$^6$ and basin pore fluids$^13$ (Kendrick et al. 2011); mantle: OIB and MORB glasses$^7$ (Kendrick et al. 2017), coated diamond$^8$ (Johnson et al. 2000; Burgess et al. 2002; Burgess et al. 2009); porphyry copper deposits$^9$ (Böhlke and Irwin 1992; Irwin and Roedder 1995; Kendrick et al. 2001ab); mixing trend 1: sedimentary assimilation with magmatic-hydrothermal fluids$^{10}$ (Polya et al. 2000); mixing trend 2: evaporite assimilation with magmatic-hydrothermal fluids$^{11}$ (Campbell et al. 1995); mixing trend 3: evaporated and seawater assimilation$^{12}$ (Richard et al. 2014); sedimentary$^{14, 15, 16}$: dolomite, limestone, sandstone, shale, chert, and fluvial lacustrine sediments (Mason 1966; Sekimoto and Ebihara 2013; Hanley and Koga 2018); scapolite$^{17}$ (Kendrick and Phillips 2009); magmatic-hydrothermal related REE phosphate deposits$^{18}$ in Sweden (Andersson 2019);
and fluids and gases from volcanic magma\textsuperscript{19} (Webster et al. 2018) are shown for comparison.
Table 1. A summary of major and halogen elements results determined by EPMA and LA-ICPMS in scapolite.

<table>
<thead>
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<th>EPMA (wt%)</th>
<th>1300m (N = 61)</th>
<th>830 m (N = 10)</th>
<th>510 m (N = 42)</th>
<th>358 m (N = 11)</th>
<th>328.7 m (N = 12)</th>
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<tbody>
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<td></td>
<td>Scp I</td>
<td>Scp I</td>
<td>Scp II</td>
<td>Scp I</td>
<td>Scp II</td>
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<tr>
<td></td>
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<td>Mean</td>
<td>Range</td>
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<td>Range</td>
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<td>0.56–0.76</td>
<td>0.63</td>
<td>0.63–0.71</td>
</tr>
<tr>
<td></td>
<td>0.65–0.75</td>
<td>0.71</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LA-ICPMS</td>
<td>1300m (N = 30)</td>
<td>830 m (N = 10)</td>
<td>510 m (N = 25)</td>
<td>358 m (N = 16)</td>
<td>328.7 m (N = 14)</td>
</tr>
<tr>
<td>Cl (wt%)</td>
<td>2.45–3.41</td>
<td>2.91</td>
<td>2.07–2.72</td>
<td>2.52</td>
<td>1.84–2.47</td>
</tr>
<tr>
<td></td>
<td>2.10–3.10</td>
<td>2.03–2.83</td>
<td>2.48</td>
<td>2.03–2.75</td>
<td>2.42</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
<td>---------</td>
<td>-----</td>
<td>---------</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>I (ppm)</td>
<td>10.8–17.9</td>
<td>13.6</td>
<td>10.1–12.0</td>
<td>10.8</td>
</tr>
<tr>
<td>Molar B/C</td>
<td>( \times 10^{-3} )</td>
<td>6.1–9.1</td>
<td>7.9</td>
<td>6.9–9.6</td>
<td>7.9</td>
</tr>
</tbody>
</table>

FeO, MgO, MnO, TiO₂, and F are generally below the detection limit (b.d.l.). Atomic formula based on Si + Al = 12 (Evans et al. 1969; Teertstra and Sherriff 1997).

aCO₂ contents are recalculated by assuming a full anion site occupancy and H₂O-free compositions (Cl + S + C = 1; Evans et al. 1969; Teertstra and Sherriff 1997).

bMe (meionite equivalent) = 100 × (Ca + Mg + Fe + Mn + Sr)/(Na + K + Ca + Mg + Fe + Mn + Sr).

cEq. An (equivalent anorthite) = 100 × (Al - 3)/3.
Table 2. Microthermometry results of skarn minerals from the Tietangdong breccia pipe.

<table>
<thead>
<tr>
<th>FIA</th>
<th>Type</th>
<th>N</th>
<th>Homogenization (°C)</th>
<th>SD (°C)</th>
<th>Halite dissolution (°C)</th>
<th>SD (°C)</th>
<th>Salinity (wt% NaCl eq.)</th>
<th>SD (wt% NaCl eq.)</th>
<th>Pressure (MPa)</th>
<th>SD (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>596.5c</td>
<td>S</td>
<td>7</td>
<td>584</td>
<td>44</td>
<td>376</td>
<td>10</td>
<td>44.4</td>
<td>0.9</td>
<td>47.0</td>
<td>3.4</td>
</tr>
<tr>
<td>596.5d</td>
<td>S</td>
<td>2</td>
<td>544</td>
<td>74</td>
<td>341</td>
<td>4</td>
<td>41.1</td>
<td>0.1</td>
<td>46.9</td>
<td>16.1</td>
</tr>
<tr>
<td>596.5e</td>
<td>S</td>
<td>6</td>
<td>571</td>
<td>35</td>
<td>467</td>
<td>5</td>
<td>54.8</td>
<td>0.3</td>
<td>44.1</td>
<td>7.8</td>
</tr>
<tr>
<td>596.5f</td>
<td>S</td>
<td>5</td>
<td>582</td>
<td>17</td>
<td>288</td>
<td>2</td>
<td>37.0</td>
<td>0.1</td>
<td>58.8</td>
<td>4.6</td>
</tr>
<tr>
<td>596.5h</td>
<td>S</td>
<td>9</td>
<td>571</td>
<td>36</td>
<td>343</td>
<td>4</td>
<td>41.3</td>
<td>0.4</td>
<td>54.4</td>
<td>0</td>
</tr>
<tr>
<td>596.5i</td>
<td>S</td>
<td>3</td>
<td>586</td>
<td>102</td>
<td>348</td>
<td>45</td>
<td>42.0</td>
<td>4.4</td>
<td>51.5</td>
<td>30.4</td>
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</table>

**Retrograde skarn stage (epidote)**

<table>
<thead>
<tr>
<th>FIA</th>
<th>Type</th>
<th>N</th>
<th>Homogenization (°C)</th>
<th>SD (°C)</th>
<th>Ice dissolution (°C)</th>
<th>SD (°C)</th>
<th>Salinity (wt% NaCl eq.)</th>
<th>SD (wt% NaCl eq.)</th>
<th>Pressure (MPa)</th>
<th>SD (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T601-537.7a</td>
<td>S</td>
<td>2</td>
<td>461</td>
<td>2</td>
<td>304</td>
<td>71</td>
<td>38.7</td>
<td>5.5</td>
<td>30.3</td>
<td>1.3</td>
</tr>
<tr>
<td>T601-537.7b</td>
<td>S</td>
<td>2</td>
<td>457</td>
<td>3</td>
<td>213</td>
<td>11</td>
<td>32.5</td>
<td>0.6</td>
<td>31.7</td>
<td>0.4</td>
</tr>
<tr>
<td>T601-537.7c</td>
<td>S</td>
<td>3</td>
<td>450</td>
<td>5</td>
<td>217</td>
<td>2</td>
<td>32.7</td>
<td>0.1</td>
<td>30.4</td>
<td>1.0</td>
</tr>
<tr>
<td>T601-537.7d</td>
<td>S</td>
<td>14</td>
<td>470</td>
<td>3</td>
<td>277</td>
<td>3</td>
<td>36.4</td>
<td>0.2</td>
<td>32.8</td>
<td>0.6</td>
</tr>
<tr>
<td>T601-537.7e</td>
<td>S</td>
<td>10</td>
<td>462</td>
<td>3</td>
<td>252</td>
<td>1</td>
<td>34.7</td>
<td>0.1</td>
<td>32.3</td>
<td>0.2</td>
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<tr>
<td>T18-2a</td>
<td>S</td>
<td>8</td>
<td>441</td>
<td>27</td>
<td>237</td>
<td>-</td>
<td>33.8</td>
<td>-</td>
<td>33.5</td>
<td>0</td>
</tr>
<tr>
<td>494.7a</td>
<td>S</td>
<td>7</td>
<td>457</td>
<td>28</td>
<td>288</td>
<td>5</td>
<td>37.1</td>
<td>0.4</td>
<td>30.2</td>
<td>6.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FIA</th>
<th>Type</th>
<th>N</th>
<th>Homogenization (°C)</th>
<th>SD (°C)</th>
<th>Salinity (wt% NaCl eq.)</th>
<th>SD (wt% NaCl eq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>03a</td>
<td>L</td>
<td>7</td>
<td>420</td>
<td>8</td>
<td>-6.0</td>
<td>9.2</td>
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</table>

**Quartz-sulfide and calcite stage (calcite)**

<table>
<thead>
<tr>
<th>FIA</th>
<th>Type</th>
<th>N</th>
<th>Homogenization (°C)</th>
<th>SD (°C)</th>
<th>Ice dissolution (°C)</th>
<th>SD (°C)</th>
<th>Salinity (wt% NaCl eq.)</th>
<th>SD (wt% NaCl eq.)</th>
<th>Pressure (MPa)</th>
<th>SD (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>512.1c</td>
<td>L</td>
<td>8</td>
<td>160</td>
<td>9</td>
<td>-4.9</td>
<td>2.3</td>
<td>7.6</td>
<td>3.1</td>
<td></td>
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</tr>
</tbody>
</table>
Table 3. Sr isotope data of the scapolite grains from the Tietangdong breccia pipe.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Comment</th>
<th>Rb/Sr</th>
<th>$^{87}$Sr/$^{86}$Sr</th>
<th>2SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>18S1-01</td>
<td>Scp I</td>
<td>0.02</td>
<td>0.7100</td>
<td>0.0001</td>
</tr>
<tr>
<td>18S1-02</td>
<td>Scp I</td>
<td>0.02</td>
<td>0.7101</td>
<td>0.0001</td>
</tr>
<tr>
<td>18S1-03</td>
<td>Scp I</td>
<td>0.02</td>
<td>0.7100</td>
<td>0.0001</td>
</tr>
<tr>
<td>18S1-04</td>
<td>Scp I</td>
<td>0.02</td>
<td>0.7101</td>
<td>0.0002</td>
</tr>
<tr>
<td>18S1-05</td>
<td>Scp I</td>
<td>0.01</td>
<td>0.7102</td>
<td>0.0002</td>
</tr>
<tr>
<td>83013-01</td>
<td>Scp I</td>
<td>0.01</td>
<td>0.7100</td>
<td>0.0002</td>
</tr>
<tr>
<td>83013-02</td>
<td>Scp I</td>
<td>0.01</td>
<td>0.7099</td>
<td>0.0002</td>
</tr>
<tr>
<td>83013-03</td>
<td>Scp I</td>
<td>0.02</td>
<td>0.7103</td>
<td>0.0002</td>
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<td>83013-04</td>
<td>Scp I</td>
<td>0.01</td>
<td>0.7104</td>
<td>0.0002</td>
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<tr>
<td>181.3-01</td>
<td>Scp I</td>
<td>0.03</td>
<td>0.7103</td>
<td>0.0003</td>
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<td>181.3-02</td>
<td>Scp I</td>
<td>0.03</td>
<td>0.7109</td>
<td>0.0002</td>
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<tr>
<td>181.3-03</td>
<td>Scp I</td>
<td>0.03</td>
<td>0.7112</td>
<td>0.0002</td>
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<tr>
<td>181.3-04</td>
<td>Scp I</td>
<td>0.03</td>
<td>0.7112</td>
<td>0.0003</td>
</tr>
<tr>
<td>83015-01</td>
<td>Scp II</td>
<td>0.03</td>
<td>0.7113</td>
<td>0.0002</td>
</tr>
<tr>
<td>83015-02</td>
<td>Scp II</td>
<td>0.03</td>
<td>0.7114</td>
<td>0.0003</td>
</tr>
<tr>
<td>83015-03</td>
<td>Scp II</td>
<td>0.05</td>
<td>0.7107</td>
<td>0.0003</td>
</tr>
<tr>
<td>510-6-01</td>
<td>Scp II</td>
<td>0.03</td>
<td>0.7110</td>
<td>0.0003</td>
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<tr>
<td>510-6-02</td>
<td>Scp II</td>
<td>0.04</td>
<td>0.7116</td>
<td>0.0003</td>
</tr>
<tr>
<td>510-6-03</td>
<td>Scp II</td>
<td>0.03</td>
<td>0.7110</td>
<td>0.0003</td>
</tr>
<tr>
<td>510-6-04</td>
<td>Scp II</td>
<td>0.03</td>
<td>0.7104</td>
<td>0.0002</td>
</tr>
</tbody>
</table>
Figure 1

[Diagram showing geological features and samples locations]

- Proterozoic sedimentary rocks
- Archean TTG-amphibolite
- Proterozoic diabase
- Granite porphyry
- Quartz porphyry
- Sunzhuang monzonite
- Mafic dikes
- Fault
- Drill core
- Analyzed sample location
- Section
- Eastern Block
- Western Block
- Nanmenshan
- XinZhuang
- Jinjiling
- Hewan
- Tietangdong
- T510
- T601-152
- T601-181.3
- 830Scp-5
- 830Scp-13
- 830Scp-15
- 830Scp-18
- 1300m
- Elevation

[Legend and labels for geological features]
Figure 2
<table>
<thead>
<tr>
<th>Stages</th>
<th>Skarn stage</th>
<th>Quartz-sulfide-calcite stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minerals</td>
<td>Prograde</td>
<td>Retrograde</td>
</tr>
<tr>
<td>Garnet</td>
<td></td>
<td>Scp I</td>
</tr>
<tr>
<td>Diopside</td>
<td></td>
<td>Scp II</td>
</tr>
<tr>
<td>Scapolite</td>
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<tr>
<td>Epidote</td>
<td></td>
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</tr>
<tr>
<td>Actinolite</td>
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<tr>
<td>Chlorite</td>
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<tr>
<td>Quartz</td>
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<td>Calcite</td>
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<td>Magnetite</td>
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<td>Hematite</td>
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<td>Pyrite</td>
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<td>Electrum</td>
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<tr>
<td>Chalcopyrite</td>
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<tr>
<td>Bornite</td>
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<td>Galena</td>
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<td>Sphalerite</td>
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<tr>
<td>Tetrahedrite</td>
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<td>Sericite</td>
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<tr>
<td>Sericite</td>
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<tr>
<td>Adularia</td>
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<tr>
<td>Ankerit</td>
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</tbody>
</table>

Figure 3
Figure 4
Figure 5
Figure 6
Figure 7

![Figure 7: Diagram showing temperature and salinity relationship with error bars for different stages of mineral formation.](image-url)
Figure 8

(a) Br ppm vs Cl wt% (b) I ppm vs Cl wt% (c) I ppm vs Br ppm (d) Br/Cl vs I/Cl × 10^6

Legend:
- 1300 m Scp I
- 830 m Scp I
- 830 m Scp II
- 510 m Scp I
- 510 m Scp II
- 358 m Scp II
- 328.7 m Scp I
Figure 9

Metamorphic rocks
Hewan granite porphyry

Error bar (2 SE)
Figure 10

![Diagram with various points and lines indicating mass fraction of vapor and halogen ratios variation of brine.](image)

This study of magmatic-hydrothermal related REE phosphate deposits in Sweden involves the following:

- **BPF** (Basin pore fluids)
- **FGVM** (Fluids and gases from volcanic magma)
- **MT1** (Mixing trend 1: magmatic hydrothermal & sediments assimilation)
- **MT2** (Mixing trend 2: magmatic hydrothermal & evaporite assimilation)
- **MT3** (Mixing trend 3: magmatic hydrothermal & seawater evaporites brines assimilation)
- **MPF** (Marine pore fluids)

Mass fraction of vapor and halogen ratios variation of brine are illustrated in the diagram, with various points and lines indicating different ratios and trends. The diagram includes labels for various points and lines, indicating different mass fractions and ratios.

Key points in the diagram include:

- **SW-Seawater**
- **Sylvite**
- **SET-Seawater evaporite trend**
- **Evaporite**
- **OM(Organic matter)**
- **PCD** (Porphyry copper deposits)
- **BPF** (Basin pore fluids)
- **FGVM** (Fluids and gases from volcanic magma)
- **Sediments**

Initial ratios and mass fractions of vapor are indicated in the diagram, with various markers and lines indicating different values for I/Cl and Br/Cl ratios.