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

24 Halogens (Cl, Br, and I) are major complexing agents for metal ions, and their ratios 25 (Br/Cl and I/Cl) have been used to determine the source and evolution of hydrothermal 26 fluid. Halogen fractionation during hydrothermal fluid evolution, however, has been 27 inferred from several studies, which poses problems in using halogen ratios as a fluid 28 tracer. The Br/Cl and I/Cl ratios of scapolite are consistent with those ratios present in the 29 coexisting fluid during the mineral's formation, making scapolite particularly useful for 30 understanding hydrothermal fluid evolution. In this paper, we present fluid inclusion 31 microthermometry, major elements, and in situ halogens and Sr isotope analysis of 32 scapolite formed from a high salinity hydrothermal fluid during the vapor-brine phase 33 separation at the Yixingzhai gold deposit, North China Craton, to better understand 34 halogen fractionation during vapor-brine phase separation. The studied scapolite has 35 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 36 37 incorporation of Br and I into the brine phase compared to Cl entering the vapor phase 38 during fluid phase separation. Based on fluid inclusion microthermometry results, the 39 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 40 41 results reveal halogen fractionation during the vapor-brine phase separation of 42 hydrothermal fluids. This view has implications for interpreting the halogen systematics 43 of scapolite and other minerals formed in similar environments, particularly when they 44 are used as a fluid tracer.



46

INTRODUCTION

47 Halogens (Cl, Br, and I) are important agents for complexation and transportation of 48 metals in hydrothermal fluid systems (Webster and Holloway 1988; Webster al. 2004). 49 The Br/Cl and I/Cl ratios in hydrothermal fluids are commonly preserved during fluid 50 migration (fluid buffered), and thus have been used as a fingerprint of the source and 51 evolution of hydrothermal fluids (Böhlke and Irwin 1992; Heinrich et al. 1993; Irwin and 52 Roedder 1995; Kendrick et al. 2002, 2013). Nonetheless, several studies have revealed 53 halogen fractionation during hydrothermal fluid evolution processes, posing a big 54 challenge in using halogen geochemistry to constrain fluid sources (Berndt and Seyfried 55 1997; Lüders et al. 2002; Kurosawa et al. 2016). Possible factors or processes that cause 56 halogen fractionation include low-pressure segregation of hydrothermal fluid from 57 magma (Bureau et al. 2000, 2010, 2016; Kurosawa et al. 2016), precipitation of 58 Cl-bearing minerals (e.g., biotite, amphibole, and halite; Markl and Bucher 1998; 59 Svensen et al. 1999; Kusebauch et al. 2015), and vapor-brine phase separation of 60 hydrothermal fluids (Ishibashi et al. 1994; Oosting and Von Damm 1996; Berndt and 61 Seyfried 1997; Lüders et al. 2002). Experimental studies suggest that Br preferentially 62 partitions into the vapor phase compared to Cl during phase separation of a hydrothermal 63 fluid system (Foustoukos and Seyfried 2007; Seo and Zajacz 2016). In contrast, other 64 studies indicate that the Br/Cl ratios in the vapor phase are lower than those in the brine 65 phase (Oosting and Von Damm 1996; Liebscher et al. 2006). Seo and Zajacz (2016) 66 proposed that the degree of Br/Cl fractionation between brine and vapor phases depends 67 on the types of alkali-halide and alkali-OH complexes in the hydrothermal system. These 68 discrepancies highlight that the mechanisms of halogen fractionation during vapor-brine

69 phase separation remain to be understood.

70	Scapolite group minerals are volatile-rich and have a diverse range of compositions
71	$[(Ca,Na)_4Al_6Si_6O_{24}(SO_4,CO_3)-Na_4Al_3Si_9O_{24}Cl]. They can form in magmatic,$
72	metamorphic, and hydrothermal environments and are stable over a wide range of
73	temperature and pressure (Shaw 1960; Evans et al. 1969; Goldsmith and Newton 1977;
74	Dong 2005; Filiberto et al. 2014; Almeida and Jenkins 2017). Previous studies suggest
75	that the Br/Cl and I/Cl ratios of scapolite are equivalent to those ratios of the coexisting
76	fluids during the scapolite formation (Pan and Dong 2003; Kendrick and Phillips 2009).
77	In addition, the chlorine contents of scapolite are correlated with the salinity of coexisting
78	hydrothermal fluids (Ellis 1978; Oliver et al. 1992, Zhu et al. 2015). Thus, halogen
79	chemistry of scapolite has been widely applied to understand the genesis of ore deposits
80	and associated fluid evolution. For instance, the composition and Br/Cl ratios of scapolite
81	have been used to quantify the assimilation of evaporites during iron skarn mineralization
82	in the Daye district, South China (Zhu et al. 2015; Zeng et al. 2019) and to identify the
83	mixing of metamorphic and magmatic fluids in the genesis of IOCG deposits in the
84	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

92 occurs in this breccia pipe and coexists with other skarn minerals. They contain 93 heterogeneous fluid inclusions assemblages, which consist of vapor-rich and daughter 94 crystal-bearing fluid inclusions (Zhang et al. 2020). This indicates that the scapolite 95 formed from a hydrothermal fluid that underwent phase separation. Thus, scapolite from 96 the Tietangdong breccia pipe can record the Br/Cl and I/Cl variation of the coexisting 97 hydrothermal fluids. This provides an excellent opportunity to elucidate the halogen fractionation behavior during fluid phase separation. In this study, we conducted fluid 98 99 inclusion microthermometry, halogen geochemistry (Cl, Br, and I), and Sr isotope 100 analysis of scapolite to provide insights into the mechanisms of halogen fractionation 101 during the phase separation of hydrothermal fluid.

102 GEOLOGICAL BACKGROUND

103 The Yixingzhai gold deposit is one of the largest gold deposits in the Taihangshan 104 district, North China Craton (Fig. 1a). It includes four breccia pipes and several 105 NW-/NNW-trend auriferous quartz veins hosted in Archean tonalite-trondhjemite-106 granodiorite (TTG) and amphibolite rocks (Fig. 1b). The Tietangdong Fe-Au skarn 107 breccia pipe $(250 \times 150 \text{ m at the surface})$ is roughly controlled by two sets of parallel 108 NW- and NE-trend faults with steep boundaries and extends more than 1400 m in depth 109 (Fig. 1c). The breccia clasts include numerous sub-angular to rounded polymictic clasts, 110 with diameters ranging from a few millimeters to several meters. They are composed of 111 prograde skarn (garnet, diopside, and scapolite), retrograde skarn (actinolite, tremolite, 112 epidote, and chlorite), TTG, amphibolite, diabase, diorite porphyry, and felsite. The 113 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).

118 Three hydrothermal alteration and mineralization stages in the Tietangdong breccia 119 pipe have been recognized by detailed field and petrographic observations. These include 120 the prograde skarn, retrograde skarn, and quartz-sulfide-calcite stages. The prograde 121 skarn stage is characterized by the formation of garnet, diopside, scapolite, and minor 122 magnetite (Figs. 2a-d). The retrograde skarn stage is represented by epidote, actinolite, 123 magnetite, and sulfide minerals, with minor electrum and late-stage scapolite (Figs. 2e-g). 124 They commonly replace or cement the prograde skarn minerals (Fig. 2a). Finally, the 125 quartz-sulfide-calcite stage is characterized by pervasive quartz, sulfides, calcite, and 126 adularia, which frequently occur in the open vugs of the breccia pipe. The mineral 127 paragenesis sequences of Tietangdong are summarized in Fig. 3, showing that the 128 scapolite coexisted with other skarn minerals in the prograde and retrograde skarn stages.

129

SAMPLES AND METHODS

130 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

136 T510-6 were taken from the 830 m and 510 m underground adits. Samples T601-152 and 137 T601-181.3 were taken from drill core T510ZK601, with mineral associations of garnet, 138 scapolite, diopside, epidote, actinolite, calcite, and quartz. Double-polished thin sections 139 were examined under an optical microscope to investigate the mineralogy and textural 140 features. Subsequently, scapolite grains with different mineral associations were extracted, 141 handpicked, and mounted in 25 mm-diameter epoxy mounts. Then, carbon-coated 142 sections and mounts were observed by back-scattered electron (BSE) and 143 cathodoluminescence (CL) imaging on scanning electron microscopes.

144 Fluid inclusion microthermometry

145 Fluid inclusion microthermometry was performed on a Linkam 600 heating-freezing 146 stage and a Linkam TS1400XY heating stage mounted on the Olympus BX53M 147 microscopes at the State Key Laboratory of Geological Processes and Mineral Resources, 148 China University of Geosciences (Wuhan). The Linkam 600 stage was calibrated at 149 -56.6 °C, 0.0 °C, and 374.1 °C using pure H₂O-CO₂ and H₂O synthetic fluid inclusion 150 standards, and the Linkam TS1400XY stage was calibrated at 374.1 °C using a pure H₂O 151 synthetic fluid inclusion standard. Fluid inclusion assemblages (FIAs), which represent a 152 group of petrographically constrained and contemporaneously entrapped fluid inclusions 153 (Goldstein and Reynolds 1994), were chosen for microthermometric measurements. A 154 cycling technique was undertaken to obtain homogenization and ice melting temperatures 155 (Goldstein and Reynolds 1994). Total uncertainties range from 2–3 °C for the heating 156 stage (temperature above 100 °C) and \pm 0.2 °C for the freezing stage (-56.6 to 0.0 °C). 157 The program HokieFlincs for the NaCl- H_2O system (Steele-MacInnis et al. 2012) was 158 used to calculate the salinity and pressure of fluid inclusions.

159 Electron probe microanalysis

160 Electron probe microanalysis (EPMA) of scapolite was conducted using a JEOL 161 JXA-8230 Superprobe at the Center for Material Research and Analysis, Wuhan 162 University of Technology. Analyses were performed using a 15 kV accelerating voltage 163 and a 20 nA beam current with a 5 µm beam to avoid potential diffusion of Na and Cl 164 (Hammerli et al. 2013). The peak counting times were 20 seconds for Sr and S, and 10 165 seconds for the other elements. The background was measured on both sides of the peak 166 for half of the peak time. The Kα line was chosen for Na, Al, Si, Mg, Fe, K, Ca, Ti, Cl, F, 167 Sr, and S. The L α line was chosen for Mn. Natural mineral standards include albite (Na, 168 Si, and Al), K-feldspar (K), plagioclase (Ca), tugtupite (Cl), celestite (Sr and S), pyrope 169 (Mg), rutile (Ti), hematite (Fe), rhodonite (Mn), and fluorite (F). The USNM R6600-1 170 scapolite (Cl: 1.43 wt%; Jarosewich et al. 1980) was used as a secondary standard. The 171 raw data were corrected using the internal ZAF routine. The detection limits of all the 172 elements were approximately 0.02 wt%. The measured value of USNM R6600-1 is 1.39 173 ± 0.05 wt% for Cl (n = 10, 2 σ ; Table S2). The mineral formula was calculated based on 174 Si + Al = 12 atom per formula unit and Cl + S + C = 1 atom per formula unit (Evans et al. 175 1969; Teertstra and Sherriff 1997). The detailed analytical method for EPMA of actinolite 176 is listed in the Supplementary Materials.

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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

181 Geological Sciences, Beijing. A laser spot size of 50 µm was used throughout these 182 measurements. A repetition rate of 8 Hz was used along with a carrier gas rate of helium 183 of 0.70 L/min and the argon make-up gas rate of 1.20 L/min to introduce the ablated 184 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 $ThO^+/Th^+ < 0.3\%$. 185 186 For each analysis cycle, a 30 seconds background signal was collected before the laser 187 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 188 backgrounds. Only ²⁹Si, ³⁵Cl, ⁷⁹Br, ⁸¹Br, and ¹²⁷I were determined to provide optimal 189 190 counting time for halogen concentrations. Furthermore, the reference materials (see 191 below) were repeatedly analyzed every 10 analyses of the studied scapolite and 192 monitored throughout the session for drift. Raw data were reduced via the software 193 package ICPMSDataCal (Liu et al. 2010). Silicon concentrations quantified by EPMA 194 were used as the internal standard for data reduction. The scapolite standards ON70 (1.94 195 wt% Cl, 1877 ppm Br; Evans et al. 1969; Teertstra and Sherriff 1997; Zhang et al. 2017a) 196 and AF8 (7.16 wt% Cl, 148 ppm Br, and 28.4 ppm I determined by bulk analysis) were 197 used as the external standard for Cl, Br, and I data reduction. AF5 (7.12 wt% Cl, 661 198 ppm Br, and 106 ppm I, bulk analysis) was used as a secondary standard. The measured 199 values of AF5 are 7.11 ± 0.59 wt% for Cl, 658 ± 56 ppm for Br, and 102 ± 10 ppm for I 200 $(n = 12, 2\sigma; Table S3)$. The scapolite Cl contents detected by LA-ICPMS are consistent 201 with the Cl concentrations obtained from EPMA within 2σ uncertainty (Fig. S1c). The 202 details on the LA-ICPMS and bulk halogen analyses on the reference materials are listed 203 in the Supplementary Materials.

204 Strontium isotope analysis of scapolite

205 Sr isotopes of scapolite were measured by a Neptune Plus MC-ICP-MS (Thermo 206 Fisher Scientific, Bremen, Germany) in combination with a Geolas HD excimer ArF laser 207 ablation system (Coherent, Göttingen, Germany) at the Wuhan Sample Solution 208 Analytical Technology Co., Ltd, Hubei, China. The Neptune Plus was equipped with nine Faraday cups fitted with $10^{11} \Omega$ resistors. The Faraday collector configuration of the mass 209 210 system was composed of an array from L4 to H3 to monitor Kr, Rb, Er, Yb and Sr. The 211 combination of the high-sensitivity X-skimmer cone and Jet-sample cone was employed. 212 In the laser ablation system, helium was used as the carrier gas for the ablation cell. Laser 213 conditions included spot diameter (120 μ m), pulse frequency (8 Hz), and fluence (~8 J/cm²). A signal smoothing device (Hu et al. 2012) was used downstream from the sample 214 215 cell to eliminate the short-term variation of the signal. The data reduction for 216 LA-MC-ICPMS analysis was conducted using ICPMSDataCal (Liu et al. 2010). The 217 interference correction strategy was the same as the one reported by Tong et al. (2016) 218 and Zhang et al. (2018). One natural feldspar megacryst (anorthite YG4301) was used as 219 the secondary standard to verify the accuracy of the calibration method for in situ Sr isotope analysis. Measured 87 Sr/ 86 Sr values of YG4301 are 0.70343 ± 0.00021 (n = 4, 2 σ), 220 which are consistent with the recommended 87 Sr/ 86 Sr values of 0.70343 \pm 0.00002 221 222 (Zhang et al. 2018).

223 **RESULTS**

Textures and geochemistry of scapolite

225 Two different types of scapolite (Scp I and Scp II) are distinguished by their mineral 226 associations. Scp I grains occur at 1300, 830, 510, and 328.7 m above sea level (a.s.l.) in 227 the Tietangdong breccia pipe (Fig. 1c). They are coarse-grained and euhedral crystals 228 (0.2-1.5 cm), which are intergrown with garnet, diopside, and magnetite at the prograde 229 skarn stage (Figs. 2a-d, 3). Some Scp I grains have been formed by the replacement of 230 plagioclase phenocrysts in the diorite fragments, with a grain size of 0.2–0.5 cm (Figs. 2b, 231 c). Scp II crystals (0.5-2 cm) filling in the voids of breccia clasts are commonly 232 associated with actinolite, epidote, and pyrite at the retrograde skarn stage (Figs. 2 e-g, 3). 233 Scp II mainly occurs at 830, 510, and 358 m a.s.l. in the Tietangdong breccia pipe (Fig. 234 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 $[Na_4Cl]Si_2$ - $[NaCa_3CO_3]Al_2$ substitution mechanism (Fig. 5a; Hassan and Buseck 1988) and show a negative correlation between Cl and equivalent anorthite

- 245 (Eq. An) (Figs. 5b, c). Scp I crystals have Me of 27.5–40.3% and Eq. An of 26.0–38.8%
- 246 (Table 1, Figs. 5a-c). They contain 22.08–23.80 wt% Al₂O₃, 52.38–57.52 wt% SiO₂,
- 247 7.16–9.17 wt% Na₂O, and 6.59–9.75 wt% CaO, with minor amounts of K₂O (0.83–2.02
- 248 wt%) and SrO (0.20–0.35 wt%). The contents of Cl, SO₃, and CO₃ in Scp I range from
- 249 2.53–3.48 wt%, 0.04–0.33 wt%, and 0.82–2.36 wt%, respectively (Table 1, Fig. 5d). Scp
- 250 II grains have 34.4–49.8% Me and 31.5–42.9% Eq. An (Table 1, Figs. 5a-c), and contain
- 251 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%,
- 253 0.06–0.50 wt%, and 1.52–2.85 wt%, respectively (Table 1, Fig. 5d).

254 Fluid inclusions

255 Three types of primary fluid inclusion are distinguished by their textural and phase 256 proportion features at room temperature. These types include daughter mineral-bearing 257 three phases (S-type), vapor-rich aqueous (V-type), and liquid-rich aqueous (L-type) fluid 258 inclusions. For each type, fluid inclusions have constant phase proportions (Fig. 6b) and 259 commonly occur in mineral growth zones (Fig. 6c). The fluid inclusions (5-15 µm 260 diameter) often display rounded or negative crystal shapes (Figs. 6a, b), but some show 261 irregular boundaries (Figs. 6c, d). S-type fluid inclusions are composed of liquid, vapor, 262 halite, sylvite, and/or other unidentified daughter crystal phases at room temperature. 263 They commonly occur in scapolite, diopside, and epidote (Figs. 6a-d). V-type fluid 264 inclusions are dominated by a vapor phase generally higher than 65% of the total volume 265 and typically coexist with S-type varieties (Figs. 6a-d). The coexistence of S- and V-type 266 fluid inclusions is interpreted as boiling FIAs in the skarn minerals (Audétat 2022; Figs. 267 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.

275 The microthermometry results are summarized in Table 2 and illustrated in Fig. 7. 276 All S-type inclusions are characterized by the final disappearance of the vapor phase after 277 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 278 279 and calculated salinities of 37.0-54.8 wt% NaCl eq. (Fig. 7). Homogenization 280 temperatures of S- and L-type inclusions in the epidote are 441–470 °C and 413–433 °C, 281 respectively (Fig. 7). The calculated salinities of S- and L-type inclusions are 32.5–38.7 282 wt% NaCl eq. and 7.9–10.5 wt% NaCl eq., respectively (Fig. 7). L-type inclusions in 283 calcite have total Homogenization temperatures of 146 to 169 °C and calculated salinity 284 of 5.4–9.9 wt% eq. (Fig. 7). Due to the unclear boundaries of the vapor phase, the V-type 285 fluid inclusions were not measured.

286 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 $6.1-11.9 \times 10^{-3}$, 91- 191×10^{-6} , and 49.9-75.5, respectively. The Scp II grains have 1.84-3.10 wt% Cl, 395-

291 806 ppm Br, and 8.4–24.4 ppm I, with Br/Cl, I/Cl, and Br/I molar ratios ranging from 292 7.4–14.7 × 10⁻³, 105–302 × 10⁻⁶, and 42.0–94.1 respectively. Zoned scapolite grains in 293 sample T510-6 show variable halogen ratios between the core and rim. The CL-bright 294 core (Scp I) has lower Br/Cl (8.6–8.9 × 10⁻³) and I/Cl (137–140 × 10⁻⁶) values, whereas 295 the CL-dark rim (Scp II) has higher Br/Cl (11.9–14.4 × 10⁻³) and I/Cl (205–302 × 10⁻⁶) 296 values (Fig. 4d). The Br and I contents of the studied scapolite grains show no correlation 297 with Cl (Figs. 8a, b), whereas Br is correlates positively with I (Figs. 8c, d).

298 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 Sr/ 86 Sr values can be considered as the initial 87 Sr/ 86 Sr ratios of scapolite. Scp I and Scp II grains have 87 Sr/ 86 Sr values ranging from 0.7099 to 0.7112 and 0.7104 to 0.7116, respectively. The 87 Sr/ 86 Sr values of all the scapolite increase with increasing Br/Cl and I/Cl values (Fig. 9).

305

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

312 average) imply that the sulfur species in the hydrothermal fluid include sulfate (e.g., SO_4^{2-} , Qiu et al. 2021), suggesting an oxidized ore-forming fluid. This view is also 313 314 confirmed by the occurrence of hematite and magnetite in these samples. The relatively 315 high Cl contents (2.19–3.48 wt%) and marialite proportions (Me = 27.5–49.8; Figs. 5b-d) 316 in scapolite suggest elevated Cl and Na concentrations in the coexisting hydrothermal 317 fluid (Ellis 1978; Oliver et al. 1994). This view is confirmed by the presence of high 318 salinities of S-type fluid inclusions in diopside and epidote (32.5-54.8 wt% NaCl eq.; 319 Table 2). The microthermometry results show that Scp I and II grains have formed from 320 high temperature (544–586 °C for Scp I, 441–470 °C for Scp II; Table 2) hydrothermal 321 fluids under low-pressure conditions (44.1–58.8 MPa for Scp I, 30.2–33.5 MPa for Scp II; 322 Table 2). The coexisting S-type and V-type fluid inclusions in diopside, scapolite, and 323 epidote imply that they form under fluid phase separation.

324 Scapolite from the Tietangdong breccia pipe has relatively high Cl and low Eq. An 325 values (Fig. 5b). These chemical characters are similar to hydrothermal scapolite from the 326 Tieshan iron skarn deposit in Hubei Province, China, the Nickel plate Au deposit in 327 British Columbia, Canada (Pan and Dong 2003), the Jinshandian iron skarn deposit in 328 Hubei Province, China (Zeng et al. 2019), and the Clarke Head metasomatic syenite in 329 Nova Scotia, Canada (Pe-Piper et al. 2019). In contrast, they are significantly distinct 330 from the metamorphic scapolite in amphibolite-facies calc-silicates at Mary Kathleen, 331 Australia (Oliver et al. 1992) and Idaho, America (Rebbert and Rice 1997). The studied 332 scapolite has relatively low $CO_3/(SO_3 + CO_3 + CI)$ ratios and high Cl contents, similar to the magmatic-hydrothermal origin scapolite from the Norrbotten district, Sweden (Fig. 5d, 333 Bernal et al. 2017). Furthermore, the ⁸⁷Sr/⁸⁶Sr ratios of scapolite (0.7099–0.7116; Table 3) 334

335 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 ⁸⁷Sr/⁸⁶Sr values of the 336 337 metamorphic rocks in this region (0.7130-0.7180; Jahn et al. 1999). The Sr isotope data 338 suggest that the studied scapolite formed from a magmatic-hydrothermal fluid that 339 interacted slightly with the Archean wall rocks (Figs. 9a, b). Taken together, we propose 340 that the studied scapolite grains formed from an oxidized, high-salinity fluid resulting 341 from the fluid phase separation of magmatic-hydrothermal fluid at high-temperature and 342 low-pressure conditions. However, the Br/Cl and I/Cl values of all the studied scapolite 343 are significantly higher than those values of the magmatic-hydrothermal fluid (Fig. 10), 344 for reasons that will be discussed later.

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

346 The significantly high Br/Cl and I/Cl values of the scapolite from the Tietangdong 347 breccia pipe may be explained by (1) large Br/Cl and I/Cl partition coefficients (>1) 348 between scapolite and fluids in Cl-poor (< 0.03 wt% Cl) meionitic scapolite groups, (2) 349 mixing of magmatic-hydrothermal fluid with external high Br/Cl and I/Cl fluids, or (3) 350 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 351 Farm (LM-Q) in the Grenville Province has unusually high Br/Cl $(39.1-54 \times 10^{-3})$ and 352 I/Cl $(226-284 \times 10^{-6})$ ratios (Kendrick and Phillips 2009; Fig. 10). These high halogen 353 354 ratios may result from the high Br/Cl and I/Cl partition coefficients (> 1) between 355 Cl-poor meionitic scapolite and fluids (Kendrick and Phillips 2009). However, high Br/Cl 356 and I/Cl ratios do not occur in the scapolite (1.79-4.13 wt% Cl, Me = 7.1-48.8%) from 357 Haliburton Highway (HAL-O), Tory Hills, Bancroft (TB-O), and Bear Lake (BL-Q) in

358 the Grenville Province (Kendrick and Phillips 2009; Fig. 10). In this study, all scapolite 359 grains from the Tietangdong breccia pipe are high Cl scapolite (2.19-3.48 wt) Cl; Me = 360 precludes the first hypothesis. 27.5-49.8%), which In the second case, 361 magmatic-hydrothermal fluid mixing with high Br/Cl sources (marine evaporites or 362 organic-rich sediment) may cause significantly high Br/Cl values of the scapolite, but 363 those mixing fluids have significantly lower or higher I/Cl ratios than the studied 364 scapolite (Zherebtsova and Volkova 1966; Polya et al. 2000; Sekimoto and Ebihara 2013; 365 Hanley and Koga 2018; mixing trend 1 and 3, Fig. 10). This precludes the second 366 hypothesis. We therefore suggest that these high Br/Cl and I/Cl values of the studied 367 scapolite most likely resulted from halogen fractionation during hydrothermal fluid 368 evolution. In this case, three processes may cause such halogen fractionation, including 369 (1) low-pressure devolatilization of a cooling magma (Bureau et al. 2000, 2010, 2016; 370 Kurosawa et al. 2016), (2) precipitation of Cl-bearing minerals (Markl and Bucher 1998; 371 Svensen et al. 1999; Kusebauch et al. 2015), and (3) phase separation of hydrothermal 372 fluid (Ishibashi et al. 1994; Oosting and Von Damm 1996; Berndt and Seyfried 1997; 373 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 $0.17-4.15 \times 10^{-3}$ and $0.84-703.20 \times 10^{-6}$, respectively (Webster et al. 2018; Fig. 10). These halogen ratios are much lower than the Br/Cl values of the studied scapolite

381 (Fig. 10). Therefore, we propose that the significantly high halogen ratios in the studied 382 scapolite are not controlled by the segregation of hydrothermal fluids from the magma at 383 low pressure.

384 Halogen fractionation in hydrothermal fluids may be attributed to the precipitation of 385 Cl-bearing minerals (such as halite, biotite, and amphibole). Several studies propose that 386 most Cl-bearing minerals (halite, biotite, and amphibole) preferentially incorporate Cl 387 into their structures rather than Br and I (Svensen et al. 2001; Mark et al. 2005; 388 Kusebauch et al. 2015). For example, the precipitation of halite possibly increases the 389 Br/Cl and I/Cl ratios of hydrothermal fluids (Andersson 2019, Michallik et al. 2021; Fig. 390 10). However, S-type fluid inclusions in the studied minerals were finally homogenized 391 by vapor disappearance after the dissolution of salt crystals (Table 2), indicating the 392 scapolite formed from a salt unsaturated fluid (Goldstein and Reynolds 1994; Driesner 393 and Heinrich 2007; Fig. 7). Precipitation of massive Cl-bearing actinolite (Cl: 0.01–0.12 394 wt%, Fig. S2, Table S4) may also elevate the Br/Cl and I/Cl ratios of the hydrothermal 395 fluids, because Cl preferentially partitions into the actinolite than Br and I (Svensen et al. 396 1999, 2001; Kusebauch et al. 2015). This view is confirmed by the higher Br/Cl and I/Cl 397 values of Scp II than Scp I (Fig. 8d). However, the Scp I grains are not intergrown with 398 any Cl-bearing minerals and have extremely high Br/Cl and I/Cl values. Thus, we 399 proposed that the precipitation of Cl-bearing minerals may not be the predominant factor 400 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 (0.196 Å for Br; 0.220 Å for I; Shannon 1976), (2) Br/I values are overall constant during 416 417 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

As summarized above, the high Br/Cl and I/Cl values of scapolite from the Tietangdong breccia pipe can be interpreted in terms of halogen fractionation due to phase separation of the magmatic-hydrothermal fluid. Based on Drummond and Ohmoto (1985), elements partition during phase separation of hydrothermal fluids is similar to

- 427 Rayleigh distillation. Thus, the Br/Cl and I/Cl values in separated brine phases can be
- 428 quantitatively described as a simple Rayleigh fractionation model:

429
$$C_{(Br/Cl)}^{Brine} = C_{(Br/Cl)}^{Initial} \times (1 - F_{Vapor})^{(1/K}_{D(Br/Cl)}^{Brine-vapor - 1)}$$
(1)

430
$$C_{(I/Cl)}^{Brine} = C_{(I/Cl)}^{Initial} \times (1 - F_{Vapor})^{(1/K}_{D(I/Cl)}^{Brine-vapor - 1)}$$
(2)

where $C_{(Br/Cl)}^{Brine}$ and $C_{(I/Cl)}^{Brine}$ represent the Br/Cl and I/Cl molar ratios of the brine, 431 respectively; C_(Br/Cl) Initial and C_(I/Cl) Initial refer to the Br/Cl and I/Cl molar ratios of the 432 433 initial hydrothermal fluids, respectively; F_{Vapor} is the mass ratio between vapor and initial 434 fluids. F_{Vapor} represents the vapor loss ratio during the phase separation of initial fluids. $K_{D(Br/Cl)}^{Brine-Vapor}$ and $K_{D(I/Cl)}^{Brine-Vapor}$ represent the Br/Cl and I/Cl exchange coefficients 435 between the brine and vapor phases. The $C_{(Br/Cl)}^{Initial}$ (1.5/1.8/2.0 × 10⁻³) and $C_{(I/Cl)}^{Initial}$ 436 $(16/30/55 \times 10^{-6})$ values were estimated from hydrothermal fluids degassed from magmas 437 438 (Johnson et al. 2000; Burgess et al. 2002; Burgess et al. 2009; Kendrick et al. 2017; Table S6). The $K_{D(Br/CL)}^{Brine-Vapor}$ is calculated from the equation proposed by Liebscher et al. 439 440 (2006):

441
$$K_{D(Br/Cl)}^{Brine-Vapor} = 0.349 \times \ln[1.697 \times (D_{Cl}^{Brine-Vapor} - 1) + e^{(1/0.394)}]$$
 (3)

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

447 The Br/Cl and I/Cl ratios of brines are estimated to increase gradually with the 448 progressive vapor loss (represented by F_{Vapor}) in the Tietangdong breccia pipe during the 449 phase separation of initial hydrothermal fluids. They can be up to 18×10^{-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.

457

IMPLICATIONS

458 The integrated study of fluid inclusion microthermometry, halogen geochemistry, and 459 Sr isotope suggests that scapolite grains from the Tietangdong breccia pipe formed from 460 an oxidized, high-temperature (544–586 °C for Scp I and 441–470 °C for Scp II), high 461 salinity (37.0-54.8 wt% NaCl eq. for Scp I and 32.5-38.7 wt% NaCl eq. for Scp II), and 462 low pressure (44.1–58.8 MPa for Scp I and 30.2–33.5 Mpa for Scp II) 463 magmatic-hydrothermal fluid at prograde and retrograde skarn stages. The studied scapolite grains have significantly high Br/Cl (6.1–14.7 \times 10⁻³) and I/Cl (91–302 \times 10⁻⁶) 464 465 values, which can be interpreted as the phase separation of magmatic-hydrothermal fluids. 466 The phase separation could trigger halogen fractionation characterized by the preferential 467 partitioning of Br and I into the brine compared to Cl. This study highlights the role of 468 fluid phase separation in causing halogen fractionation, thus providing new insights into 469 using halogens as a fluid tracer to determine the source and evolution of hydrothermal 470 fluids under complex geological environments.

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FIGURE CAPTIONS

739 Figure 1. (a) A sketch map showing the tectonic divisions of the North China craton 740 (NCC) and the location of the Taihangshan district (modified from Li et al. 2012). 741 Geological map (b) and A-A' cross-section (c) of the Tietangdong breccia pipe showing 742 the sample locations (modified from Jing 1985) 743 744 Figure 2. Photographs and microphotographs showing the mineralogy and texture of the 745 scapolite samples. (a) Scp I coexisting with garnet which is cemented by actinolite and 746 epidote. (b) Plagioclase phenocrysts in diorite breccia replaced by Scp I grains. (c) 747 Magnetite intergrown with Scp I. (d) Euhedral Scp I intergrown with garnet. (e-f) Scp II 748 grains intergrown with massive actinolite, epidote, and pyrite. (g) Scp II intergrown with 749 actinolite. Act-actinolite, Ep-epidote, Grt-garnet, Di-diopside, Mag-magnetite, Py-pyrite. 750 751 Figure 3. Paragenetic sequence of the Tietangdong breccia pipe. The thickness of the 752 lines represents the relative contents of minerals. 753 754 Figure 4. CL and BSE images showing scapolite textures (Scp I and Scp II). (a) 755 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 756 757 Br/Cl and I/Cl values, whereas the dark rim displays high halogen ratios. 758 759 Figure 5. Distribution of major elements in Scp I and Scp II. (a) AI/(AI + Si) vs. Me of

760 the scapolite. The solid line showing [Na₄Cl]Si₂-[NaCa₃CO₃]Al₂ and

[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.

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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.

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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.

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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

and Scp II show two trends.

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

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791 Figure 10. I/Cl vs. Br/Cl diagram (molar ratios) for scapolite in the Tietangdong breccia 792 pipe. The blue (brine trend) and gray dotted (vapor trend) lines represent the Rayleigh 793 fractionation modeling of halogens fractionation during hydrothermal fluid phase 794 separation. Halogen reservoirs include seawater¹ (Riley and Chester 1971); seawater evaporation trajectory² (Zherebtsova and Volkova 1966); sylvite³ (Holser, 1979); 795 evaporite⁴ and organic matter⁵ (Kendrick and Burnard 2013); marine pore fluids⁶ and 796 basin pore fluids¹³ (Kendrick et al. 2011); mantle: OIB and MORB glasses⁷ (Kendrick et 797 al. 2017), coated diamond⁸ (Johnson et al. 2000; Burgess et al. 2002; Burgess et al. 2009); 798 porphyry copper deposits⁹ (Böhlke and Irwin 1992; Irwin and Roedder 1995; Kendrick et 799 800 al. 2001ab); mixing trend 1: sedimentary assimilation with magmatic-hydrothermal fluids¹⁰ (Polya et al. 2000); mixing trend 2: evaporite assimilation with 801 magmatic-hydrothermal fluids¹¹ (Campbell et al. 1995); mixing trend 3: evaporated and 802 seawater assimilation¹² (Richard et al. 2014); sedimentary^{14, 15, 16}: dolomite, limestone, 803 804 sandstone, shale, chert, and fluvial lacustrine sediments (Mason 1966; Sekimoto and Ebihara 2013; Hanley and Koga 2018); scapolite¹⁷ (Kendrick and Phillips 2009); 805 magmatic-hydrothermal related REE phosphate deposits¹⁸ in Sweden (Andersson 2019); 806

- 807 and fluids and gases from volcanic magma¹⁹ (Webster et al. 2018) are shown for
- 808 comparison.

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TABLES

810 **Table 1.** A summary of major and halogen elements results determined by EPMA and LA-ICPMS in scapolite.

	1300m (N	= 61)	830 m (N = 10)			510 m (N = 42)				358 m (N = 11)		328.7 m (N = 12)		
EPMA (Wt%)	Sep I		Scp I		Sep II		Scp I		Scp II		Scp II		Scp I	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
SiO ₂	52.76-57.52	54.94	52.38-52.82	52.66	51.39-52.64	52.01	53.31-53.46	53.38	51.84-54.9	53.23	53.26-54.92	54.04	53.04-54.87	53.73
Al_2O_3	22.08-23.80	22.86	23.27-23.60	23.47	23.79–24.46	24.11	23.33-23.60	23.47	23.12-24.43	23.75	22.56-23.27	22.98	22.94-23.58	23.32
CaO	6.59–9.68	7.92	8.50-8.61	8.54	9.87-10.93	10.42	8.43-8.77	8.60	9.01-12.27	10.92	8.39–9.72	8.98	8.40-9.75	9.19
SrO	0.20-0.35	0.26	0.24–0.34	0.29	0.20-0.30	0.25	0.22-0.25	0.24	0.20-0.31	0.25	0.21-0.29	0.25	0.20-0.29	0.25
Na ₂ O	7.36–9.17	8.43	7.78-8.01	7.91	6.45-7.06	6.70	7.44–7.55	7.49	5.76-7.62	6.41	7.35-8.16	7.74	7.16-8.47	7.59
K ₂ O	0.97-2.02	1.61	1.52-1.60	1.56	1.55-1.79	1.68	1.58-1.63	1.61	1.28-1.66	1.44	1.12-1.36	1.25	0.83-1.58	1.35
Cl	2.53-3.48	3.15	2.91-3.02	2.95	2.39-2.68	2.49	3.05-3.08	3.07	2.19-2.90	2.45	2.49-2.83	2.66	2.56-2.94	2.75
SO ₃	b.d.10.28	0.13	0.18-0.22	0.20	0.15-0.27	0.20	0.29–0.33	0.31	0.13-0.50	0.24	0.06-0.14	0.10	0.09-0.32	0.24
Sub total	97.68-102.00	99.36	97.60–97.62	97.61	96.75–98.81	97.89	98.07–98.25	98.16	96.84-100.50	98.74	97.31–98.54	98.03	97.68–99.42	98.52
- Cl = O	0.57 - 0.78	0.71	0.66-0.68	0.67	0.54-0.60	0.56	0.69–0.70	0.69	0.49–0.65	0.55	0.56-0.64	0.60	0.58-0.66	0.62
$\rm CO_2(calc)^a$	0.82-2.36	1.38	1.40-1.63	1.55	2.01-2.58	2.32	1.32-1.33	1.32	1.52-2.85	2.44	1.97-2.45	2.18	1.65-2.35	1.92
Total	97.88–103.00	99.93	98.32–98.58	98.49	98.57–100.48	99.65	98.69–98.89	98.79	98.74–101.91	100.70	99.04–100.00	99.62	98.83-100.52	99.82
Me ^b	27.5-39.2	32.0	34.6-35.2	35.0	40.4-44.7	42.8	35.5-36.7	36.1	37.2–49.8	45.4	34.4-40.2	37.0	34.2-40.3	37.8
Eq. An ^c	26.0-38.8	31.6	36.8-38.7	37.8	40.4-42.9	41.3	35.9-37.2	36.5	33.6-42.8	37.9	31.5-35.5	33.5	33.2-37.3	35.4
Al/(Al+Si)	0.32-0.35	0.33	0.34-0.35	0.34	0.35-0.36	0.35	0.34-0.34	0.34	0.33-0.36	0.34	0.33-0.34	0.33	0.33-0.34	0.34
Cl/(Cl+CO ₃)	0.64-0.88	0.79	0.75–0.78	0.76	0.61-0.69	0.65	0.80-0.80	0.80	0.56-0.76	0.63	0.63–0.71	0.67	0.65–0.75	0.71
LA-ICPMS	1300m (N	= 30)		830 m	(N = 19)		51	0 m (N =	= 25)		358 m (N	= 16)	328.7 m (N	(=14)
Cl (wt%)	2.45-3.41	2.91	2.07-2.72	2.52	1.84-2.47	2.10	3.03-3.10	3.07	1.94-3.04	2.48	2.03-2.83	2.42	2.20-2.75	2.55

Br (ppm)	389–650	512	402–488	448	522-623	586	585-620	602	503-806	597	395–663	539	476–659	565
I (ppm)	10.8-17.9	13.6	10.1-12.0	10.8	18.5–23.2	20.1	14.1–15.2	14.6	13.3–24.4	17.6	8.4–19.3	13.3	11.4–16.1	13.3
Molar Br/Cl $\times 10^{-3}$	6.1–9.1	7.9	6.9–9.6	7.9	10.7–14.7	12.5	8.6-8.9	8.7	7.4–14.4	10.8	8.0-12.1	9.9	8.2–11.9	9.9
Molar I/Cl $\times 10^{-6}$	91–156	132	109–140	120	235–302	269	127–140	134	124–302	201	105–214	153	118–191	147

812 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

813 Sherriff 1997).

 a CO₂ contents are recalculated by assuming a full anion site occupancy and H₂O-free compositions (Cl + S + C = 1; Evans et al. 1969; Teertstra and

815 Sherriff 1997).

816 ^bMe (meionite equivalent) = $100 \times (Ca + Mg + Fe + Mn + Sr)/(Na + K + Ca + Mg + Fe + Mn + Sr)$.

817 °Eq. An (equivalent anorthite) = $100 \times (A1 - 3)/3$.

Table 2. Microthermometry results of skarn minerals from the Tietangdong breccia pipe.

Prograde skarn stage (diopside)										
FIA	Туре	Ν	Homogenization (°C)	SD (°C)	Halite dissolution (°C)	SD (°C)	Salinity (wt% NaCl eq.)	SD (wt% NaCl eq.)	Pressure (MPa)	SD (MPa)
596.5c	S	7	584	44	376	10	44.4	0.9	47.0	3.4
596.5d	S	2	544	74	341	4	41.1	0.1	46.9	16.1
596.5e	S	6	571	35	467	5	54.8	0.3	44.1	7.8
596.5f	S	5	582	17	288	2	37.0	0.1	58.8	4.6
596.5h	S	9	571	36	343	4	41.3	0.4	54.4	0
596.5i	S	3	586	102	348	45	42.0	4.4	51.5	30.4
Retrograde skarn stage (epidote)										
T601-537.7a	S	2	461	2	304	71	38.7	5.5	30.3	1.3
T601-537.7b	S	2	457	3	213	11	32.5	0.6	31.7	0.4
T601-537.7c	S	3	450	5	217	2	32.7	0.1	30.4	1.0
T601-537.7d	S	14	470	3	277	3	36.4	0.2	32.8	0.6
T601-537.7e	S	10	462	3	252	1	34.7	0.1	32.3	0.2
T18-2a	S	8	441	27	237	-	33.8	-	33.5	0
494.7a	S	7	457	28	288	5	37.1	0.4	30.2	6.6
FIA	Туре	Ν	Homogenization (°C)	SD (°C)	Ice dissolution (°C)	SD (°C)	Salinity (wt% NaCl eq.)	SD (wt% NaCl eq.)		
03a	L	7	420	8	-6.0	1.0	9.2	1.9		
Quartz-sulfide and calcite stage (calcite)										
512.1c	L	8	160	9	-4.9	2.3	7.6	3.1		

Sample no.	Comment	Rb/Sr	⁸⁷ Sr/ ⁸⁶ Sr	2SE
18S1-01	Scp I	0.02	0.7100	0.0001
18S1-02	Scp I	0.02	0.7101	0.0001
18S1-03	Scp I	0.02	0.7100	0.0001
18S1-04	Scp I	0.02	0.7101	0.0002
18S1-05	Scp I	0.01	0.7102	0.0002
83013-01	Scp I	0.01	0.7100	0.0002
83013-02	Scp I	0.01	0.7099	0.0002
83013-03	Scp I	0.02	0.7103	0.0002
83013-04	Scp I	0.01	0.7104	0.0002
181.3-01	Scp I	0.03	0.7103	0.0003
181.3-02	Scp I	0.03	0.7109	0.0002
181.3-03	Scp I	0.03	0.7112	0.0002
181.3-04	Scp I	0.03	0.7112	0.0003
83015-01	Scp II	0.03	0.7113	0.0002
83015-02	Scp II	0.03	0.7114	0.0003
83015-03	Scp II	0.05	0.7107	0.0003
510-6-01	Scp II	0.03	0.7110	0.0003
510-6-02	Scp II	0.04	0.7116	0.0003
510-6-03	Scp II	0.03	0.7110	0.0003
510-6-04	Scp II	0.03	0.7104	0.0002

829 Table 3. Sr isotope data of the scapolite grains from the Tietangdong breccia pipe.830





Stages	Skarn	stage	Quartz-sulfide-calcite			
Minerals	Prograde	Retrograde	stage			
Garnet						
Diopside	Carl	Carl				
Scapolite	Scpi	Scpli				
Epidote						
Actinolite						
Chlorite						
Quartz						
Calcite						
Magnetite						
Hematite			_			
Pyrite						
Electrum						
Chalcopyrite						
Bornite						
Galena						
Sphalerite						
Tetrahedrite						
Sericite						
Adularia						
Ankerit						









Figure 7





Figure 10

