13	Abstract
12	[†] Corresponding author: shundayuan@cugb.edu.cn
11	
10	3 China University of Geosciences, Beijing 100083, China
9	Canada
8	2 Department of Earth & Planetary Sciences, McGill University, 3450 University Street, Montreal, QC H3A 0E8,
7	of Geological Sciences, Beijing 100037, China
6	1 MNR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy
5	Yuan, ^{3,†}
4	Jiaxin Wang, ^{1,2} A.E. Williams-Jones, ² A. Timofeev, ² Xueni Zhang, ³ Jiajun Liu, ^c Shunda
3	
2	Deposits: Insights From Experiments and Modelling
1	The Role of Scandium Chloride and Hydroxide Complexes in the Formation of Scandium
_	

Although scandium is commonly concentrated to economic levels by magmatic processes, 14 hydrothermal fluids also play an important role in its concentration. Indeed, the most important 15 source of scandium is currently the Bayan Obo deposit in China, where scandium is extracted from 16 hydrothermally produced aggirine. In order to know how and why scandium is concentrated by 17 hydrothermal fluids, it is necessary to understand the speciation of scandium in hydrothermal 18 fluids. In a recently published study, we showed that scandium forms stable species with fluoride 19 ions and proposed that such species may have been responsible for the hydrothermal transport of 20 21 scandium in deposits like Bayan Obo. Chloride ions, which have been shown to form stable complexes with the other rare earth elements (REE), however, are much more abundant in most 22 hydrothermal fluids than fluoride ions, as are hydroxide ions, particularly at high pH. We, therefore, 23 24 conducted solubility experiments designed to investigate the stability of scandium chloride and hydroxide complexes in hydrothermal fluids. The experiments investigating the role of chloride 25

species considered the solubility of Sc₂O_{3(s)} in the H₂O-NaCl-HCl system at 100, 150, 300 and 350 26 °C and saturated water vapor pressure. These experiments showed that scandium concentration is 27 independent of chloride concentration over the range of chlorinity investigated, i.e., up to 3.6 m 28 Cl⁻ and that scandium, therefore, does not form stable complexes with chloride ions. In order to 29 evaluate the role of hydroxide species in scandium transport and avoid the effect of chloride ions 30 in the complexation, a second set of experiments was conducted that determined the solubility of 31 32 Sc₂O_{3(s)} in H₂O-NaClO₄-HClO₄ solutions at 100, 150, 200 and 250 °C, and saturated water vapor pressure. The results of these experiments showed that the solubility of $Sc_2O_{3(s)}$ depends on pH 33 and temperature. Based on the former dependence, two scandium hydroxide complexes, Sc(OH)²⁺ 34 and Sc(OH)₃°, were identified at low and higher pH, respectively. The formation constant (log β) 35 determined for Sc(OH)²⁺ is 10.29 ± 0.07 , 10.32 ± 0.07 , 10.35 ± 0.19 , and 10.91 ± 0.20 at 100, 150, 36 200, and 250 °C, respectively. That of Sc(OH)₃° is 27.22±0.68, 26.66±1.35, 27.04±0.13, and 37 28.02 ± 0.14 at the same temperatures, respectively. These results demonstrate that, unlike the case 38 for the other rare earth elements, chloride plays a negligible role in transporting scandium in 39 hydrothermal fluids. Instead, they show that scandium hydroxide complexes can be important in 40 the transport of scandium and could have contributed significantly to the formation of deposits 41 42 like those at Bayan Obo.

43

Introduction

Scandium is a rare earth element (REE) that, because of a combination of low density and high
melting point, is used to produce the light high tensile strength aluminum alloys that are required
by the automotive and aerospace industries to help address the issue of global warming (Klimpel

et al., 2021; Wang et al., 2021). Previous studies have shown that scandium is concentrated mainly
in ferromagnesian minerals, particularly clinopyroxene (Williams-Jones and Vasyukova, 2018;
Halkoaho et al., 2020; Wang et al., 2020). Currently, 90 % of global scandium production is from
the Bayan Obo REE deposit, China (the largest REE deposit in the world), where it is concentrated
in aegirine, which is interpreted to have formed by the hydrothermal alteration of the host dolomite
(Smith et al., 2015; Williams-Jones and Vasyukova, 2018). This raises the question of how
scandium is transported in hydrothermal fluids.

In a recent experimental study (Wang et al., 2022), we investigated the solubility and 54 speciation of scandium in fluoride-bearing aqueous fluids at elevated temperature, partly because 55 Sc^{3+} is a hard acid and should form strong complexes with a hard base like F⁻ (Pearson, 1963; 56 Williams-Jones and Migdisov, 2014) and partly because fluorite is a common gangue mineral in 57 58 deposits like Bayan Obo (Smith et al., 2015). Numerous studies, however, have shown that the borderline base, chloride, is the dominant ligand involved in metal complexation in most 59 hydrothermal fluids (Heinrich and Seward, 1990; Fein et al., 1992; Seward et al., 2014; Migdisov 60 et al., 2016). Furthermore, a number of studies of REE complexation have shown that REE 61 chloride species are the dominant REE complexes, at least at acidic to near neutral conditions 62 (Migdisov et al., 2008; Mayanovic et al., 2009; Williams-Jones et al., 2012; Migdisov and 63 Williams-Jones, 2014; Migdisov et al., 2016), and that their stability increases with increasing 64 temperature (Gammons et al., 1996; Migdisov et al., 2009; Migdisov et al., 2016). For the reasons 65 given above, it is reasonable to conclude that scandium should form stable complexes with chloride 66 ions and that such complexes might be the dominant means of scandium transport in hydrothermal 67 fluids. 68

Another ligand that might be important in the transport of scandium, particularly at high pH, is the hydroxide ion, because like the fluoride ion, it is a hard base (Pearson, 1963; Williams-Jones and Migdisov, 2014). Indeed, at ambient temperature, scandium forms very strong complexes with OH⁻ (Wood and Samson, 2006; Williams-Jones and Vasyukova, 2018) and extrapolations of the ambient temperature formation constants to elevated temperature suggest that their stability remains high or increases with increasing temperature (Shock et al., 1997).

Currently, the only information available on the thermodynamic properties of scandium 75 chloride species is from experiments conducted at ambient temperature and, even for this 76 temperature, there is little agreement among the studies reporting information on these properties 77 (Paul, 1962; Reed et al., 1964; Samodelov, 1964; Alimarin et al., 1965; Sekine and Hasegawa, 78 79 1966). As noted above, Shock et al. (1997) estimated formation constants for scandium hydroxide species for elevated temperature based on extrapolations from ambient temperature but, as 80 discussed by Wood and Samson (2006), the hydrolysis constants reported by Shock et al. (1997) 81 may overestimate the true values. Moreover, as shown by Migdisov et al. (2009) for the other REE, 82 83 extrapolations of this type may lead to differences of several orders of magnitude between the theoretically predicted formation constants and those experimentally determined. 84

In this contribution, we evaluate the potential role of chloride and hydroxide complexes in
the hydrothermal transport of scandium from the results of experiments that measured the
solubility of Sc₂O_{3(S)} in the H₂O-NaCl-H₂O and H₂O-NaClO₄-HClO₄ systems at temperatures
between 100 and 350 °C and between 100 and 250 °C, respectively. These results show that,
contrary to expectation, scandium does not form stable complexes with chloride ions at elevated
temperature for the range of chlorinity commonly observed in nature. Scandium, however, does
© 2023. This manuscript version is made available under the CC-BY-NC-ND 4.0 license
http://creativecommons.org/licenses/by-nc-nd/4.0/

91	form stable species with hydroxide ions; at the conditions of the experiments, $Sc(OH)^{2+}$ and
92	$Sc(OH)_3$ ° are the dominant scandium species. Using the thermodynamic data extracted from the
93	experiments, we model the transport of scandium in hydrothermal fluids and evaluate the processes
94	of fluid rock interaction that might lead to scandium mineral deposition.
95	Experimental method
96	We investigated the solubility of scandium oxide $(Sc_2O_{3(s)})$ in H ₂ O-NaCl-HCl solutions at 100,
97	150, 300, and 350 °C, and in H ₂ O-NaClO ₄ -HClO ₄ solutions at 100, 150, 200, and 250 °C, both at
98	saturated water vapor pressure. In the first set of experiments, the chlorinity varied between 0.001
99	and 3.6 m and in the second set of experiments the $pH_{25^{\circ}C}$ varied between 1.6 and 4.5. Two sets of
100	experimental solutions, prepared using nanopure water, were employed in the experiments: (1)
101	solutions in which chloride concentration and pH were controlled using NaCl-HCl mixtures (trace
102	metal grade NaCl and HCl, Fisher Chemical); and (2) solutions in which pH and ionic strength
103	were controlled using HClO ₄ -NaClO ₄ mixtures (NaClO ₄ HPLC grade, Fisher Chemical; HClO ₄
104	trace metal grade, Fisher Chemical). The first set of experimental solutions was used to investigate
105	the solubility of scandium as a function of chloride concentration and the second set of solutions
106	was used to determine the effect of hydroxide on scandium solubility, without the presence of
107	chloride ions (the perchlorate ion is very stable and does not decompose to yield chloride ions;
108	Rudolph and Pye, 2000).
109	The experiments were performed in titanium autoclaves (Fig. 1) treated with nitric acid to

approximately 55 cm³. At the beginning of an experiment, scandium oxide solid ($Sc_2O_{3(s)}$ Alfa

110

© 2023. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

produce a protective layer of TiO₂ on the internal surfaces. The volumes of the autoclaves were

Aesar, 99.999% purity) was placed in quartz tubes fused shut at the base and capped with quartz 112 wool (Fig. 1). These quartz holders were placed in the autoclaves to which 14 ml of experimental 113 solution of variable chloride concentration or pH was added (Fig. 1). After sealing with a carbon 114 ring, the autoclaves were placed in a muffle furnace that had been preheated to the temperature of 115 interest. The furnace was modified by inserting an aluminum box with 1 cm thick walls to reduce 116 thermal gradients in the autoclaves. The internal temperature during runs was measured with a 117 thermocouple placed inside the box and controlled to an accuracy of ± 1 °C. On the completion of 118 each experiment, the autoclaves were quenched rapidly in a cold-water bath to room temperature 119 120 (~ 15 min). The quartz holders were then removed from the autoclaves, and 3 ml of the experimental solution was pipetted into a clean test tube to measure its pH and chloride 121 122 concentration. Approximately 5 ml of nitric acid (HNO₃ trace metal grade, Fisher Chemical) was added to the remaining solution to dissolve any scandium on the autoclave walls. The autoclave 123 was sealed and left for 24 h to ensure complete dissolution of the scandium. The ~16 ml of solution 124 (11 ml of experimental solution and 5 ml of nitric acid) was then removed from the autoclave and 125 introduced into a clean test tube for analysis of the scandium concentration. Before an experiment 126 and after each removal of solution from and addition of acid to an autoclave, the autoclave was 127 128 weighed to accurately determine the mass of scandium dissolved and, in turn, its concentration in the solution at the end of an experiment. The time required to reach equilibrium was determined 129 for each temperature investigated from sets of kinetic experiments with durations of 1 to 14 days. 130 After 7 days, the scandium concentration reached a steady state concentration, confirming the 131 attainment of equilibrium (Fig. 2). All subsequent experiments were of greater than 10 days 132 duration. 133

134	The pH of the experimental solutions was measured at ambient temperature using a glass
135	pH electrode (Fisher Scientific, precision of ± 0.01 pH units), which was calibrated using a series
136	of NaCl-HCl or NaClO ₄ -HClO ₄ solutions. The concentration of Cl ⁻ in the experimental solutions
137	was determined using a UV-visible spectrometer that had been calibrated with a series of NaCl
138	solutions for which the chloride concentration was known. Scandium concentrations were
139	measured using ICP-MS. The experimental and standard solutions were diluted using a 2% nitric
140	acid blank solution and were matrix-matched with a Ga internal standard (Fisher scientific, NIST
141	traceable certified standard) to correct for instrumental drift. After the experiments, the reacted
142	solid (Sc_2O_3) was analyzed by X-ray diffraction. No other solids were detected.

143

RESULTS

144 *Calculation of ion activity*

145 The activity of the aqueous species was calculated using the extended Debye-Hückel equation

146 (Helgeson et al., 1981):

147
$$\log \gamma_{n} = -\frac{A \cdot [z_{n}]^{2} \cdot \sqrt{I}}{1 + B \cdot \mathring{a} \cdot \sqrt{I}} + b_{\gamma} \cdot I$$
(1)

where A and B are the solvent parameters, å is the ion size parameter for the electrolyte, z is the charge of the ion, and *I* represents the ionic strength of the solution that considers all dissolved components. The parameter $b\gamma$ is the extended term, which depends on the nature of the background electrolyte and extends the application of Equation (1) to provide accurate estimates of activity coefficient up to roughly 10 mol/l. Values of $b\gamma$ for the H₂O-NaClO₄-HClO₄ solutions were taken from Migdisov and Williams-Jones (2007) and for the H₂O-NaCl-HCl solutions were taken from Oelkers and Helgeson (1991). The values of å were set at 9, 3.5, 4, 3, 4.5 Å for H⁺,

OH⁻, Na⁺, Cl⁻, ClO₄⁻, respectively (Kielland, 1937; Garrels and Christ, 1965). Thermodynamic data
for the aqueous species other than those involving scandium were taken from Johnson et al. (1992),
Sverjensky et al. (1997), and Shock et al. (1997).

158 Identification of dissolved Sc species

The scandium species responsible for the observed scandium concentrations were determined from 159 trends observed in the experimental data reported in Table 1 (for H₂O-NaCl-HCl solutions) and 160 161 Table 2 (for H₂O-NaClO₄-HClO₄), i.e., the slope of the logarithm of scandium concentration with respect to the logarithm of chloride concentration for the H₂O-NaCl-HCl solutions (Fig. 3) and pH 162 for the H₂O-NaClO₄-HClO₄ solutions (Fig. 4). From Figure 3, it is evident that the concentration 163 of scandium was independent of chloride concentration at all temperatures investigated, indicating 164 that, if scandium formed complexes with chloride, they were unstable and not detectable. However, 165 scandium concentration was not independent of pH in the chloride ion absent experiments. At 100 166 and 150 °C, the scandium concentration increased linearly with increasing H⁺ activity (decreasing 167 pH) over the full range of pH investigated (1.8 to 3.9 at 100 °C and 1.5 to 3.6 at 150 °C), and at 168 169 200 and 250 °C, it showed the same linear trend with the logarithm of hydrogen ion activity but only for values above -3 (Fig. 4). At pH values above 3, scandium concentration was independent 170 of pH. The slope of the dependence of the logarithm of scandium molality on the logarithm of 171 hydrogen ion activity in the 100 and 150 °C experiments and at low hydrogen ion activity in the 172 experiments at 200 and 250 °C was approximately 2, which is consistent with the dissolution 173 reaction: 174

175
$$Sc_2O_{3(s)} + 4H^+ = 2Sc(OH)^{2+} + H_2O$$
 (2)

176 $\log k_2 = \log a_{\text{Sc(OH)}}^{2+} - 4\log a_{\text{H}}^+$ © 2023. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

177	As noted above, at 200 and 250 °C, the	he scandium concentration was independent of pH at
178	pH values > 3 (Fig. 4C, D). We, therefore,	conclude that at this higher pH, the neutral scandium
179	hydroxide complex is the dominant scandid	am species as illustrated by the reaction:
180	$Sc_2O_{3(s)} + 3H_2O = 2Sc(OH)_3^{\circ}$	(3)

 $\log k_3 = \log a_{\rm Sc(OH)3}^{\circ}$

182 The results of these experiments show that scandium forms stable complexes with

183 hydroxide ions, namely $Sc(OH)^{2+}$ and $Sc(OH)_3^{\circ}$, and that these are the dominant scandium

184 species in chloride-bearing solutions at elevated temperatures, with $Sc(OH)_3^\circ$ being favoured by

185 higher temperature and higher pH.

186 *Formation constants and data optimization*

187 In order to make our data accessible for incorporation into thermodynamic databases, we calculated the formation constants of $Sc(OH)^{2+}$ and $Sc(OH)_3^{\circ}$. The raw experimental data for 188 scandium oxide solubility in H₂O-NaClO₄-HClO₄ solutions were processed with the Optim A 189 190 program in the HCh software package (Shvarov, 2015). This program computes the standard molal Gibbs free energy for the species of interest, in this case $Sc(OH)^{2+}$ and $Sc(OH)_3^{\circ}$, by minimizing 191 the sum of the squared deviations of the concentrations of aqueous species in equilibrium in the 192 experimental solutions at the same temperature and pressure for variable values of the independent 193 parameter (pH). The formation constants for $Sc(OH)^{2+}$ and $Sc(OH)_3^{\circ}$, Reactions (4) and (5) were 194 195 evaluated as follows:

196 $Sc^{3+} + OH^{-} = Sc(OH)^{2+}$ (4)

197 $\log \beta_4 = \log a_{\rm Sc(OH)}^{2^+} - \log a_{\rm Sc}^{3^+} - \log a_{\rm OH}^{-1^+}$

^{© 2023.} This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

198
$$Sc^{3+} + 3OH^{-} = Sc(OH)_{3}^{\circ}$$
 (5)

199 $\log \beta_5 = \log a_{\rm Sc(OH)3}^{\circ} - \log a_{\rm Sc}^{3+} - 3\log a_{\rm OH}^{-1}$

200 The Gibbs free energy changes ($\Delta G_r(T)$) for Reactions (4) and (5) were calculated using the standard molal Gibbs free energy of the other species involved in the reactions, namely Sc³⁺ and 201 OH⁻. Formation constants (log β) were, in turn, calculated from the values of $\Delta G_r(T)$ using the 202 relationship log $\beta = -\Delta G_r(T)/2.303$ RT (Table 3). The standard molal Gibbs free energy for the 203 species Sc³⁺ and OH⁻ were obtained from Shock et al. (1997) and the HCh database, respectively. 204 The formation constants for $Sc(OH)^{2+}$ and $Sc(OH)_3^{\circ}$ were fitted to the Ryzhenko-Bryzgalin 205 (MRB) equation of state in order to allow them to be calculated for temperatures not considered 206 in the experiments (Ryzhenko et al., 1985; Borisov and Shvarov, 1992; Shvarov and Bastrakov, 207 2015). The parameters derived from the MRB equation of state for $Sc(OH)^{2+}$ and $Sc(OH)_3^{\circ}$ are 208 listed in Table 4. These parameters were used to calculate the equilibrium constants (log k) for 209 Reaction (2) and Reaction (3) reported in Table 5. Thermodynamic data for scandium oxide 210 $(Sc_2O_{3(s)})$ were taken from Pankratz (1982). The best fit lines to the experimental data shown in 211 Fig. 4 were calculated using these equilibrium constants and, as is evident, fit the data remarkably 212 213 well.

214

DISCUSSION

215 *Comparison to previous studies*

As mentioned earlier, the complexation of scandium with chloride ions has been investigated
experimentally at 25 °C (Paul, 1962; Reed et al., 964; Samodelov, 1964; Alimarin et al., 1965;
Sekine and Hasegawa, 1966) and the formation constants for ScCl²⁺, ScCl₂⁺, ScCl₃⁰ reported in
© 2023. This manuscript version is made available under the CC-BY-NC-ND 4.0 license

http://creativecommons.org/licenses/by-nc-nd/4.0/

these studies are -0.80 to 1.45, -0.84 to 1.35, -1.40 to 0.16, respectively. These low and even 219 220 negative formation constants indicate that the corresponding scandium chloride complexes are relatively unstable and that chloride complexation does not play a significant role in transporting 221 scandium at ambient temperature (Wood and Samson, 2006; Williams-Jones and Vasyukova, 222 2018). The results of our study show that scandium concentration is independent of chloride 223 concentration up to 350 °C and vapor-saturated water pressure, even at high chloride molality (up 224 225 to 3.6 mol/l). Thus, chloride complexation also does not play a significant role in scandium transport at high temperature (Fig. 3). This contrasts strongly with the behavior of the other rare 226 227 earth elements, which form relatively strong complexes with chloride ions and are generally thought to be transported in hydrothermal fluids mainly by forming such complexes (Migdisov et 228 229 al., 2009; Williams-Jones et al., 2012; Migdisov and Williams-Jones, 2014; Migdisov et al., 2016). 230 The likely reason for our failure to detect chloride complexes of scandium relates to the fact that the stability of REE chloride species decreases strongly with decreasing ionic radius of the REE 231 from light to heavy REE (Migdisov et al., 2016). The ionic radius of scandium is the smallest of 232 233 all the REE, 15% less than that of the next smallest REE, lutetium and, thus, scandium would be expected to be the least likely of the REE to form stable complexes with chloride ions. Because of 234 235 its small ionic radius and hard-soft-acid-base principles (Pearson, 1963; Williams-Jones and 236 Migdisov, 2018), scandium, however, is predicted to form very stable complexes with the hard base, OH⁻, and OH⁻ would therefore out compete Cl⁻ in forming stable complexes with scandium. 237 Scandium hydroxide speciation has been investigated experimentally in numerous studies at 238 ambient temperature, and thermodynamic data have been reported for ScOH²⁺, Sc(OH)₂⁺, Sc(OH)₃° 239 and Sc(OH)₄ at this temperature (e.g., Ivanov-Emin et al., 1960; Ivanov-Emin et al., 1968; 240 © 2023. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

241 Aveston, 1966; Antonovich, and Nazarenko, 1968; Akalin, 1971; Travers et al., 1976; Brown et

al., 1983; Stryapkov et al., 1996). The available data were reviewed by Baes and Mesmer (1986), 242 who recommended values of the 25 °C stability constants for these species, and more recently by 243 Wood and Samson (2006), who supported these recommendations. Shock et al. (1997) used the 244 values recommended by Baes and Mesmer (1986) for ScOH²⁺, Sc(OH)₂⁺, Sc(OH)₃° and Sc(OH)₄⁻ 245 (which they express as $ScOH^{2+}$, ScO^+ , $HScO_2^{\circ}$, and ScO_2^{-} , respectively), in conjunction with 246 247 correlation algorithms, to determine values for the parameters of the Helgeson-Kirkham-Flowers (HKF) equation (Helgeson et al., 1981) and enable estimation of the corresponding hydrolysis 248 constants at elevated temperature and pressure. In Table 6, we report hydrolysis constants for 249 ScOH²⁺ and Sc(OH)₃° for the temperatures of our experiments, estimated using the HKF 250 parameters reported by Shock et al. (1997), and in Figure 5, we compare these constants with those 251 252 extracted from our experimental data. From this comparison, it is evident that our constants for $ScOH^{2+}$ are quite similar to those calculated from Shock et al. (1997), whereas for $Sc(OH)_3^\circ$ they 253 are consistently higher and at 100 °C, the difference is greater than a log unit. 254

255 An important difference in the findings of our study from those for ambient temperature is that, whereas $Sc(OH)_2^+$ is relatively important at this temperature, it was not shown to be stable at 256 the higher temperatures of our experiments. It is, however, predicted to be stable at these higher 257 temperatures by calculations made using the values of the HKF parameters reported by Shock et 258 al. (1997), which were based on extrapolations of experimental data reported for 25 °C. Indeed, 259 according to these predictions, $Sc(OH)_2^+$ is responsible for up to ~ 35% of the dissolved scandium 260 at temperatures ≥ 100 °C, albeit for a narrow pH interval (Fig. 6). These observations suggest that 261 either we did not conduct experiments for pH conditions corresponding to those of the 262 © 2023. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

predominance pH for Sc(OH)₂⁺ or, much more likely, that this species is simply not stable at elevated temperature and that with increasing pH the hydrolysis of scandium proceeds from Sc(OH)²⁺ to Sc(OH)₃° directly. In summary, the results of our study show that, at least up to a pH of 5, scandium in chloride-bearing hydrothermal fluids is transported dominantly as Sc(OH)²⁺ and Sc(OH)₃° and that Sc(OH)₃° is the predominant species in fluids with a pH > ~4 at 100 °C or > ~3 at 250 °C (Fig. 6).

269 *Geological implications*

270 The data collected in this study demonstrate that, although scandium chloride complexes cannot mobilize scandium, complexes involving hydroxide may fulfill this role. To gain an insight 271 into the likely behavior of scandium as hydroxide species in hydrothermal systems, we modeled 272 the dissolution Sc₂O_{3(s)} as a function of pH and temperature, two parameters commonly invoked 273 to explain metallic mineral deposition from hydrothermal fluids. The results of this modeling are 274 illustrated in Figure 7 and show that at a pH of 2 and a temperature of 100 °C, hydrothermal fluids 275 can transport about 110 ppm scandium as hydroxide species (ScOH²⁺). This concentration, 276 however, decreases to ~2 ppm at the same pH, if the temperature is increased to 250 °C. A similar 277 effect is observed with a change in pH. Thus, at 100 °C, the scandium concentration drops from 278 279 110 ppm to <1 ppm as the pH increases from 2 to 3. At higher pH, however, scandium 280 concentration increases with increasing temperature, i.e., there is a gradual change from retrograde 281 to prograde solubility. The other important conclusion is that at higher pH, scandium solubility is 282 effectively independent of pH; this corresponds to the change in the predominant species from $Sc(OH)^{2+}$ to $Sc(OH)_3^0$ (Figs. 4 and 7). Thus, for natural systems the overarching conclusion is that 283 284 temperature is the main control of scandium solubility.

To investigate the role of hydrothermal transport in scandium ore genesis, we constructed a 285 fluid-rock interaction model, in which we monitored the reaction of 1 kg aliquots of scandium-286 bearing ore fluid with 1 kg hydroxyapatite-bearing calcite rock (90% calcite and 10% 287 hydroxyapatite) at 400 °C. For this model, we assumed that the scandium ore fluid (containing 2 288 289 m NaCl, 60 wt% CO₂, at 400 °C, 1.0 kbar and a pH of 3) initially contained 0.80 ppm scandium, which is the concentration that would be present in the fluid at 400 °C and a pH of 3, based on an 290 291 extrapolation of our experimental data using the Bryzgalin-Ryzhenko parameters listed in Table 4. The choice of P-T conditions was guided by the pressure (0.7 to 1.0 kbar) and temperature (430 to 292 360 °C) inferred for the formation of the aegirine-apatite veins of the Bayan Obo REE deposit 293 294 (Smith and Henderson, 2000); aggirine is the main host for scandium in the deposit, which as noted earlier, is responsible for 90% of global scandium production. The NaCl and CO₂ concentrations 295 296 were guided by the salinity (NaCl 5–15 wt. %) and CO₂ content (mean 59 wt. %) of fluid inclusions in the aegirine-apatite veins of the Bayan Obo REE deposit (Smith and Henderson, 2000; Fan et 297 al., 2004, 2006; Qin et al, 2007). The only other deposit of hydrothermal origin that has been mined 298 299 for scandium is the Zhovti Vody deposit in Ukraine, in which the main ore mineral was also 300 aegirine, which, as at Bayan Obo, was accompanied by apatite; the aegirine replaced amphibole in 301 magnetite amphibolites (Tarkhanov et al., 1992; Williams-Jones and Vasyukova, 2018). Although 302 it is not possible to model the formation of these deposits directly, the modeling presented here provides an idea of some of the factors that may have controlled their formation. 303

The thermodynamic data for pretulite (ScPO₄), a mineral that could potentially form
 scandium ores, if aegirine were not present to sequester the scandium prior to saturation of the
 fluid with pretulite, and hydroxyapatite, were taken from Gavrichev (2010) and Robie and
 © 2023. This manuscript version is made available under the CC-BY-NC-ND 4.0 license
 http://creativecommons.org/licenses/by-nc-nd/4.0/

Hemingway (1995). Interaction of the first aliquot of fluid with the rock led immediately to the 307 precipitation of pretulite and the addition of scandium to the rock (Fig. 8A). With increasing 308 fluid/rock ratio, the scandium content of the rock increases sharply and reaches a concentration of 309 0.5 wt. % Sc₂O₃ at a fluid/rock ratio of 412, corresponding to the final consumption of calcite (Fig. 310 311 8B). Most significantly, the Sc_2O_3 concentration in the rock reaches 150 ppm at a fluid/rock ratio of 101 (Fig. 8B), which is comparable to the scandium concentration in the aegirine of the Bayan 312 Obo and Zhovti Vody deposits (169 ppm Sc_2O_3 in the massive ores and 101 ppm Sc_2O_3 in the 313 banded ores at Bayan Obo, Zhao, 1987; and a mean concentration of 161 ppm Sc at Zhovti Vody, 314 Williams-Jones and Vasyukova, 2018). This fluid/rock ratio is within the range of fluid/rock ratios 315 that might be predicted for the Bayan Obo REE ores (e.g., a ratio of 100, assuming a Ce content 316 of the ore of 4 wt% Ce and a concentration of 400 ppm Ce in the fluid, Zhao, 1987; Migdisov et 317 al., 2009). The dominant scandium hydroxide species in the ore fluid was Sc(OH)₃° (Fig. 8C) and 318 the pH was buffered to a constant value of 5.4 after reaction of the rock with the first aliquot until 319 complete replacement of the calcite by pretulite at a fluid/rock ratio of 412 (Fig. 8D). The 320 321 simulations were repeated for a scandium ore fluid with a pH value of 4 and produced similar results, although the fluid/rock ratio required to produce a rock containing 150 ppm Sc_2O_3 is a little 322 higher (115, Fig. 9). In summary, our simulations indicate that scandium hydroxide species can 323 mobilize scandium in concentrations sufficient to form an economic deposit and that, in the 324 absence of aegirine (or any other clinopyroxene, Williams-Jones and Vasyukova, 2018), pretulite 325 would be the principal scandium ore mineral in an apatite-bearing ore. 326

327	Conclusions
328	The results of this study show that complexation with chloride ions does not play a role in the
329	hydrothermal transport of scandium in solutions containing up to 3.6 M NaCl at temperatures up
330	to 350 °C. They also show, however, that scandium forms stable complexes with hydroxide ions
331	$(Sc(OH)^{2+} and Sc(OH)_3^{\circ} but not Sc(OH)_2^{+})$ and that $Sc(OH)_3^{\circ}$ is the principal scandium species at
332	pH > \sim 4 at 100 °C and > \sim 3 at 250 °C. Simulations of natural systems provide evidence that
333	hydrothermal fluids, in which scandium is transported as hydroxide species, can mobilize this
334	metal in concentrations sufficient to form economic deposits like Bayan Obo, that in apatite-
335	bearing deposits, which do not contain aegirine, pretulite would be the main ore mineral and finally
336	that fluid/rock interaction can be an important driver of scandium ore formation.
337	Acknowledgements
338	The experimental part of this study was carried out in the Hydrothermal Laboratory of the
339	Department of Earth and Planetary Sciences at McGill University. Funding for the research was
340	
540	provided by the National Natural Science Foundation of China (92062218, 41672095), the
341	provided by the National Natural Science Foundation of China (92062218, 41672095), the National Nonprofit Institute Research Grant of CAGS (KK1910), a NSERC Discovery grant to
341 342	provided by the National Natural Science Foundation of China (92062218, 41672095), the National Nonprofit Institute Research Grant of CAGS (KK1910), a NSERC Discovery grant to AEW-J, and a scholarship to JW from the China Scholarship Council (CSC). The study
341 342 343	provided by the National Natural Science Foundation of China (92062218, 41672095), the National Nonprofit Institute Research Grant of CAGS (KK1910), a NSERC Discovery grant to AEW-J, and a scholarship to JW from the China Scholarship Council (CSC). The study benefitted from discussions with Olga Vasyukova, Junfeng Shen and Haylea Nisbet. The
341 342 343 344	provided by the National Natural Science Foundation of China (92062218, 41672095), the National Nonprofit Institute Research Grant of CAGS (KK1910), a NSERC Discovery grant to AEW-J, and a scholarship to JW from the China Scholarship Council (CSC). The study benefitted from discussions with Olga Vasyukova, Junfeng Shen and Haylea Nisbet. The manuscript was improved significantly with the help of the comments of the Economic Geology
 341 342 343 344 345 	provided by the National Natural Science Foundation of China (92062218, 41672095), the National Nonprofit Institute Research Grant of CAGS (KK1910), a NSERC Discovery grant to AEW-J, and a scholarship to JW from the China Scholarship Council (CSC). The study benefitted from discussions with Olga Vasyukova, Junfeng Shen and Haylea Nisbet. The manuscript was improved significantly with the help of the comments of the Economic Geology Reviewers, Taras Bryndzia and Marion Louvel, Associate Editor Paul Spry and Editor Larry

347

348	REFERENCES
349	Akalin, S., 1971, Hydrolysis of Sc ³⁺ and the stabilities of scandium (III)-Tiron chelates in aqueous
350	solution: Journal of Inorganic and Nuclear Chemistry, v. 33, p. 4171-4180.
351	Alimarin, I.P., Belyavskaya, T.A., Brikina, G.D., 1965, Investigation of the complex formation of
352	scandium by the ion exchange method: Vestnik Moskovskogo Universiteta, Series. 2, p. 69-
353	72.
354	Antonovich, V.P., and Nazarenko, V.A., 1968, Spectrophotometric determination of the
355	hydrolysis constants of scandium ions: Russian Journal of Inorganic Chemistry, v. 13, p. 940-
356	941.
357	Aveston, J., 1966, Hydrolysis of scandium (III): ultracentrifugation and acidity measurements.
358	Journal of the Chemical Society A: Inorganic, Physical, Theoretical, p. 1599-1601.
359	Baes J.C.F., and Mesmer, R.E., 1986, The Hydrolysis of Cations: Krieger Publishing Company,
360	Malabar, Florida, 489 p.
361	Borisov, M.V., and Shvarov, Y.V., 1992, Thermodynamics of Geochemical Processes: Moscow
362	State University Publishing House, Moscow, 254 p.
363	Brown, P.L., Ellis, J., and Sylva, R.N., 1983, The hydrolysis of metal ions. Part 6. Scandium (III).
364	Journal of the Chemical Society: Dalton Transactions, no. 1, p. 35-36.
365	Fan, H.R., Xie, Y.H., Wang, K.Y., Tao, K.J., and Wilde, S.A., 2004, REE daughter minerals
366	trapped in fluid inclusions in the giant Bayan Obo REE-Nb-Fe deposit, Inner Mongolia, China:
367	International Geology Review, v. 46, p. 638-645.

- 368 Fan, H.R., Hu, F.F., Yang, K.F., and Wang, K.Y., 2006, Fluid unmixing/immiscibility as an ore-
- 369forming process in the giant REE–Nb–Fe deposit, Inner Mongolian, China: evidence from
- 370 fluid inclusions: Journal of Geochemical Exploration, v. 89, p.104-107.
- 371 Fein, J.B., Hemley, J.J., d'Angelo, W.M., Komninou, A., and Sverjensky, D.A., 1992,
- Experimental study of iron-chloride complexing in hydrothermal fluids: Geochimica et
 Cosmochimica Acta, v. 56, p. 3179-3190.
- 374 Gammons, C.H., Wood, S.A., and Williams-Jones, A.E., 1996, The aqueous geochemistry of the
- 375 rare earth elements and yttrium: VI. Stability of neodymium chloride complexes from 25 to
- 376 300 C: Geochimica et Cosmochimica Acta, v. 60, p. 4615-4630.
- 377 Garrels, R.M., and Christ, C.L., 1965, Solutions, minerals, and equilibria, 450 p.
- Grammaccioli, C.M., Diella, V., and Demartin, F., 1999, The role of fluoride complexes in REE
 geochemistry and the importance of 4f electrons: some examples in minerals: European
- 380 Journal of Mineralogy, v. 11, p. 983-992.
- 381 Grammaccioli, C.M., Diella, V., and Demartin, F., 2000, The formation of scandium minerals as
- an example of the role of complexes in the geochemistry of rare earths and HFS elements:
 European Journal of Mineralogy, v. 12, p. 795-808.
- Halkoaho, T., Ahven, M., Rämö, O.T., Hokka, J., and Huhma, H., 2020, Petrography,
 geochemistry, and geochronology of the Sc-enriched Kiviniemi ferrodiorite intrusion, eastern
 Finland: Mineralium Deposita, v. 55, p. 1-20.
- Hefter, G.T., 1984, Acidity constant of hydrofluoric acid: Journal of Solution Chemistry, v. 13, p.
 457–470.

389	Helgeson, H.C., Kirkham, D.H., and Flowers, G.C., 1981, Theoretical prediction of the
390	thermodynamic behavior of aqueous electrolytes by high pressures and temperatures; IV,
391	Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard
392	and relative partial molal properties to 600 °C and 5kb: American Journal of Science, v. 281,
393	p. 1249-1516.
394	Heinrich, C.A., and Seward, T.M., 1990, A spectrophotometric study of aqueous iron (II) chloride
395	complexing from 25 to 200 °C: Geochimica et Cosmochimica Acta, v. 54, p. 2207-2221.
396	Johnson, J. W., Oelkers, E. H., and Helgeson, H. C., 1992, SUPCRT92: a software package for
397	calculating the standard molal thermodynamic properties of minerals, gases, aqueous species,
398	and reactions from 1 to 5000 bar and 0 to 1000 °C: Computer and Geosciences, v. 18, p. 899–
399	947.
400	Kestin, J., Sengers, J., and Kampgar-Parsi, B., 1984, Thermo- physical properties of fluid H2O:
401	Journal of Physical and Chemical Reference data, v. 13, p. 175-183.
402	Kielland, J., 1937, Individual activity coefficients of ions in aqueous solutions: Journal of the
403	American Chemical Society, v. 59, p. 1675-1678.
404	Klimpel, F., Bau, M., and Graupner, T., 2021, Potential of garnet sand as an unconventional
405	resource of the critical high-technology metals scandium and rare earth elements: Scientific
406	reports, v. 11, p. 1-10.
407	Li, X.C., Yang, K.F., Spandler, C., Fan, H.R., Zhou, M.F., Hao, J.L., and Yang, Y.H., 2021, The
408	effect of fluid-aided modification on the Sm-Nd and Th-Pb geochronology of monazite and
409	bastnäsite: Implication for resolving complex isotopic age data in REE ore systems:
410	Geochimica et Cosmochimica Acta, v. 300, p. 1-24.
	© 2023. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

- 411 Marshall, W.L., and Franck, E.U., 1981, Ion product of water substance, 0-1000 °C, 1-10,000 bars.
- 412 New international formulation and its background: Journal of Physical and Chemical
 413 Reference Data, v. 10, p. 295-304.
- 414 Mayanovic, R.A., Anderson, A.J., Bassett, W.A. and Chou, I.M., 2009, The structure and stability
- 415 of aqueous rare-earth elements in hydrothermal fluids: new results on neodymium (III) aqua
- and chloroaqua complexes in aqueous solutions to 500 °C and 520 MPa: Chemical Geology,
 v. 259, p. 30-38.
- 418 Migdisov, A.A., and Williams-Jones, A.E., 2007, An experimental study of the solubility and
- speciation of neodymium (III) fluoride in F-bearing aqueous solutions, Geochimica et
 Cosmochimica Acta, v. 71, p. 3056-3069.
- Migdisov, A.A., Williams-Jones, A.E., Normand, C., and Wood, S.A., 2008, A spectrophotometric
 study of samarium (III) speciation in chloride solutions at elevated temperatures: Geochimica
 et Cosmochimica Acta, v. 72, p. 1611-1625.
- 424 Migdisov, A.A., Williams-Jones, A.E., and Wagner, T., 2009, An experimental study of the
- solubility and speciation of the Rare Earth Elements (III) in fluoride-and chloride-bearing
 aqueous solutions at temperatures up to 300 C: Geochimica et Cosmochimica Acta, v. 73, p.
 7087-7109.
- 428 Migdisov, A., Williams-Jones, A.E., Brugger, J., and Caporuscio, F.A., 2016, Hydrothermal
- transport, deposition, and fractionation of the REE: Experimental data and thermodynamic
 calculations: Chemical Geology, v. 439, p. 13-42.
- 431 Nikolaychuk, P.A., 2016, The revised potential-pH diagram of Sc-H2O system: Scientific
- 432 statements, v. 37, p. 70-87.

^{© 2023.} This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

- 433 Oelkers, E.H., and Helgeson, H.C., 1991, Calculation of activity coefficients and degrees of
- 434 formation of neutral ion pairs in supercritical electrolyte solutions: Geochimica et
 435 Cosmochimica Acta, v. 55, p. 1235-1251.
- Pankratz, L.B., 1982, Thermodynamic properties of elements and oxides (No. 672): US
 Department of the Interior, Bureau of Mines, p. 364-365.
- Paul, A.D., 1962, The chloride and bromide complexing of scandium (III) and yttrium (III) in
 aqueous solution: The Journal of Physical Chemistry, v. 66, p. 1248-1252.
- 440 Pearson, R.G., 1963, Hard and soft acids and bases: Journal of the American Chemical society, v.
- 441 85, p. 3533-3539.
- 442 Qin, C.J., Qiu, Y.Z., Zhou, G.F., Wang, Z.G., Zhang, T.R., and Xiao, G.W., 2007, Fluid inclusion
- study of carbonatite dykes/veins and ore-hosted dolostone at the Bayan Obo ore deposit: Acta
 Petrologica Sinica, v. 23, p. 0161-68.
- Reed, G.L., Sutton, K.J., and Morris, D.F.C., 1964, Stability constants of scandium (III) chloride
- 446 complexes: Journal of Inorganic and Nuclear Chemistry, v. 26, p. 1227-1231.
- 447 Rudolph, W.W., and Pye, C.C., 2000, Raman spectroscopic measurements of scandium (III)
- 448 hydration in aqueous perchlorate solution and ab initio molecular orbital studies of scandium
- (III) water clusters: does Sc (III) occur as a hexaaqua complex?: The Journal of Physical
 Chemistry A, v. 104, p. 1627-1639.
- 451 Ryzhenko, B.N., Bryzgalin, O.V., Artamkina, I.Y., Spasennykh, M.Y., and Shapkin, A.I., 1985,
- 452 An electrostatic model for the electrolytic dissociation of inorganic substances dissolved in
- 453 water: Geochemistry International, v. 22, p. 138-144.

- 454 Samodelov, A.P., 1964, State and complex formation of scandium in solutions of mineral acids:
 455 Soviet Radiochemistry, v. 6, p. 548-560.
- 456 Sekine, T., and Hasegawa, Y., 1966, Studies of Scandium in Various Solutions. I. An Ion-
- 457 Exchange Study of Scandium (III) Chloride and Nitrate Complexes: Bulletin of the Chemical
- 458 Society of Japan, v. 39, p. 240-243.
- 459 Shock, E.L., Sassani, D.C., Willis, M., and Sverjensky, D.A., 1997, Inorganic species in geologic
- 460 fluids: correlations among standard molal thermodynamic properties of aqueous ions and
- 461 hydroxide complexes: Geochimica et Cosmochimica Acta, v. 61, p. 907-950.
- 462 Shvarov, Y., 2015, A suite of programs, OptimA, OptimB, OptimC, and OptimS compatible with
- the Unitherm database, for deriving the thermodynamic properties of aqueous species from
 solubility, potentiometry and spectroscopy measurements: Applied Geochemistry, v. 55, p.
 17-27.
- Smith, M.P., and Henderson, P., 2000, Preliminary fluid inclusion constraints on fluid evolution
 in the Bayan Obo Fe-REE-Nb deposit, Inner Mongolia, China: Economic Geology, v. 95, p.
 1371-1388.
- Smith, M.P., Campbell, L.S., and Kynicky, J., 2015, A review of the genesis of the world class
 Bayan Obo Fe–REE–Nb deposits, Inner Mongolia, China: Multistage processes and
 outstanding questions: Ore Geology Reviews, v. 64, p. 459-476.
- 472 Stryapkov, A.V., Koshei, E.V., and Stryapkova, R.Z., 1996, Hydrolytic precipitation of scandium
- 473 from nitrate, chloride and sulfate solutions: Izvestiya Ministerstva Nauki-Akademii Nauk
- 474 Respubliki Kazakhstan Seriya Khimicheskaya, v. 4, p. 60-65 (in Russian).

- 475 Sverjensky, D.A., Shock, E.L., and Helgeson, H.C., 1997, Prediction of the thermodynamic
 476 properties of aqueous metal complexes to 1000 °C and 5 kb: Geochimica et Cosmochimica
 477 Acta, v. 61, p. 1359-1412.
- Travers, J.G., Dellien, I., Hepler, L.G., 1976, Scandium: Thermodynamic properties, chemical
 equilibria, and standard potentials: Thermochimica Acta, v. 15, p. 89-104.
- 480 Vasyukova, O.V., and Williams-Jones, A.E., 2018, Direct measurement of metal concentrations
- 481 in fluid inclusions, a tale of hydrothermal alteration and REE ore formation from Strange
- 482 Lake, Canada: Chemical Geology, v. 483, p. 385-396.
- Wang, J.X., Williams-Jones, A.E., Timofeev, A., Yuan, S.D., and Liu, J.J., 2022, An experimental
- 484 investigation of the solubility and speciation of scandium in fluoride-bearing aqueous liquids
 485 at temperatures up to 250 °C: Geochimica et Cosmochimica Acta, v. 330, p. 67-79.
- 486 Wang, L., Wang, P., Chen, W.Q., Wang, Q.Q., and Lu, H.S., 2020, Environmental impacts of
- 487 scandium oxide production from rare earths tailings of Bayan Obo Mine: Journal of Cleaner
 488 Production, v. 270, p. 122464.
- Wang, Z., Li, M.Y.H., Liu, Z.R.R., and Zhou, M.F., 2021, Scandium: Ore deposits, the pivotal
- 490 role of magmatic enrichment and future exploration: Ore Geology Reviews, v. 128, p. 103906.
- 491 Williams-Jones, A.E., Migdisov, A.A., and Samson, I.M., 2012, Hydrothermal mobilisation of the
- 492 rare earth elements–a tale of "ceria" and "yttria": Elements, v. 8, p. 355-360.
- 493 Williams-Jones, A.E., and Vasyukova. O.V., 2018, The economic geology of scandium, the runt
- 494 of the rare earth element litter: Economic Geology, v. 113, p. 973-988.
- 495 Wood, S.A., and Samson, I.M., 2006, The aqueous geochemistry of gallium, germanium, indium

496 and scandium: Ore Geology Reviews, v. 28, p. 57-102.

^{© 2023.} This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

497	
498	Figure captions
499	Fig. 1 A schematic diagram of the titanium autoclave employed in this study. The autoclave was
500	loaded with a quartz tube containing Sc ₂ O ₃ solid.
501	
502	Fig. 2 The logarithm of scandium molality as a function of the duration of the experiments in
503	days at constant temperature (100 °C), chloride concentration (0.05 mol/l) and pH (3), and
504	saturated water vapor pressure. Scandium reached a steady state concentration in the solution
505	after 7 days, indicating the attainment of equilibrium.
506	
507	Fig. 3 The logarithm of scandium molality as a function of the concentration of NaCl at 100,
508	150, 300, and 350 °C.
509	
510	Fig. 4 The logarithm of scandium molality with respect to pH at (A) 100, (B) 150, (C) 200, and
511	(D) 250 °C. The dashed lines indicate the logarithm of scandium molality calculated from the
512	values of logK for Reaction (2) and Reaction (3). The filled blue circles indicate the scandium
513	molality measured in experiments in the system H2O-NaCl-HCl.
514	
515	Fig. 5 The logarithms of the scandium hydrolysis constants versus temperature, determined
516	experimentally in this study and calculated from Shock et al. (1997) for (A) Sc(OH) ²⁺ and (B)
517	$Sc(OH)_3^{\circ}$.
518	

519 Fig. 6 A comparison of the distribution of scandium hydroxide complexes as a function of pH at

520 (A) 100, (B) 150, (C) 200, (D) 250 $^{\circ}$ C based on the parameters of HKF from this study to that

521 form Shock et al. (1997).

522

Fig. 7 The concentration of scandium in equilibrium with Sc₂O₃ (solid) as a function of pH for
temperatures between 100 and 250°C.

525

526 Fig. 8 Results of the thermodynamic modeling of the reaction, at 250 °C, 500 bar and an initial pH

of 2, of a scandium ore fluid containing 1 m NaCl and 1 ppm Sc, with a rock containing 90 wt.%

528 calcite and 10 wt.% hydroxyapatite. A) the moles of the different minerals present in the rock, B)

529 the scandium content of the rock, C) the scandium speciation, and D) the pH, all as a function of

530 the fluid/rock ratio.

531

Fig. 9 The scandium content of a rock containing 90 wt.% calcite and 10 wt.% hydroxyapatite as

a function of the fluid/rock ratio after reaction with a fluid at 100 and 200°C and an initial pH of

534 2, that contains 1 m NaCl and variable concentrations of scandium.



Figure 1. A schematic diagram of the titanium autoclave employed in this study. The autoclave was loaded with a quartz tube containing Sc_2O_3 solid.



Figure 2. The logarithm of scandium molality as a function of the duration of the experiments in days at constant temperature (100 °C), chloride concentration (0.05 mol/l) and pH (3), and saturated water vapor pressure. The uncertainty associated with each value is less than the diameter of the corresponding symbol. Scandium reached a steady state concentration in the solution after 7 days, indicating the attainment of equilibrium.



Figure 3. The logarithm of scandium molality as a function of the concentration of NaCl at 100, 150, 300, and 350 °C. The uncertainty associated with each value is less than the diameter of the corresponding symbol.

Wang, J., Williams-Jones, A., Timofeev, A., Zhang, X., Liu, J., and Yuan, S., 2023, The Role of Scandium Chloride and Hydroxide Complexes in the Formation of Scandium Deposits: Insights from Experiments and Modeling: Economic Geology, v. 118, p. 1995-2004



Figure 4. The logarithm of scandium molality with respect to the logarithm of the activity of H+ at (A) 100, (B) 150, (C) 200, and (D) 250 °C. The dashed lines indicate the logarithm of scandium molality calculated from the values of log K for Reaction (2) and Reaction (3). The filled blue circles indicate the scandium molality measured in experiments in the system H₂O-NaCl-HCl. The uncertainty associated with each value is less than the diameter of the corresponding symbol.



Figure 5. Logarithms of scandium hydrolysis constants versus temperature, determined experimentally in this study and calculated from Shock et al. (1997) for (A) $Sc(OH)^{2+}$ and (B) $Sc(OH)_3^{\circ}$.

Wang, J., Williams-Jones, A., Timofeev, A., Zhang, X., Liu, J., and Yuan, S., 2023, The Role of Scandium Chloride and Hydroxide Complexes in the Formation of Scandium Deposits: Insights from Experiments and Modeling: Economic Geology, v. 118, p. 1995-2004



Figure 6. A comparison of the distribution of scandium hydroxide complexes as a function of pH at (A) 100, (B) 150, (C) 200, (D) 250 °C, based on the results of this study to those extrapolated from ambient temperature using the HKF parameters reported by Shock et al. (1997).



Figure 7. The concentration of scandium in equilibrium with Sc_2O_3 (solid) as a function of pH for the temperatures investigated experimentally (100 to 250°C) and extrapolated from the experimental data (up to 400 °C).

Wang, J., Williams-Jones, A., Timofeev, A., Zhang, X., Liu, J., and Yuan, S., 2023, The Role of Scandium Chloride and Hydroxide Complexes in the Formation of Scandium Deposits: Insights from Experiments and Modeling: Economic Geology, v. 118, p. 1995-2004



Figure 8. Results of the thermodynamic modeling of the reaction, at 400 °C, 1.0 kbar and an initial pH of 3, of a scandium ore fluid containing 2 m NaCl, 60 wt. % CO₂ and 0.82 ppm Sc, with a rock containing 90 wt.% calcite and 10 wt.% hydroxyapatite. A) the moles of the different minerals present in the rock, B) the scandium oxide content of the rock, C) the scandium speciation, and D) the pH, all as a function of the fluid/rock ratio.

Wang, J., Williams-Jones, A., Timofeev, A., Zhang, X., Liu, J., and Yuan, S., 2023, The Role of Scandium Chloride and Hydroxide Complexes in the Formation of Scandium Deposits: Insights from Experiments and Modeling: Economic Geology, v. 118, p. 1995-2004



Figure 9. The scandium oxide content of a rock containing 90 wt.% calcite and 10 wt.% hydroxyapatite as a function of the fluid/rock ratio after reaction with a fluid at 400°C having an initial pH of 3 or 4, a content of 2 m NaCl and 60 wt. % CO_2 , and a scandium concentration established by $Sc_2O_{3(s)}$ solid saturation.