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An experimental study of the solubility and speciation of the scandium in fluoride-bearing aqueous solutions at temperatures up to 250 °C

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ABSTRACT

The solubility of ScF_3 (solid) and the speciation of scandium in fluoride-bearing aqueous solutions with HF concentrations from 0.53 mmol/kg to 645.12 mmol/kg was investigated at temperatures from 100 to 250 ^oC and vapor-saturated water pressure. The results of the experiments show that ScF_2^+ and ScF_3^o are the dominant species in fluoride-bearing solutions at the conditions investigated. The logarithm of the formation constant (logβ) of ScF_2^+ ($Sc_3^+ + 2F^- \rightleftharpoons ScF_2^+$) is 12.10±0.01, 12.73±0.01, 13.60±0.02, and 14.77±0.01 at 100, 150, 200, and 250 °C, respectively. That of ScF_3^0 ($Sc_3^+ + 3F^- \rightleftharpoons ScF_3^0$) is 17.28±0.04, 17.76 ±0.08, 18.58±0.03, and 19.82±0.01 at the same temperatures, respectively.

In this contribution, we show that scandium fluoride complexes are more stable than scandium hydroxide complexes and Sc^{3+} at temperature from 100 to 250^{o}C in fluoride bearing acidic hydrothermal fluids. Modeling of the transport and deposition of scandium using the results of this study provided evidence that although fluid mixing leads to the deposition of scandium minerals, fluid-rock interaction is a potentially more effective method of scandium mineral deposition, particularly if the rock is enriched in phosphate. Our study provides the essential thermodynamic data needed to better understand the

factors controlling the transport and deposition of scandium in natural fluoride-bearing hydrothermal systems.

INTRODUCTION

Scandium is a rare metal considered to be critical because of its importance to industrial progress and in emerging technologies, particularly those relating to the environment and national security (Levard et al., 2018; USGS, 2018; Chakhmouradian et al., 2015). The main use of scandium is in nonferrous alloys and solid oxide fuel cells, for which demand is increasing rapidly (Williams-Jones and Vasyukova, 2018). Most important among the former are the aluminum-scandium alloys that have been long used in the aerospace sector and are increasingly sought after by the automotive industry, as it moves to replace steel with much lighter alloys having high tensile strength (Siegfried et al., 2018; Williams-Jones and Vasyukova, 2018). Scandium is in high demand as a scandia-stabilised electrolyte for use in solid oxide fuel cells because of its capacity to improve conductivity and lower the operating temperature, thereby extending cell life (Williams-Jones and Vasyukova, 2018). Currently, most of the World's supply of scandium (~ 90%) is as a by-product of the mining of the other rare earths at Bayan Obo in China (Wang et al., 2011) where, unlike the rest of the rare earth element family, it is concentrated in aegirine, rather than in bastnäsite-(Ce) and monazite-(Ce), the main hosts for these elements (Williams-Jones and Vasyukova, 2018). The high price for scandium, coupled with a limited and erratic supply and high demand, have created a strong need to find new resources of this critical metal and thus an improved understanding of the processes that concentrate it to mineable levels. In this and other deposits, hydrothermal processes commonly have played an important role in concentrating the scandium to exploitable levels. Unfortunately, because of a lack of reliable thermodynamic data for aqueous scandium species at elevated temperature, it is currently not possible to model scandium behavior in hydrothermal fluids and develop the models needed to predict its economic concentration.

Because scandium has a high charge to radius ratio (Z/r), it is classified as a hard cation in hard-soft-acid-base (HSAB) terminology (Pearson, 1963; Williams-Jones and Migdisov, 2014) and should form strong complexes with hard ligands, such as fluoride, hydroxide, sulfate, and phosphate. Furthermore, as elevated scandium concentrations are commonly associated with the emplacement of alkaline igneous rocks and carbonatites having high fluorine concentrations, it is reasonable to propose that complexation with fluoride could explain the mobility of scandium in this environment. Indeed, this may have been the case for Bayan Obo, which is interpreted to be a carbonatite-related hydrothermal deposit and contains abundant fluorite. Further support for the hypothesis that fluoride could be an important ligand for scandium complexation in hydrothermal fluids is provided by thermodynamic data for fluoride scandium species at ambient temperature (Wood and Samson, 2006; Williams-Jones and Vasyukova, 2018). In addition, by analogy with the behavior of the other REEs (Migdisov et al., 2009; Williams-Jones et al., 2012; Loges et al., 2013), it is reasonable to predict that fluoride scandium species will be more stable at elevated temperature. Because of its much smaller cation size than the other REEs and its quite different behavior in nature (e.g., Sc is a compatible element concentrating in ferromagnesian minerals, whereas the other REE are incompatible and concentrate as REE minerals; Williams-Jones and Vasyukova, 2018), it is nonetheless possible that its high temperature complexation will also be different from that of the other REEs. It is, thus, essential that we begin to experimentally investigate the speciation of scandium at elevated temperature and provide thermodynamic data for species that could potentially play an important role in its transport and deposition by hydrothermal fluids.

In this contribution, we evaluate the speciation of scandium in fluoride-bearing solutions at temperatures from 100 to 250ºC, and provide the thermodynamic properties of the dominant fluoride scandium species. Using these new thermodynamic data we provide a simple example of how they can be used to evaluate the controls on hydrothermal scandium transport and deposition in nature. This study represents an important first step in providing the thermodynamic data needed to model and thereby advance understanding of hydrothermal scandium ore-formation.

2. EXPERIMENTAL METHOD

The experiments involved measuring the solubility of synthetic ScF_3(solid) (99.99%, Alfa Aesar) in aqueous solutions of variable HF concentration at temperatures from 100 to

250°C, at saturated water vapor pressure. The method employed in the experiments is similar to that used in previous studies by our group (e.g., Migdisov and Williams-Jones, 2007; Timofeev et al., 2017) for studying Nd speciation in fluoride-bearing aqueous solutions. Readers are referred to these papers for details not covered in the following summary.

The fluoride concentration was controlled by dissolving known amounts of NaF in nano-pure de-ionized water and ranged from 0.53 mmol/kg to 645.12 mmol/kg. The pH of each solution was then reduced to a value close to the pre-selected value for the corresponding experiment, by adding an appropriate amount of trace metal grade $HClO_4$ (Fisher Scientific). The pH at the temperature of interest ranged from 0.66 to 6.48, although for the majority of the experiments the pH was in the range 1 - 2. The ionic strength of the experimental solutions was adjusted by adding a predetermined amount of $NaClO_4$, approximately equivalent to that of NaF, to each experimental solution containing >20 mmol/kg NaF, to ensure the predominance of ClO_4^-, a noncomplexing ligand, over HF as the background electrolyte. The experimental solutions were stored in polyethylene containers.

The experiments were performed by placing tiny sealed Teflon holders containing ScF_3 powder into Teflon reactors (50 cm^3 Teflon test tubes) and adding 14 ml of experimental solution to them (Fig. 1). The reactors were then placed in titanium autoclaves (Grade 2ASTM B348, Fig. 1) and, to balance the pressure inside and outside the reactors during an experiment, solution identical in composition to that used in the experiment was added to the autoclaves (Fig. 1). As ultra-fine particles of ScF_3(s) may have become attached to the outsides of the Teflon holders during their filling, the reactor-bearing autoclaves were heated to a temperature of 250 °C for one week to dissolve these particles. A fresh solution was then added to each reactor and the autoclaves were heated to the target temperature. The heating of the autoclaves prior to and during the experiments was done in a Fisher Isotemp 838F forced draft oven controlled to a temperature of ± 1 °C.

The minimum time required to attain a steady state concentration, assumed to represent the equilibrium solubility, was determined from a series of experiments of variable duration performed at 100°C with a starting solution containing 0.02 mol/kg HF, having a pH of 1.2. The duration of the experiments ranged from 1 to 13 days, with a steady state concentration, being reached after 7 days (Fig. 2). To ensure all the subsequent experiments on which this study is based reached equilibrium, they were of two weeks duration. After an experiment, the autoclave was quenched in cold water to room temperature and opened, and the ScF_3-bearing Teflon holder within the larger Teflon reactor was removed in less than 30 min to minimize ScF_3 (solid) precipitation. The experimental solution was then removed and stored for subsequent analysis. A 3 mL aliquot of fluid was used for pH and fluoride concentration measurement. The pH (25 °C) of the experimental solution was determined potentiometrically using a HF-resistant glass pH electrode (8172BNWP, Fisher Scientific). The acidity of this aliquot of experimental solution was then neutralized by adding to it 3 ml of TISAB II (Deionized water >84%, sodium acetate 8%, sodium chloride 6%, acetic acid 1%, CDTA <1%, Supplier: Thermo Fisher Scientific) solution and the fluoride concentration measured using a Thermo Scientific Orion fluoride ion selective electrode (ASTMD 1179, Fisher Scientific). This electrode was calibrated with several sodium fluoride solutions containing between 0.05 and 0.0005 mol/kg NaF that were prepared by serial dilution. After removal of the experimental solution from a Teflon reactor, 5mL of trace metal grade HNO_3 was added to the reactor and allowed to remain there for a minimum of two hours to dissolve any Sc-bearing precipitates that may have formed on the inside walls during quenching. The concentrations of scandium in the experimental and washing solutions were determined using ICP-MS spectroscopy (McGill and UQAM, Montreal). The autoclaves and Teflon reactors were cleaned using 5% HNO3 (trace metal grade) and nano-pure de-ionized water for later use. In order to ensure that the only solid present during the experiments was ScF_3(s), the solid remaining after a reaction was analyzed by X-ray diffraction (XRD). The XRD spectra showed no evidence of additional solids (Supplementary Fig. 1), confirming that the solubility measured corresponded to that of ScF_3(s).

3. RESULTS

3.1. Identification of dissolved scandium species

The results of the experiments, which were conducted at temperatures between 100 and

250 °C, are reported in Table1 and are used here to identify the dominant species present in the experimental solutions at the different experimental conditions. For this purpose, the logarithm of the concentration of scandium measured in the experimental solutions was plotted as a function of the logarithm of the HF activity and pH_T (Fig. 3). Two distinct trends are evident in the data for 100 and 150ºC. At low HF activity (< ~0.01 at 100℃, mol/kg; < ~0.03 mol/kg at 150℃,), the logarithm of scandium concentration, dissolved as $ScF_3(s)$ has a slope of approximately negative one with respect to the logarithm of HF activity. This suggests that in this species Sc is bound to two atoms of F, which corresponds to the simple dissociation reaction:

$$ScF_{3(s)} + H^+ = ScF_2^+ + HF$$

$$\log K_1 = \log a_{ScF2^+} + \log a_{HF} - \log a_{H^+} \qquad (1)$$

Moreover, the logarithm of scandium concentration at low pH with constant HF has a slope of approximately negative one (Fig. 3a$_2$, b$_2$), which confirms that this scandium complex formed via Reaction (1). In contrast to the population of scandium data at low HF activity, the population at higher HF activity shows a much weaker dependence on HF activity, with the slope of the logarithm of scandium activity relative to the logarithm of HF activity being zero (Fig. 3a$_1$, b$_1$). This indicates that the solubility of the ScF_3 (solid) was controlled mainly by the reaction:

$$ScF_{3s} = ScF_3^0$$

$$\log K_2 = \log a_{ScF3^0} \qquad (2)$$

Furthermore, as in the pH dependent experiments with high HF activity, the distribution of yellow triangle symbols (Fig. 3a$_1$, b$_1$) shows that Reaction (2) is not pH dependent.

At higher temperature, 200 and 250℃, the slope in the logarithm of scandium activity versus the logarithm of HF activity is approximately negative one for all concentrations of HF considered in the study (Fig. 3c$_1$, d$_1$). This suggests that the solubility of the ScF_3 (solid) at high temperature was mainly controlled by Reaction (1). Support for this interpretation is provided by the results of a series of experiments carried out at constant HF (logaHF=-2), but variable pH (Fig. 3c2, d2). These results show that the solubility of ScF_3 solid decreases with increasing pH from ~1 to 2.5. It is also worth noting that the higher temperature pH dependence experiments with high HF activity (the yellow triangle symbols, Fig. 3c2, d2) show that the high HF activity limit of the data defining a negative one trend in Fig. 3c1 and Fig. 3d1 coincides with a change in predominance from ScF_2^+ to ScF_3^0. This interpretation is also supported by the two distinct trends that are evident in the the plots of the data as a function of pH at constant HF activity (Fig. 3a2, b2, c2, d2).

3.2. Methods used and data treatment

As discussed in the preceding section, the results of our experiments show that ScF_3 solid dissolves in HF-bearing solutions by forming the species ScF_2^+ and ScF_3^0. The standard Gibbs free energy of the two species was determined using the optimization code "OptimA", which is part of the HCh software package (Shvarov, 2010) and involved minimizing the sum of squared deviations of the experimentally determined concentrations of the above species from their concentrations determined by calculating the equilibrium composition of the solution in all experiments performed for the same isotherm. Inputs to the code included the molality of Sc measured after each experiment, the molality of NaF in the experimental solution, as well as the molality of $NaClO_4$ and $HClO_4$. The molality of $HClO_4$ was calculated from the pH measured after each experiment and an assumption that $HClO_4$ dissociates completely; the $NaClO_4$ molality was determined by subtracting the $HClO_4$ molality from the total ClO_4^- molality of the experimental solution. Aqueous species considered during the optimization were H^+, OH^-, F-, Na^+, NaOH, NaF, HF, ClO_4^-, thermodynamic data for which were obtained from Ryzhenko (1965), Ryzhenko et al. (1991), Johnson et al. (1992), Sverjensky et al. (1997), and Shock et al. (1997).

The activity of the ions was calculated using the extended Debye-Hückel equation (Helgeson et al., 1981):

$$\log \gamma_n = -\frac{A \cdot [z_n]^2 \cdot \sqrt{I}}{1 + B \cdot å \cdot \sqrt{I}} + b_\gamma \cdot I \qquad (3)$$

in which A and B are solvent parameters, $b\gamma$ is the extended parameter, which depends on the nature of the background electrolyte, $\mathring{a}$ is the distance of closest approach, which is specific to the ion of interest, z is the charge of the ion, and I the true ionic strength, determined after consideration of all the dissolved components. The values of $b\gamma$, the extended parameter, were taken from Migdisov and Williams-Jones (2007), who determined the best fit of $b\gamma$ values for ClO_4^- in a chemically similar system. The distances of closest approach ($\mathring{a}$), were set at 9 Å for H+ (Kielland, 1937; Garrels and Christ, 1965), 3.5 Å for F^- and OH^- (Garrels and Christ, 1965), 4 Å for Na^+ (Garrels and Christ, 1965) and at 4.5 Å for ClO_4^- and ScF_2^+ (Kielland, 1937). The Haar–Gallagher–Kell (Kestin et al., 1984) and Marshall and Franck (1981) models were used to determine the thermodynamic properties and dissociation constant of H_2O under our experimental conditions, respectively. Thermodynamic data for scandium fluoride solid powder (ScF_3) were taken from Spedding (1974).

The values of $\triangle G_r(T)$ for the reactions:

$$Sc_3^+ + 2F^- = ScF_2^+ \qquad (4)$$

$$Sc_3^+ + 3F^- = ScF_3^o \qquad (5)$$

which were responsible for the formation of ScF_2^+ and ScF_3^o, were calculated using the standard Gibbs free energy for the species Sc_3^+ and F^- reported in Shock (1997) and Shock and Helgeson (1988), respectively. The values of $\triangle G_r(T)$ were then converted to a formation constant (logβ) using the relationship $\triangle Gr(T) = -RT\ln K$. These formation constants are shown in Table 2 together with their uncertainty for them calculated using the OptimA program.

All calculated formation constants were fitted separately for ScF_2^+ and ScF_3^0 to the Ryzhenko-Bryzgalin (MRB) equation of state (Ryzhenko et al., 1985) modified by Borisov and Shvarov (1992). The parameters derived from the MRB model for ScF_2^+ and ScF_3^0 are listed in Table 3 and were used to calculate equilibrium constants (log K) for the scandium fluoride dissolution reactions (Table 4). Uncertainties in the equilibrium constants were obtained by adjusting the measured scandium activity to the same pH(T) and hydrofluoric acid activity of each data point using Reactions (1) and (2) by determining their standard deviation, and propagating this deviation to the equilibrium constant. The best fit points to the experimental data shown in Fig. 3a_1, b_1, c_1, d_1 were calculated on the basis of these equilibrium constants.

4. DISCUSSION

4.1. Comparison to previous studies

The experiments conducted in this study were the first to investigate the speciation of scandium in HF-bearing solutions at elevated temperature. In contrast, there have been five studies of scandium speciation at ambient temperature (Kury et al., 1959; Aziz and Lyle, 1969; Hancock et al., 1980; Yuchi et al., 1987). These studies all reported formation constants for ScF^{2+} and, with the exception of Ivanov-Emin et al. (1976), also reported formation constants for two or more of the species ScF_2^+, ScF_3^0 and ScF_4^- (Table 5). The results of these studies are reviewed in Wood and Samson (2006), who on the basis of a careful evaluation of the data recommended formation constants (log β) for ScF^{2+}, ScF_2^+ and ScF_3^0 (Table 5). As discussed earlier, we only detected ScF_2^+ and ScF_3^0 in our study. Our failure to detect ScF^{2+} may be because the stability of this species decreases with increasing temperature and it was not the dominant species at the conditions of any of our experiments. Similarly, we conclude that the reason that ScF^{4-} was not detected is that the F^- activity was too low to stabilize ScF^{4-}; at the acid conditions of our experiments HF is strongly associated, which suppresses the F- activity even at high total fluorine concentration. Hancock et al (1980) speculated that polynuclear scandium fluorine complexes might form at ambient temperature, showing that their experimental data could be explained satisfactorily by formation of the $Sc_2F_3^{3+}$. At higher temperature, polynuclear species are more labile (less stable), due to the decrease in the dielectric constant of water with increasing temperature and the corresponding large increase in electrostatic repulsion (Seward et al., 2014; Brugger et al., 2014). For this reason, and in the absence of any direct evidence for polynuclear species, we propose that mononuclear species governed the solubility of the scandium in our experiments.

In order to compare the formation constants of ScF_2^+ and ScF_3^0 determined in our study with those from previous studies at ambient temperature, we extrapolated our formation constants to 25ºC using the MRB model (Ryzhenko et al., 1985). The values for the corresponding model parameters are tabulated in Table 3 and the resulting formation constants at 25 ºC reported in Table 5, where they can be compared with those previously reported for ambient temperature. From this table, it is evident that the extrapolated formation constants for both ScF_2^+ and ScF_3^0 are in good agreement with those from the ambient temperature studies, providing confidence that the formation constants determined for higher temperature in this study reliably predict the behavior of scandium in fluoride-bearing hydrothermal fluids at temperatures up to at least 250 °C.

4.2 The relative importance of hydroxide and fluoride complexes

As discussed in the introduction of this paper, Sc^{3+} is a hard acid, which is why it was predicted and shown in this paper to form strong complexes F^-. It should therefore form strong complexes with other hard bases. The only base for which there are thermodynamic data for scandium species, however, is OH^-. Formation constants have been determined experimentally for $Sc(OH)^{2+}$, $Sc(OH)_2^+$, $Sc(OH)_3^0$ and $Sc(OH)_4^-$) at ambient temperature and used by Shock et al. (1997) to predict the thermodynamic properties of these species at elevated temperature and pressure. We have therefore employed these data to assess the relative importance of fluoride and hydroxide complexes in the transport of scandium. For this purpose, we constructed binary diagrams showing the predominance of the different fluoride and hydroxide species discussed above as a function of log aF$^-$ and pH (Fig. 5a - d) at temperature from 100 to 250ºC and 500bar. The diagrams in Figure 5 show that ScF_3^0 has a large field of predominance at acidic to neutral pH that extends to relatively low fluoride activity, albeit much higher HF activity. Immediately below this field, at low pH, the dominant species is ScF_2^+ that has a much smaller predominance field, which increases with increasing temperature and passes at low fluoride activity into the predominance field of the simple ion or, at higher pH, those of the scandium hydroxide species. Scandium hydroxide species increase in importance with increasing pH, reflecting the increase in the OH^- activity, with species having higher ligand number predominating at higher pH.

4.3 Application to natural systems

Two of the more common processes by which hydrothermal ore deposits are interpreted to form are mixing of the ore fluid (commonly acidic) with a second fluid and interaction of the ore fluid with its host rock. In order to assess the efficacy of these processes in concentrating scandium, we used our data to model two scenarios. In the first scenario, one liter of an acidic (pH ~2.1) fluid containing 500 ppm HF, 1.5m NaCl, and 0.01m HCl, that was scandium saturated (~140 ppm) with respect to Sc_2O_3 solid, was mixed iteratively with 1 ml aliquots of a brine containing 0.75 m NaCl and 1m $CaCl_2$ at 250ºC and 500bar (Fig. 6a). The starting concentration of HF in the first solution corresponds to that measured in fluid inclusions in the Capitan Pluton (Banks et al., 1994), which contains significant REE mineralization, the concentration of 1.5m NaCl reflects the salinity of many ore fluids, and the concentration of 0.01m HCl was adopted to buffer the pH to a value of X. Although the second fluid is slightly more saline, the main difference is that it contains appreciable $CaCl_2$, a salt commonly present in hydrothermal fluids. This was to induce deposition of fluorite, a mineral that is found in many REE deposits, including those of scandium. In the second scenario, 1 liter of an acidic fluid identical to that used in the first model was reacted iteratively with aliquots of rock containing 5 mg of fluorapatite (Fig. 6b). As in the first scenario, the temperature was 250 ºC and the pressure was 500 bar. The ore mineral was pretulite, one of a very small number of scandium minerals for which the thermodynamic properties are known. Thermodynamic data for Sc_2O_3 solid and pretulite were taken from Pankratz (1982), and Gavrichev (2010), respectively and those for fluorapatite and fluorite were taken from Robie and Hemingway, (1995), whereas thermodynamic data for the other aqueous species not considered in this study were obtained from Shock et al., (1997) and Sverjensky et al. (1997).

The results of two models clearly demonstrate the conditions under which scandium deposition is favored. In the fluid mixing model, small amounts of Sc_2O_3 precipitate soon after mixing begins, whereas fluorite precipitation only begins after mixing of the ore fluid with 830 milliters of the second brine. Increases in pH are relatively minor and concentrations of ScF_3^0 and ScF_2^+ decrease slowly with progressive mixing. However, the sum of concentration of ScF_3^0 and ScF_2^+, the dominant scandium species in solution, remains significant and greater that the amount of the precipitated Sc_2O_3(solid), which reaches a maximum of 9.15×10^{-4} moles after reaction with 1000 milliliters of brine, corresponding to deposition of less than half of the scandium initially in solution. Thus, we suggest that fluorine could not play a key role in transport scandium in acid fluoride bearing hydrothermal system, and that the removal of fluorine via precipitation of fluorite could not act as a means of depositing scandium. By contrast, reaction of the acidic fluid with apatite leads to deposition of appreciable quantities of pretulite immediately. As a result, the concentrations of the scandium species in solution decrease by more than four orders of magnitude after interacting with just 550mg of apatite, whereas the amount of precipitated pretulite is greater than 3×10^{-3} moles. As the case in the first model, the fluorite postdates scandium mineral deposition.

5. CONCLUSIONS

The experimental data obtained in this study show that significant concentrations of scandium can be dissolved in acidic fluoride-bearing aqueous fluids as ScF_2^+ at low fluoride concentration and ScF_3^0 species at higher fluoride concentration at temperatures up to 250ºC. Scandium-fluoride complexes predominate over scandium-hydroxide complexes and Sc^{3+} at a fluoride activity of greater than $\sim10^{-6}$ at temperature from 100 to 150ºC and $\sim10^{-7}$ at temperature from 200 to 250ºC in acidic hydrothermal fluids. Simple models of scandium transport and deposition based on the species ScF_2^+ and ScF_3^0 formation constants confirmed in our study show that although fluid-mixing may lead to the deposition of scandium minerals, interaction of the ore-fluid with a rock containing a depositional ligand like phosphate may be a more efficient scandium concentrating process.

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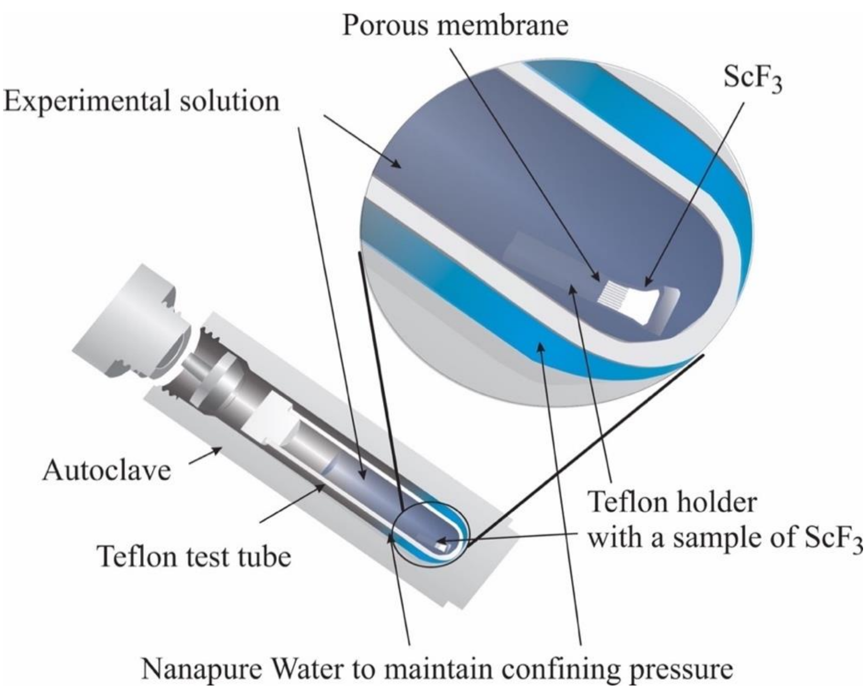


Figure 1. A sketch of the experimental set-up.

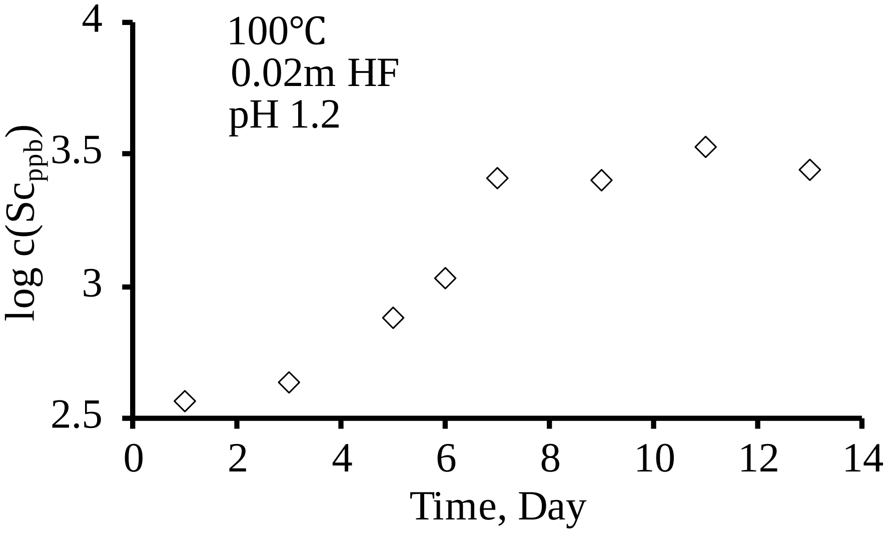


Figure 2. Results from a series of experiments illustrationg the solubility of ScF$_3$(solid) as a function of time in an aqueous solution at 100 ^{o}C containing 0.02m HF. The data suggest that a steady state (dashed line) was attained after 7 days at 100^{o}C.

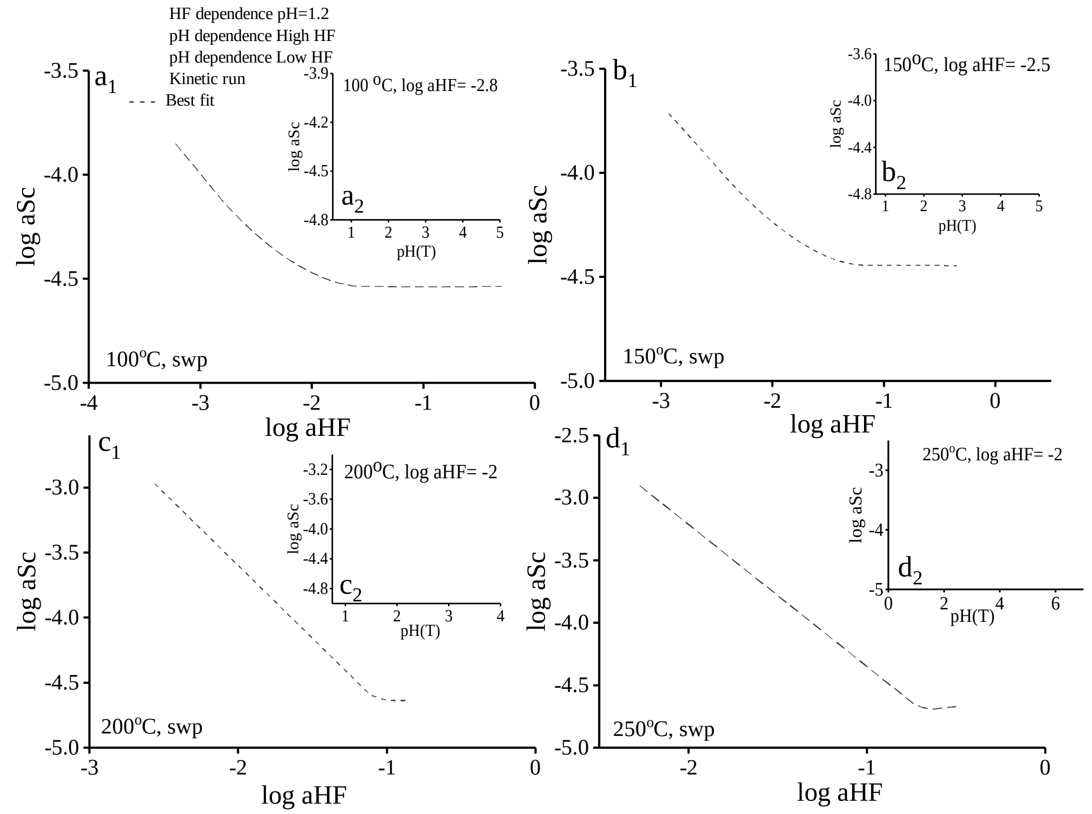


Figure 3. The logarithm of Sc activity as a function of the activity of HF at (a_1) 100, (b_1) 150, (c_1) 250, and (d^1) 250°C.

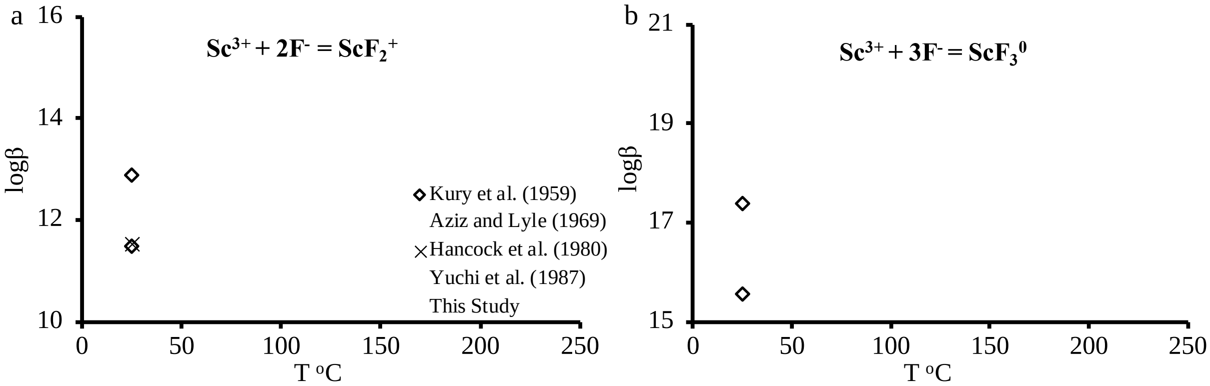


Fig. 4. Logarithms of formation constants from this study for (a) ScF_2^+ and (b) ScF_3^0 as a function of temperature and extrapolated to 25°C using the BRM model. Also shown for comparison are the corresponding formation constants at 25°C reported by other studies.

Wang, J., Williams-Jones, A., Timofeev, A., Liu, J., and Yuan, S., 2022, An experimental investigation of the solubility and speciation of scandium in fluoride-bearing aqueous liquids at temperatures up to 250° C: Geochimica et Cosmochimica Acta, v. 330, p. 67-79.

Fig

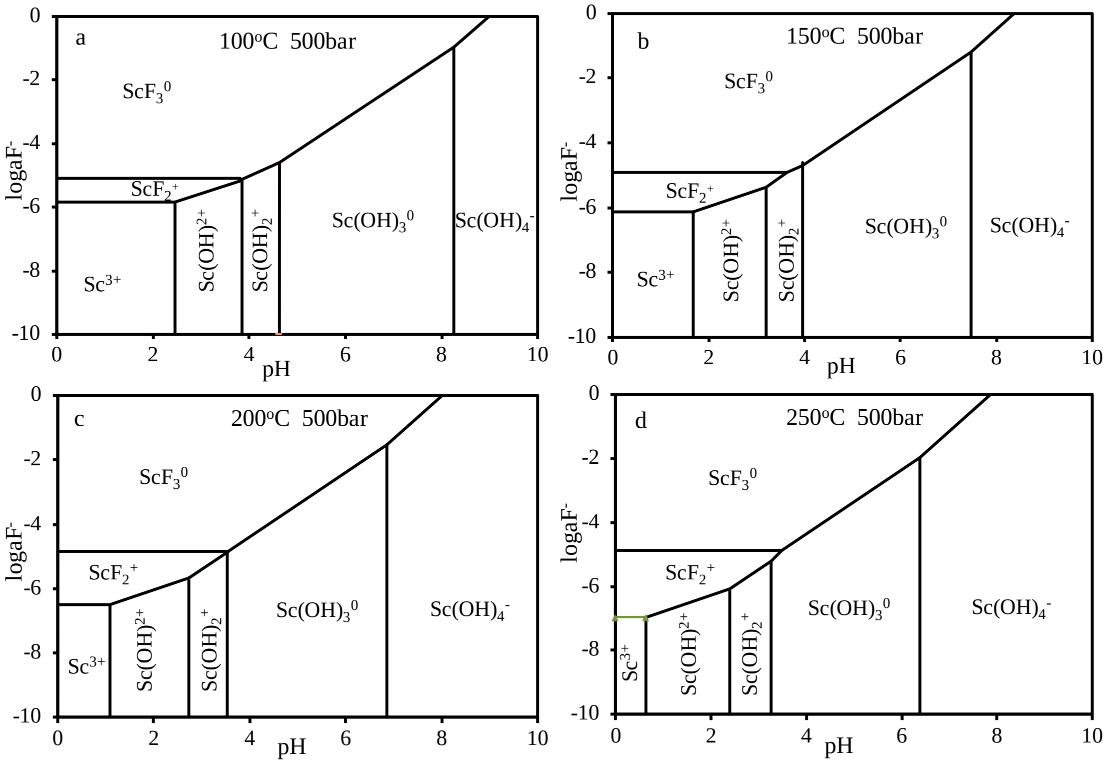


Figure 5. A Log aF^- versus pH diagram showing the fields of predominance of scandium fluoride and hydroxide complexes (a) at 100°C and 500bar, (b) at 150°C and 500bar, (c) at 200°C and 500bar, (d) and at 250°C and 500bar.

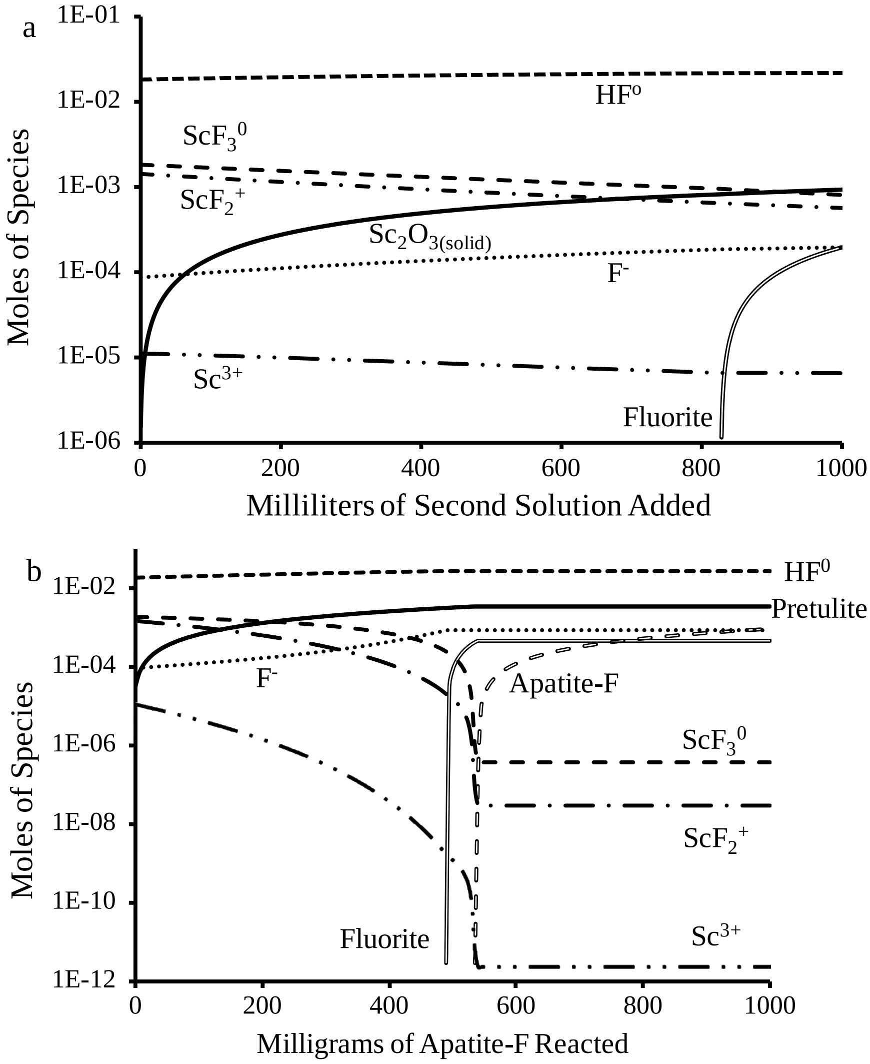
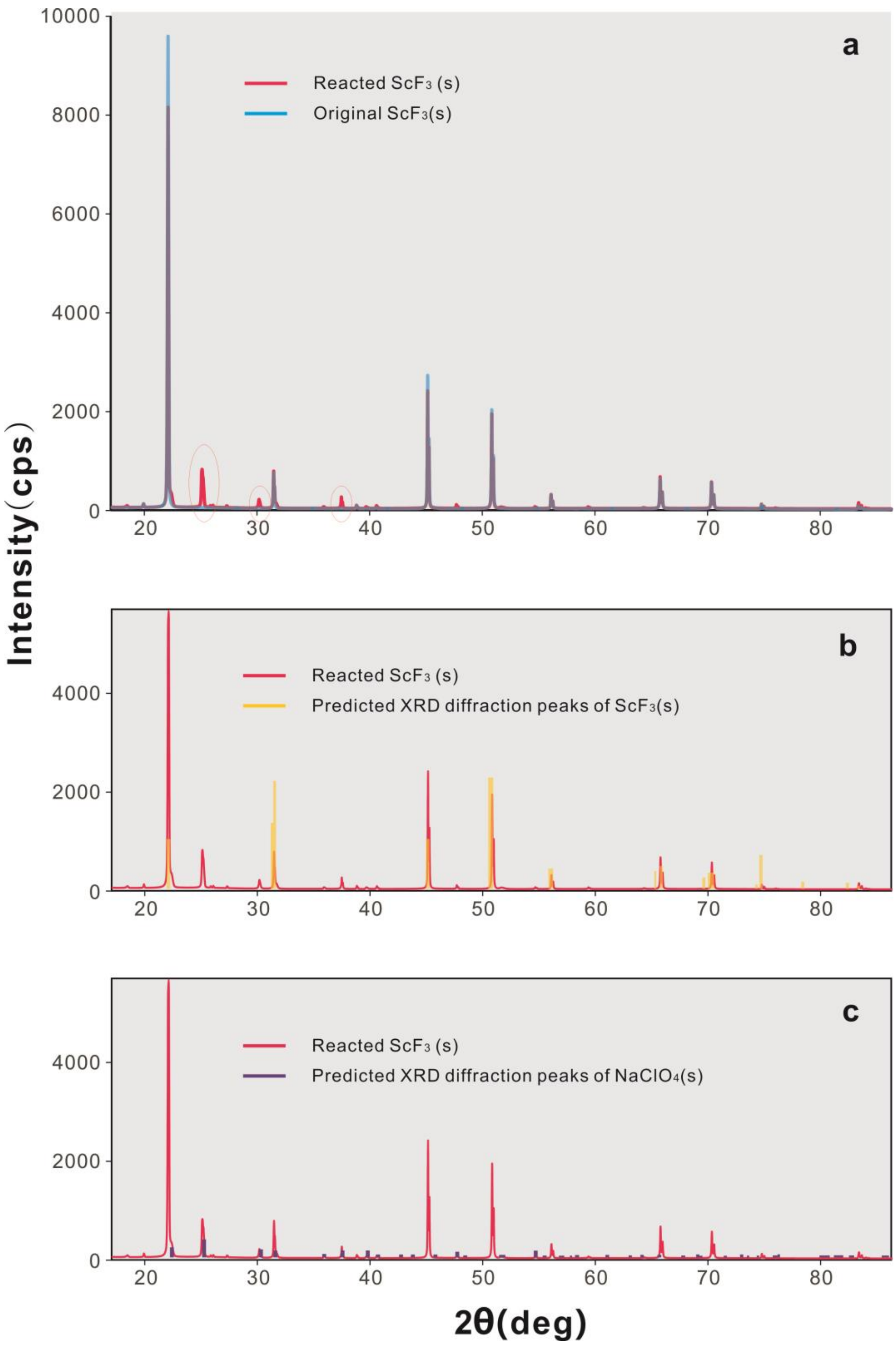


Figure 6. Cumulative concentrations of aqueous species and solids precipitated at 250 °C and 500 bar from a fluid containing 500ppm HF, 1.5m NaCl, and 0.01m HCl and saturated with respect to scandium (a) during progressive mixing with a brine containing 0.75m NaCl, and 1m $CaCl_2$, (b) and during progressive interaction with fluorapatite.

Wang, J., Williams-Jones, A., Timofeev, A., Liu, J., and Yuan, S., 2022, An experimental investigation of the solubility and speciation of scandium in fluoride-bearing aqueous liquids at temperatures up to 250° C: Geochimica et Cosmochimica Acta, v. 330, p. 67-79.



Supplementary Fig. 1. X-ray diffractograms of the ScF$_3$(s) reactant following completion of an experiment.

Wang, J., Williams-Jones, A., Timofeev, A., Liu, J., and Yuan, S., 2022, An experimental investigation of the solubility and speciation of scandium in fluoride-bearing aqueous liquids at temperatures up to 250° C: Geochimica et Cosmochimica Acta, v. 330, p. 67-79.

Table 1
Composition of the experimental solutions after equilibration with $ScF_{3(s)}$ at the pressure of saturated water vapor.

T (ºC)	Total F (mmol/kg)	Sc, 10^{-6}	pH (T)	$NaClO_4$ (mmol/kg)
100	18.04	0.80	1.23	20.26
100	18.86	1.20	1.24	20.26
100	18.51	0.97	1.25	20.26
100	9.53	1.10	1.24	0.00
100	1.14	5.77	1.19	0.00
100	19.47	1.11	1.25	20.28
100	4.68	2.00	1.27	0.00
100	1.87	2.60	1.28	0.00
100	0.53	10.10	1.28	0.00
100	0.70	8.05	1.28	0.00
100	5.96	1.77	1.29	0.00
100	0.89	6.65	1.26	0.00
100	86.12	0.90	1.25	100.28
100	431.78	1.38	1.32	502.72
100	82.54	0.95	1.30	103.17
100	17.96	0.71	1.28	20.26
100	9.00	0.74	1.28	0.00
100	379.57	1.61	0.66	502.72
100	69.27	1.50	2.35	103.17
100	22.97	1.32	1.41	23.00
100	11.31	1.40	1.70	0.00
100	7.03	1.93	2.27	0.00
100	2.96	1.23	2.56	0.00
100	2.90	1.15	3.23	4.13
100	12.91	5.35	4.70	4.07
100	2.97	1.00	4.42	3.93
100	112.09	1.19	1.41	104.79
100	104.50	1.12	1.64	109.61
100	100.28	1.36	2.47	105.38
100	99.45	1.22	3.15	100.16
100	94.65	1.50	3.54	108.12
100	86.12	0.90	1.25	100.28
150	17.71	3.74	1.24	20.07
150	18.91	3.01	1.24	20.07
150	17.62	3.71	1.26	20.07
150	17.93	3.97	1.25	20.07
150	89.47	1.30	1.23	100.28
150	52.03	1.35	1.22	50.39
150	18.58	2.09	1.24	20.07
150	9.61	3.92	1.25	0.00

150	17.71	1.48	1.25	20.07
150	18.91	1.60	1.34	20.07
150	17.70	1.58	1.29	20.07
150	17.93	3.03	1.30	20.07
150	17.81	4.44	1.28	20.07
150	17.81	7.39	1.28	20.07
150	645.13	1.50	1.35	1001.80
150	80.78	1.04	1.31	103.17
150	44.90	2.29	1.29	50.58
150	44.45	1.59	1.29	50.58
150	1.13	12.76	1.29	0.00
150	0.93	11.48	1.29	0.00
150	630.76	1.75	1.34	1001.80
150	75.29	1.48	1.26	103.17
150	29.60	3.14	1.45	30.01
150	3.32	4.05	1.58	0.00
150	3.10	1.54	2.07	0.00
150	3.08	0.99	2.57	0.00
150	2.97	1.09	4.36	4.07
150	2.98	1.16	4.89	3.93
150	3.22	7.16	1.24	0.00
150	2.37	8.90	1.24	0.00
150	1.79	9.88	1.23	0.00
150	125.81	1.35	1.44	104.79
150	108.01	1.75	1.81	109.61
150	101.53	1.68	2.94	105.38
150	104.91	1.32	3.16	100.16
150	96.62	1.48	3.99	108.12
200	100.78	1.27	1.28	103.17
200	50.43	2.69	1.24	50.58
200	20.27	6.89	1.24	20.26
200	10.58	10.26	1.26	0.00
200	6.07	28.55	1.27	0.00
200	3.33	34.02	1.27	0.00
200	2.68	43.21	1.27	0.00
200	44.99	4.12	1.21	205.30
200	143.26	1.00	1.02	502.72
200	121.92	1.10	1.09	501.15
200	183.14	0.97	3.67	206.50
200	170.90	1.03	3.59	206.50
200	112.33	1.46	1.38	104.79
200	98.99	1.12	4.13	100.16
200	9.41	6.69	1.26	0.00
200	24.17	4.11	1.62	25.05
200	4.38	2.94	1.77	4.13
200	69.69	2.51	3.89	109.61

200	15.77	5.29	3.12	20.03
250	297.22	1.81	1.36	501.15
250	58.62	4.94	1.21	50.58
250	23.73	11.25	1.25	20.26
250	22.11	35.39	1.25	20.35
250	9.91	40.62	1.26	0.00
250	6.84	44.11	1.25	0.00
250	5.38	61.89	1.24	0.00
250	95.35	4.86	1.28	103.17
250	98.57	5.10	1.26	103.17
250	8.11	33.27	1.77	0.00
250	284.61	0.88	1.62	502.72
250	348.60	0.67	3.59	504.28
250	358.67	0.53	3.85	504.28
250	190.75	0.73	4.06	206.50
250	179.45	1.10	4.03	206.50
250	106.10	8.89	1.28	104.79
250	101.44	3.85	1.50	109.61
250	32.75	14.05	1.22	33.17
250	7.75	26.06	1.46	0.00
250	15.48	2.58	3.07	0.00
250	33.42	22.91	6.48	34.02
250	13.17	5.84	5.15	4.13
250	7.41	4.01	5.32	4.07

Table 2

Formation constants (logβ) for the scandium species in this study at temperature from 100 to 250°C.

T (°C)	100		150		200		250	
$Sc_3^+ + 2F^- = ScF_2^+$	12.10	±0.01	12.73	±0.01	13.60	±0.02	14.77	±0.01
$Sc_3^+ + 3F^- = ScF_3^0$	17.28	±0.04	17.76	±0.08	18.58	±0.03	19.82	±0.01

Table 3

Bryzgalin-Ryzhenko parameters derived for scandium species based on the formation constants determined in this study.

	pK(298)	A(zz/a)	B(zz/a)
ScF_2^+	11.739	2.538	0.00
ScF_3^0	17.480	3.098	0.00

Table 4

Equilibrium constants (logk) and their associated uncertainty for the ScF_3 dissolution reactions, (1) and (2).

T (°C)	100		150		200		250	
$ScF_3(s) + H^+ = ScF_2^+ + HF$	-5.88	±0.14	-5.25	±0.14	-4.64	±0.18	-4.02	±0.2
$ScF_3(s) = ScF_3^0$	-4.55	±0.24	-4.56	±0.12	-4.51	±0.15	-4.40	±0.28

Table 5

Summary of formation constants from the literature for fluoride complexes of Sc^{3+}.

Medium	T (°C)	logβ				
		ScF^{2+}	**ScF_2^+**	**ScF_3^0**	**ScF_4^-**	**Source**
0.5 M $NaClO_4$	25	6.19	11.47	15.55	18.4	Kury et al. (1959)
0	25	7.08	12.89	17.37	20.22	Kury et al. (1959)
0.5 M $NaClO_4$	25	6.17	11.44	15.46	18.49	Aziz and Lyle (1969)
0.01-0.1 M $ScCl_3$	25	6.28	-	-	-	Ivanov Et al. (1976)
0.5 M $NaClO_4$	25	6.18	11.52	15.8	-	Hancock et al. (1980)
0.1 M KNO_3	25	6.22	11.52	15.47	-	Yuchi et al. (1987)
0.1-0.5 ClO_4^-	**25**		**11.105**	**17.150**		**This Study**