**Experimental Determination of Contaminant Metal Mobility as a Function of
Temperature, Time and Solution Chemistry**

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INTRODUCTION

Strontium is significantly more mobile than other hazardous radioactive metals. Its partitioning between aqueous and solid phases is controlled by reactions that occur at the interface between natural waters and minerals. At a groundwater site in Hanford (200-BP-5), the aerial extent of the ^{90}Sr plume is 100 times larger than the aerial extent of the ^{137}Cs and the ^{239}Pu plumes. Similarly, contaminated, perched watertables at INEL have much higher aqueous concentrations of ^{90}Sr than ^{137}Cs , presumably because Cs is preferentially sorbed to solids (Duncan 1995). Under high physical flow conditions, such as those in the highly fractured rock at Hanford and INEL, ^{90}Sr present in plumes may spread off-site and cause contamination of aquifers or other water sources. Geochemical factors that may contribute to the overall mobility of Sr in natural waters are the solubilities of phases such as strontianite (SrCO_3) and formation of strong complexes with sulfate and nitrate.

Although ^{90}Sr is mobilized in natural waters in these examples, significant concentrations may also be present in solid phases. Sorption experiments using a wide variety of substrates at room temperature have shown that Sr is removed from solution under certain conditions (Malati 1966; Schindler and Gamsjager 1969; Tadros and Lyklema 1969; Fordham 1973; Huang and Stumm 1973; Kinniburgh et al. 1975; Fuerstenau et al. 1981; Yanagi et al. 1989; Park et al. 1992; Liang et al. 1993; Adeleye et al. 1994; Axe and

Anderson 1995; Gorturk et al. 1995). Additionally, strontianite (SrCO_3) may precipitate at low Sr concentrations in the pH range of waters in contact with basaltic rocks, which varies between pH 8 and 10. Waters contain variable amounts of carbonate owing to atmospheric interactions; the partial pressure of CO_2 is about $10^{-3.5}$ atm in air and commonly as high as $10^{-2.5}$ atm in soils.

The objective of this work is to determine the fundamental data needed to predict the behavior of strontium at temperature and time scales appropriate to thermal remediation. Our approach combines macroscopic sorption/precipitation and desorption/dissolution kinetic experiments, which track changes in solution composition, with direct molecular characterization of strontium in the solid phase using X-ray absorption spectroscopy. These experiments will be used to identify mechanistic geochemical reactions and their thermochemical properties that will be incorporated into geochemical computer codes. This report consists of two sections: **1.** A description of the preliminary results of strontium sorption to kaolinite and goethite from pH 4 to 10 at 25, 50, and 80 °C and atmospheric $\text{CO}_2(\text{g})$; and **2.** A review of the available thermodynamic data in the Fe-Sr-Na- NO_3 - CO_2 - H_2O system.

STRONTIUM SORPTION TO GOETHITE AND KAOLINITE

AT 25, 50, AND 80°C.

Experimental Methods

Synthetic goethite (Schwertmann and Cornell 1991) and a natural kaolinite were the mineral phases studied in these static batch sorption experiments. The goethite was prepared by mixing 100 ml of 1N $\text{Fe}(\text{NO}_3)_3$ with 180 ml of 5 N KOH with vigorous stirring in a 2L polypropylene bottle. Formation of brown-red ferrihydrite was immediate. The ferrihydrite suspension was then diluted to 2L with distilled and deionized water and then placed into a 70°C oven for 60 hours. Formation of the goethite was evident by the transformation of the brown-red solid to a mustard colored solid. The goethite was then separated from the supernatant and washed with water until the a turbid goethite suspension formed, which was then centrifuged at 2000 rpm for 20 minutes. The goethite was then dried in an oven at 40°C. Finally, the purity and crystallinity of the synthetic goethite was verified by X-ray diffraction.

The kaolinite used for these studies was procured from the University of Missouri-Columbia, Source Clay Minerals Repository. It is a “well crystallized” Kaolin (KGa-lb) from Washington County, Georgia, USA. The purity and crystallinity of the mineral was verified by X-ray diffraction and used without further purification in the sorption experiments.

Suspensions with a mass-to-volume ratio of 10 g/L were reacted for 2 days at 25, 50 and 80°C. The solutions were 0.10 N NaNO₃ with initial Sr concentrations ranging from 10⁻⁷ to 10⁻⁴ M and pH varying between 4 and 10. Initial Sr concentrations ranged from undersaturated to supersaturated with respect to strontianite, SrCO₃(s) (Fig. 1). Experimental samples were prepared by weighing 0.25 ± 0.01 g of the solid into each 50 ml poly-carbonate tube with a sealing o-ring cap and then adding 25 ml of 0.10 N NaNO₃. The solutions were then spiked a Sr atomic absorption standard (J.T. Baker, 99.99+%, 1000 ppm) to yield the desired initial concentration. The solutions were then allowed to react in a constant temperature water bath, after which each solution was adjusted to the desired pH using NaOH and HNO₃. During pH adjustments and measurements experimental temperatures were maintained. Once the solutions were adjusted to their desired pH, they were sealed, shaken vigorously by-hand, and then reacted for 2 days in a constant temperature orbital shaker water bath (200 rpm). Following reaction, the final pH of each solution was measured and a 2.5 ml assay was taken from each solution. The assays were then filtered through 4.1 nm pore size centrifugal filters to remove all suspended material. The filtrates were then analyzed for Al, Fe, Si and Sr concentrations with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The analytical detection limits of Al, Fe, Si and Sr are 0.02, 0.01, 0.02, and 0.001 ppm respectively. Concentration ten times the analytical detection limits were reproducible to less than 2%.

Sr K-edge X-Ray Absorption Spectroscopy (XAS) spectra were collected

for two Sr-adsorbed two samples of goethite and and one sample of kaolinite in May 1997. 32 and 36 scans were run on the goethite samples and 16 scans on the kaolinite. The data were averaged, filtered and fitted in k-space.

Results

Figures 2-7 show the results of Sr sorption to goethite and kaolinite at atmospheric $p\text{CO}_2(\text{g})$ as a function of pH and temperature. In the presence of goethite, significant strontium-uptake occurs at 25, 50, and 80°C from solutions containing $\text{pH} > 8$ and $[\text{Sr}]_i = 10^{-7}$ to 10^{-4} M (Fig. 2 and 3). The absolute strontium-uptake increases with increasing $[\text{Sr}]_i$ at constant temperature and at $\text{pH} > 8$. There is a slight increase in strontium-uptake with increasing temperature for experiments with $[\text{Sr}]_i = 10^{-6}$, 10^{-5} , and 10^{-4} M. At $[\text{Sr}]_i = 10^{-7}$ M, any temperature dependence of strontium-uptake is masked by analytical uncertainty. The final dissolved strontium concentrations approach or exceed strontianite saturation at $\text{pH} > 7$ (Fig. 4). With the exception of pH 4 experiments, dissolved iron concentrations are less than the analytical detection limit.

Similar to goethite, significant strontium-uptake occurs at 25, 50, and 80°C from solutions containing $\text{pH} > 8$ and $[\text{Sr}]_i = 10^{-6}$ to 10^{-7} M (Fig. 5 and 6). Minimal strontium is removed from solutions containing $[\text{Sr}]_i = 10^{-7}$ from pH 4 to 10. The absolute strontium-uptake increases with increasing $[\text{Sr}]_i$ at constant temperature and at $\text{pH} > 8$. In contrast to strontium-uptake on goethite, strontium-uptake on kaolinite has a complex dependence on

temperature. At $[\text{Sr}]_i$ of 10^{-4}M , there is no temperature dependence for strontium-uptake. However at $[\text{Sr}]_i = 10^{-7}$ to 10^{-5}M , strontium-uptake is higher at 50°C than at 25 and 80°C . Figure 7 shows the relative saturation of the aqueous solutions with respect to strontianite, kaolinite, gibbsite, and quartz from pH 4 to 10 and 25 , 50 and 80°C . After two days of reaction, final solutions approach or exceed strontianite saturation at $\text{pH} > 7$, are saturated with respect to gibbsite, but are undersaturated with respect kaolinite and quartz.

The preliminary x-ray absorption spectroscopy results show first shell of about 8-9 oxygen atoms at about $2.6\text{\AA}$ around the central Sr atom. We were unable to obtain useful information beyond the first shell, due to low signal/noise ratio. Future samples will need greater surface loading and will need to be run for longer scan times to acquire second shell information. Part of the problem in obtaining structural information for Sr beyond the first shell by XAS is the possibility that Sr^{2+} remains relatively hydrated when it adsorbs. If this is the case, it would be useful to apply other, complementary spectroscopic tools such as Infra-Red (IR), Raman and Nuclear Magnetic Resonance(NMR), to the problem of determining the nature and structure of the Sr - surface species.

We have already begun to investigate these other possibilities. We have also obtained some preliminary NMR spectra for kaolinite, using ^{27}Al and ^{29}Si . The early results indicate that ^{29}Si NMR might be a promising tool for kaolinite and montmorillonite. Goethite cannot be run as

Fe³⁺ is paramagnetic. The ²⁷Al NMR spectra showed a homogeneous octahedral environment for both the “clean” kaolinite and the Sr - sorbed kaolinite. The ²⁹Si NMR, however, appears to be promising, showing the possible formation of an amorphous silicate layer at the surface of the Sr - sorbed kaolinite, which is absent in the case of the “clean” kaolinite.

If indeed, Sr remains relatively hydrated. at the surface, then IR vibrational frequencies should be observed at about 3597-3496 cm⁻¹, where the -OH stretching frequency for Sr(OH)₂ is located. Unfortunately, this is also the frequency range where bulk water has a broad -OH stretching peak, and can mask the Sr-OH peak. We are currently in the process of developing an experimental protocol for eliminating the problem with the bulk H₂O peak.

Discussion

Strontium uptake on goethite and kaolinite at pH > 8 maybe due to the formation of strontium surface complexes at metal-oxygen and/or metal-carbonate sites. In the absence of strontium and carbonate, goethite's zero point of charge (zpc) occurs at pH_{zpc} = 9.0 (Zeltner and Anderson 1988). In the presence of atmospheric CO₂(g), the goethite pH_{zpc} shifts to lower pH due to the formation of carbonate-surface species (van Geen et al. 1994). Surface complexation reactions important for strontium sorption may include the deprotonation of the neutral iron site:

sorption of carbonate at the neutral iron site:

and the sorption of strontium to these sites:

Strontium sorption on kaolinite is more complex than goethite. In the absence of strontium, reported values for kaolinite's zero point of charge range from pH_{zpc} 3.3 to 5.0 (Schroth and Sposito 1997). Kaolinite's low pH_{zpc} is attributed to permanent structural charge from isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral layer. Strontium's interaction at the surface appears to be site specific, because significant uptake does not from pH 4 to 7. Strontium-uptake at pH > 8 maybe due to its specific sorption at specific $>\text{AlO}^-$ and $>\text{SiO}^-$ sites at the kaolinite surface. The surface reactivity of aluminum- and silica-oxide yield negatively charged sites at pH > 9.1 (Huang and Stumm 1973) and pH > 7.0 (Schindler and Gamsjager 1972), respectively. It is also likely that carbonate sorbs to kaolinite surface sites and enhances strontium-uptake. Surface complexation reactions important for strontium sorption may include the deprotonation of the neutral aluminum and silica sites:

sorption of carbonate at the neutral aluminum and silica sites:

and the sorption of strontium to these sites:

The stoichiometry of kaolinite surface sites as a function of pH and $\text{pCO}_2(\text{g})$ is not known. The sites proposed above simply represent a correlation of strontium-uptake from our experiments and protonation-deprotonation of kaolinite and its constituent oxide components. Direct spectroscopic data is needed to identify the atomic structure of the surface complexes.

Another possible mechanism controlling the uptake of strontium in our experiments is the precipitation of strontianite. In our goethite and kaolinite experiments, strontium-uptake begins in solutions undersaturated with respect to strontianite and increases in more supersaturated solutions. We know that strontium-uptake is enhanced by kaolinite and goethite, because strontium is not removed from solution over the same experimental run conditions in the absence of solid phases. It is possible that ternary strontium-carbonate complexes form at the kaolinite and goethite surfaces, and that they provide the needed “seed carbonate” to precipitate strontianite. This idea builds for direct observation of multinuclear-cobalt-surface

complexes on kaolinite (O'Day et al. 1994) and the formation of a mixed nickel-aluminum hydroxide during pyrophyllite dissolution and nickel-uptake (Scheidegger et al. 1996). We expect strontium-uptake to involve the formation of multinuclear- strontium-carbonate complexes because strontianite is much less soluble than $\text{Sr}(\text{OH})_2(\text{s})$. Direct spectroscopic analysis of the reaction products will be able to distinguish between strontium-carbonate and mixed strontium-aluminum hydroxide.

The observed increase of strontium-uptake with increasing initial strontium concentration in the solution at constant temperature reflects lack of equilibrium and possibly the dependence of the strontium-uptake rate on the net Gibbs free energy of reaction, ΔG_r :

$$\text{Rate}_{\text{Sr-uptake}} = -d[\text{Sr}]/dt = -k_{\text{Sr-uptake}} * [1 - \exp(\Delta G_r/RT)]^m \quad 13.$$

where $k_{\text{Sr-uptake}}$, n and m are empirical constants. In the batch experiments, the saturation index is not held constant. Therefore the rate of strontium-uptake decreases as strontium is removed from the solution. Calcite (CaCO_3) precipitation and dissolution rates are classic examples of reaction rates that are driven by deviation from equilibrium (Morse 1983; Inskeep and Bloom 1985).

The temperature dependence of strontianite solubility increases by about 0.2 orders of magnitude from 25 to 80°C. Therefore it is not surprising that we do not see a marked change in strontium-uptake to goethite at 25, 50 and 80°C and kaolinite at 25 and 80°C. Additional experiments are needed to verify the slight increase in strontium-uptake in the presence of goethite with

increasing temperature and the significant increase in strontium-uptake in the presence of kaolinite at 50 °C.

REVIEW OF THERMODYNAMIC AND SORPTION DATA FOR THE FE-SR- NA-NO₃CO₂-H₂O SYSTEM

The chemical system of interest is Fe-Sr-Na-NO₃-CO₂-H₂O because our initial experiments will involve Sr sorption onto goethite (α-FeOOH) in the presence of CO₂ with the ionic strength buffered by NaNO₃. Oxidizing conditions will be maintained through continuous contact with the atmosphere and the lack of a reducing agent in the system. The experimental matrix will, in part, be set up according to scoping calculations made using preliminary thermodynamic and surface complexation data for this system. We have therefore reviewed some of the available data and begun to compile data bases for our use. Our preliminary data bases will allow us to plan our initial experiments, and to identify additional data needs. As our experimental program progresses, we will modify the data bases with our acquired data and revised models.

For our initial data base, we chose version data0.com.V8.R6 of the GEMBOCHS data base (Johnson and Lundeen, 1997) and the surface complexation data base associated with the The Geochemist's Workbench applications package (Bethke, 1996). The GEMBOCHS data base is maintained to support the EQ3/6 geochemical modeling code package (Wolery, 1992;

Wolery and Daveler, 1992). Data base data0.com.V8.R6 was specially formatted to work with The Geochemist's Workbench applications, and was altered to include the mineral and aqueous complex data discussed herein. The surface complexation data, altered from the original data base supplied with The Geochemist's Workbench applications package, is being stored as a separate data base.

Thermodynamic data for aqueous and solid reactions, excluding surface complexation reactions, for the subsystems $\text{Sr-CO}_2\text{-H}_2\text{O}$, $\text{Fe-CO}_2\text{-H}_2\text{O}$, $\text{Sr-NO}_3\text{-H}_2\text{O}$, $\text{Fe-NO}_3\text{-H}_2\text{O}$ are discussed below. Surface complexation data for Sr, CO_3 , Na, and NO_3 are then reviewed.

$\text{Sr-H}_2\text{O-CO}_2$

Thermodynamic data for the solids Sr, SrO and Sr(OH)_2 were taken directly from data0.com.V8.R6, and are listed in Appendix A. Owing to the extremely high solubilities of these solids, and the pH and Sr concentrations that we will use in our experiments, we do not anticipate the precipitation of any of these phases.

Data for the $\text{Sr-H}_2\text{O-CO}_2$ chemical subsystem were taken mainly from Busenberg, Plummer and Parker (1984). They published log K values at 25°C for the reactions shown in Table 1. Log K at elevated temperatures were expressed in the form of a polynomial in temperature. Log K at 60 and 100°C were calculated using these polynomials and entered directly into the data base.

Table 1. Thermodynamic data for Sr aqueous species and strontianite from Busenberg, Plummer and Parker (1984).

Reaction	log K (Busenberg et al., 1984)*		
	25°C	60°C	100°C
$\text{SrCO}_3^\circ + \text{H}^+ = \text{Sr}^{2+} + \text{HCO}_3^-$	7.5237	6.8764	6.3166
$\text{SrHCO}_3^+ = \text{Sr}^{2+} + \text{HCO}_3^-$	-1.1846	-1.7049	-2.2996
$\text{SrOH}^+ + \text{H}^+ = \text{Sr}^{2+} + \text{H}_2\text{O}$	13.1751	13.1708	13.1669
$\text{SrCO}_3(\text{stront.}) + \text{H}^+ = \text{Sr}^{2+} + \text{HCO}_3^-$	1.0583	0.6831	0.1792

* reactions re-written in terms of basis species HCO_3^- when necessary, using association constants for reaction $\text{CO}_3^{2-} + \text{H}^+ = \text{HCO}_3^-$ from data0.com.V8.R6. Data for SrOH^+ obtained as described in text. Stront. = strontianite.

Busenberg, Plummer and Parker (1984) obtained stability data for SrHCO_3^+ and SrCO_3° as a function of temperature using potentiometric methods. The log K's for SrCO_3° agree extremely well with log K values in the data0.com.V8.R6 data base which are referenced to Sverjensky et al. (1994). This paper, however, has never been published, and only a table of data was available without reference to the source of the data. The correspondence of values suggests that the source of the data is Busenberg, Plummer and Parker (1984).

Busenberg, Plummer and Parker's (1984) thermodynamic data for Sr^{2+} matches closely that in the data0.com.V8.R6 data base. The Sr^{2+} data in the current data base was therefore retained (Appendix A). They also measured strontianite solubility as a function of temperature. Their measured free energy of formation for strontianite is about 8 kJ/mol less stable than values in SUPCRT92¹ referenced to earlier work, although the difference amounts to only a 0.6% difference in the mineral's free energy. Plummer and Busenberg's values were selected, as shown in Table 1.

The 25°C association constant for SrOH^+ in data0.com.V8.R6 (written in terms of the OH^- ion) equals 0.71; the source of the data is Baes and Mesmer (1976). In comparison, Busenberg, Plummer and Parker (1984) selected a constant at 25°C of 0.82 from Sillen and Martell (1964). This log K, combined with ΔH°_f at 298.15 K (4.81 kJ/mol) from the same reference, was used by Busenberg et al. in the van't Hoff equation to estimate the temperature dependence of the equilibrium constant. The difference in the 25°C equilibrium constants is rather small, and probably within error limits. Owing to the advantage of knowing the temperature dependence of K, the data0.com value was replaced with the Sillen and Martell 25°C value and the van't Hoff relation was used to generate log K values at 25, 60 and 100°C. Values of a (the ion size parameter in the Debye-Hückel activity coefficient equation) for SrOH^+ , SrHCO_3^+ and SrCO_3° were selected by analogy to similar

¹SUPCRT92 is the fundamental data base for minerals, gases and ions on which the data0.com

species in the data0.com.V8.R6 data base; they do not equal those values used by Busenberg, Plummer and Parker. In data0.com, the value of Δ is chosen according to the valence of the aqueous species. However, the inaccuracies incurred in adhering to the data0.com formula will probably be small, and comparative consistency with the remainder of the data set is maintained.

Fe-H₂O-CO₂

Standard molal thermodynamic properties of **Fe³⁺** were taken from Helgeson (1985). Shock and Helgeson (1988) determined the equation of state parameters necessary to predict the properties of **Fe³⁺** at elevated temperature, Data at 25°C for Fe hydroxide aqueous species **Fe(OH)₄⁻**, **Fe(OH)₃⁰**, **Fe(OH)₂⁺** and **FeOH²⁺** are from Baes and Mesmer (1976). These data are taken directly from the data0.com.V8.R6 data base, and are listed in Appendix A.

Multinuclear species were not considered; Fe concentrations are expected to be very low in our experiments, and data for multinuclear species tends to be suspect. Only log K at 25°C are available for these species, so we must determine or estimate **Fe³⁺** speciation data at temperatures up to 80°C.

Goethite thermodynamic data in data0.com.V8.R6 (Appendix A) is from Barany (1965) (heat of formation by solution calorimetry) and King and Weller (1970) (low temperature heat capacity and entropy). The sample of goethite used by Barany was a natural sample ground to minus 325-mesh and dried at 125°C before use. Corrections were made for small amounts of Mn,

data base is built (Johnson, Oelkers and Helgeson, 1992). See also Johnson and Lundeen (1997).

Mg and Al impurities. The calorimetric reaction scheme required the heats of formation of ferric oxide and water. The value for hematite in data0.com.V8.R6 is 620 cal/mol more negative than that used by Barany in the reaction scheme, and the value for water was essentially identical. Thus, the heat of formation determined by Barany is generally consistent with other data in data0.com. King and Weller (1970) measured the low temperature heat capacity of a natural sample of goethite (dried at 120°C) from which its entropy was determined.

The temperature dependence of goethite solubility is estimated using a constant enthalpy approximation. We must evaluate the adequacy of the constant enthalpy approximation, which is generally used up to a temperature of about 80°C. In addition, Bruno et al. (1992) found it necessary to correct the solubility constant for hematite used in their experiments for particle-size effects according to a method from Schindler (1967). If found necessary and appropriate, corrections to the goethite data for particle size will also be made.

The FeCO_3^+ species in the data0.com.V8.R6 data base was rejected because it was crudely estimated using correlations between the stability constants of carbonate and oxalate complexes by Turner, Whitfield and Dickson (1981). We plan to use data for the Fe-carbonate aqueous species Fe(OH)CO_3° and $\text{Fe(CO}_3)_2^-$ from Bruno et al. (1992) which they obtained from hematite solubility experiments under constant CO_2 pressure. However, we

found an error in their published data. We are now awaiting corrected values from Bruno. This data must then be extrapolated to elevated temperature.

Sr-NO₃OH₂O

Data for aqueous species SrNO_3^+ is a 25°C log K value of 0.8 from Smith and Martell (1976) for the reaction $\text{SrNO}_3^+ = \text{Sr}^{2+} + \text{NO}_3^-$ (Appendix A). Calculations using this equilibrium constant suggest that the SrNO_3^+ aqueous species will complex about 20 mol% of the total Sr in a 0.1 molal NaNO_3 solution. This indicates that formation of SrNO_3^+ must be explicitly accounted for when regressing surface complexation data from experiments using nitrate as a component of a background electrolyte.

J. Rard (LLNL; pers. comm.) reviewed osmotic and activity coefficient data in the literature to attempt to qualitatively evaluate the strength of the SrNO_3^+ complex, and thus the reliability of the association constant. Rard concluded that the degree of association was generally consistent with the activity and osmotic coefficients of related electrolytes at 25°C.

Fe-NO₃-H₂O

Data for FeNO_3^{2+} in data0.com.V8.R6 is from Smith and Martell (1976) (Appendix A). Unlike SrNO_3^+ , FeNO_3^{2+} is predicted to complex an extremely small proportion of total Fe^{3+} and NO_3^- in a 0.1 molal NaNO_3 solution in equilibrium with goethite at 25°C. Further work will therefore not be required to refine data for this species.

Surface complexation data. In our experimental study, we will be concerned about the potential for surface complexation of Sr, CO_3 , Na, and NO_3 . Available surface complexation data for each of these species will be discussed below. The notation ">" denotes a surface species; >(w) and >(s) refer to weak and strong surface sites as defined by the diffuse double layer model of Dzombak and Morel (1990).

Dzombak and Morel (1990) fit experimental data from Kolarik (1961) to obtain intrinsic surface complexation constants for Sr sorption onto hydrous ferric oxides, assuming a generalized two-layer surface complexation model. The surface reactions and their complexation constants at 25°C are listed in Table 2.

In deriving complexation constants from experimental data, Dzombak and Morel restricted potential Sr aqueous species to Sr^{2+} and SrOH^+ ($\text{Sr}^{2+} + \text{OH}^- = \text{SrOH}^+$; $\log K (25^\circ\text{C}) = 0.7$ at $I=0$). As mentioned previously, this constant was changed to 0.8 in the data base, so there is not rigorous agreement between data0.com and the thermodynamic data set used by Dzombak and Morel. However, the impact will probably be of little consequence because the SrOH^+ complex does not become a significant aqueous complex of Sr until pH is greater than about 12, which is beyond the pH anticipated for our experiments.

The experiments of Kolarik (1961) used by Dzombak and Morel did not

Table 2. Sr surface complexation reactions and complexation constants from Dzombak and Morel (1990); see text for explanation of modified values.

	Dzombak and Morel (1990)	Modified Dzombak and Morel
Surface complexation reaction	log K	log K
$>(\text{s})\text{FeOH} + \text{Sr}^{2+} =$ $>(\text{s})\text{FeOHSr}^{2+}$	5.01	5.87
$>(\text{w})\text{FeOH} + \text{Sr}^{2+} =$ $>(\text{w})\text{FeOSr}^+ + \text{H}^+$	-6.58	-5.72
$>(\text{w})\text{FeOH} + \text{Sr}^{2+} + \text{H}_2\text{O} =$ 20	-17.60	-16.74

specifically exclude CO_2 , nor did Dzombak and Morel consider the possibility of formation of Sr-carbonate aqueous species. They did, however, find evidence that the solubility of solid SrCO_3 was not exceeded. The availability of thermodynamic data for Sr-carbonate aqueous species (see earlier section) will allow us to evaluate the potential for their formation and their impact on derived complexation constants.

Complexation constants that are derived by obtaining the best fit to experimental data are sensitive to the sorbent's protonation and deprotonation constants used in the fit. As will be discussed in the next section, the Dzombak and Morel constants for Sr were modified (see Table 2) to adjust for this effect.

Dzombak and Morel's data set lacks surface complexation constants for carbonate species, yet we plan to run experiments in the presence of atmospheric CO_2 . Waite et al. (1994) fit carbonate sorption data from Zachara et al. (1987) to obtain data for carbonate surface complexes. They used a two-site diffuse double layer model. Their calculated point of zero charge (PZC) equals 7.8 (Table 3; $\text{PZC} = 0.5 * (\log K \text{ of } >\text{FeOH} \text{ protonation} - \log K \text{ of } >\text{FeOH} \text{ deprotonation})$). Van Geen, Robertson and Leckie (1994) focused on complexation of carbonate species at the goethite surface, using a single-site diffuse double layer model. Their PZC equals 8.97 (Table 3). The PZC obtained by using the protonation and deprotonation constants of Dzombak and Morel equals 8.11.

Our preliminary experimental results suggest that the PZC for the goethite prepared for our study is 8.5 or greater. Both the Dzombak and Morel and Waite et al. PZC values are significantly lower than our early experiments suggest. Therefore, we will use the constants of Van Geen et al. (Table 3) for our scoping calculations. Later revisions in data will be made as we begin to acquire our own complexation data for our goethite samples.

Dzombak and Morel (1990) assumed the presence of both strong and weak sites for surface complexes, whereas Van Geen et al. used a one-site model in which no distinction was made between strong and weak sites. Data base requirements necessitated that the data for carbonate surface species had to be input to the Dzombak and Morel data base using the two-site designation. Accordingly, the complexation constants for strong and weak carbonate surface species are equal, and the concentrations of strong and weak complexes of the same species should be added together to obtain the total molality of that surface species. Dzombak and Morel (1990) also used the same protonation/deprotonation constants for the weak and strong sites.

Table 3. Surface complexation reactions related to carbonate sorption onto hydrous ferric oxides.

	log K		
Surface complexation reaction	Dzombak and Morel*	Waite et al. I=0.1	Van Geen et al.-intrinsic*
$>\text{FeOH} + \text{H}^+ = >\text{FeOH}_2^+$	7.29	6.51	7.91
$>\text{FeOH} = >\text{FeO}^- + \text{H}^+$	-8.93	-9.13	-10.02
$>\text{FeOH} + \text{H}^+ + \text{HCO}_3^- = >\text{FeCO}_3\text{H}^0 + \text{H}_2\text{O}$	—	9.266	10.45
$>\text{FeOH} + \text{HCO}_3^- = >\text{FeCO}_3^- + \text{H}_2\text{O}$	—	1.276	2.38
Model	Gen. Diffuse double layer; 2-site	Diffuse double layer; 2-site	Diffuse double layer; 1-site
* reaction constants for weak and strong surface sites assumed to be equal			

Given that we have altered the complexation constants of protonation and deprotonation constants from those in Dzombak and Morel, we should reference all other surface complexation reactions in The Geochemist's

Workbench data base to those reactions. A rigorous approach would require regressing all sorption data with the new constants. At this point, however, we are restricting our attention to surface complexation reactions in the chemical system Fe-Sr-Na-NO₃-CO₂-H₂O. In addition, such a massive undertaking is not required at this point for our preliminary scoping calculations. The difference in the PZC between the Dzombak and Morel and Van Geen protonation/deprotonation constants equals 0.86 log units. Correspondingly, the original Sr surface complexation constants in Dzombak and Morel were increased by 0.86 log units to obtain the “modified” complexation constants listed in Table 2. The modified complexation constants reproduced the sorption curve fits published in Dzombak and Morel. It was therefore concluded that the modified Sr complexation constants are quite adequate for our initial calculations.

Although Van Geen, Robertson and Leckie have data for carbonate complexation onto goethite at 25°C, they did not consider the possibility that Fe-carbonate aqueous species may have formed in solution. Bruno et al. (1992) measured aqueous complexation constants for Fe carbonates. However, as previously mentioned, the published aqueous complexation constants are in error, and Bruno will send us corrected data. Additional information from Bruno must be obtained as well, including the protonation/deprotonation constants that he used.

When the data for Bruno is finalized, we can evaluate whether Van Geen’s solutions might have been impacted by Fe-carbonate formation, and

whether it would have affected their selection of surface species and their sorption data. Van Geen used much lower CO₂ pressures ($<5 \times 10^{-6}$ to 0.04 atm) than Bruno (0.3 and 0.97 atm). Van Geen used the surface species $>\text{FeCO}_3\text{H}^\circ$ and $>\text{FeCO}_3^-$ to fit his sorption data on goethite, whereas Bruno used the surface species $>\text{FeOH-HCO}_3^-$ (equivalent to $>\text{FeCO}_3^-$ minus 1 H₂O) and $>\text{FeOH}_2\text{CO}_2^+$ for sorption onto hematite. Hematite and goethite are commonly thought to sorb similarly. Bruno's work was limited to pH values less than about 7.1, whereas VanCeen's went slightly higher to 7.6. Bruno found the neutral species dominant at 25°C up to pH = 6, at which point the negative species was dominant.

Na is commonly assumed to be non-sorbing, and is commonly used as a component in background electrolytes. However, Rundberg, Albinsson and Vannerberg (1994) reported results of Na sorption experiments onto goethite at 25°C in NaClO₄ mediums with ionic strengths of 0.005 to 0.016. Potentiometric titrations located the zero point of charge at a pH of about 8.45 (as compared, for example, to Dzombak and Morel's 8.1 and Van Geen's 8.9). Rundberg's experiments showed that, as would be expected, no Na sorption occurred below the zero point of charge; in fact, cation exclusion was observed below the zero point of charge. Rundberg used the triple layer model to establish a surface complexation constant equal to 15 (log K=1.2) for the reaction $>\text{FeO}^- + \text{Na}^+ = >\text{FeONa}^\circ$.

Whether the Na surface complex will compete for Sr to a significant degree in our experiments using NaNO₃ as a background electrolyte is still in question. In future work, we may have to re-fit Rundberg's data to obtain complexation constants according to the diffuse double layer model which we are using to make our scoping calculations. We can then evaluate whether Na sorption may affect Sr sorption onto goethite.

For reference, Dzombak and Morel only considered sorption of one monovalent cation, Ag⁺, for which they found that a single strong site best fit experimental data.

Nitrate (NO₃) is normally assumed to be non-sorbing, and is commonly used as a component of a background electrolyte in surface complexation experiments. No data has been found for the possibility that NO₃ may sorb in given situations.

CONCLUSIONS AND FUTURE EXPERIMENTS

There are three major conclusions from these preliminary strontium sorption experiments: 1. Strontium-uptake may occur at metal-oxygen or metal-carbonate surface sites, or as a strontium-carbonate surface precipitate; 2. Sorption or precipitation kinetics probably control strontium partitioning between waters and kaolinite and goethite; and 3. Changes in temperature may not effect strontium-uptake.

Future research will be directed toward spectroscopic analysis of reaction run products to determine the molecular structure of strontium at goethite and kaolinite surfaces. It may not be necessary to determine the molecular structure above 25°C, because macroscopic batch experiments do not indicate a change in reaction mechanism. However, additional batch experiments are needed to verify the significant increase in strontium-uptake in the presence of kaolinite at 50°C.

Future sorption experiments will determine the rate of strontium-uptake to kaolinite and goethite in flow-through reactors from conditions undersaturated to supersaturated with respect to strontianite at 25, 50, 80°C. The advantage of flow-through reactors over batch reactors is the solution composition can be held constant over the duration of the experiment. This allows the effect of saturation on the overall uptake rate to be investigated. These experiments will be followed by long-term desorption experiments. Batch sorption experiments will be conducted as needed to support the kinetic experiments and spectroscopic analysis.

The data survey revealed that the following should be acquired, estimated, or further evaluated:

- thermodynamic data for Fe^{3+} -hydroxide aqueous complexes at elevated temperature
- thermodynamic data for Fe^{3+} -carbonate aqueous species; should be available from J. Bruno (1997; pers. comm.)

- thermodynamic data for SrNO_3^+ as a function of temperature
- thermodynamic data for goethite at elevated temperature as a function of particle size
- surface complexation constants for Sr, Na, CO_3 and NO_3 as a function of temperature

In summary, data to be used in our preliminary scoping calculations can be found in: Appendix A (thermodynamic data for gases, aqueous species and minerals); Table 1 (Sr aqueous complexes and strontianite); Table 2 (Sr complexation constants for hydrous ferric oxides modified from Dzombak and Morel, 1990) and Table 3 (carbonate complexation constants and protonation/deprotonation constants for hydrous ferric oxides from Van Geen et al., 1994).

REFERENCES

- Adeleye, A. A., Clay, P. G., Oladipo, M. O. A. (1994). "Sorption of cesium, strontium and europium ions on clay minerals." *J. Mat. Sci.* **29**: 954-958.
- Axe, L., Anderson, P.R. (1995). "Sr diffusion and reaction within Fe oxides: Evaluation of the rate-limiting mechanism for sorption." *J. Colloid Interface Sci.* **175**: 157-165.
- Baes, C.F., Jr. and Mesmer, R.F. (1976) *The Hydrolysis of Cations*: Wiley, New York, 489 pp.
- Barany, R. (1965) "Heats of formation of goethite, ferrous vanadate, and manganese molybdate." *U.S. Dept. Interior, Bur. Mines, Rent. of Investigations* 6618, 10 p.
- Bethke, C.M. (1996) *Geochemical Reaction Modeling*. Oxford Univ. Press, New York, 397 pp.
- Bruno, J., Stumm, W., Wersin, P. and Brandberg, F. (1992) *Geochim., et Cosmochim. Acta*, **56**: 1139-1147.
- Busenberg, E., Plummer, L.N. and Parker, V.B. (1984) "The solubility of strontianite (SrCO_3) in CO_2 - H_2O solutions between 2 and 91°C, the

- association constants of $\text{SrHCO}_3^+(\text{aq})$ and $\text{SrCO}_3^\circ(\text{aq})$ between 5 and 80°C, and an evaluation of the thermodynamic properties of $\text{Sr}^{2+}(\text{aq})$ and $\text{SrCO}_3(\text{cr})$ at 25°C and 1 atm total pressure." Geochim. et Cosmochim. Acta, 48: 2021-2035.
- Duncan, P. R. (1995). An evaluation of the potential for remediating hazardous metals and radionuclides in aquifers and the subsurface: A summary report., INEL, Biotechnology Group.
- Dzombak, D.A. and Morel, F.M.M. (1990) *Surface Complexation Modeling: Hydrous Ferric Oxide*: John Wiley, New York, 393 pp.
- Fordham, A. W. (1973). "The location of iron-55, strontium-85, and iodide-25 sorbed by kaolinite and dickite particles." Clays Clay Min. **21**: 175-184.
- Fuerstenau, D. W., Monmohan, D., Raghavan, S., Ed. (1981). The adsorption of alkline earth metal ions at the rutile/aqueous solution interface. Adsorption From Aqueous Solutions. New York, Plenum Press.
- Gorturk, H., Eylem, C., Erten, H. N. (1995). "Radiochemical studies of the sorption behavior of strontium and barium." J. Radioanalytical Nuclear Chem. **198**: 449.
- Helgeson, H.C. (1985) "Errata II: Thermodynamics of minerals, reactions, and aqueous solutions at high pressures and temperatures" Am. J. Sci. **285**: p. 845-855.
- Huang, C. P., Stumm, W. (1973). "Specific adsorption of cations on hydrous- $\gamma\text{Al}_2\text{O}_3$." J. Colloid Interface Sci. **43**: 409-420.
- Inskip, W. P., Bloom P. R. (1985). "An evaluation of rate equations for calcite precipitation kinetics at PCO_2 less than 0.01 atm and pH greater than 8." Geochim. Cosmochim. Acta **49**: 2165-2180.
- Johnson, J.W. and Lundeen, S. R. (1997) "GEMBOCHS thermodynamic datafiles for use with the EQ3/6 software package" Lawrence Livermore National Laboratory UCRL-ID, in prep.
- Johnson, J.W., Oelkers, E.H. and Helgeson, H.C. (1992) "SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C." Computers & Geosciences, 18: 899-947.
- King, K.G. and Weller, W.W. (1970) "Low-temperautre heat capacities and entropies at 298.15°K of goethite and pyrophyllite." U.S. Dept. Interior, Bur Mines. Rept. of Investigations **7389**: 6.
- Kinniburgh, D. G., Syers, J. K., Jackson M. L. (1975). "Specific adsorption of trace amounts of calcium and strontium by hydrous oxides of iron and aluminum." Soil Sci. Soc. Am. T. **39**: 464-470.
- Kolarik, Z. (1961) "Sorption radioaktiver Isotopen an niederschlagen. VI. System Eisen(III)-Hydroxyd-Strontiumnitratlosung und die allgemein gesetzmassigkeiten der sorption am Eisen(III)-Hydroxyd." Collection Szech Chem. Commun **27**: 929-933.

- Liang, T., Hsu, C, Liou, D. (1993). "Modified freundlich sorption of cesium and strontium on Wyoming bentonite." Applied Radiation and Isotopes **44**: 1205-1208.
- Lyklema, J. (1969). "The electrical double layer on silica in the presence of bivalent counter-ions." J. Electroanal. Chem. **22**: 1-7.
- Malati, M. A. (1966). "The role of hydration in the adsorption of alkaline earth ions onto quartz." J. Colloid Interface Sci. **22**: 306-307.
- Morse, J. W., Ed. (1983). The kinetics of calcium carbonate dissolution and precipitation. Carbonates: Mineralogy and Chemistry; Reviews in Mineralogy.
- O'Day, P. A., Brown, G. E. Jr., Parks, G. A. (1994). "X-ray absorption spectroscopy of cobalt(II) multinuclear surface complexes and surface precipitates on kaolinite." J. Colloid Interface Sci. **165**: 269-289.
- Park, D. K., Woo, S. I., Tanaka, T., Kamiyama, H. (1992). "Sorption and desorption behaviour of 60-Co, 85-Sr, and 137-Cs in a porous tuff. Mechanisms and kinetics." J. Nuclear Sci. Technol. **29**: 1184-1193.
- Rundberg, R.S., Albinsson, Y. and Vannerberg, K. (1994) "Sodium adsorption onto goethite as a function of pH and ionic strength." Radiochim. Acta **66/67**: 333-339.
- Scheidegger, A. M., Lamble, G. M., Sparks, D. L. (1996). "Investigation of Ni sorption on pyrophyllite: An XAFS study." Environ. Sci. Technol. **30**: 548-554. Schindler, P.W., 1967, Heterogeneous equilibria involving oxides, hydroxides, carbonates, and hydroxide carbonates. In *Equilibrium Concepts in Natural Water Systems*, (W. Stumm, ed.): Advances in Chemistry Series 67, Am. Chem Soc., p. 196.
- Schindler, p. W., Gamsjager H. (1972). "Acid-base reactions of the TiO₂(Anatase)-water interface and the point of zero charge of TiO₂ suspensions." Kolloid-Z.A. Polym. **250**: 759-763.
- Schroth, B. K., Sposito G. (1997). "Surface charge properties of kaolinite." Clays Clay Minerals **45**: 85-91.
- Schwertmann, U., Cornell, R. M. (1991). Iron Oxides in the Laboratory: Preparation and Characterization. New York City, VCH Publishers, Inc.
- Shock, E.L. and Helgeson, H.C. (1988) "Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5kb and 1000C." Geochim. et Cosmochim. Acta **52**: 2009-2036.
- Sillen, L.G. and Martell, A.E. (1964) *Stability constants of metal-ion complexes: Chem. Soc. Spec. Pub.* 17, London.
- Smith, R.M., and Martell, A.E. (1976) *Critical Stability Constants, Inorganic Complexes*, Vol. 4: Plenum, New York, 4, 257 p.
- Sverjensky, D.A. (1994) "Thermodynamic properties of aqueous inorganic metal complexes." draft for *Geochim. et Cosmochim. Acta*.

- Turner, D.R., Whitfield, M. and Dickson, A.G. (1981) "The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm pressure." Geochim. et Cosmochim. Acta **45**: 855-881.
- van Geen, A., Robertson A. P., Leckie J. O. (1994). "Complexation of carbonate species at the goethite surface: Implications for adsorption of metal ions in natural waters." Geochim. Cosmochim. Acta **58**: 2073-2086.
- Wolery T.J. (1992) "EQ3NR, a computer program for geochemical aqueous speciation-solubility calculations: Theoretical manual, user's guide, and related documentation (Version 7.0)" Lawrence Livermore National Laboratory UCRL-MA-110662 PT III.
- Wolery T.J. and Daveler S.A. (1992) "EQ6, a computer program for reaction path modeling of aqueous geochemical systems: Theoretical manual, user's guide, and related documentation (Version 7.0)." Lawrence Livermore National Laboratory UCRL-MA-110662 PT TV.
- Yanagi, T., Watanabe M., Yamamoto K. (1989). "Sorption behavior of cesium and strontium ions on mixtures of clay sorbates." J. Nuclear Sci. Technol. **26**: 861-864.
- Zachara, J.M., Girvin, D.C., Schmidt, R.L. and Resch, C.T. (1987) "Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions." Environ. Sci. Tech. **21**: 589-594.
- Zeltner, W. A., Anderson M. A. (1988). "Surface charge development at the goethite/aqueous solution interface: Effects of CO₂ adsorption." Langmuir **4**: 469-474.

Figure 1. Strontianite solubility at 25°C and atmospheric CO₂(g). Strontianite solubility increases by only 0.2 log units at 80 ° C

Figure 2. Strontium-uptake at goethite interface as a function of pH at 25, 50 and 80 ° C from solutions containing initial strontium concentrations A $[Sr]_i = 10^{-4} \text{ M}$, B $[Sr]_i = 10^{-5} \text{ M}$, C $[Sr]_i = 10^{-6} \text{ M}$, D $[Sr]_i = 10^{-7} \text{ M}$.

Figure 2 (continued).

Figure 3. Strontium-uptake at geothite interface as a function of pH and initial strontium concentration at **A** 25 ° C, **B** 50 ° C, and **C** 80 ° C.

Figure 4. Final solution composition of the strontium-goethite experiments plotted as relative saturation with respect to strontianite ($\log Q/K$) versus pH.

Figure 5. Strontium-uptake at kaolinite surface as a function of pH at 25, 50 and 80 °C from solutions containing initial strontium concentrations A $[Sr]_i = 10^{-4} \text{ M}$, B $[Sr]_i = 10^{-5} \text{ M}$, C $[Sr]_i = 10^{-6} \text{ M}$, D $[Sr]_i = 10^{-7} \text{ M}$.

Figure 5 (continued).

Figure 6. Strontium-uptake at kaolinite surface as a function of pH and initial strontium concentration at **A** 25°C, **B** 50°C, and **C** 80°C.

Figure 7. Final solution composition of the strontium-kaolinite experiments plotted as relative saturation ($\log Q/K$) versus pH with respect to **A** strontianite, **B** kaolinite, **C** gibbsite, and **D** quartz.

Figure 7. (continued)

Appendix A. Thermodynamic data for relevant gases, aqueous species and solids from GEMBOCHS thermodynamic data file version data0.com.V8.RG.

Gas

CO₂(g)

mole wt.= 44.0098 g

3 species in reaction

-1.0000 H₂O 1.0000 H⁺ 1.0000 HCO₃⁻
 -7.6765 -7.8136 -8.0527 -8.3574
 -8.7692 -9.2165 -9.7202 -10.3393

* gflag = 1 [reported delG_{0f} used]
 * extrapolation algorithm: supcrt92 [92joh/oel]
 * reference-state data source = 82wag/eva
 * delG_{0f} = -94.254 kcal/mol
 * delH_{0f} = -94.051 kcal/mol
 * S_{0PrTr} = 51.085 cal/(mol*K)

Aqueous species

CO₂(aq)

charge= 0.0 ion size= 3.0 Å mole wt.= 44.0098 g

3 species in reaction

-1.0000 H₂O 1.0000 H⁺ 1.0000 HCO₃⁻
 -6.5804 -6.3447 -6.2684 -6.3882
 -6.7235 -7.1969 -7.7868 -8.5280

* gflag = 1 [reported delG_{0f} used]
 * extrapolation algorithm: supcrt92 [92joh/oel]
 * reference-state data source = 89sho/hel
 * delG_{0f} = -92.250 kcal/mol
 * delH_{0f} = -98.900 kcal/mol
 + S_{0PrTr} = 28.100 cal/(mol*K)

CO₃⁻

charge= -2.0 ion size= 4.5 Å mole wt.= 60.0092 g

2 species in reaction

-1.0000 H⁺ 1.0000 HCO₃⁻
 10.6241 10.3288 10.1304 10.0836
 10.2003 10.4648 10.8707 11.4638

* gflag = 1 [reported delG_{0f} used]
 * extrapolation algorithm: supcrt92 [92joh/oel]
 * reference-state data source = 88sho/hel
 * delG_{0f} = -126.191 kcal/mol

```

*      delH0f = -161.385 kcal/mol
*      S0PrTr = -11.950 cal/(mol*K)

HCO3-
  charge= -1.0   ion size= 4.0 A   mole wt.= 61.0171 g
  3 elements in species
  1.0000 c      1.0000 H      3.0000 O
*  gflag = 1 [reported delG0f used]
*  extrapolation algorithm: supcrt92 [92joh/oel]
*  reference-state data source = 88sho/hel
*      delG0f = -140.282 kcal/mol
*      delH0f = -164.898 kcal/mol
*      S0PrTr = 23.530 cal/(mol*K)

```

```

NO3-
  charge= -1.0   ion size= 3.0 A   mole wt.= 62.0049 g
  4 species in reaction
-1.0000 H+      -1.0000 H2O      1.0000 NH3(aq)
 2.0000 O2(aq)
-68.1779 -62.1001 -54.8254 -47.8997
-40.7634 -34.8282 -29.7190 -25.1037
*  gflag = 1 [reported delG0f used]
*  extrapolation algorithm: supcrt92 [92joh/oel]
*  reference-state data source = 88sho/hel
*      delG0f = -26.507 kcal/mol
*      delH0f = -49.429 kcal/mol
*      S0PrTr = 35.120 cal/(mol*K)

```

```

Sr++
  charge= 2.0   ion size= 5.0 A   mole wt.= 87.6200 g
  1 elements in species
  1.0000 Sr
*  gflag = 1 [reported delG0f used]
*  extrapolation algorithm: supcrt92 [92joh/oel]
*  reference-state data source = 88sho/hel
*      delG0f = -134.760 kcal/mol
*      delH0f = -131.670 kcal/mol
*      S0PrTr = -7.530 cal/(mol*K)

```

```

SrNO3+
  charge= 1.0   ion size= 4.0 A   mole wt.= 149.6249 g
  2 species in reaction
 1.0000 NO3-      1.0000 Sr++
 500.0000 -0.8000 500.0000 500.0000
 500.0000 500.0000 500.0000 500.0000
*  gflag = 3 [reported logK data used]

```

```

* logk source = 76smi/mar
* logk = 0.8000
* logk reference reaction:
* 1.0000 SrNO3+ - 1.0000 NO3-
* -1.0000 Sr++
* calculated g-h-s values:
* delG0f = -162.358 kcal/mol
* delH0f = N/A
* S0PrTr = N/A

```

```

Fe(OH)4-
charge= -1.0 ion size= 4.0 A mole wt.= 123.8764 g
3 species in reaction
-4.0000 H+ 1.0000 Fe+++ 4.0000 H2O
500.0000 21.6000 500.0000 500.0000
500.0000 500.0000 500.0000 500.0000
* gflag = 3 [reported logK data used]
* logk source = 76bae/mes
* logk = -21.6000
* logk reference reaction:
* 1.0000 Fe(OH)4- -4.0000 H2O
* -1.0000 Fe+++ 4.0000 H+
* calculated g-h-s values:
* delG0f = -201.403 kcal/mol
* delH0f = N/A
* S0PrTr = N/A

```

```

Fe(OH)2+
charge= 1.0 ion size= 4.0 A mole wt.= 89.8617 g
3 species in reaction
-2.0000 H+ 1.0000 Fe+++ 2.0000 H2O
500.0000 5.6700 500.0000 500.0000
500.0000 500.0000 500.0000 500.0000
* gflag = 3 [reported logK data used]
* logk source = 76bae/mes
* logk = 5.6700
* logk reference reaction:
* -1.0000 Fe(OH)2+ -2.0000 H+
* 1.0000 Fe+++ 2.0000 H2O
* calculated g-h-s values:
* delG0f = -109.760 kcal/mol
* delH0f = N/A
* S0PrTr = N/A

```

```

Fe(OH)3(aq)
charge= 0.0 ion size= 3.0 A mole wt.= 106.8690 g

```

3 species in reaction
 -3.0000 H+ 1.0000 Fe+++ 3.0000 H2O
 500.0000 12.0000 500.0000 500.0000
 500.0000 500.0000 500.0000 500.0000
 * gflag = 3 [reported logK data used]
 * logk source = 76bae/mes
 * logk = -12.0000
 * logk reference reaction:
 * 1.0000 Fe(OH)3(aq) -3.0000 H2O
 * -1.0000 Fe+++ 3.0000 H+
 * calculated g-h-s values:
 delG0f = -157.812 kcal/mol
 * delH0f = N/A
 * S0PrTr = N/A

Fe(OH)2+
 charge= 1.0 ion size= 4.0 A mole wt.= 89.8617 g
 3 species in reaction
 -2.0000 H+ 1.0000 Fe+++ 2.0000 H2O
 500.0000 5.6700 500.0000 500.0000
 500.0000 500.0000 500.0000 500.0000
 * gflag = 3 [reported logK data used]
 * logk source = 76bae/mes
 * logk= 5.6700
 * logk reference reaction:
 * -1.0000 Fe(OH)2+ -2.0000 H+
 * 1.0000 Fe+++ 2.0000 H2O
 * calculated g-h-s values:
 delG0f = -109.766 kcal/mol
 * delH0f = N/A
 * S0PrTr = N/A

FeNO3++
 charge= 2.0 ion size= 4.5 A mole wt.= 117.8519 g
 2 species in reaction
 1.0000 Fe+++ 10000 NO3-
 500.0000 -1.0000 500.0000 500.0000
 500.0000 500.0000 500.0000 500.0000
 * gflag = 3 [reported logK data used]
 * logk source = 76smi/mar
 * logk = 1.0000
 * logk reference reaction:
 * 1.0000 FeNO3++ -1.0000 Fe+++
 * -1.0000 NO3-
 * calculated g-h-s values:
 delG0f = -31.991 kcal/mol

```
*      delH0f =    N/A
*      S0PrTr =    N/A
```

Solids

```
Sr                                type=
  formula=
  mole vol.= 33.921 cc    mole wt.= 87.6200 g
  4 species in reaction
-2.0000 H+          -0.5000 O2(aq)          1.0000 H2O
  1.0000 Sr++
    155.0673 141.7816 126.4636 112.4267
    98.5549 87.5495 78.5682 71.0407
* gflag = 1 [reported delG0f used]
* extrapolation algorithm: Cp integration
* reference-state data source = 92gre/fug
*   delG0f =    0.000 kj/mol
*   delH0f =    0.000 kj/mol
*   S0PrTr =   55.700 j/(mol*K)
```

```
Sr(NO3)2                        type=
  formula=
  mole vol.= 0.000 cc    mole wt.= 211.6299 g
  2 species in reaction
  1.0000 Sr++          2.0000 NO3-
    0.8834  1.1493  1.3565  1.4728
    1.4879  1.3599 500.0000 500.0000
* gflag = 1 [reported delG0f used]
* extrapolation algorithm: constant enthalpy approximatio
* reference-state data source = 79rob/hem
*   delG0f = -779.086 kj/mol
*   delH0f = -978.311 kj/mol
*   S0PrTr =  194.560 j/(mol*K)
```

```
Sr(NO3)2:4H2O                  type=
  formula=
  mole vol.= 128.950 cc    mole wt.= 283.6910 g
  3 species in reaction
  1.0000 Sr++          2.0000 NO3-          4.0000 H2O
    -0.0505  0.6976  1.6233  2.5854
    3.6602  4.5745 500.0000 500.0000
* gflag = 1 [reported delG0f used]
* extrapolation algorithm: constant enthalpy approximatio
* reference-state data source = 82wag/eva
*   delG0f = -1730.390 kj/mol
*   delH0f = -2155.787 kj/mol
```

* S0PrTr = 369.000 j/(mol*K)

Sr(OH)2 type=
 formula=
 mole vol.= 33.550 cc mole wt.= 121.6347 g
 3 species in reaction
 -2.0000 H+ 1.0000 Sr++ 2.0000 H2O
 30.0065 27.5229 24.7298 22.2571
 19.9113 18.1259 500.0000 500.0000
 * gflag = 1 [reported delG0f used]
 * extrapolation algorithm: constant enthalpy approximat
 * reference-state data source = 85cha/dav
 * delG0f = -881.098 kj/mol
 * delH0f = -968.892 kj/mol
 * S0PrTr = 97.069 j/(mol*K)

SrO type=
 formula=
 mole vol.= 20.686 cc mole wt.= 103.6194 g
 3 species in reaction
 -2.0000 H+ 1.0000 H2O 1.0000 Sr++
 45.7951 41.8916 37.4018 33.3030
 29.2655 26.0638 23.4377 21.2066
 * gflag = 1 [reported delG0f tied]
 * extrapolation algorithm: Cp integration
 + reference-state data source = 82wag/eva
 * delG0f = -561.900 kj/mol
 * delH0f = -592.871 kj/mol
 * S0PrTr = 54.400 j/(mol*K)

Goethite type=
 formula= FeOOH
 mole vol.= 20.820 cc mole wt.= 88.8537 g
 3 species in reaction
 -3.0000 H+ 1.0000 Fe+++ 2.0000 H2O
 1.5252 0.5345 -0.6000 -1.6142
 -2.6004 -3.3990 500.0000 500.0000
 * gflag = 1 [reported delG0f used]
 * extrapolation algorithm: constant enthalpy approximat
 * reference-state data source = 79rob /hem
 * delG0f = -488.550 kj/mol
 * delH0f = -559.328 kj/mol
 * S0PrTr = 60.380 j/(mol*K)

Siderite type=
 formula= FeCO3

mole vol.= 29.378 cc mole wt.= 115.8562 g
 3 species in reaction
 -1.0000 H+ 1.0000 Fe++ 1.0000 HCO3-
 0.2914 -0.1920 -0.8309 -1.4967
 -2.2685 -3.0240 -3.8241 -4.7626
 * gflag = 1 [reported delG0f used]
 * extrapolation algorithm: supcrt92 [92joh/oel]
 * reference-state data source = 78hel/del
 * delG0f = -162.414 kcal/mol
 * delH0f = -179.173 kcal/mol
 * S0PrTr = 25.100 cal/(mol*K)

Data references

76bae/mes

Baes, C.F.Jr., and Mesmer, R.E., 1976, The hydrolysis of cations: Wiley-Interscience, New York, 489 p.

85cha/dav

Chase, M.W., Davies, C.A., Downey, J.R., Frurip, D.J., McDonald, R.A., and Syverud, A.N., 1985, Janaf thermochemical tables 3rd ed., 1985 supplement: J. Phys. Chem. Ref. Data, 14, 1856 p.

92gre/fug

Grenthe, I., Fuger, J., Konings, R. J.M., Lemirej R. J., Muller, A.B., Nguyen-Trung, C., and Wanner, H., 1992, Chemical Thermodynamics, Volume 1: Chemical Thermodynamics of Uranium: North-Holland, Amsterdam, 1, 714 p.

92joh/oel

Johnson, J.W., Oelkers, E.H., and Helgeson, H.C., 1992, SUPCRT92: A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C: Computers Geosci., 18, 899-947.

79rob/hem

Robie, R.A., Hemingway, B.S., and Fisher, J.R., 1979, Thermodynamic properties of minerals and related substances at 298.15K and 1 bar (10⁵ Pascals) pressure and at higher temperatures: U.S.G.S. Bull. 1452 (with corrections), 1452, 1456 p.

89sho/hel

Shock, E.L., Helgeson, H.C., and Sverjensky, D.A., 1989, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species: Geochim. Cosmochim. Acta, 53, 2157-2183.

88sho/hel

Shock, E.L., and Helgeson, H.C., 1988, Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5kb and 1000°C: Geochim. Cosmochim. Acta, 52, 2009-2036.

76smi/mar

Smith, R.M., and Martell, A.E., 1976, Critical Stability Constants, Vol. 4: Inorganic Complexes: Plenum, New York, 4, 257 p.

82wag/eva

Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Chumey, K.L., and Nuttall, R.L., 1982, The NBS tables of chemical thermodynamic properties, selected values for inorganic and cl and c2 organic substances in SI units: J. Phys. Chem. Ref. Data, V. 11, supp. 2, 392 p.

Key

$\text{delGof} = \Delta G_f^\circ$ = apparent standard molal Gibbs free energy of formation from the elements at the reference temperature (298.15K) and pressure (1 bar)

$\text{delHof} = \Delta H_f^\circ$ = apparent standard molal enthalpy of formation from the elements at the reference temperature (298.15K) and pressure (1 bar)

$\text{SOPrTr} = S^\circ$ = standard molal entropy at the reference temperature (298.15K) and pressure (1 bar)

gflag- denotes the thermodynamic data used to calculate ΔG_f°

gflag = 1 means the the reported value of ΔG_f° is used

* gflag = 1 [reported delGof used]

gflag = 3 means that ΔG_f° is computed from reported equilibrium constant

* gflag = 3 [reported logK data used]

extrapolation algorithms - the methods used to extrapolate thermodynamic properties to temperatures and pressures above the reference condition

supcrt92 [92joh/oel] and Cp integration: coefficients in heat capacity power functions are used to calculate properties at elevated temperature and pressure. The reference [92joh/oel] refers to the SUPCRT92 software package which contains heat capacity coefficients and power functions

- * extrapolation algorithm: supcrt92 [92joh/oel]
- * extrapolation algorithm: Cp integration

constant enthalpy approximation: When heat capacity coefficients are lacking, the enthalpy is assumed to be invariant with respect to temperature; e.g.

- * extrapolation algorithm: constant enthalpy approximation