PAUL SCHERRER INSTITUT	Registrierung TM-44-12-05

Titel	**The PSI/Nagra Chemical Thermodynamic Database 12/07 (Update of the Nagra/PSI TDB 01/01): Data Selection for Silicon**	Ersetzt -
Autoren/ Autorinnen	**Wolfgang Hummel**	Erstellt 4. June 2014

Summary:

Data reported in the literature for dissolved silica and aqueous metal silicate complexes have been reviewed by the author.

Literature reviewed in OECD NEA's books "Chemical Thermodynamics of Uranium" by GRENTHE et al. (1992), "Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium" by GUILLAUMONT et al. (2003), "Chemical Thermodynamics of Nickel" by GAMSJÄGER et al. (2005), "Chemical Thermodynamics of Zirconium" by BROWN et al. (2005) and "Chemical Thermodynamics of Thorium" by RAND et al. (2009) have been considered in this review. The updated database is called PSI/Nagra Chemical Thermodynamic Database 12/07.

This is the 4th of a continuing series of reports concerning the PSI/Nagra Chemical Thermodynamic Database 12/07.

Verteile	Abt.	Empfänger / Empfängerinnen	Expl.	Abt.	Empfänger / Empfängerinnen	Expl
	44	B. Baeyens	1	Nagra	V. Cloet	1
		U. Berner	1		L. Johnson	1
		S. Churakov	1		J. Mibus	1
		E. Curti	1		J. Schneider	1
		R. Dähn	1		B. Schwyn	1
		T. Gimmi	1		P. Zuidema	1
		M. Glaus	1			
		W. Hummel	1	New Bern	F.J. Pearson	1
		G. Kosakowski	1			
		D. Kulik	1			
		M. Marques	1			
		W. Pfingsten	1			
		T. Thoenen	1			
		J. Tits	1			
		L. Van Loon	1			
		E. Wieland	1			

	Expl.
Bibliothek	2
Reserve	4
Total	29
Seiten	40
Beilagen	-

Informationsliste

D	1	2	3	4	5	8	9	A

Visum ~~Abt./Laborleitung~~:

Silica and silicates

8.1 Elemental silicon

Silicon metal and gas are not relevant under environmental conditions. Hence, the gas phase Si(g) is not included in the data base. For the same reason SiF_4(g), selected by GRENTHE et al. (1992), is also not included in the data base. The absolute entropy and heat capacity of Si(cr) are included as they are used for the calculation of certain thermodynamic reaction properties. The selected values are taken from CODATA (COX et al. 1989).

$$S_m°(\text{Si, cr, 298.15 K}) = (18.810 \pm 0.08)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}°(\text{Si, cr, 298.15 K}) = (19.789 \pm 0.030)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

8.2 Silica (quartz)

The selected values for SiO_2(cr), quartz, are taken from CODATA (COX et al. 1989).

$$\Delta_f H_m°(\text{SiO}_2\text{, cr, 298.15 K}) = -(910.700 \pm 1.0)\ \text{kJ} \cdot \text{mol}^{-1}$$

$$S_m°(\text{SiO}_2\text{, cr, 298.15 K}) = (41.460 \pm 0.20)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p,m}°(\text{SiO}_2\text{, cr, 298.15 K}) = (44.602 \pm 0.30)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

and the Gibbs energy of formation calculated from the above values and $S_m°$ (Si, cr, 298.15 K)

$$\Delta_f G_m°(\text{SiO}_2\text{, cr, 298.15 K}) = -(856.287 \pm 1.0)\ \text{kJ} \cdot \text{mol}^{-1}$$

8.3 Silica compounds and aqueous species

8.3.1 Silica compounds

Dissolution of silica in water in the pH range where $Si(OH)_4$(aq) is the dominant aqueous silica species can be expressed by the reaction

$$SiO_2(s) + 2\ H_2O(l) \Leftrightarrow Si(OH)_4(aq)$$

Taking the activity of the solid phase and water to be 1, as well as the activity coefficient of $Si(OH)_4$(aq) leads to

$$K_s = m_{Si(dissolved)}$$

where m is the measured concentration of dissolved silica in moles/kg H_2O.

New solubility data for quartz at 21, 50, 75 and 96°C have been reported by RIMSTIDT (1997). Note, that the duration of his solubility experiments at 21°C lasted for more than 13 years! These solubility data show excellent internal consistency and fit a straight line (RIMSTIDT 1997):

$$\log_{10} m_{Si(dissolved)} = -0.076 - 1093.711 / T$$

This means that in the temperature range 21 – 96°C a two-term approximation of temperature dependence is sufficient, i.e. the integrated van't Hoff equation including only $\log_{10}K_s°$ and $\Delta_r H_m°$:

$$\log_{10}K_s°(\text{Quartz, cr, 298.15 K}) = -3.744$$

$$\Delta_r H_m°(\text{Quartz, cr, 298.15 K}) = 20.939\ \text{kJ} \cdot \text{mol}^{-1}$$

RIMSTIDT (1997) critically evaluated all the quartz solubility data from the literature and fitted all reliable literature data up to 300°C together with his own results to the van't Hoff equation:

$$\log_{10}m_{Si(dissolved)} = -(0.0254 \pm 0.0247) - (1107.12 \pm 10.77) \;/\; T$$

This function predicts that the solubility of quartz at 25°C is 11.0 ± 1.1 ppm "SiO_2". Note that all uncertainties given by RIMSTIDT (1997) are expressed as ± 1 standard deviation. This results in:

$$\log_{10}K_s°(\text{Quartz, cr, 298.15 K}) = -(3.739 \pm 0.087)$$

$$\Delta_rH_m°(\text{Quartz, cr, 298.15 K}) = (21.196 \pm 0.41)\ \text{kJ} \cdot \text{mol}^{-1}$$

where the uncertainties are now expressed as 2 standard deviations (95% confidence level).

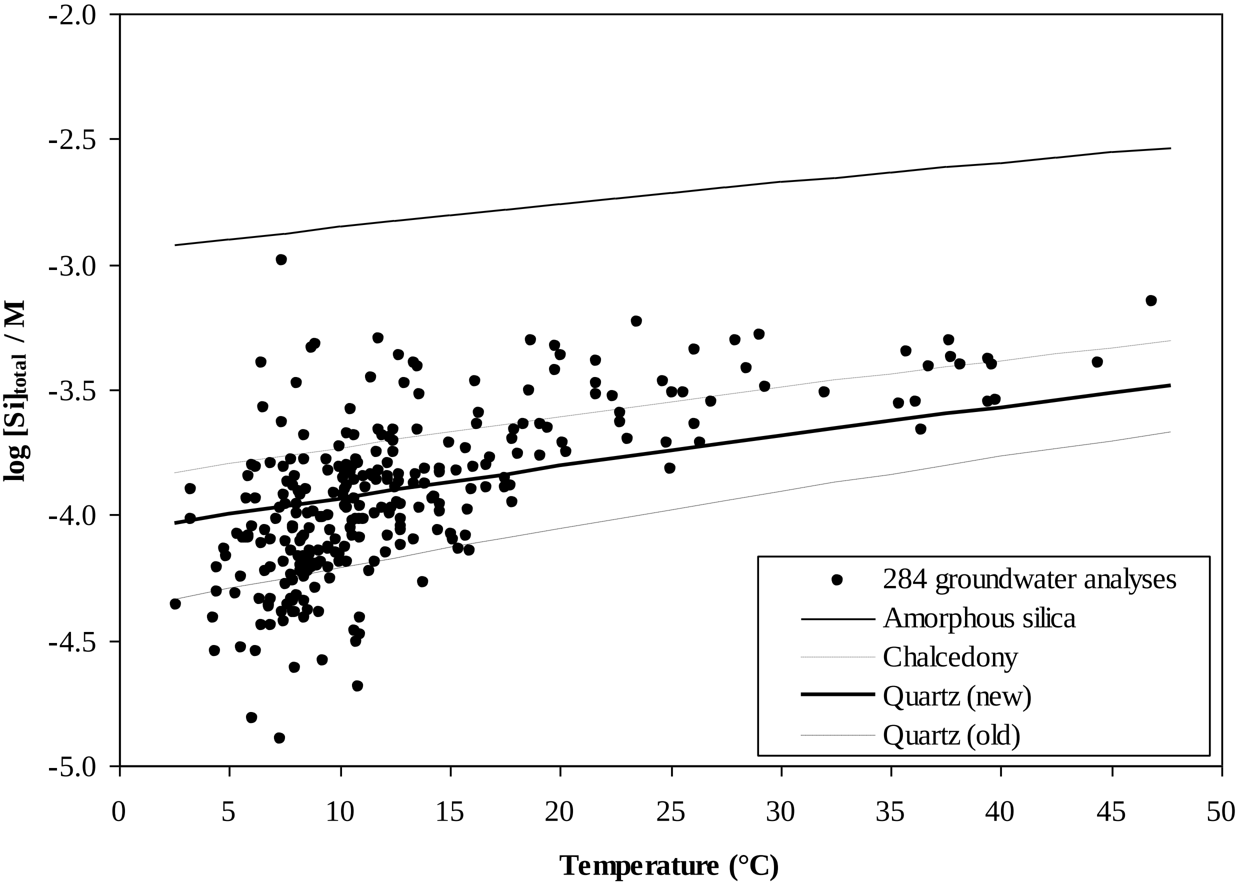

Fig. 8.1: Temperature dependence of total dissolved silica in Swiss groundwaters. The solubility of amorphous silica and quartz (new) is calculated with the integrated van't Hoff equation using $\log_{10}K_s°$ and $\Delta_rH_m°$ selected in this review. Note that the four term temperature functions of GUNNARSSON & ARNORSSON (2000) give identical results in this temperature range. The solubility of chalcedony and quartz (old) is calculated with the temperature function given by NORDSTROM et al. (1990).

GUNNARSSON & ARNORSSON (2000) discussed and simultaneously fitted the new data of RIMSTIDT (1997), their own experiments on amorphous silica, and all reliable published solubility data of quartz and amorphous silica in pure water in the temperature range 0 to 350°C at 1 bar below 100°C and at P_{sat} at higher temperatures. Their results are:

$$\log_{10}K_s\,(\text{Quartz, cr}) = -34.188 + 197.47 / T - 5.851 \cdot 10^{-6}\,T^2 + 12.245 \log_{10}T$$

$$\log_{10}K_s\,(\text{Silica, am}) = -8.476 - 485.24 / T - 2.268 \cdot 10^{-6}\,T^2 + 3.068 \log_{10}T$$

which results in:

$$\log_{10}K_s°(\text{Quartz, cr, 298.15 K}) = -(3.746 \pm 0.087)$$

$$\log_{10}K_s°(\text{Silica, am, 298.15 K}) = -(2.714 \pm 0.044)$$

$$\Delta_r H_m°(\text{Quartz, cr, 298.15 K}) = (20.637 \pm 0.41) \ \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m°(\text{Silica, am, 298.15 K}) = (14.594 \pm 0.21) \ \text{kJ} \cdot \text{mol}^{-1}$$

No uncertainty estimates are given by GUNNARSSON & ARNORSSON (2000) except the information that the residuals of the data points used for the regressions are all within 500 J / mole for amorphous silica whereas the quartz residuals are within 1000 J / mole. As the quartz data fitted by GUNNARSSON & ARNORSSON (2000) are essentially the same as the ones used by RIMSTIDT (1997) we used the uncertainty estimates of RIMSTIDT (1997) for the quartz parameters and half the quartz uncertainties as uncertainty estimates for amorphous silica parameters.

The solubility of amorphous silica has not changed at T < 200°C compared with earlier results. However, the solubility of quartz is significantly higher than given in most previous compilations, e.g. by NORDSTROM et al. (1990). The old quartz solubility constant at 25°C was based on rather dubious data not in accord with most data measured at other temperatures (RIMSTIDT 1997).

Based on the old quartz solubility almost all groundwaters had been calculated to be significantly supersaturated with respect to quartz (Figs. 8.1 and 8.2). In an attempt to remedy this disturbing situation the solubility of chalcedony has been widely used in speciation calculations. However, the chalcedony data are based on measurements of a few ill-defined samples, as discussed by RIMSTIDT (1997). Using the new quartz solubility in speciation calculations the situation has changed, most groundwaters are now saturated or only slightly supersaturated with respect to quartz (Figs. 8.1 and 8.2). Hence, the dubious value of chalcedony solubility has been removed from the data base.

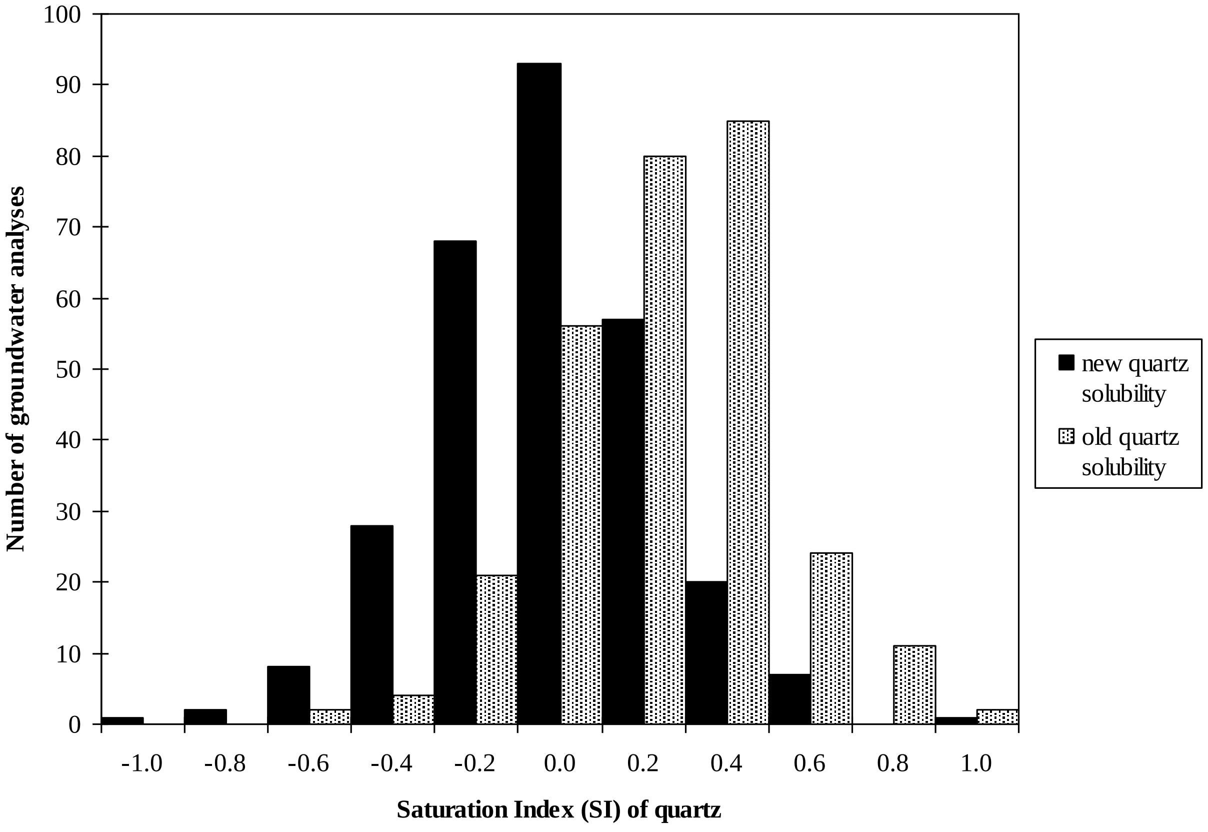

Fig. 8.2: Histogram of quartz saturation indices calculated for 284 Swiss groundwater analyses shown in Fig. 8.1.

8.3.2 Aqueous silica species

In aqueous media, silicon exists exclusively in the +IV oxidation state. The relevant species in solutions at pH < 9 is $Si(OH)_4(aq)$.

The thermodynamic properties of this species are based on

- CODATA (COX et al. 1989) values for Si(cr) (see 8.1), $SiO_2(cr)$ (see 8.2), $H_2O(l)$, $O_2(g)$, $H_2(g)$ with their given uncertainties
- and the temperature dependent solubility of quartz, $SiO_2(cr) + 2\ H_2O(l) \Leftrightarrow Si(OH)_4(aq)$, expressed as $\log_{10}K_s(T) = A + B / T - C \cdot T^2 + D \cdot \log_{10}T$ with uncertainty estimates as discussed above (see 8.3.1).

They are calculated as follows ($R = 8.314510\ J \cdot K^{-1} \cdot mol^{-1}$ and $T^o = 298.15$ K):

$$\log_{10}K_s(T^\circ) = -(3.74634 \pm 0.08715)$$

$$\Delta_r G_m^\circ = -R \cdot T^o \cdot \ln(10) \cdot \log_{10}K_s(T^o) = (21.3843 \pm 0.4975)\ kJ \cdot mol^{-1}$$

$$\Delta_r H_m^\circ = R \cdot (T^o)^2 \cdot \ln(10) \cdot \partial \log_{10}K_s(T)/\partial T$$

$$= R \cdot (-\ln(10) \cdot B + 2 \cdot \ln(10) \cdot C \cdot (T^o)^3 + D \cdot T^o) = (20.6368 \pm 0.4124)\ kJ \cdot mol^{-1}$$

$$\Delta_r S_m^\circ = (\Delta_r H_m^\circ - \Delta_r G_m^\circ) / T^o \cdot 1000 = -(2.5071 \pm 2.1672)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$\Delta_r C_{p,m}^\circ = \partial \Delta_r H_m(T)/\partial T = R\ (6 \cdot \log_e 10 \cdot C \cdot (T^o)^2 + D) \cdot 1000 = 42.0659\ J \cdot K^{-1} \cdot mol^{-1}$$

$$\Delta_f G_m^\circ(Si(OH)_4(aq)) = \Delta_r G_m^\circ + \Delta_f G_m^\circ(\text{Quartz}) + 2 \cdot \Delta_f G_m^\circ(H_2O(l))$$

$$= (21.384 \pm 0.498) - (856.287 \pm 1.002) - 2 \cdot (237.140 \pm 0.041) = -(1309.183 \pm 1.120)\ kJ \cdot mol^{-1}$$

$$\Delta_f H_m^\circ(Si(OH)_4(aq)) = \Delta_r H_m^\circ + \Delta_f H_m^\circ(\text{Quartz}) + 2 \cdot \Delta_f H_m^\circ(H_2O(l))$$

$$= (20.637 \pm 0.412) - (910.700 \pm 1.000) - 2 \cdot (285.830 \pm 0.040) = -(1461.723 \pm 1.082)\ kJ \cdot mol^{-1}$$

$$\Delta_f S_m^\circ(Si(OH)_4(aq)) = \Delta_r S_m^\circ + \Delta_f S_m^\circ(\text{Quartz}) + 2 \cdot \Delta_f S_m^\circ(H_2O(l))$$

$$= -(2.507 \pm 2.167) - (182.502 \pm 0.200) - 2 \cdot (163.307 \pm 0.030) = -(511.623 \pm 2.177)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$S_m^\circ(Si(OH)_4(aq)) = \Delta_f S_m^\circ(Si(OH)_4(aq)) + S_m^\circ(Si(cr)) + 2 \cdot S_m^\circ(O_2(g)) + 2 \cdot S_m^\circ(H_2(g))$$

$$= -(511.623 \pm 2.177) + (18.810 \pm 0.080) + 2 \cdot (205.152 \pm 0.005) + 2 \cdot (130.680 \pm 0.003)$$

$$= (178.851 \pm 2.178)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$\Delta_f C_{p,m}^\circ(Si(OH)_4(aq)) = \Delta_r C_{p,m}^\circ + \Delta_f C_{p,m}^\circ(\text{Quartz}) + 2 \cdot \Delta_f C_{p,m}^\circ(H_2O(l))$$

$$= 42.066 - 4.565 + 2 \cdot 31.826 = 101.153\ J \cdot K^{-1} \cdot mol^{-1}$$

$$C_{p,m}^\circ(Si(OH)_4(aq)) = \Delta_f C_{p,m}^\circ(Si(OH)_4(aq)) + C_{p,m}^\circ(Si(cr)) + 2 \cdot C_{p,m}^\circ(O_2(g)) + 2 \cdot C_{p,m}^\circ(H_2(g))$$

$$= 101.153 + 19.789 + 2 \cdot 29.378 + 2 \cdot 28.836 = 237.370\ J \cdot K^{-1} \cdot mol^{-1}$$

In ordinary groundwater the species $Si(OH)_4(aq)$ predominates. In alkaline waters a deprotonated species gains importance and at very high pH a second deprotonation step is observed. The thermodynamic data are taken from NEA auxiliary data (GRENTHE et al. 1992):

$Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+$ $\log_{10}\beta_1° = -9.81 \pm 0.02$ $\Delta_r H_m° = 25.6 \pm 2.0 \text{ kJ} \cdot \text{mol}^{-1}$

$Si(OH)_4(aq) \Leftrightarrow SiO_2(OH)_2^{2-} + 2\,H^+$ $\log_{10}\beta_2° = -23.14 \pm 0.09$ $\Delta_r H_m° = 75 \pm 15 \text{ kJ} \cdot \text{mol}^{-1}$

Both $\log_{10}\beta°$ values result from extrapolations to $I = 0$ of experimental data in NaCl media using SIT. From the slopes of these extrapolations GRENTHE et al. (1992) obtained $\Delta\varepsilon = 0.04 \pm 0.03 \text{ kg} \cdot \text{mol}^{-1}$ and $0.14 \pm 0.07 \text{ kg} \cdot \text{mol}^{-1}$, respectively. Assuming $\varepsilon(Si(OH)_4(aq), NaCl) = 0$ GRENTHE et al. (1992) derived $\varepsilon(SiO(OH)_3^-, Na^+) = -0.08 \pm 0.03 \text{ kg} \cdot \text{mol}^{-1}$ and $\varepsilon(SiO_2(OH)_2^{2-}, Na^+) = -0.10 \pm 0.07 \text{ kg} \cdot \text{mol}^{-1}$ and commented the results as follows: "The first value is more negative than would be expected from comparison with other ion interaction coefficients for species of the same charge and similar size."

However, measurements of the solubility of amorphous silica in 1 and 3 M NaCl (ZARUBIN & NEMKINA 1990) indicate that the assumption $\varepsilon(Si(OH)_4(aq), NaCl) = 0$ is not valid.

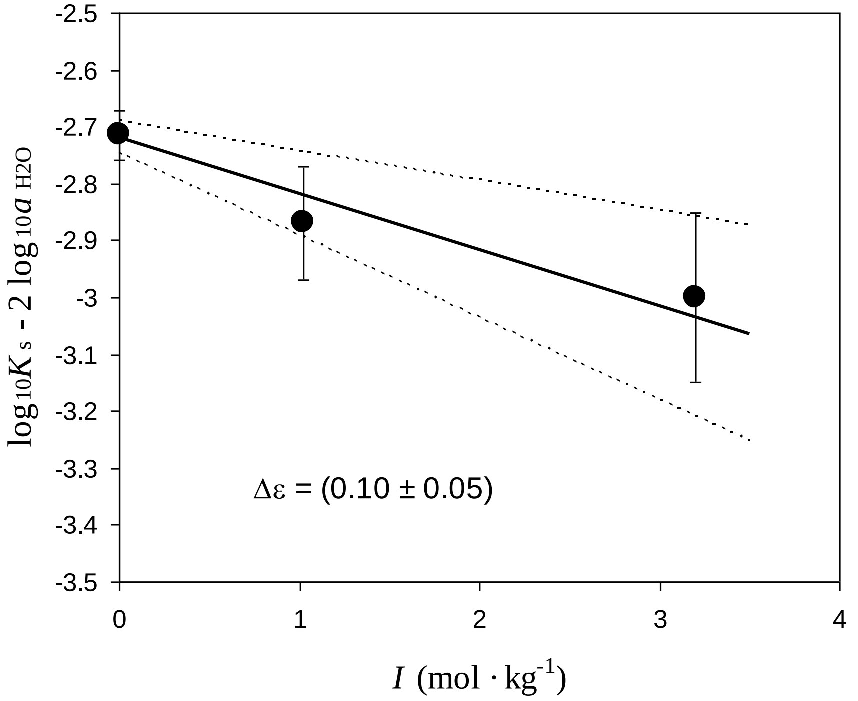

Fig. 8.3: Evaluation of the ion interaction coefficient of $Si(OH)_4(aq)$ in NaCl media using solubility data of amorphous silica of ZARUBIN & NEMKINA (1990) (1 and 3 M NaCl) and GUNNARSSON & ARNORSSON (2000) ($I = 0$).

Table 8.1: Data for the reaction $SiO_2(am) + 2\,H_2O(l) \Leftrightarrow Si(OH)_4(aq)$ in NaCl media.

I (M)	I (m)	$\log_{10}K_s$ (M)	± (est.)	$\log_{10}K_s$ (m)	$\log_{10}K_s$ (m) – 2 $\log_{10} a_{H2O}$	Reference
0	0	-2.714	0.044	-2.714	-2.714	GUNNARSSON & ARNORSSON (2000)
1	1.02	-2.88	0.10	-2.898	-2.869	ZARUBIN & NEMKINA (1990)
3	3.20	-3.05	0.15	-3.106	-3.000	ZARUBIN & NEMKINA (1990)

For the reaction

$$SiO_2(am) + 2\,H_2O(l) \Leftrightarrow Si(OH)_4(aq)$$

the solubility data of ZARUBIN & NEMKINA (1990) and GUNNARSSON & ARNORSSON (2000) were used to evaluate the SIT interaction coefficient of $Si(OH)_4(aq)$ according to the equation

$$\log_{10}K_s - 2\log_{10}a_{H2O} = \log_{10}K_s^\circ - \Delta\varepsilon \cdot I\,(m).$$

The values of $\log_{10}K_s$ (M) in 1 and 3 M NaCl were estimated from total dissolved silica measured at pH 8.5 (ZARUBIN & NEMKINA 1990) assuming that about 10% of dissolved silica is $SiO(OH)_3^-$ in that pH range. The values given in Table 8.1 are numerically identical with $[Si(OH)_4(aq)]$ values calculated at pH < 7 by extrapolating a polynomial fit of experimental data in the range 8.3 < pH < 10.2 given by ZARUBIN & NEMKINA (1990).

Rather large uncertainties were assigned to the $\log_{10}K_s$ (M) values in 1 and 3 M NaCl because of the mentioned estimation and extrapolation procedures and the small experimental data set they are based on.

The $\log_{10}K_s$ value at $I = 0$ from GUNNARSSON & ARNORSSON (2000) is more precise than the other two values (Table 8.1) and essentially acts as a fixed value in the SIT regression procedure. Hence, the only new result of the weighted linear regression (Fig. 8.3) is the slope $\Delta\varepsilon = \varepsilon(Si(OH)_4(aq), NaCl) = 0.10 \pm 0.05$ kg · mol^{-1}. Using this value the SIT interaction coefficients of $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$ were re-evaluated resulting in:

$$\varepsilon(Si(OH)_4(aq), NaCl) = 0.10 \pm 0.05\ kg \cdot mol^{-1}$$

$$\varepsilon(SiO(OH)_3^-, Na^+) = 0.02 \pm 0.05\ kg \cdot mol^{-1}$$

$$\varepsilon(SiO_2(OH)_2^{2-}, Na^+) = 0.00 \pm 0.08\ kg \cdot mol^{-1}$$

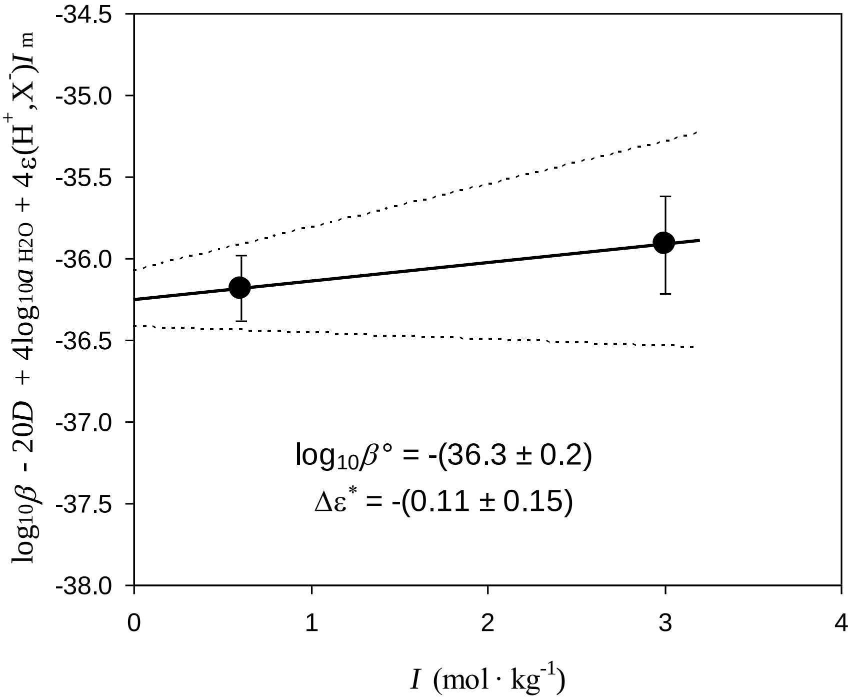

Fig. 8.4: Extrapolation to $I = 0$ of experimental data for the formation of $Si_4O_8(OH)_4^{4-}$ using SIT. The data are taken from LAGERSTRÖM (1959) (3 m $NaClO_4$) and SJÖBERG et al. (1985). (0.6 M NaCl).

In the pH range above 10.5, and 10 millimolar and higher concentrations of dissolved silica, polymeric silicate species predominate.

In the first reliable potentiometric study of this system published half a century ago (LAGERSTRÖM 1959) the results were interpreted in terms of dimeric and tetrameric silicate species, where $Si_4O_8(OH)_4^{4-}$ was the dominating species at pH > 11.

Stability constants for six polymeric species, i.e two dimers, two trimers, and two tetramers have been reported and accepted by NEA as auxiliary data (GRENTHE et al. 1992). The NEA data selection is based on the seminal paper of SJÖBERG et al. (1985) who did a combined potentiometric and ^{29}Si NMR study. SJÖBERG et al. (1985) conclude that "within the concentration ranges studied, the main polysilicate complex is tetrameric." In the pH range 11.0 – 12.2 "the prevailing species are the tetramer and the monomer $SiO(OH)_3^-$."

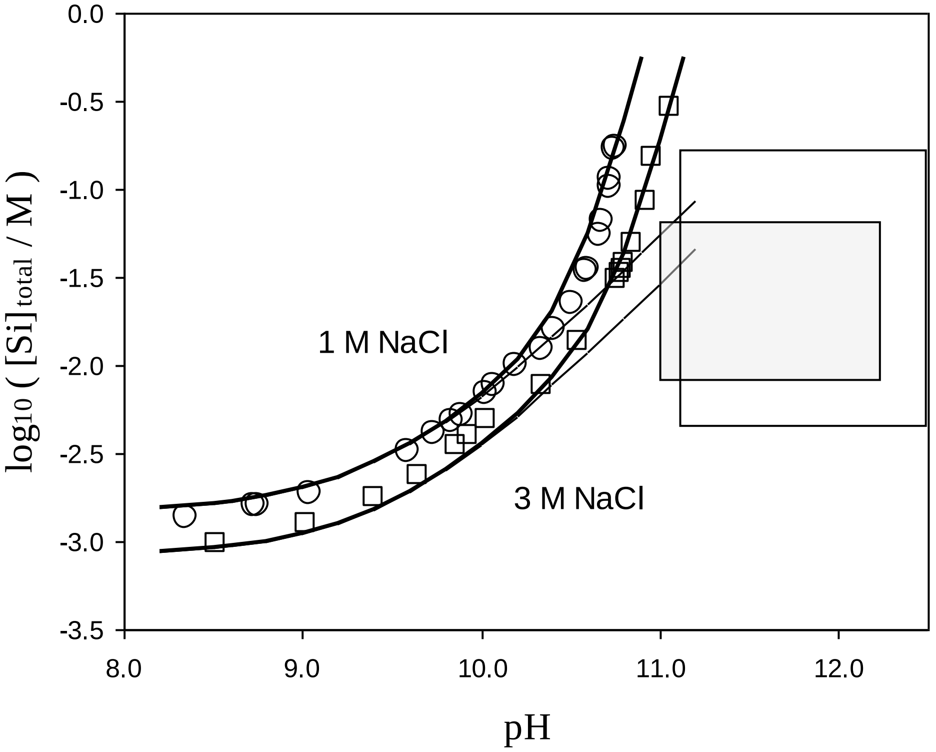

Fig. 8.5: Solubility of SiO_2(am) in NaCl media. Experimental data taken from ZARUBIN & NEMKINA (1990), 1 M NaCl: circles, 3 M NaCl: squares. Thin solid lines: Calculated solubility using only the monomeric species $Si(OH)_4$(aq) and $SiO(OH)_3^-$ with stability constants and SIT parameters selected here. Thick solid lines: The tetrameric species $Si_4O_8(OH)_4^{4-}$ is added. White rectangle: Range of experimental study of Lagerström (1959). Grey rectangle: Range of experimental study of SJÖBERG et al. (1985).

Hence, the two equilibrium constants reported for the reaction

$$4\ Si(OH)_4(aq) \Leftrightarrow Si_4O_8(OH)_4^{4-} + 4\ H^+ + 4\ H_2O(l)$$

in 3 m (molal) $NaClO_4$, $\log_{10}\beta = -32.48$ (LAGERSTRÖM 1959) and in 0.6 M NaCl, $\log_{10}\beta = -32.81$ (SJÖBERG et al. 1985) were extrapolated to $I = 0$ using SIT with uncertainties assigned in the present review (Fig. 8.4). Note that the resulting stability constant

$$\log_{10}\beta^\circ = -(36.3 \pm 0.2)$$

is the same as the one selected by GRENTHE et al. (1992). From the slope $\Delta\varepsilon^* = \Delta\varepsilon + 4\ \varepsilon(H^+, X^-) = \varepsilon(Si_4O_8(OH)_4^{4-}, Na^+) - 4\ \varepsilon(Si(OH)_4(aq), NaCl) = -(0.11 \pm 0.15)\ kg \cdot mol^{-1}$ the SIT interaction coefficient for the tetramer was obtained assuming that $\varepsilon(Si(OH)_4(aq), NaCl) = \varepsilon(Si(OH)_4(aq), NaClO_4) = 0.10 \pm 0.04\ kg \cdot mol^{-1}$:

$$\varepsilon(Si_4O_8(OH)_4^{4-}, Na^+) = 0.29 \pm 0.17\ kg \cdot mol^{-1}$$

Using a very simple model comprising only the monomeric species $Si(OH)_4(aq)$ and $SiO(OH)_3^-$ and the tetramer $Si_4O_8(OH)_4^{4-}$ with stability constants and SIT interaction coefficients derived in this review the solubility of $SiO_2(am)$ in NaCl media (ZARUBIN & NEMKINA 1990) is reproduced sufficiently well (Fig. 8.5).

Adding the other polymeric species selected by GRENTHE et al. (1992) to the model with SIT interaction coefficients adjusted in analogy to the new evaluations discussed above does not significantly change the overall picture shown in Fig. 8.5. Depending on the choice of the estimated SIT interaction coefficients the measured silica solubilities are slightly to significantly overestimated. However, as already discussed by SJÖBERG et al. (1985) all these other polymers were found to remain minor species in the entire range of experimental studies indicated in Fig. 8.5.

A more recent paper proposing an aqueous thermodynamic model for polymerised silica species (FELMY et al. 2001) includes nine polymeric silicate species, i.e. two dimers, two trimers, four tetramers and one hexamer. The reasoning for the selection of this set of species is based on new ^{29}Si NMR data, whereas the actual stability constants were fitted to the $SiO_2(am)$ solubility data of ZARUBIN & NEMKINA (1990) using the Pitzer formalism for ionic strength effects. A good fit is reported for the 3 M NaCl data, whereas the model calculations for 1 M NaCl deviate from experimental data at pH > 10.5, increasingly underestimating the measured solubilities with increasing pH.

The effect of the highly charged polymeric silica species on the speciation model strongly depends on the chosen ionic strength correction model and the estimated SIT or Pitzer parameters. On the other hand, dissolved silica concentrations in natural waters seldom exceed 0.1 mol even when contacted with highly basic solutions, because of the precipitation of calcium or other silicate-containing solid phases. Hence, the very simple model used in this review, including only one polymeric species, $Si_4O_8(OH)_4^{4-}$, besides the monomeric species $Si(OH)_4(aq)$, $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$ seems to be sufficient for all practical purposes of environmental modelling.

8.4 Metal silicate compounds and complexes

8.4.1 Calcium and magnesium

8.4.1.1 Aqueous Ca and Mg silicates

The results of potentiometric titrations of $Si(OH)_4(aq)$ in the presence of Ca^{2+} and Mg^{2+} in 1 M $NaClO_4$ up to pH 9 are reported by SANTSCHI & SCHINDLER (1974). In order to avoid the formation of polymeric silicate species as well as the precipitation of amorphous silica, the total ligand concentration did not exceed $2.3 \cdot 10^{-3}$ M. In preliminary experiments it was found that the complexes formed are rather weak. Comparatively high concentrations of both the reacting metal ions and the inert salt were therefore required.

The results of this experimental study are not unambiguous in terms of the speciation model. Two limiting situations are discussed by SANTSCHI & SCHINDLER (1974). Based on chemical arguments, the most probable interpretation of the experimental data could be done in terms of two equilibria:

$$M^{2+} + SiO(OH)_3^- \Leftrightarrow MSiO(OH)_3^+ \qquad (a)$$

$$M^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow MSiO_2(OH)_2(aq) \qquad (b)$$

Values for the stability constants are extrapolated from 1 M $NaClO_4$ to zero ionic strength by the SIT formalism using $\varepsilon(Ca^{2+}, ClO_4^-) = 0.27 \pm 0.03$ kg · mol^{-1} and $\varepsilon(Mg^{2+}, ClO_4^-) = 0.33 \pm 0.03$ kg · mol^{-1} (GRENTHE et al. 1992), and $\varepsilon(SiO(OH)_3^-, Na^+) = 0.02 \pm 0.05$ kg · mol^{-1} and $\varepsilon(SiO_2(OH)_2^{2-}, Na^+) = 0.00 \pm 0.08$ kg · mol^{-1} derived in this review and the following guesses for $\varepsilon(CaSiO(OH)_3^+, ClO_4^-) = 0.3 \pm 0.1$ kg · mol^{-1}, $\varepsilon(MgSiO(OH)_3^+, ClO_4^-) = 0.4 \pm 0.2$ kJ · mol^{-1} and $\varepsilon(MSiO_2(OH)_2(aq), NaClO_4) = 0.2 \pm 0.2$ kg · mol^{-1}. Note that the results presented below depend on these guesses.

Ca	$\log_{10}K°(\text{eq.a}) = 1.2 \pm 0.1$	and	$\log_{10}K°(\text{eq.b}) = 4.6 \pm 0.2$
Mg	$\log_{10}K°(\text{eq.a}) = 1.5 \pm 0.2$	and	$\log_{10}K°(\text{eq.b}) = 5.7 \pm 0.2$

Although the stoichiometry of these complexes and their stability constants have not been explored by other studies we decided to include them in our data base. If these complexes are found to be of crucial importance in some systems, additional experimental studies are recommended.

8.4.1.2 Solid Ca and Mg silicates

Thermodynamic data for the Mg silicate solids chrysotile, sepiolite, and kerolite have been selected by NORDSTROM et al. (1990). We did not explore the thermodynamics of these sheet silicates and decided not to include them in the data base.

Calcium silicate hydrates (CSH) and calcium aluminium silicate hydrates (CASH) are important solid phases in cementitious systems. However, these phases form solid solutions (KULIK & KERSTEN 2001) and their appropriate thermodynamic representation is the subject of ongoing research (e.g. LOTHENBACH et al. 2008; www.empa.ch/cemdata/).

8.4.2 Nickel

8.4.2.1 Aqueous nickel silicates

The complexation behaviour of Ni^{2+} with $Si(OH)_4(aq)$ has been studied as a function of ionic strength from 0.20 to 1.00 M ($NaClO_4$) at pH 4.55 and 25°C by a solvent extraction technique (PATHAK & CHOPPIN 2006a). The authors concluded that Ni^{2+} forms a 1:1 complex, $NiSiO(OH)_3^+$, as the predominant species and interpreted their data in terms of the equilibrium

$$Ni^{2+} + SiO(OH)_3^- \Leftrightarrow NiSiO(OH)_3^+$$

The equilibrium constants $\log_{10}\beta$ derived at different ionic strengths have been fitted by PATHAK & CHOPPIN (2006a) with an extended Debye-Hückel expression similar to the SIT formalism and the authors obtained a value of $\log_{10}\beta° = 6.34 \pm 0.03$ at zero ionic strength.

An analogous complexation study of Co^{2+} with $Si(OH)_4(aq)$ using the same method under the same conditions (PATHAK & CHOPPIN 2006b) resulted in $\log_{10}\beta° = 5.61 \pm 0.03$ for $CoSiO(OH)_3^+$.

Re-analyses of the experimental data published by PATHAK & CHOPPIN (2006a, 2006b) in the present review using the SIT formalism (Fig. 8.6) resulted in:

$$\log_{10}\beta° = 6.34 \pm 0.10 \text{ and } \Delta\varepsilon = 0.18 \pm 0.13 \text{ kg} \cdot \text{mol}^{-1} \text{ for } NiSiO(OH)_3^+$$

$$\log_{10}\beta° = 5.62 \pm 0.11 \text{ and } \Delta\varepsilon = 0.30 \pm 0.13 \text{ kg} \cdot \text{mol}^{-1} \text{ for } CoSiO(OH)_3^+$$

Using $\varepsilon(Ni^{2+}, ClO_4^-) = 0.37 \pm 0.03$ kg · mol^{-1} (GAMSJÄGER et al. 2005), $\varepsilon(Co^{2+}, ClO_4^-) = 0.34 \pm 0.03$ kg · mol^{-1} (GRENTHE et al. 1992) and $\varepsilon(SiO(OH)_3^-, Na^+) = 0.02 \pm 0.05$ kg · mol^{-1} derived in this review we calculate

$$\varepsilon(NiSiO(OH)_3^+, ClO_4^-) = 0.57 \pm 0.15 \text{ kg} \cdot \text{mol}^{-1}$$

$$\varepsilon(CoSiO(OH)_3^+, ClO_4^-) = 0.66 \pm 0.15 \text{ kg} \cdot \text{mol}^{-1}$$

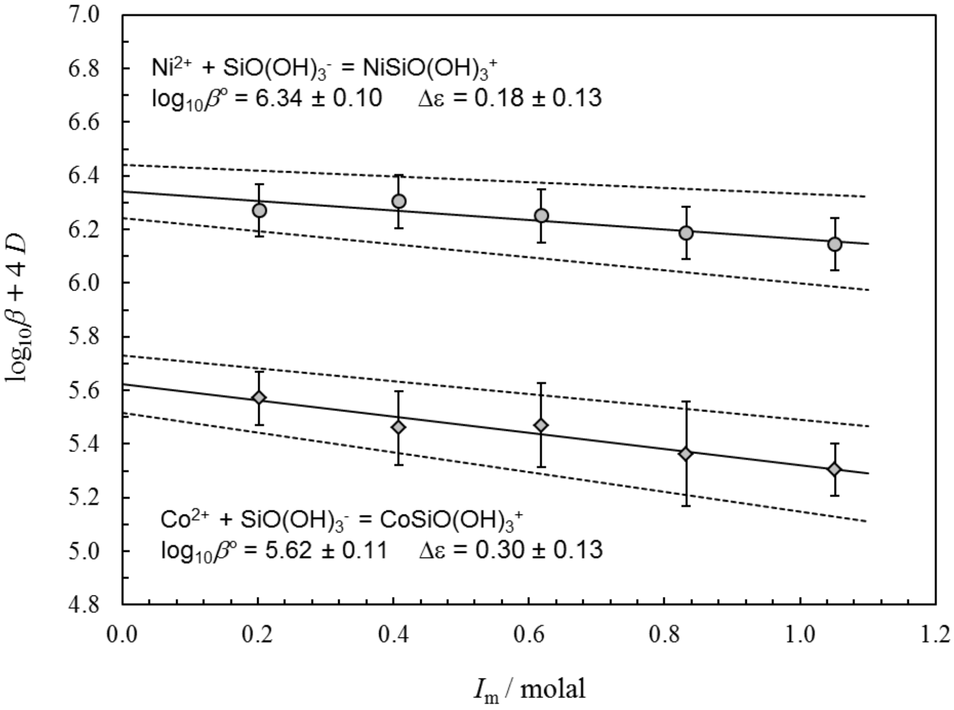

Fig. 8.6: Extrapolation to $I = 0$ of experimental data for the formation of $NiSiO(OH)_3^+$ and $CoSiO(OH)_3^+$ using SIT. The data are taken from PATHAK & CHOPPIN (2006a, 2006b).

The equilibrium constants reported by PATHAK & CHOPPIN (2006a, 2006b) are not unreasonable compared with other metal – silicate complexes, but as we have not yet any independent confirmation of these results, the complex $NiSiO(OH)_3^+$ has been included in our data base as "supplemental data" with a value of $\log_{10}\beta° = 6.3$.

8.4.2.2 Solid nickel silicates

Thermodynamic data for Ni_2SiO_4(cr) have been selected by GAMSJÄGER et al. (2005). The thermodynamic data have been derived from heat capacity measurements in the temperature range from 270 to 1570 K and from solution calorimetry in a molten oxide solvent at 965 K. There is no indication that Ni_2SiO_4(cr) forms at ambient conditions and consequently, no solution study in aqueous media is known.

Liebenbergite (Ni_2SiO_4) is an end-member of a complex solid-solution system known as the olivine group of minerals of the general formula X_2SiO_4, where X is a divalent metal cation (Mg, Fe, Mn, Ni, Ca and Co). The pure nickel olivine does not occur naturally; only liebenbergite of an approximate formula $Ni_{1.5}Mg_{0.5}SiO_4$ has been reported (GAMSJÄGER et al. 2005).

We conclude that liebenbergite is of no importance for thermodynamic models at ambient conditions and thus, the thermodynamic data for Ni_2SiO_4(cr) are not included in our data base.

8.4.3 Aluminium

8.4.3.1 Aqueous aluminium silicates

Several studies have been published reporting experimental data on Al silicate complexation

BROWNE & DRISCOLL (1992) applied a fluorescent probe technique to study trace level concentrations of Al(III) (0.3-10 μM) with $[Si(OH)_4]_{tot}$ varying between 0.10 and 0.27 mM at pH 4.0 – 5.5 and 0.01 M ionic strength. At pH 4 – 5 the data were interpreted in terms of the following mononuclear reaction:

$$Al^{3+} + Si(OH)_4(aq) \Leftrightarrow AlSiO(OH)_3^{2+} + H^+$$

They reported $\log_{10}K° = -(1.07 \pm 0.06)$ at infinite dilution. At pH 5.5 the authors inferred in addition two dinuclear Al-Si stoichiometries from the experimental data.

FARMER & LUMSDON (1994) measured the shift in $\log[H^+]$ in Al(III) solutions with and without added silicic acid in 0.1 M $NaClO_4$. In this study, more concentrated solutions were used ($[Al]_{tot}$ = 0.5-2.0 mM and $[Si(OH)_4]_{tot}$ =1.33 mM) and the pH range was quite narrow (pH 3.75-4.11). They reported $\log_{10}K° = -(2.50 \pm 0.05)$ at infinite dilution, a value more than one magnitude lower than the one published by BROWNE & DRISCOLL (1992).

POKROVSKI et al. (1996) studied the formation of $AlSiO(OH)_3^{2+}$ by measuring the pH variation of a 0.005 M silicic acid solution as a slightly acidic Al^{3+} solution was added. This allowed a wider concentration range in Al(III) to be studied (3 points with $[Al]_{tot}$ = 0.023, 0.0100 and 0.0160 M). Again a limited pH range was studied (pH = 3.710-3.448) in 0.1 M KCl medium. The reported stability constant at $I = 0$ is $\log_{10}K° = -(2.38 \pm 0.10)$.

SPADINI et al. (2005) studied the Al – Si complexation by potentiometric titrations in 0.6 M NaCl using a hydrogen electrode with OH^- ions being generated coulometrically. The total concentrations were varied within the limits $0.3 < [Si]_{tot} < 2.5$ mM, $0.5 < [Al]_{tot} < 2.6$ mM and $2 \leq -\log[H^+] \leq 4.2$. A complex formation constant $\log_{10}K = -(2.75 \pm 0.1)$ was reported for I = 0.6 M NaCl and 25.0°C.

The data of FARMER & LUMSDON (1994), POKROVSKI et al. (1996) and SPADINI et al. (2005) were used in the present review for a SIT analysis (Fig. 8.7). As can be seen in Fig. 8.7 the data of

BROWNE & DRISCOLL (1992) is far away of all the others and has not been considered in the final SIT analysis. The results are

$$\log_{10}K^\circ = -(2.39 \pm 0.12) \text{ and } \Delta\varepsilon = -(0.61 \pm 0.36).$$

For the equilibrium

$$Al^{3+} + SiO(OH)_3^- \Leftrightarrow AlSiO(OH)_3^{2+}$$

we calculate a stability constant of $\log_{10}\beta^\circ = 7.42 \pm 0.12$ from the above result.

Using $\varepsilon(H^+, Cl^-) = 0.12 \pm 0.01$ kg · mol^{-1} and $\varepsilon(Al^{3+}, Cl^-) = 0.33 \pm 0.02$ kg · mol^{-1} (GRENTHE et al. 1992), and $\varepsilon(Si(OH)_4(aq), NaCl) = 0.10 \pm 0.05$ kg · mol^{-1} derived in this review we calculate

$$\varepsilon(AlSiO(OH)_3^{2+}, Cl^-) = -(0.30 \pm 0.36) \text{ kg} \cdot \text{mol}^{-1}$$

POKROVSKI et al. (1996) studied in addition the temperature dependence of the equilibrium $Al^{3+} + Si(OH)_4(aq) \Leftrightarrow AlSiO(OH)_3^{2+} + H^+$ at 25, 90 and 150°C and found a linear dependence of $\log_{10}K$ on reciprocal temperature, $\log_{10}K = -3473$ K/T + 9.25, which results in $\Delta_rH_m^\circ = 66.6 \pm 3.0$ kJ · mol^{-1}.

This value was later confirmed by measurements at 300°C (SALVI et al. 1998).

Hence, we accept this result and using $\Delta_rH_m^\circ = 25.6 \pm 2.0$ kJ · mol^{-1} for $Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+$ we calculate $\Delta_rH_m^\circ = 41.0 \pm 3.0$ kJ · mol^{-1} for $Al^{3+} + SiO(OH)_3^- \Leftrightarrow AlSiO(OH)_3^{2+}$.

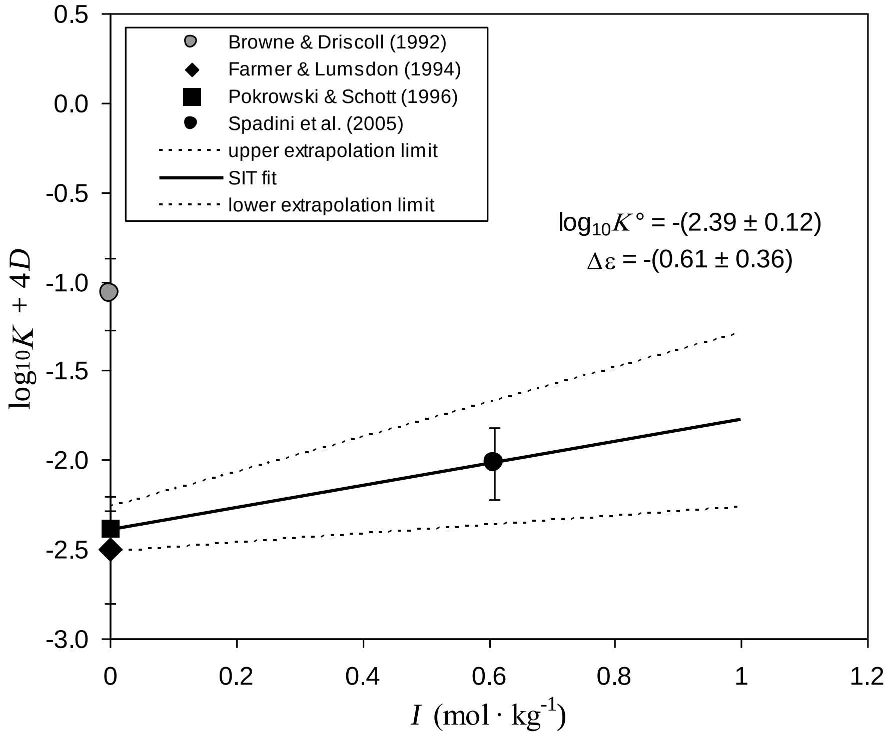

Fig. 8.7: SIT analysis of the equilibrium $Al^{3+} + Si(OH)_4(aq) \Leftrightarrow AlSiO(OH)_3^{2+} + H^+$. The data of BROWNE & DRISCOLL (1992) has not been included in the regression analysis.

All the studies discussed so far have been carried out in the acidic pH range $3.5 < pH < 5.5$.

The first study of aluminium silicate complexation by potentiometric titrations in the alkaline region, $9 < pH < 13$, at 25 and 75°C was mentioned by POKROVSKI et al. (1998). In this extended abstract the authors claim to be able to interpret their (not yet published) experimental data in terms of the equilibrium

$$Al(OH)_4^- + Si(OH)_4(aq) \Leftrightarrow Al(OH)_3SiO(OH)_3^- + H_2O(l)$$

with $\log_{10}K° = 3.64 \pm 0.20$.

The same group also claims to have found this complex to be the dominating aqueous aluminium-silicate species in the neutral to basic pH region at 300°C (SALVI et al. 1998).

Hence, we decided to include this complex in the previous version of our data base (TDB Version 01/01) as guidelines for modellers, or as “supplemental data” as this data category is named in the present version.

To the best of our knowledge, the potentiometric data and their interpretation mentioned in the extended abstract (POKROVSKI et al. 1998) have never been published as a full paper.

However, shortly after the finalisation of TDB Version 01/01 the same group published a Raman spectroscopic study of aluminium-silicate complexes at 20°C in basic solutions, $12.4 < pH < 14.3$ (GOUT et al. 2000).

The measurements in “ultra basic solutions” at pH about 14 have been interpreted by GOUT et al. (2000) in terms of the equilibrium

$$Al(OH)_4^- + SiO_2(OH)_2^{2-} \Leftrightarrow SiAlO_3(OH)_4^{3-} + H_2O(l)$$

The value of the apparent equilibrium constant for this reaction (for $I = 1.2$ M) was calculated by the authors as $K = 3.4 \pm 0.2$. We did not make any attempt to extrapolate this value to zero ionic strength, but included the value $\log_{10}K = 0.53$ as “supplemental data” in the present version of our data base.

In their section “basic pH (≈ 12.5)” GOUT et al. (2000) write that “calculations using the equilibrium constant of the reaction derived above imply that the complex $SiAlO_3(OH)_4^{3-}$ is minor in these solutions and, therefore, cannot account for the observed amounts of complexes Al and Si. Thus, the important quantities of complexed Al and Si at pH 12.5 are due to the formation of other complexes, between $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$ and $Al(OH)_4^-$. However, it was impossible to derive the stoichiometry and charge of these complexes from our measurements, because the amount of complexed and free Al and Si do not show any regular dependence on component concentrations. This strongly suggests the formation of several, likely polymerized, Al – Si species. This conclusion is also in agreement with our potentiometric and NMR measurements which demonstrated the existence of different polynuclear Al – Si complexes at $m_{(Al,Si)} > 0.006m$ (POKROVSKI et al. 1998). Complementary studies are necessary to determine the nature of these complexes and their stabilities.”

Although GOUT et al. (2000) never mention it explicitly, in their statement cited above they implicitly retract the complex $Al(OH)_3SiO(OH)_3^-$ and its associated stability constant $\log_{10}K° = 3.64 \pm 0.20$ published in their extended abstract (POKROVSKI et al. 1998). Consequently, we removed this complex and its stability constant from our data base.

We are left with some sobering statements concerning Al – Si complexation: The complex $AlSiO(OH)_3^{2+}$ is fairly well established in acidic solutions, but as it predominates at pH < 5 it is of little importance for groundwater modelling. The complex $SiAlO_3(OH)_4^{3-}$ was identified in "ultra basic solutions" at pH about 14; it may hardly be of any importance in environmental modelling. In neutral to basic solutions there is qualitative evidence of polynuclear Al – Si complexes but no quantitative data are available.

8.4.3.2 Solid aluminium silicates

Thermodynamic data are available for the mineral kaolinite ($Al_2Si_2O_5(OH)_4$) (NORDSTROM et al. 1990):

$$Al_2Si_2O_5(OH)_4(s) + 6\,H^+ \Leftrightarrow 2\,Al^{3+} + 2\,Si(OH)_4(aq) + H_2O(l)$$

$$\log_{10}{}^*K_{s,0}^\circ\text{ (Kaolinite, cr, 298.15 K)} = 7.435$$

$$\Delta_r H_m^\circ\text{(Kaolinite, cr, 298.15 K)} = -35.3\text{ kcal}\cdot\text{mol}^{-1} \rightarrow -147.7\text{ kJ}\cdot\text{mol}^{-1}$$

The stability constant for kaolinite is derived from measured solubilities (MAY et al. 1986) and thus, the kaolinite data were included in our data base.

Aluminium silicate minerals, especially clay minerals, are of great importance in determining the chemistry of water in many rock types. A number of characteristics of these minerals renders excessively difficult the collection of reliable thermodynamic data and their proper use in geochemical modelling.

One characteristic is that many react so slowly at laboratory and normal groundwater temperatures that frequently it is not possible to attain equilibrium in reasonable experimental times. Thus, high temperature data extrapolated to lower temperatures are often used for groundwater modelling.

Another characteristic is that many clay minerals have highly variable chemical compositions and they are never found in nature in bigger crystals than the nanometre scale. Based on these facts and on thermodynamic reasoning LIPPMANN (1982) concluded that "virtually all clay minerals are more or less metastable or even completely unstable. Nevertheless, they persist through geological times. They owe their existence and their many-varied properties not to thermodynamic equilibrium but to the kinetic inhibitions inherent in ordinary-temperature conditions".

Thirty years later LIPPMANN's (1982) conclusions seem still to be valid and we decided not to include in our data base the many thermodynamic data derived from calorimetric measurements (GAILHANOU et al. 2007, 2009, 2012, 2013).

8.4.4 Iron

Four studies have been published reporting experimental data on Fe(III) silicate complexation: absorbance measurements with a spectrophotometer at *I* = 0.1 M (WEBER & STUMM 1965; PORTER & WEBER 1971), spectrophotometric analyses at *I* = 0.1 M and polarography at *I* = 0.15 M (OLSON & O'MELIA 1973), and determination of amorphous silica solubility in acidified ferric nitrate solutions at *I* < 0.08 M (REARDON 1979). For the equilibrium

$$Fe^{3+} + SiO(OH)_3^- \Leftrightarrow FeSiO(OH)_3^{2+}$$

the following constants are derived for zero ionic strength: $\log_{10}K^\circ = 10.0$ (WEBER & STUMM 1965), 9.5 (PORTER & WEBER 1971), 9.6 and 9.8 from spectrophotometric and polarographic data, respectively (OLSON & O'MELIA 1973), and 9.8 from silica solubility data (REARDON 1979). These constants are in close agreement and an unweighted mean is $\log_{10}K° = 9.7 \pm 0.3$.

Note that all these studies have been carried out at pH < 4. No conclusions can be drawn from these investigations whether bidentate Fe(III) complexes with $SiO_2(OH)_2^{2-}$ form at high pH in analogy with Ca and Mg complexation, or whether a complex of the stoichiometry $Fe(OH)_nSiO(OH)_3^{2-n}$ dominates in neutral and alkaline groundwater in analogy with Al.

No thermodynamic data concerning Fe(II) silicate complexation have been found in the literature.

8.4.5 Europium, Americium and Curium

Silicate complextion of europium, americium and curium often has been studied by the same groups using the same experimental methods and hence, they are discussed together in this section.

JENSEN & CHOPPIN (1996) studied the interaction of Eu(III) with silicic acid in aqueous solutions of 0.1 M ionic strength by solvent extraction. The authors interpreted the results of their solvent extraction study, carried out at pH 4, 6 and 9, in terms of 1:1 and 1:2 complexes according to the equilibrium

$$Eu^{3+} + n\, SiO(OH)_3^- \Leftrightarrow Eu(SiO(OH)_3)_n^{3-n}$$

The following constants are reported (Table 1 in JENSEN & CHOPPIN 1996): at pH 4 and 0.1 M NaCl $\log_{10}\beta_1 = 7.16 \pm 0.34$, at pH 6 and 0.1 M $NaClO_4$ $\log_{10}\beta_1 = 7.36 \pm 0.15$ and at pH 9 and 0.1 M $NaClO_4$ $\log_{10}\beta_1 = 7.25 \pm 0.13$ and $\log_{10}\beta_2 = 11.7 \pm 0.4$. Extrapolating these values to zero ionic strength gives: $\log_{10}\beta_1° = 7.82 \pm 0.34$, 8.02 ± 0.15 and 7.91 ± 0.15, and $\log_{10}\beta_2° = 12.8 \pm 0.4$.

For the complex $EuSiO(OH)_3^{2+}$ a mean value $\log_{10}\beta_1° = 7.92 \pm 0.20$ is obtained from the reported results.

The existence of the complex $Eu(SiO(OH)_3)_2^+$ at pH 9 could not be confirmed by other studies carried out in the neutral and basic pH range (STEINLE et al. 1997; PANAK et al. 2005; WANG et al. 2005). Hence, this complex and its stability constant has been removed in the current version of our database.

STEINLE et al. (1997) studied the interaction of Cm(III) with orthosilicic acid in aqueous solutions of ionic strength 0.1 M $NaClO_4$ by time-resolved laser fluorescence spectroscopy (TRLFS). Data obtained in the pH range 5.0 – 5.5 were interpreted in terms of the equilibrium

$$Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$$

with $\log_{10}\beta_1 = 7.4 \pm 0.2$ (extrapolated to zero ionic strength: $\log_{10}\beta_1° = 8.1 \pm 0.2$).

Above pH 5.5 a further Cm species was detected which the authors interpreted as probably due to sorption of Cm to a polymeric silicate species.

WADSAK et al. (2000) reported experimental data on Am(III) silicate complexation. The authors interpreted the results of their solvent extraction study, carried out at pH 3.0 – 3.8 in 0.1 M $NaClO_4$ solutions, in terms of a 1:1 complex according to the equilibrium

$$Am^{3+} + SiO(OH)_3^- \Leftrightarrow AmSiO(OH)_3^{2+}$$

The following constant has been reported for zero ionic strength: $\log_{10}\beta_1° = 8.20 \pm 0.04$ (1 σ).

PANAK et al. (2005) investigated the complexation of Cm(III) with aqueous silicic acid in the pH range 1.5 – 9.0 in 0.03 M NaCl by time-resolved laser fluorescence spectroscopy (TRLFS). The silicate concentration was varied from under- to over-saturation with respect to the solubility of amorphous silica. Three different complexation products were observed: Cm-silicate(I), Cm-silicate(II) and Cm-silicate(III).

Cm-silicate(I) appears in both, under- and over-saturation of silicic acid only as a minor fraction at pH 4 – 7 and could be interpreted in terms of the equilibrium

$$Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$$

with $\log_{10}\beta_1 = 7.32 \pm 0.08$ (extrapolated to zero ionic strength: $\log_{10}\beta_1^\circ = 7.74 \pm 0.08$). Considering its assigned uncertainty, this value is quite different from the value reported earlier from the same lab using the same experimental method (STEINLE et al. 1997). This discrepancy is not discussed and although two co-authors are identical, the earlier publication of STEINLE et al. (1997) is not even mentioned by PANAK et al. (2005).

Cm-silicate(II) and Cm-silicate(III) were found to be colloidal. Cm-silicate(II) shows spectroscopic characteristics varying with the experimental conditions, whereas Cm-silicate(III), which formed exclusively with polysilicic acid, remained consistent and stable. The existence of a species $Cm(SiO(OH)_3)_2^+$, in analogy to the species $Eu(SiO(OH)_3)_2^+$ proposed by JENSEN & CHOPPIN (1996), could not be confirmed.

WANG et al. (2005) studied the complexation of Cm(III) and Eu(III) with dissolved silica by solubility measurement and time-resolved laser fluorescence spectroscopy (TRLFS) in basic solutions (pH 7.5 – 12) over a range of total silica concentrations at different electrolyte ($NaNO_3$) concentrations. The authors conclude: “The increase in solubility of the $Eu(OH)_3$ / silica precipitates at high pH values indicated the possible formation of strong Eu-silicate aqueous complexes. The presence of these strong complexes was confirmed by TRLFS measurements of both Eu(III) and Cm(III) silicate solutions. The complexes present at the high pH values appeared to be fully coordinated with silicates and possibly nitrates in concentrated $NaNO_3$. The changes in fluorescence lifetime, fluorescence intensity and the concentrations of the monomeric and polymeric silicates suggested that the Cm(III) complex(es) in basic solution mostly involve polysilicates.”

PATHAK & CHOPPIN (2006c) measured the complex formation of silicate with U(VI), Cm(III) and Eu(III) in the temperature range 5 – 45°C in an aqueous medium of 0.20 M ($NaClO_4$) ionic strength and pH ≈ 3.5 by solvent extraction. Enthalpies of reaction were derived from the temperature variation of the obtained stability constants.

The stability constants at 25°C and 0.2 M $NaClO_4$ reported for the equilibria

$$Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$$

$$Eu^{3+} + SiO(OH)_3^- \Leftrightarrow EuSiO(OH)_3^{2+}$$

are $\log_{10}\beta_1 = 7.83 \pm 0.02$ and 7.79 ± 0.01, respectively (Table 1 in PATHAK & CHOPPIN 2006c). A re-evaluation in the present review of the experimental data given in graphical form in Figs. 2 and 3 of PATHAK & CHOPPIN (2006c) resulted in $\log_{10}\beta_1 = 7.82 \pm 0.02$ and 7.79 ± 0.02 (1 σ), respectively. Considering the errors induced by digitising graphical data the results are identical with the values published by PATHAK & CHOPPIN (2006c). Extrapolation of these values to zero ionic strength using the SIT equation with the Debye-Hückel term only yielded $\log_{10}\beta_1^\circ = 8.64 \pm 0.04$ and 8.61 ± 0.04 (2 σ), respectively.

In their Table 2 PATHAK & CHOPPIN (2006c) reported enthalpies of reaction for Cm(III) and Eu(III) as $\Delta_r H_m = 15.8 \pm 2.0$ and $14.5 \pm 1.0\ \mathrm{kJ \cdot mol^{-1}}$, respectively. A re-evaluation in the present review by least squares fits of the experimental data given in Table 1 of PATHAK & CHOPPIN (2006c) resulted in $\log_{10}\beta_1$ (25°C) = 7.86 ± 0.02 kJ · mol^{-1} and $\Delta_r H_m$ = 15.8 ± 1.9 kJ · mol^{-1} (1 σ), for Cm(III) and $\log_{10}\beta_1$ (25°C) = 7.78 ± 0.01 and $\Delta_r H_m$ = 14.1 ± 0.8 kJ · mol^{-1} (1 σ) for Eu(III). Within the statistical uncertainties these re-evaluated values are identical with the values published by PATHAK & CHOPPIN (2006c).

Hence, the values $\Delta_r H_m$ = 15.8 ± 4.0 kJ · mol^{-1} (2 σ) for Cm(III) and $\Delta_r H_m$ = 14.5 ± 2.0 kJ · mol^{-1} (2 σ) for Eu(III) are included as supplemental data in our database. In addition, an estimate $\Delta_r H_m \approx 15$ kJ · mol^{-1} for Am(III), Pu(III) and Np(III) is added as supplemental data to our database.

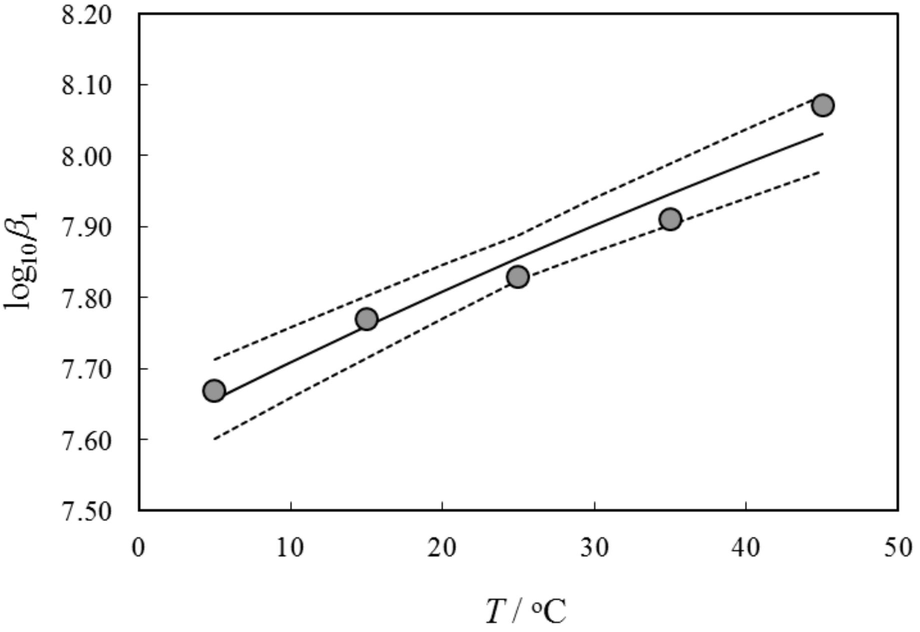

Fig. 8.8: Temperature dependence of the stability constant for the equilibrium $Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$. Data taken from Table 1 in PATHAK & CHOPPIN (2006c). An unweighted least squares fit gives: $\log_{10}\beta_1$ (25°C) = 7.86 ± 0.02 and $\Delta_r H_m$ = 15.8 ± 1.9 kJ · mol^{-1}. The dotted lines are the 1 σ standard deviations extrapolated from 25°C to lower and higher temperatures.

THAKUR et al. (2007) measured the complex formation of silicate with Am(III), Cm(III) and Eu(III) at pH 3.5 and in ionic strengths of 0.20 – 1.00 M ($NaClO_4$) by the solvent extraction method. Hence, they used the same experimental set-up as PATHAK & CHOPPIN (2006c) in order to study the same equilibria. Instead of temperature variation at constant ionic strength (PATHAK & CHOPPIN 2006c) now the ionic strength was varied at constant temperature.

The authors reported for I = 0.20 M $\log_{10}\beta_1$ = 8.02 ± 0.10, 7.78 ± 0.08 and 7.81 ± 0.11 for Am(III), Cm(III) and Eu(III), respectively. While the values reported for Cm(III) and Eu(III) are virtually the same as the values reported by PATHAK & CHOPPIN (2006c), the stability constant of Am(III) is higher than the others. Experimental solvent extraction data for I = 0.20 M are given in graphical form in Fig. 3 of THAKUR et al. (2007). These data were digitised and the stability constants re-evaluated in the present review. The results are: $\log_{10}\beta_1$ = 7.77 ± 0.06, 7.79 ± 0.03 and 7.83 ± 0.03 for Am(III), Cm(III) and Eu(III), respectively. Considering their assigned uncertainties all these values are the same, especially the stability constants of Am(III) and Cm(III) are undistinguishable. However, while the values for Cm(III) and Eu(III) re-evaluated in this review are the same as reported by THAKUR et al. (2007), the value for Am(III) is at variance. Assuming that the experimental data shown in Fig. 3 of THAKUR et al. (2007) are correct, the $\log_{10}\beta_1$ value for Am(III) given in Table 1 of THAKUR et al. (2007) is incorrect.

Unfortunately, experimental solvent extraction data are published only for I = 0.20 M (Fig. 3 in THAKUR et al. 2007) but no experimental data are published for I = 0.50, 0.75 and 1.00 M. Hence, the $\log_{10}\beta_1$ values given for these higher ionic strengths in Table 1 of THAKUR et al. (2007) cannot be checked for correctness by re-evaluating the original experimental data. Inspecting Table 1 of THAKUR et al. (2007) one recognises that the $\log_{10}\beta_1$ values for Cm(III) and Eu(III) are very similar at all ionic strengths, differing by not more than 0.03 log units, while the Am(III) values are all systemically higher, differing from the Cm(III) data by 0.24, 0.27, 0.28 and 0.30 log units with increasing ionic strength. It seems that all $\log_{10}\beta_1$ values reported for Am(III) in Table 1 are affected by the same systematic error in data evaluation and thus, they are not considered further in this review.

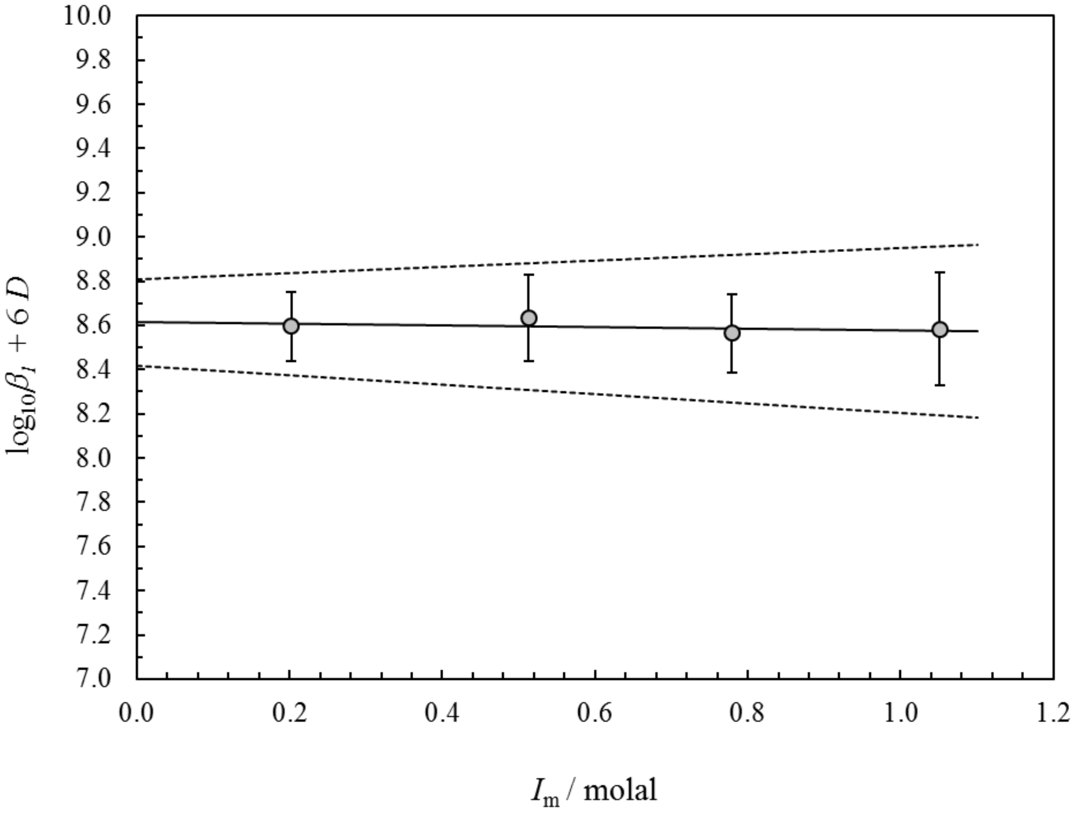

Fig. 8.9: Extrapolation to I = 0 of experimental data for the formation of $Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$ using SIT. The data are taken from THAKUR et al. (2007).

The $\log_{10}\beta_1$ values for Cm(III) and Eu(III) given in Table 1 of THAKUR et al. (2007) were used for SIT regression analyses in the present review (Fig. 8.9). The results are for

$$Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$$

$$Eu^{3+} + SiO(OH)_3^- \Leftrightarrow EuSiO(OH)_3^{2+}$$

$$\log_{10}\beta_1^\circ = 8.61 \pm 0.19 \text{ and } \Delta\varepsilon = 0.04 \pm 0.31 \text{ kg} \cdot \text{mol}^{-1} \text{ for } CmSiO(OH)_3^{2+}$$

$$\log_{10}\beta_1^\circ = 8.67 \pm 0.24 \text{ and } \Delta\varepsilon = 0.07 \pm 0.37 \text{ kg} \cdot \text{mol}^{-1} \text{ for } EuSiO(OH)_3^{2+}$$

Using $\varepsilon(Cm^{3+}, ClO_4^-) = \varepsilon(Eu^{3+}, ClO_4^-) = \varepsilon(Am^{3+}, ClO_4^-) = 0.49 \pm 0.03$ kg · mol^{-1} (GAMSJÄGER et al. 2005), and $\varepsilon(SiO(OH)_3^-, Na^+) = 0.02 \pm 0.05$ kg · mol^{-1} derived in this review we calculate

$$\varepsilon(CmSiO(OH)_3^{2+}, ClO_4^-) = 0.55 \pm 0.32 \text{ kg} \cdot \text{mol}^{-1}$$

$$\varepsilon(EuSiO(OH)_3^{2+}, ClO_4^-) = 0.58 \pm 0.38 \text{ kg} \cdot \text{mol}^{-1}$$

Using the value $\log_{10}\beta_1 = 7.77 \pm 0.06$ re-evaluated for Am(III) at $I = 0.20$ M in this review, $\log_{10}\beta_1° = 8.59 \pm 0.2$ is estimated for $I = 0$.

Note that the $\log_{10}\beta_1°$ values reported in THAKUR et al. (2007), i.e. 8.23 ± 0.09, 7.94 ± 0.06 and 8.04 ± 0.08 for Am(III), Cm(III) and Eu(III), respectively, are incorrect. Probably the authors neglected the term Δz^2 in the extended Debye-Hückel expression and thus effectively used $\Delta z^2 = -1$ instead of the correct value $\Delta z^2 = -6$. By chance, this incorrectly extrapolated values "agree well with the reported values at $I = 0.00$" for Am(III), 8.20 ± 0.04 (WADSAK et al. 2000), for Cm(III), 7.74 ± 0.08 (PANAK et al. 2005), and Eu(III), 7.98 ± 0.06 (JENSEN & CHOPPIN 1996), and the error went unnoticed.

Table 8.2: Stability constants $\log_{10}\beta_1°$ for the reaction $Me^{3+} + SiO(OH)_3^- \Leftrightarrow MeSiO(OH)_3^{2+}$ (Me = Eu, Am, Cm) extrapolated to zero ionic strength.

			$\log_{10}\beta_1°$		
Reference	Lab	Method	Eu(III)	Am(III)	Cm(III)
JENSEN & CHOPPIN (1996)	Choppin's lab	Solvent extr.	7.92 ± 0.20		
PATHAK & CHOPPIN (2006c)	Choppin's lab	Solvent extr.	8.61 ± 0.04		8.64 ± 0.04
THAKUR et al. (2007)	Choppin's lab	Solvent extr.	8.67 ± 0.24	8.59 ± 0.2	8.61 ± 0.19
WADSAK et al. (2000)	University Vienna	Solvent extr.		8.20 ± 0.08	
STEINLE et al. (1997)	INE Karlsruhe	TRLFS			8.1 ± 0.2
PANAK et al. (2005)	INE Karlsruhe	TRLFS			7.74 ± 0.08

An overview over the stability constants discussed here for the equilibrium $Me^{3+} + SiO(OH)_3^- \Leftrightarrow MeSiO(OH)_3^{2+}$ (Me = Eu, Am, Cm) (Table 8.2) reveals two contradicting results:

On the one hand, stability constants obtained by the same method for different metal cations do not show any statistically significant difference or trend with respect to Eu(III), Am(III) and Cm(III) (PATHAK & CHOPPIN 2006c, THAKUR et al. 2007).

On the other hand, values reported from the same lab, obtained with the same experimental method for the same metal cation show statistically significant differences, for Eu(III) (JENSEN & CHOPPIN (1996) versus PATHAK & CHOPPIN (2006c) and THAKUR et al. (2007)) as well as for Cm(III) (STEINLE et al. (1997) versus PANAK et al. (2005)). In both cases, these differences are not discussed or not even mentioned in subsequently published papers.

In summary, based on the available data there is no reason to discern between Eu(III), Am(III) and Cm(III) with respect to the reaction $Me^{3+} + SiO(OH)_3^- \Leftrightarrow MeSiO(OH)_3^{2+}$. If we take just one of the almost identical values from PATHAK & CHOPPIN (2006c) and THAKUR et al. (2007), in order not to give them too much weight, and average this value with the other values given in Table 8.2, a common value $\log_{10}\beta_1° = 8.1 \pm 0.4$ is obtained. This value is included in our database for Eu(III), Am(III) and Cm(III), and as an estimate (supplemental data) for Pu(III) and Np(III).

8.4.6 Zirconium

No information about aqueous zirconium silicate complexes could be found in the literature during the present review.

Thermodynamic data for twelve zirconium silicate compounds have been selected in the NEA review of zirconium (Brown et al. 2005). However, none of these data are included in our data base (see Table 8.4) for reasons discussed in section 1.7.2 of Thoenen (2014).

8.4.7 Thorium

Rai et al. (2008) studied the solubility of ThO_2(am) in alkaline silica solutions, pH 10 – 13.3, at room temperature (22 ± 2°C) in a controlled atmosphere chamber containing an inert gas. Freshly precipitated ThO_2(am) was washed and the precipitate then suspended in appropriate Na_2SiO_3 solutions. Either the sodium silicate concentration was varied at constant pH or the pH was varied at constant sodium silicate concentration. The solubility experiments from undersaturation lasted from 7 to 487 days. The maximum Na concentration measured in these experiments was 0.4 M.

The experimental data were interpreted by Rai et al. (2008) in terms of the equilibrium

$$\mathrm{ThO_2(am)} + 3\ \mathrm{Si(OH)_4(aq)} + \mathrm{H_2O} \Leftrightarrow \mathrm{Th(OH)_3(SiO(OH)_3)_3^{2-}} + 2\ \mathrm{H^+}$$

with $\log_{10}{}^{*}K_{s,0}^{\circ} = -(18.5 \pm 0.7)$.

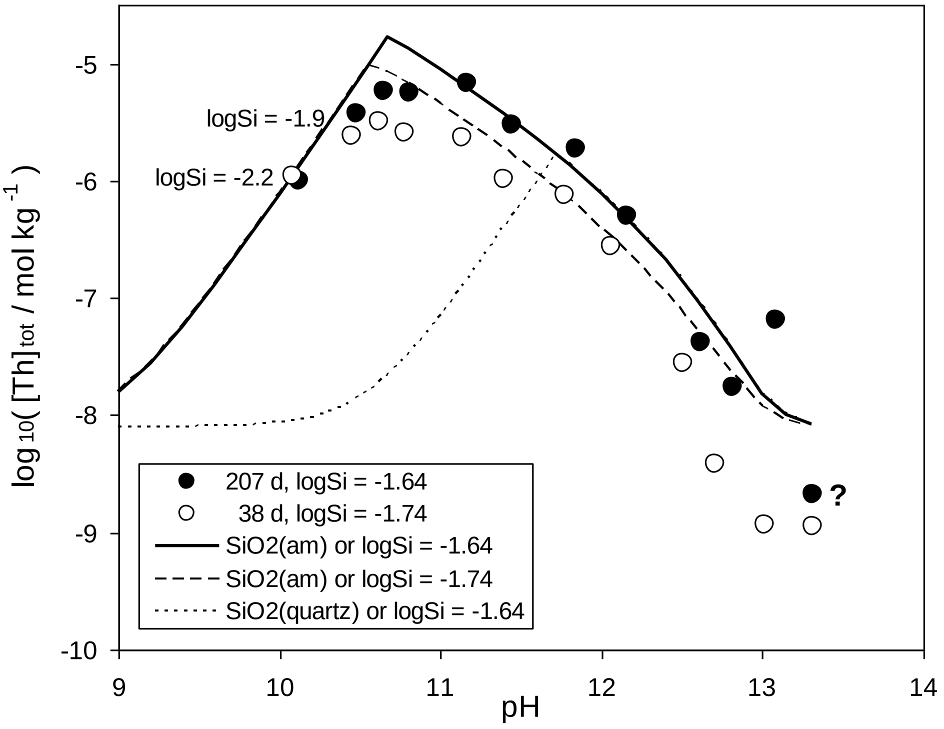

Fig. 8.10: Solubility of ThO_2(am) as a function of pH and time at fixed aqueous Na_2SiO_3 concentration of approximately 0.018 mol·dm^{-3} (38 days reaction time) or 0.023 mol·dm^{-3} (207 days reaction time), except where shown explicitly otherwise. Data points taken from Table 11 in Rai et al. (2008). Data point with question mark refers to log[Th] given as < -8.677. Lines calculated in the present review with a simplified speciation model discussed in the text.

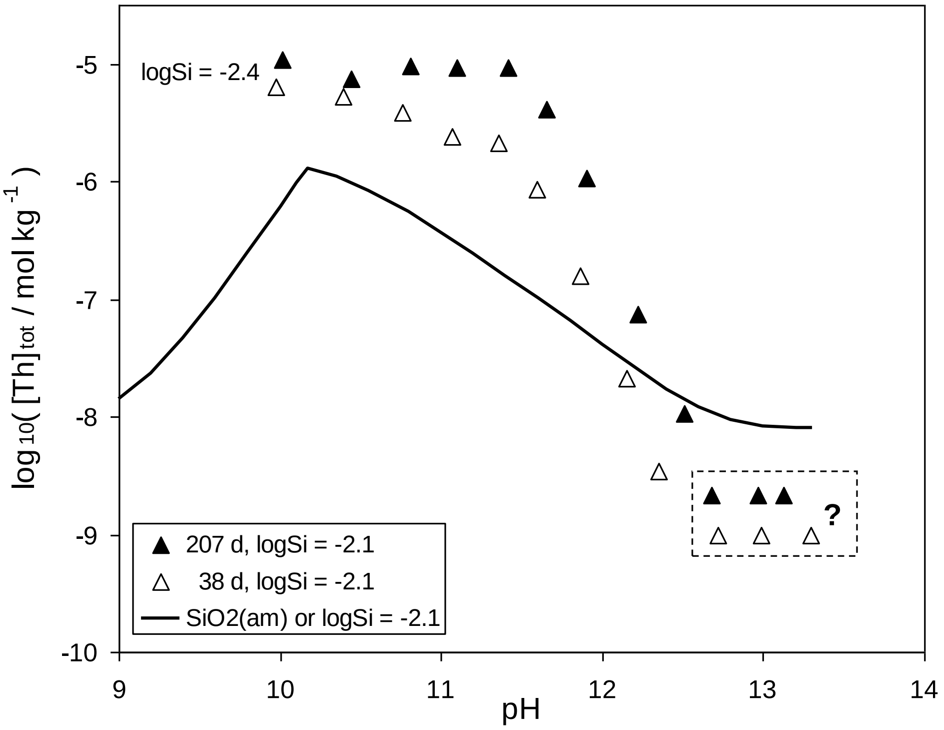

Fig. 8.11: Solubility of ThO_2(am) as a function of pH and time at fixed aqueous Na_2SiO_3 concentration of approximately 0.008 mol·dm^{-3}, except where shown explicitly otherwise. Data points taken from Table 12 in RAI et al. (2008). Data points in the dashed box with question mark refers to log[Th] given as < -8.667 and < -9.000. Lines calculated in the present review with a simplified speciation model discussed in the text.

RAI et al. (2008) assumed $\log_{10}K_{s,0}° = -46.7$ for the solubility product $ThO_2(am) + 2\ H_2O \Leftrightarrow Th^{4+} + 4\ OH^-$ and obtained for

$$Th^{4+} + 3\ Si(OH)_4(aq) + 3\ H_2O \Leftrightarrow Th(OH)_3(SiO(OH)_3)_3^{2-} + 6\ H^+$$

$$\log_{10}K° = -(27.8 \pm 0.7)$$

Note that the solubility product $\log_{10}K_{s,0}° = -46.7$ is numerically identical with the solubility product $\log_{10}{}^{*}K_{s,0}° = 9.3 \pm 0.9$ for $ThO_2(am, hyd, fr) + 4\ H^+ \Leftrightarrow Th^{4+} + 2\ H_2O$ selected by RAND et al. (2009) and included in our data base.

In the present review the solubility products given above were used together with equilibrium constants for $SiO(OH)_3^-$, $SiO_2(OH)_2^{2-}$ and $Th(OH)_4(aq)$, and the solubility of SiO_2(am) as included in our data base in order to calculate the solubility of ThO_2(am) (Figs. 8.10 and 8.11). The tetramer $Si_4O_8(OH)_4^{4-}$ was not included in this simplified speciation model as Fig. 6 in RAI et al. (2008) shows that polymeric silica species contribute less than 10% to the total silica speciation at these low total silica concentrations. The agreement between measured data points and calculated Th concentration is good in Fig. 8.10 and poor in Fig. 8.11.

The data points with question marks in Figs. 8.10 and 8.11 refer to the unresolved question of detection limits. RAI et al. (2008) state that their detection limit for measured Th concentrations is $10^{-9.67}$, and indeed in their Table 9 (Set II) several numbers log[Th] < -9.67 appear. On the other hand, in Table 8 (Set I) log[Th] goes a low as -10.363. No detection limits in Set I? In Table 11 (Set

III) we find one number log[Th] < -8.677 (question mark in Fig. 8.10). Does this indicate a detection limit one order of magnitude higher than stated in the text? In Table 12 (Set IV) we find three numbers log[Th] < -8.667 and three numbers log[Th] < -9.000 (dashed box with question mark in Fig. 8.11). Yet other detection limits? All these data should perhaps not be included in thermodynamic modelling.

The thermodynamic interpretation of experimental data by RAI et al. (2008) has several further shortcomings.

First of all, measurements at generally low ionic strength (the maximum Na concentration was 0.4 M) were interpreted in terms of both, the Pitzer and SIT formalism. The authors were aware of the fact that the results of the speciation calculations are insensitive to the Pitzer or SIT coefficients used. Nevertheless, they give Pitzer and SIT coefficients for $Th(OH)_3(SiO(OH)_3)_3^{2-}$ which are mere guesses. The SIT coefficient is not included in our data base.

Secondly, the authors claim to have included the solubility of quartz in their speciation model (Table 4 in RAI et al. (2008)). This cannot be correct. Using the solubility of quartz in our simplified speciation model results in calculated total silica incompatible with measurements and totally wrong Th solubility at pH < 11 (dotted line in Fig. 8.10).

Thirdly, the calculated Th concentration show in Fig. 6 of RAI et al. (2008) could be reproduced in the present review only in the pH range 11.5 – 13. Below pH 11.5 the calculated curve of RAI et al. (2008) exhibits a parabolic shape which is incompatible with the effect of SiO_2(am) solubility which leads to the sharp edge in Fig 8.10 and a solubility limited total Si concentration at pH < 10.7. The measured log[Si] numbers shown in Fig. 8.10 are in perfect agreement with concentrations calculated with our simplified speciation model. This is not mentioned and was probably not recognised by RAI et al. (2008).

Last but not least there is a discrepancy of measured and calculated Th concentrations in data set IV (Fig. 8.11) and RAI et al. (2008) comment “it was surprising to find disagreement in this set, and exact reasons for this are not known”. A closer look at Fig. 8.11 here and Fig. 11 in RAI et al. (2008) reveals even stranger disagreements. In Fig. 11 again the parabolic line appears, with a maximum Th concentration at pH 10.5 about one order of magnitude lower than calculated with our simplified speciation model (Fig. 8.11). The only difference between calculations shown in Fig. 8.10 and Fig. 8.11 is the total concentration of dissolved silica. Hence, it is unclear why we calculated something totally different than RAI et al. (2008) in this case, whereas the calculated curves in the first case (Fig. 8.10) agree well, at least at pH > 11.5. But the data shown in Fig. 8.11 may hide some more fundamental problems than differences in speciation calculations. The long-term solubility experiments (207 days) result in almost the same dissolved Th concentrations as the data shown in Fig. 8.10 although the total dissolved silica concentration differs by a factor of four. Furthermore, although the measured silica concentration at pH 10 (log[Si] = -2.4) agrees well with the one calculated as a result of solubility limitation by SiO_2(am), the total dissolved Th concentration is not lower than the other values at higher pH, in contrast to the effects seen in Fig. 8.10. Both effects cannot be explained by the formation of a single thorium silicate complex.

In summary, the experimental data of RAI et al. (2008) show strong thorium silicate complex formation in alkaline solutions, and their thermodynamic interpretation is not unreasonable. We included their equilibrium constant in our data base, but because of the shortcomings discussed above, as “supplemental data”.

RAND et al. (2009) selected in their NEA review of thorium standard molar enthalpies of formation for the minerals $ThSiO_4$(huttonite) and $ThSiO_4$(thorite). Neither solubility products nor standard molar Gibbs free energies of formation are known for these solids and RAND et al. (2009) concluded that both compounds are metastable towards quartz and thorium dioxide under standard conditions. Therefore, they are not included in our data base (see Table 8.4).

8.4.8 Uranium

8.4.8.1 Aqueous uranium silicates

Seven papers have been published until 2007 reporting experimental data on U(VI) silicate complexation (Table 8.3). Five of these papers, i.e. PORTER & WEBER (1971), SATOH & CHOPPIN (1992), JENSEN & CHOPPIN (1998), MOLL et al. (1998) and HRNECEK & IRLWECK (1999) have been discussed in detail and some data re-evaluated by GUILLAUMONT et al. (2003). The experimental data in these papers have been interpreted in terms of the equilibrium

$$UO_2^{2+} + Si(OH)_4(aq) \Leftrightarrow UO_2SiO(OH)_3^+ + H^+$$

and the equilibrium constants reported ($\log_{10}{}^*K$) and extrapolated to zero ionic strength ($\log_{10}{}^*K°$) by GUILLAUMONT et al. (2003) are shaded in Table 8.3. For the equilibrium

$$UO_2^{2+} + SiO(OH)_3^- \Leftrightarrow UO_2SiO(OH)_3^+$$

$\log_{10}\beta_1°$ values were calculated using $\log_{10}\beta° = -(9.81 \pm 0.02)$ for $Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+$ (last column in Table 8.3).

Table 8.3: Equilibrium constants $\log_{10}{}^*K$ for the reaction $UO_2^{2+} + Si(OH)_4(aq) \Leftrightarrow UO_2SiO(OH)_3^+ + H^+$ and $\log_{10}\beta_1$ for the reaction $UO_2^{2+} + SiO(OH)_3^- \Leftrightarrow UO_2SiO(OH)_3^+$. Data taken from Table 9-34 of GUILLAUMONT et al. (2003) are shaded.

Reference	Ionic medium $NaClO_4$	T (°C)	$\log_{10}{}^*K$	$\log_{10}{}^*K°$	$\log_{10}\beta_1$	$\log_{10}\beta_1°$
PORTER & WEBER (1971)	0.2 M	25	-(1.98 ± 0.13)	-(1.71 ± 0.13)		8.10 ± 0.13
SATOH & CHOPPIN (1992)	0.2 M	25	-(2.01 ± 0.09)	-(1.74 ± 0.09)		8.07 ± 0.09
JENSEN & CHOPPIN (1998)	0.1 M	25	-(2.92 ± 0.06)	-(2.65 ± 0.06)		7.16 ± 0.06
MOLL et al. (1998)	0.3 M	20	-(1.74 ± 0.20)	-(1.44 ± 0.20)		8.37 ± 0.20
HRNECEK & IRLWECK (1999)	0.2 M	25	-(2.21 ± 0.06)	-(1.94 ± 0.06)		7.87 ± 0.06
YUSOV & FEDOSEEV (2005)	0.2 M	?	-(2.56 ± 0.09)	-(2.29 ± 0.09)		7.52 ± 0.09
PATHAK & CHOPPIN (2006c)	0.2 M	25			6.87 ± 0.04	7.42 ± 0.04

YUSOV & FEDOSEEV (2005) studied the interaction of UO_2^{2+} ions with orthosilicic acid $Si(OH)_4$ and polymeric silicic acids in solutions of I = 0.1 – 0.2 M $NaClO_4$ in the pH range 1.7 – 4.3 by spectrophotometry. They reported a value of $\log_{10}{}^*K = -(2.56 \pm 0.09)$ at I = 0.2 and $\log_{10}{}^*K° = -(2.29 \pm 0.09)$ extrapolated to zero ionic strength, converted to $\log_{10}\beta_1° = 7.52 \pm 0.09$.

YUSOV & FEDOSEEV (2005) found that for the monomers and oligomers with n ≤ 4, $^{*}K$ is the same within the determination error. For polymeric silicic acids with n > 100 the data varied beyond the error limits; the apparent constant $^{*}K$ decreased with an increase of polymerization. Based on these results the authors state that "the inconsistency of the data from different papers (see Table 8.3) cannot be attributed to the polymerization of $Si(OH)_4$. In particular, the lowest and the highest $\log_{10}{}^{*}K$ values (-2.92, JENSEN & CHOPPIN (1998) and -1.74, MOLL et al. (1998)) were obtained in experiments with monomeric $Si(OH)_4$. The inconsistency is apparently associated with the procedures used." YUSOV & FEDOSEEV (2005) conclude: "We believe that the observed discrepancies are due to the complexity of the system under consideration; it is difficult to adequately take into account all the factors. This is especially difficult in experiments with trace amounts of a radionuclide when its behaviour can also be affected by sorption and other difficult-to-control factors."

PATHAK & CHOPPIN (2006c) measured the complex formation of silicate with U(VI) in the temperature range 5 – 45°C in an aqueous medium of 0.20 M ($NaClO_4$) ionic strength and pH ≈ 3.5 by solvent extraction. The enthalpy of reaction was derived from the temperature variation of the obtained stability constants.

The stability constant at 25°C and 0.2 M $NaClO_4$ reported for the equilibrium

$$UO_2^{2+} + SiO(OH)_3^- \Leftrightarrow UO_2SiO(OH)_3^+$$

is $\log_{10}\beta_1 = 6.87 \pm 0.02$ (Table 1 in PATHAK & CHOPPIN 2006c). A re-evaluation in the present review of the experimental data given in graphical form in Fig. 1 of PATHAK & CHOPPIN (2006c) resulted in $\log_{10}\beta_1 = 6.85 \pm 0.02$ (1 σ). Considering the errors induced by digitising graphical data this result is identical with the value published by PATHAK & CHOPPIN (2006c).

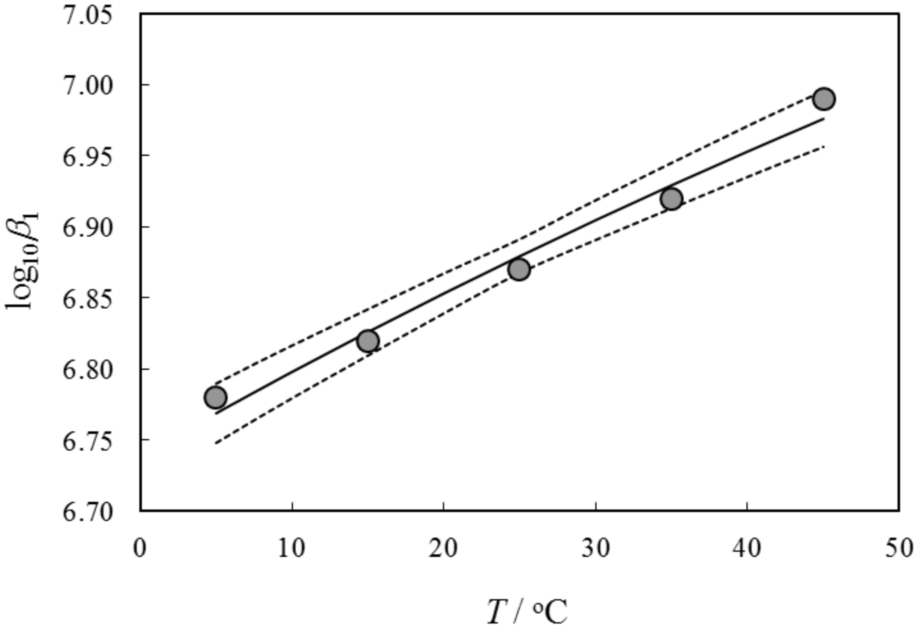

Fig. 8.12: Temperature dependence of the stability constant for the equilibrium $UO_2^{2+} + SiO(OH)_3^- \Leftrightarrow UO_2SiO(OH)_3^+$. Data taken from Table 1 in PATHAK & CHOPPIN (2006c). An unweighted least squares fit gives: $\log_{10}\beta_1$ (25°C) = 6.88 ± 0.02 and $\Delta_rH_m = 8.8 \pm 0.7$ kJ · mol^{-1} (1 σ). The dotted lines are the 1 σ standard deviations extrapolated from 25°C to lower and higher temperatures.

In their Table 2 PATHAK & CHOPPIN (2006c) reported the enthalpy of reaction for U(VI) as $\Delta_r H_m = 8.3 \pm 0.7$ kJ · mol^{-1}. A re-evaluation in the present review by least squares fits of the experimental data given in Table 1 of PATHAK & CHOPPIN (2006c) resulted in $\log_{10}\beta_1$ (25°C) = 6.88 ± 0.02 and $\Delta_r H_m = 8.8 \pm 0.7$ kJ · mol^{-1} (1 σ) (Fig. 8.12). Within the statistical uncertainties these re-evaluated values are identical with the values published by PATHAK & CHOPPIN (2006c). Hence, the value $\Delta_r H_m = 8.3 \pm 2.0$ kJ · mol^{-1} (2 σ) is included as supplemental data in our database.

Considering the discussion of YUSOV & FEDOSEEV (2005) about possible reasons for the observed discrepancies in reported equilibrium constants there seems no convincing argument to exclude any value given in Table 8.3, despite the variation of more than one order of magnitude. Furthermore, there is no good argument for any weighting scheme and thus, an unweighted average of the values in Table 8.3 was calculated: $\log_{10}\beta_1° = 7.8 \pm 0.4$.

8.4.8.2 Solid uranium silicates

GUILLAUMONT et al. (2003) discuss solubility data for a number of solid U(VI) silicates, i.e. $(UO_2)_2SiO_4\cdot 2H_2O$ (soddyite), $Ca(UO_2)_2(SiO_3OH)_2\cdot 5H_2O$ (uranophane), $Na(UO_2)(SiO_3OH)\cdot 2H_2O$ (sodium boltwoodite) and $Na_2(UO_2)_2(Si2O_5)_3\cdot 4H_2O$ (sodium weeksite).

In all cases, no solubility constant was included in their tables of selected values.

In the case of soddyite, GUILLAUMONT et al. (2003) conclude “in view of the non-concordant solubility constants (of two studies), this review does not recommend a value, but suggests that the average value … with increased uncertainty … may be used as a guideline until it has been confirmed. The estimated uncertainty covers the uncertainty ranges of the two studies.”

For the other three U(VI) silicates, GUILLAUMONT et al. (2003) also provide solubility constants with the proviso “for reasons discussed in Appendix A concerning the purity of the phases and the calculations, and the fact that the solutions are probably supersaturated with respect to silica, these values are not selected, but can be used in scoping calculations.”

All four solubility constants given in the text of GUILLAUMONT et al. (2003, p. 254-257) are included as supplemental data in our database (Table 8.5).

Coffinite, $USiO_4$(s), is an abundant mineral in reduced sedimentary uranium deposits. This mineral generally forms small crystals and is almost always associated with amorphous $USiO_4$, uraninite, UO_2(s), and auxiliary minerals. Coffinite minerals have been synthesised only with difficulty because many particular conditions are necessary: reducing media, basic pH ($7 < pH < 10$), solutions rich in dissolved silica. Coffinite minerals are always obtained in association with UO_2(s) and SiO_2(s). Therefore, it is very difficult to determine thermodynamic data for pure coffinite experimentally.

LANGMUIR (1978) proposed an estimation procedure where he assumed an average aqueous silica concentration of 10^{-3} M (60 ppm as SiO_2) for the coffinite – uraninite equilibrium

$$USiO_4(s) + 2\,H_2O(l) \Leftrightarrow UO_2(s) + Si(OH)_4(aq)$$

In this equilibrium the only aqueous species is $Si(OH)_4$(aq) and thus, the equilibrium constant equals the assumed silica concentration of 10^{-3} M. The ionic strength dependence of an equilibrium involving only neutral species is minimal and as a good approximation we can assume

$$\log_{10}K° \text{ (298.15 K)} \quad = \quad -3.0$$

In order to derive from this equilibrium a solubility constant for coffinite a further assumption has to be made about the nature of the involved U(IV) oxide and its associated solubility constant. Following the discussion in GUILLAUMONT et al. (2003) about the solubility of U(IV) oxide this review chose UO_2(am,hyd) as the appropriate solid and the solubility constant $\log_{10}K_{s,0}° = 1.5 \pm 1.0$) given by GUILLAUMONT et al. (2003) for the equilibrium

$$UO_2(am,hyd) + 4\ H^+ \Leftrightarrow U^{4+} + 2\ H_2O$$

Combining this solubility equilibrium with the above described $USiO_4$(s) – UO_2(s) equilibrium this review obtained for the solubility equilibrium

$$USiO_4(s) + 4\ H^+ \Leftrightarrow U^{4+} + Si(OH)_4(aq)$$

the new equilibrium constant $\log_{10}K_{s,0}° = -(1.5 \pm 1.0)$ which is included as supplemental data in our database.

8.4.9 Neptunium and Plutonium

Silicate complextion of neptunium and plutonium often has been studied using the same experimental methods by the same groups and hence, they are discussed together in this section.

No information about aqueous Np(III) and Pu(III) silicate complexes could be found in the literature during the present review. On the other hand, silicate complexation with Eu(III), Am(III) and Cm(III) is well established (see section 8.4.5) and these elements are considered as reasonably good chemical analogues for Pu(III) and Np(III). Therefore, we included the values

$$\log_{10}\beta_1° = 8.1 \pm 0.4 \text{ and } \Delta_r H_m° \approx 15\ \text{kJ}\cdot\text{mol}^{-1}$$

as estimates (supplemental data) in our data base for the equilibria

$$Np^{3+} + SiO(OH)_3^- \Leftrightarrow NpSiO(OH)_3^{2+}$$

$$Pu^{3+} + SiO(OH)_3^- \Leftrightarrow PuSiO(OH)_3^{2+}$$

The first paper reporting experimental data on Pu(IV) silicate complexation was published by PAZUKHIN et al. (1990). The system Pu(IV) nitrate – sodium silicate was studied by potentiometric and spectrophotometric methods. Addition of sodium silicate to a Pu(IV) solution is proposed to form a complex in which the mole ratio Pu:silicate is 1:8 at pH 1.36. The authors report a value $K = 5$. However, the equilibrium this value refers to and the stoichiometry of the complex are not defined in the paper. SHILOV & FEDOSEEV (2003) later comment on this paper: “we think that the authors dealt with colloid solutions in which Pu(IV) was sorbed on polysilicic acid particles”. The paper of PAZUKHIN et al. (1990) is not considered further in this review.

YUSOV et al. (2004) studied the hydrolysis and interaction of Np(IV) and Pu(IV) with orthosilicic acid, $Si(OH)_4$(aq), in 0.1 – 1.0 M (H,Na)ClO_4 solutions. Spectrophotometry was used to study the reactions at about 10^{-4} M Np(IV) and Pu(IV) concentrations. Formation of the complexes $NpSiO(OH)_3^{3+}$ and $PuSiO(OH)_3^{3+}$ is demonstrated in the presence of 0.005 – 0.016 M $Si(OH)_4$(aq) in the p[H^+] range 1.0 – 2.2 and 0.3 – 1.4, respectively. Equilibrium constants at different ionic strengths are given in Table 2 of YUSOV et al. (2004). From these data this review calculated by SIT analysis (Fig. 8.13)

$$\log_{10}K° = 1.34 \pm 0.18 \text{ and } \Delta\varepsilon = -(0.29 \pm 0.29)\ \text{kg}\cdot\text{mol}^{-1}$$

for the reaction

$$Np^{4+} + Si(OH)_4(aq) \Leftrightarrow NpSiO(OH)_3^{3+} + H^+$$

Using $\varepsilon(Np^{4+}, ClO_4^-) = 0.84 \pm 0.06$ kg · mol^{-1} (GUILLAUMONT et al. 2003), $\varepsilon(H^+, ClO_4^-) = 0.14 \pm 0.02$ kg · mol^{-1} (GRENTHE et al. 1992) and $\varepsilon(SiO(OH)_4(aq), NaClO_4) = \varepsilon(SiO(OH)_4(aq), NaCl) = 0.10 \pm 0.05$ kg · mol^{-1} derived in this review we calculate

$$\varepsilon(NpSiO(OH)_3^{3+}, ClO_4^-) = 0.51 \pm 0.30 \text{ kg} \cdot \text{mol}^{-1}.$$

Likewise, from the data given in Table 2 of YUSOV et al. (2004) this review calculated by SIT analysis (Fig. 8.13)

$$\log_{10}K° = 2.07 \pm 0.18 \quad \text{and} \quad \Delta\varepsilon = -(0.16 \pm 0.27) \text{ kg} \cdot \text{mol}^{-1}$$

for the reaction

$$Pu^{4+} + Si(OH)_4(aq) \Leftrightarrow PuSiO(OH)_3^{3+} + H^+$$

Using $\varepsilon(Pu^{4+}, ClO_4^-) = 0.82 \pm 0.07$ kg · mol^{-1} (GUILLAUMONT et al. 2003), and the other values as above we calculate

$$\varepsilon(PuSiO(OH)_3^{3+}, ClO_4^-) = 0.62 \pm 0.28 \text{ kg} \cdot \text{mol}^{-1}.$$

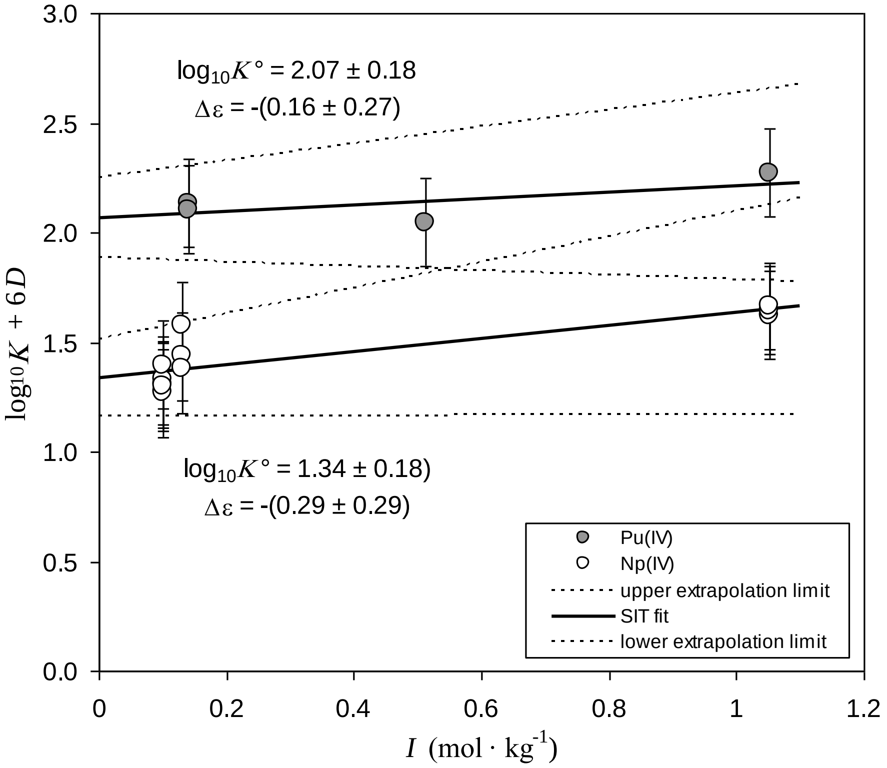

Fig. 8.13: SIT analysis of the equilibrium $An^{4+} + Si(OH)_4(aq) \Leftrightarrow AnSiO(OH)_3^{3+} + H^+$ where An is Np(IV) or Pu(IV). The experimental data are taken from YUSOV et al. (2004).

For the reactions

$$Np^{4+} + SiO(OH)_3^- \Leftrightarrow NpSiO(OH)_3^{3+}$$

$$Pu^{4+} + SiO(OH)_3^- \Leftrightarrow PuSiO(OH)_3^{3+}$$

this review calculated $\log_{10}\beta_1° = 11.15 \pm 0.18$ for Np(IV) and $\log_{10}\beta_1° = 11.88 \pm 0.18$ for Pu(IV) using $\log_{10}\beta_1° = 9.81 \pm 0.02$ for $SiO(OH)_3^- + H^+ \Leftrightarrow Si(OH)_4(aq)$ as ancillary data.

The values estimated by YUSOV et al. (2004), $\log_{10}\beta_1° = 11.2$ for Np(IV) and $\log_{10}\beta_1° = 11.8$ for Pu(IV), are consistent with the SIT analysis in this review. Because no independent confirmation of these results is yet available the values estimated by YUSOV et al. (2004) were included in our data base as "supplemental data".

SHILOV & FEDOSEEV (2003) studied radiometrically the solubility of hydrated Pu(IV) oxide in 0.09-0.9 M NaOH containing 0.01-1 M Na_2SiO_3 and in 0.1-0.2 M $NaClO_4$ containing 0.01-0.09 M Na_2SiO_3 (pH 11 and 9). They stated that the experimental log-log dependence of the Pu(IV) solubility in 0.90 and 0.09 M NaOH (pH 13.8 an 12.8) on the silicate concentration "is almost linear" and interpreted these data in terms of the equilibrium

$$\text{Pu(IV)} + n\ \text{SiO}_3^{2-} \Leftrightarrow \text{Pu}^{\text{IV}}(\text{SiO}_3^{2-})_n$$

with n = 0.7 and 1.2, respectively. They further stated that "although the plutonium solubility at pH 11 also increased with increasing Na_2SiO_3 concentration, strong scattering of the experimental points was observed. At pH 9, the solubility was almost independent of the Na_2SiO_3 concentration".

A plot of all experimental data published in Table 2 (after filtration) of SHILOV & FEDOSEEV (2003) shows (Fig. 8.14) that "almost linear" in the cases pH 13.8 and 12.8 and "almost independent" at pH 9 are euphemisms.

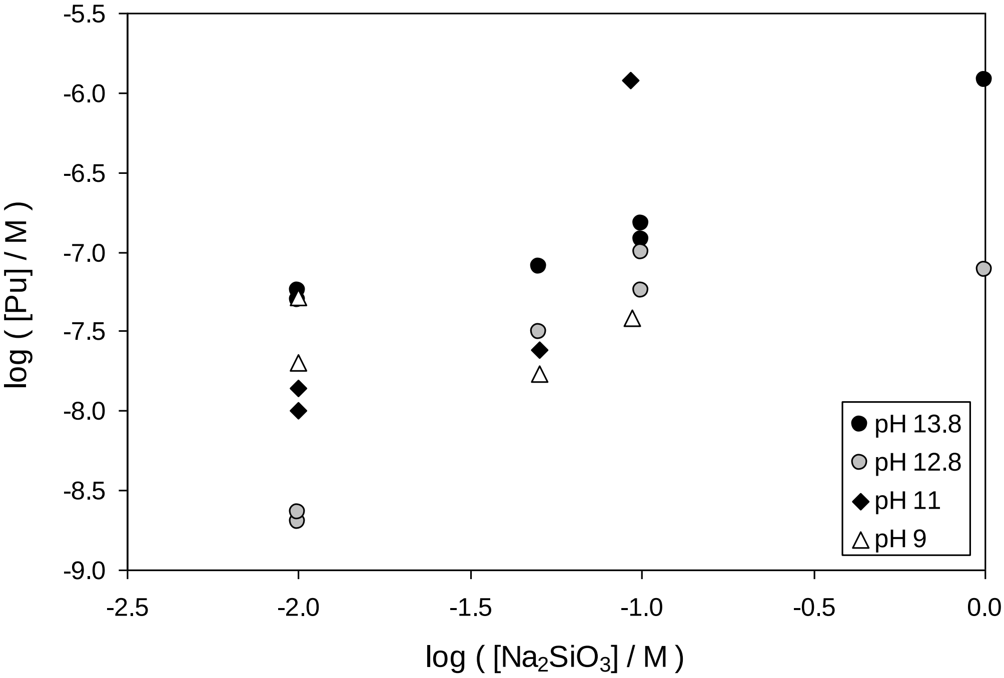

Fig. 8.14: Plutonium(IV) concentration in Na_2SiO_3 solution after filtration at different pH values. Data taken from Table 2 of SHILOV & FEDOSEEV (2003).

The data at 0.01 M Na_2SiO_3 concentration do not show any systematic pH dependence, and the log mean value of the measured Pu(IV) concentrations is -7.8 ± 0.5. This is the same value as measured without addition of Na_2SiO_3 (-7.9 ± 0.5, derived from Table 1 in SHILOV & FEDOSEEV 2003). With increasing Na_2SiO_3 concentration there seems to be a systematic increase in measured Pu concentrations, which could be due to Pu silicate complex formation. However, the scatter and some erratic data points (Fig. 8.14) prevent any meaningful interpretation of these data in terms of a simple thermodynamic equilibrium.

PATHAK & CHOPPIN (2007) studied the complexation behaviour of NpO_2^+ with silicic acid using solvent extraction at ionic strengths varying from 0.10 to 1.00 M $NaClO_4$ at p[H^+] 3.68 ± 0.08 and 25°C. The stability constant value for the 1:1 complex

$$NpO_2^+ + SiO(OH)_3^- \Leftrightarrow NpO_2SiO(OH)_3(aq)$$

was found to decrease with increase in ionic strength. The values have been fitted in the SIT model expression and the results obtained by the authors are

$$\log_{10}\beta_1° = 7.04 \pm 0.02 \text{ and } \Delta\varepsilon = 0.14 \pm 0.03 \text{ kg} \cdot \text{mol}^{-1}.$$

Using $\varepsilon(NpO_2^+, ClO_4^-) = 0.25 \pm 0.05$ kg · mol^{-1} (GUILLAUMONT et al. 2003) and $\varepsilon(SiO(OH)_3^-, Na^+) = 0.02 \pm 0.05$ kg · mol^{-1} derived in this review we calculate

$$\varepsilon(NpO_2SiO(OH)_3(aq), NaClO_4) = 0.41 \pm 0.06 \text{ kg} \cdot \text{mol}^{-1}.$$

Compared with stability constants for the analogous U(VI), Np(VI) and Pu(VI) silicate complexes (Table 8.5) the stability constant obtained by PATHAK & CHOPPIN (2007) seems exceptionally high. Also the SIT coefficient derived for the neutral species $NpO_2SiO(OH)_3(aq)$ seems a bit high.

According to a speciation diagram given by PATHAK & CHOPPIN (2007) for 1×10^{-3} M silicate and 1×10^{-4} M carbonate the species $NpO_2SiO(OH)_3(aq)$ predominates, at least up to pH 8. On the other hand, SHILOV et al. (2003) who also attempted to study the complex formation of Np(V) with silicate ions could not detect any interaction of Np(V) with silicate at pH 10.3. They found only the complex $NpO_2CO_3^-$ by spectrophotometry and state that "the presence of this complex is caused by an impurity of dissolved CO_2; … under the conditions studied, only Np(V) carbonate and hydroxide complexes were revealed".

Considering this conflicting evidence about the complexation strength of Np(V) silicate we included the value obtained by PATHAK & CHOPPIN (2007) as supplemental data ($\log_{10}\beta_1° = 7.0$) in our data base.

YUSOV & FEDOSEEV (2003) studied the reaction of Pu(VI) with orthosilicic acid (at concentrations 0.004 – 0.025 mol·dm^{-3}) in a 0.2 M $NaClO_4$ solution at pH 3 – 8 by spectrophotometry.

Data in the pH range 4.5 – 5.5 were interpreted by the authors in terms of the equilibrium

$$PuO_2^{2+} + Si(OH)_4(aq) \Leftrightarrow PuSiO(OH)_3^+ + H^+$$

with $\log_{10}K_1 = -(3.91 \pm 0.17)$. They combined this value obtained at $I = 0.2$ M $NaClO_4$ with $\log_{10}\beta_1° = -9.81 \pm 0.02$ for $Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+$ at $I = 0$ and reported $\log_{10}\beta_1 = 5.90$ for

$$PuO_2^{2+} + SiO(OH)_3^- \Leftrightarrow PuSiO(OH)_3^+$$

This erroneous value was later corrected (without any comment) to $\log_{10}\beta_1° = 6.17 \pm 0.17$ (YUSOV et al. 2005).

"For comparison with the spectrophotometric data, we (YUSOV & FEDOSEEV 2003) performed the experiment on estimation of the stability constant of the Pu(VI) complex with $OSi(OH)_3^-$ by the potentiometric method like POKROVSKI et al. (1996) studied the Al(III) complexes with $OSi(OH)_3^-$." They obtained $\log_{10}K_1 = -3.53$ and -3.71 in two experiments in a 0.207 M $NaClO_4$ solution (which gives $\log_{10}\beta_1° = 6.55$ and 6.37, respectively) and state "though these values somewhat exceed the values of the constants obtained from spectrophotometric data, they show reasonable agreement with them."

Considering that (a) these values are considerably lower than the stability constants obtained for the analogous U(VI) and Np(VI) complexes, (b) this is the only study reporting Pu(VI) complexation data and (c) the authors seem to trust their spectrophotometric data more than their potentiometric "estimation", we decided to include a value of $\log_{10}\beta_1° \approx 6$ as supplemental data in our database.

At pH > 5.5 YUSOV & FEDOSEEV (2003) interpreted their spectrophotometric data in terms of the formation of either $PuO_2SiO_2(OH)_2(aq)$ or $PuO_2(OH)SiO(OH)_3(aq)$. Since the formation of these complexes differs just by the absence or presence of one water molecule and hence, the equilibrium constant should be the same, it is unclear why YUSOV & FEDOSEEV (2003) report $\log_{10}\beta_2 \approx 12.6$ for

$$PuO_2^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow PuO_2SiO_2(OH)_2(aq)$$

but $\log_{10}\beta_2 \approx 13$ for

$$PuO_2^{2+} + SiO_2(OH)_2^{2-} + H_2O \Leftrightarrow PuO_2(OH)SiO(OH)_3(aq).$$

The first value (≈12.6) is obtained with the same mix of data at $I = 0.2$ M and $I = 0$ as above and thus should be ≈12.9. The derivation of the second value (≈13) is unclear. Nevertheless, the value ≈12.6, as given in the abstract of YUSOV & FEDOSEEV (2003), is included as a "placeholder" in our database.

SHILOV et al. (2004) studied the complexation of Np(VI) in silicate solutions in the presence of carbonate at pH 10.5 – 12.0 by spectrophotometry. The authors conclude from optical density data the occurrence of a fast competition reaction between carbonate and silicate

$$NpO_2(CO_3)_3^{4-} + SiO_3^{2-} \Leftrightarrow NpO_2SiO_3(aq) + 3\ CO_3^{2-}$$

and reported $\log_{10}\beta = 16.5$ at pH 10.13 in 0.1 M $NaClO_4$ solution for the equilibrium

$$NpO_2^{2+} + SiO_3^{2-} \Leftrightarrow NpO_2SiO_3(aq)$$

In order to obtain this value they used $\log_{10}\beta_3 = 20.41$ ($I = 0.1$) for the equilibrium $NpO_2^{2+} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{4-}$, which is one order of magnitude at variance with the value selected in our database ($\log_{10}\beta_3 = 19.04$ at $I = 0.1$). In addition, while their dissociation constants of carbonic acid are almost identical with our values, the cumulative dissociation constant of "metasilicic acid" taken from a Russian "Chemist's Handbook", $\log_{10}\beta_2° = -21.45$, is two orders of magnitude different from our established value $\log_{10}\beta_2° = -23.14 \pm 0.09$. It is not clear what "dissociation constants of metasilicic acid" means, as SHILOV et al. (2004) write in the introductory part of their paper about "silicate solutions in which both metasilicate SiO_3^{2-} and orthosilicate SiO_4^{4-} ions (and protonated species of the latter) can exist."

Hence, the value $\log_{10}\beta = 16.5$ might be grossly wrong but it is the only one reported so far for Np(VI) complexation with silicic acid at high pH, and thus the value $\log_{10}\beta \approx 16.5$ is included for the equilibrium $NpO_2^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow NpO_2SiO_2(OH)_2(aq)$ as a "placeholder" in our database.

In the last paper of this series, YUSOV et al. (2005) studied the complexation of Np(VI) in silicate solutions in the acid and neutral pH range by spectrophotometry. The interaction at pH < 4.5 is described by the equilibrium

$$NpO_2^{2+} + Si(OH)_4(aq) \Leftrightarrow NpSiO(OH)_3^{+} + H^{+}$$

with $\log_{10}K_1 = -(2.88 \pm 0.12)$ at ionic strength $I = 0.1 – 0.2$ ($\log_{10}K_1° = -(2.61 \pm 0.12)$ recalculated to $I = 0$). Using the dissociation constant $\log_{10}\beta_1° = -9.81 \pm 0.02$ for $Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^{-} + H^{+}$ the authors obtained $\log_{10}\beta_1 = 7.20 \pm 0.12$ for

$$NpO_2^{2+} + SiO(OH)_3^{-} \Leftrightarrow NpSiO(OH)_3^{+}$$

The value $\log_{10}\beta_1 = 7.2$ is included in our database as supplemental data.

YUSOV et al. (2005) further write: "We attempted to reveal the neutral complex with monomeric silicic acid, $NpO_2SiO_2(OH)_2(aq)$. However, in the solution containing 4.5 × 10^{-4} M Np(VI) and 0.002 M $Si(OH)_4$ [at such concentration, $Si(OH)_4$ does not polymerize] and pH ≈ 7.5, we failed to detect the complexation because of the strong effect of the hydrolysis." This result sheds doubts on results reported earlier by the same group (YUSOV & FEDOSEEV 2003) for $PuO_2SiO_2(OH)_2(aq)$ at pH > 5.5 using the same experimental set-up (see above). The hydrolysis effects of Np(VI) and Pu(VI) are rather similar, and the stability constants reported for Np(VI) – silicate complexes are even higher than for Pu(VI). So why should hydrolysis prevent the detection of a $NpO_2SiO_2(OH)_2(aq)$ complex, while under very similar conditions a stability constant for the (perhaps weaker?) $PuO_2SiO_2(OH)_2(aq)$ complex was reported?

The discussion in YUSOV et al. (2005) becomes even stranger in the section "Regular trends in interaction of actinide ions with silicate ions in the series U(VI) – Np(VI) – Pu(VI)": "As we reported (SHILOV et al. 2004), at pH > 10 Np(VI) forms the silicate complex $NpO_2SiO_3(aq)$ with the stability constant $\log_{10}\beta = 16.5$ ($I = 0.1$). … Similar experiments with Pu(VI) gave an appreciably lower value: $\log_{10}\beta = 14.4$, which is close to the stability constant of the Pu(VI) complex with another double-charged anion, $SiO_2(OH)_2^{2-}$, arising at pH ≈ 7: $\log_{10}\beta = 12.6$ ($I = 0.2$) (YUSOV & FEDOSEEV 2003)."

The value $\log_{10}\beta = 14.4$ for a complex $PuO_2SiO_3(aq)$ appears here out of the blue, without any further comment or reference. And the authors seem to be convinced that SiO_3^{2-} and $SiO_2(OH)_2^{2-}$ are structurally different anions really existing in silicate solutions and forming metal – silicate complexes with rather different stabilities. However, there is no indication of a ligand SiO_3^{2-} existing in aqueous solution where silicon is coordinated to just three oxygen atoms (like in CO_3^{2-}) instead of four as in $SiO_2(OH)_2^{2-}$. Sometimes in the chemical thermodynamic literature SiO_3^{2-} is used as an alternative expression to $SiO_2(OH)_2^{2-}$ where formally one H_2O is "subtracted". The stability constants for equilibria formulated with these alternative expressions are the same, only $\Delta_f G_m$ values derived therefrom are different because of the inclusion or exclusion of the formal H_2O. Hence, the value $\log_{10}\beta = 14.4$ referring to "$PuO_2SiO_3(aq)$" is not considered in our database.

Table 8.4: Silicon and silicate data selected by NEA (GRENTHE et al. 1992; BROWN et al. 2005; GAMSJÄGER et al. 2005; RAND et al. 2009) but not included in TDB Version 12/07. For explanations see text.

Gases	$Si(g)$, $SiF_4(g)$
Solids	$Ni_2SiO_4(cr)$, $ZrSiO_4(cr)$, $Ca_2ZrSi_3O_{12}(cr)$, $Ca_3ZrSi_2O_9(cr)$, $Sr_6ZrSi_5O_{18}(cr)$, $SrZrSi_2O_7(cr)$, $Na_2ZrSiO_5(cr)$, $Na_2ZrSi_2O_7(cr)$, $Na_4Zr_2Si_3O_{12}(cr)$, $Na_2ZrSi_3O_9\cdot 2H_2O(cr)$, $Na_2ZrSi_4O_{11}(cr)$, $Na_2ZrSi_6O_{15}\cdot 3H_2O(cr)$, $Cs_2ZrSi_2O_7(cr)$, $ThSiO_4$(huttonite), $ThSiO_4$(thorite),
Aqueous species	$Si_2O_3(OH)_4^{2-}$, $Si_2O_2(OH)_5^{-}$, $Si_3O_6(OH)_3^{3-}$, $Si_3O_5(OH)_5^{3-}$, $Si_4O_7(OH)_5^{3-}$

Table 8.5: Selected silica and silicate data. Core data are bold and supplemental data in italics. New or changed data with respect to TDB Version 01/01 (HUMMEL et al. 2002) are shaded.

	TDB Version 01/01				TDB Version 12/07				
Name	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	S_{m}° [J · K^{-1} · mol^{-1}]	$C_{\mathrm{p,m}}^{\circ}$ [J · K^{-1} · mol^{-1}]	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	S_{m}° [J · K^{-1} · mol^{-1}]	$C_{\mathrm{p,m}}^{\circ}$ [J · K^{-1} · mol^{-1}]	**Species**
Si(cr)	0.0	0.0	**18.810 ± 0.08**	**19.789 ± 0.030**	0.0	0.0	**18.810 ± 0.08**	**19.789 ± 0.030**	Si(cr)
Quartz	**-856.287 ± 1.0**	**-910.700 ± 1.0**	**41.460 ± 0.20**	**44.602 ± 0.30**	**-856.287 ± 1.0**	**-910.700 ± 1.0**	**41.460 ± 0.20**	**44.602 ± 0.30**	Quartz
Si(OH)4	-1309.183	-1461.723	178.851	237.370	-1309.183 ± 1.1	-1461.723 ± 1.1	178.851 ± 2.2	237.370	Si(OH)$_4$(aq)

	TDB Version 01/01		TDB Version 12/07		
Name	$\log_{10}\beta^{\circ}$	$\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	$\log_{10}\beta^{\circ}$	$\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\circ}$ [kJ · mol^{-1}]	**Reaction**
SiO(OH)3-	-9.81 ± 0.02	25.6 ± 2.0	-9.81 ± 0.02	25.6 ± 2.0	$Si(OH)_4(aq) \Leftrightarrow SiO(OH)_3^- + H^+$
SiO2(OH)2-2	-23.14 ± 0.09	75 ± 15	-23.14 ± 0.09	75 ± 15	$Si(OH)_4(aq) \Leftrightarrow SiO_2(OH)_2^{2-} + 2\ H^+$
Si4O8(OH)4-4	-	-	-36.3 ± 0.2	-	$4\ Si(OH)_4(aq) \Leftrightarrow Si_4O_8(OH)_4^{4-} + 4\ H^+ + 4\ H_2O(l)$
CaSiO(OH)3+	1.2 ± 0.1	-	1.2 ± 0.1	-	$Ca^{2+} + SiO(OH)_3^- \Leftrightarrow CaSiO(OH)_3^+$
CaSiO2(OH)2	4.6 ± 0.2	-	4.6 ± 0.2	-	$Ca^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow CaSiO_2(OH)_2(aq)$
MgSiO(OH)3+	1.5 ± 0.2	-	1.5 ± 0.2	-	$Mg^{2+} + SiO(OH)_3^- \Leftrightarrow MgSiO(OH)_3^+$
MgSiO2(OH)2	5.7 ± 0.2	-	5.7 ± 0.2	-	$Mg^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow MgSiO_2(OH)_2(aq)$
NiSiO(OH)3+	-	-	*6.3*	-	$\mathit{Ni^{2+} + SiO(OH)_3^- \Leftrightarrow NiSiO(OH)_3^+}$
AlSiO(OH)3+2	7.4 ± 0.2	-	7.4 ± 0.1	41.0 ± 3.0	$Al^{3+} + SiO(OH)_3^- \Leftrightarrow AlSiO(OH)_3^{2+}$
Al(OH)6SiO-	3.6 ± 0.2	-	-	-	$Al(OH)_4^- + Si(OH)_4(aq) \Leftrightarrow Al(OH)_3SiO(OH)_3^- + H_2O(l)$

	TDB Version 01/01		**TDB Version 12/07**		
Name	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ · mol^{-1}]	$\log_{10}\beta°$	$\Delta_r H_m°$ [kJ · mol^{-1}]	**Reaction**
AlSiO3(OH)4-3	-	-	*0.53*	-	$Al(OH)_4^- + SiO_2(OH)_2^{2-} \Leftrightarrow AlSiO_3(OH)_4^{3-} + H_2O(l)$
FeSiO(OH)3+2	9.7 ± 0.3	-	9.7 ± 0.3	-	$Fe^{3+} + SiO(OH)_3^- \Leftrightarrow FeSiO(OH)_3^{2+}$
EuSiO(OH)3+2	7.9 ± 0.2	-	8.1 ± 0.4	*14.5 ± 2.0*	$Eu^{3+} + SiO(OH)_3^- \Leftrightarrow EuSiO(OH)_3^{2+}$
Eu(SiO(OH)3)2+	12.8 ± 0.4	-	-	-	$Eu^{3+} + 2\ SiO(OH)_3^- \Leftrightarrow Eu(SiO(OH)_3)_2^+$
AmSiO(OH)3+2	8.1 ± 0.2	-	8.1 ± 0.4	*15*	$Am^{3+} + SiO(OH)_3^- \Leftrightarrow AmSiO(OH)_3^{2+}$
CmSiO(OH)3+2	-	-	8.1 ± 0.4	*15.8 ± 4.0*	$Cm^{3+} + SiO(OH)_3^- \Leftrightarrow CmSiO(OH)_3^{2+}$
PuSiO(OH)3+2	-	-	*8.1 ± 0.4*	*15*	$Pu^{3+} + SiO(OH)_3^- \Leftrightarrow PuSiO(OH)_3^{2+}$
NpSiO(OH)3+2	-	-	*8.1 ± 0.4*	*15*	$Np^{3+} + SiO(OH)_3^- \Leftrightarrow NpSiO(OH)_3^{2+}$
UO2SiO(OH)3+	-	-	7.8 ± 0.4	*8.3 ± 2.0*	$UO_2^{2+} + SiO(OH)_3^- \Leftrightarrow UO_2SiO(OH)_3^+$
NpO2SiO(OH)3+	-	-	*7.2*	-	$NpO_2^{2+} + SiO(OH)_3^- \Leftrightarrow NpO_2SiO(OH)_3^+$
NpO2SiO2(OH)2	-	-	*≈16.5*	-	$NpO_2^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow NpO_2SiO_2(OH)_2(aq)$
PuO2SiO(OH)3+	-	-	*≈ 6*	-	$PuO_2^{2+} + SiO(OH)_3^- \Leftrightarrow PuO_2SiO(OH)_3^+$
PuO2SiO2(OH)2	-	-	*≈12.6*	-	$PuO_2^{2+} + SiO_2(OH)_2^{2-} \Leftrightarrow PuO_2SiO_2(OH)_2(aq)$
NpO2SiO(OH)3	-	-	*7.0*	-	$NpO_2^+ + SiO(OH)_3^- \Leftrightarrow NpO_2SiO(OH)_3(aq)$
NpSiO(OH)3+3	-	-	*11.2*	-	$Np^{4+} + SiO(OH)_3^- \Leftrightarrow NpSiO(OH)_3^{3+}$
PuSiO(OH)3+3	-	-	*11.8*	-	$Pu^{4+} + SiO(OH)_3^- \Leftrightarrow PuSiO(OH)_3^{3+}$
Th(OH)3(SiO(OH)3)3-2	-	-	*-27.8 ± 0.7*	-	$Th^{4+} + 3\ Si(OH)_4(aq) + 3\ H_2O(l) \Leftrightarrow Th(OH)_3(SiO(OH)_3)_3^{2-} + 6\ H^+$

	TDB Version 01/01		**TDB Version 12/07**		
Name	$\mathbf{log_{10}}\boldsymbol{K}_{\mathbf{s,0}}\mathbf{°}$	$\mathbf{\Delta_r}\boldsymbol{H}_{\mathbf{m}}\mathbf{°}$ [kJ · mol^{-1}]	$\mathbf{log_{10}}\boldsymbol{K}_{\mathbf{s,0}}\mathbf{°}$	$\mathbf{\Delta_r}\boldsymbol{H}_{\mathbf{m}}\mathbf{°}$ [kJ · mol^{-1}]	**Reaction**
Quartz	(-3.746)[a]	20.637	(-3.746)[a]	20.637	$SiO_2(cr) + 2\ H_2O(l) \Leftrightarrow Si(OH)_4(aq)$
SiO2(am)	(-2.714)[b]	14.594	(-2.714)[b]	14.594	$SiO_2(am) + 2\ H_2O(l) \Leftrightarrow Si(OH)_4(aq)$
Kaolinite	7.435	-147.7	7.435	-147.7	$Al_2Si_2O_5(OH)_4 + 6H^+ \Leftrightarrow 2\ Al^{3+} + 2\ Si(OH)_4(aq) + H_2O(l)$
Soddyite	-	-	*6.2 ± 1.0*	-	$(UO_2)_2SiO_4{\cdot}2H_2O(cr) + 4\ H^+ \Leftrightarrow 2\ UO_2^{2+} + Si(OH)_4(aq) + 2\ H_2O(l)$
Uranophane	-	-	*9.4 ± 0.5*	-	$Ca(H_3O)_2(UO_2)_2(SiO_4)_2{\cdot}3H_2O(cr) + 6\ H^+ \Leftrightarrow Ca^{2+} + 2\ UO_2^{2+} + 2\ Si(OH)_4(aq) + 5\ H_2O(l)$
Na-Boltwoodite	-	-	*> 5.8*	-	$Na(H_3O)UO_2SiO_4{\cdot}H_2O(cr) + 3\ H^+ \Leftrightarrow Na^+ + UO_2^{2+} + Si(OH)_4(aq) + 2\ H_2O(l)$
Na-Weeksite	-	-	*1.5 ± 0.1*	-	$Na_2(UO_2)_2(Si_2O_5)_3{\cdot}4H_2O(cr) + 6\ H^+ + 5\ H_2O(l) \Leftrightarrow 2\ Na^+ + 2\ UO_2^{2+} + 6\ Si(OH)_4(aq)$
USiO4(s)	(-3.0)[c]	-	*-1.5 ± 1.0*	-	$USiO_4(s) + 4\ H^+ \Leftrightarrow U^{4+} + Si(OH)_4(aq)$

[a] Temperature dependence of $\log_{10}K_{s,0}$ (Quartz, cr) = $-34.188 + 197.47 / T - 5.851{\cdot}10^{-6}\ T^2 + 12.245 \log_{10}T$

[b] Temperature dependence of $\log_{10}K_{s,0}$ (Silica, am) = $-8.476 - 485.24 / T - 2.268{\cdot}10^{-6}\ T^2 + 3.068 \log_{10}T$

[c] Based on ($\Delta_fG_m°$, $USiO_4$, s) = -(1856.1 ± 11.4)

Table 8.6: Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg · mol^{-1}] for silicate species. All data included in TDB Version 12/07 are derived or estimated in this review. Data estimated according to HUMMEL (2009) are shaded. Supplemental data are in italics.

j k→ **↓**	**Cl$^-$** $\varepsilon_{j,k}$	**ClO$_4^-$** $\varepsilon_{j,k}$	**Na$^+$** $\varepsilon_{j,k}$	**K$^+$** $\varepsilon_{j,k}$	**NaCl** $\varepsilon_{j,k}$	**NaClO$_4$** $\varepsilon_{j,k}$
Si(OH)4	0	0	0	0	0.10 ± 0.05	0
SiO(OH)3-	0	0	0.02 ± 0.05	-	0	0
SiO2(OH)2-2	0	0	0.00 ± 0.05	-	0	0
Si4O8(OH)4-4	0	0	0.29 ± 0.17	-	0	0
CaSiO(OH)3+	0.05 ± 0.10	*0.3 ± 0.1*	0	0	0	0
CaSiO2(OH)2	0	0	0	0	0	*0.2 ± 0.2*
MgSiO(OH)3+	0.05 ± 0.10	*0.4 ± 0.2*	0	0	0	0
MgSiO2(OH)2	0	0	0	0	0	*0.2 ± 0.2*
NiSiO(OH)3+	*0.05 ± 0.10*	*0.57 ± 0.15*	*0*	*0*	*0*	*0*
AlSiO(OH)3+2	-0.30 ± 0.36	0	0	0	0	0
AlSiO3(OH)4-3	*0*	*0*	*-0.15 ± 0.10*	-	*0*	*0*
FeSiO(OH)3+2	0.15 ± 0.10	0.4 ± 0.1	0	0	0	0
EuSiO(OH)3+2	0.15 ± 0.10	0.58 ± 0.32	0	0	0	0
AmSiO(OH)3+2	0.15 ± 0.10	*0.55 ± 0.3*	0	0	0	0
CmSiO(OH)3+2	0.15 ± 0.10	0.55 ± 0.32	0	0	0	0
PuSiO(OH)3+2	*0.15 ± 0.10*	*0.55 ± 0.3*	*0*	*0*	*0*	*0*
NpSiO(OH)3+2	*0.15 ± 0.10*	*0.55 ± 0.3*	*0*	*0*	*0*	*0*
UO2SiO(OH)3+	0.05 ± 0.10	0.2 ± 0.1	0	0	0	0
NpO2SiO(OH)3+	*0.05 ± 0.10*	*0.2 ± 0.1*	*0*	*0*	*0*	*0*
NpO2SiO2(OH)2	*0*	*0*	*0*	*0*	*0*	*0.41 ± 0.06*
PuO2SiO(OH)3+	*0.05 ± 0.10*	*0.2 ± 0.1*	*0*	*0*	*0*	*0*
PuO2SiO2(OH)2	*0*	*0*	*0*	*0*	*0*	*0*
NpO2SiO(OH)3	*0*	*0*	*0*	*0*	*0*	*0*
NpSiO(OH)3+3	*0.25 ± 0.10*	*0.51 ± 0.30*	*0*	*0*	*0*	*0*
PuSiO(OH)3+3	*0.25 ± 0.10*	*0.62 ± 0.28*	*0*	*0*	*0*	*0*
Th(OH)3(SiO(OH)3)3-2	*0*	*0*	*-0.10 ± 0.10*	-	*0*	*0*

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