Clays and Clay Minerals, Vol. 50, No. 5, 657–666, 2002.

STABILITY OF MAGADIITE BETWEEN 20 AND 100°C

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Abstract—New experimental data with respect to the solubility of natural and synthesized magadiite at elevated temperatures and in alkaline solutions are presented. The results show that the solubility of magadiite increases according to the expression $\ln(K_{mag}) = -8146 \cdot T(K)^{-1} - 5.71$ from 20 to 100°C ($\Delta G^0_R(K_{mag}) = 19.6 \pm 0.3$ and $\Delta H^0_R(K_{mag}) = 16.2 \pm 0.4$ kcal mol^{-1}). The experimental results and the related data from the literature suggest that the formation of magadiite may be favored by a decrease of temperature and pH (pH >9) as well by large amounts of Na^+ ions and low ionic strength. These effects are related to the value of $\Delta H^0_R(K_{mag})$, the distribution of dissolved silica species, the stoichiometry of magadiite, and the occurrence of negatively-charged species, respectively.

Key Words—Alkaline Solutions, Amorphous Silica, Magadiite, Monosilicic Acid, Polysilicic Acids, Solubility.

INTRODUCTION

Magadiite ($NaSi_7O_{13}(OH)_3 \cdot 4H_2O$) is a common Na silicate mineral in terrestrial alkaline lakes. It was first observed by Eugster (1967) at Lake Magadi in the East African rift valley, which is a classic locality example for the formation of recent, or sub-recent silicates and other minerals (*e.g.* Eugster, 1970; Jones *et al.*, 1977). Magadiite has been found at other locations such as Trinity County, California (McAtee *et al.*, 1968), at Alkali-Lake in Oregon (Rooney *et al.*, 1969), at Kanem near Lake Chad (Maglione, 1970; Eugster and Maglione, 1979), at alkali lakes in Wyoming (Surdam *et al.*, 1972), and in South Carolina (Houser, 1982).

Magadiite is frequently associated with amorphous silica, quartz and Na silicate minerals, like kenyaite ($NaSi_{11}O_{20.5}(OH)_4 3H_2O$). In several cases the Na silica paragenesis is related to deposits of Na and Ca carbonates, zeolites, or various Mg silicates (*e.g.* Iler, 1979; Hay, 1986; Fritz *et al.*, 1987; Manega and Bieda, 1987; Barth-Wirsching and Höller, 1989). In general, these solids have been formed in strong alkaline solutions with a large dissolved silica content. Although their occurrence and stability have been studied previously, the factors for their formation in the system Na_2O-SiO_2-H_2O, especially with respect to alkaline solutions, are still a matter of debate. This is due to missing solubility data at elevated temperatures, and to the fact that the complex behavior of dissolved silica in alkaline solutions has barely been considered.

The present study gives solubilities for magadiite up to 100°C. The results are applied to model considerations, which account for complexing of silica in alkaline environments.

SILICA SPECIES IN THE SYSTEM Na_2O-SiO_2-H_2O

The chemistry of silica is somewhat complicated insofar as a number of different ions, polymers and complexes with cations may be formed as a function of pH and the silica concentration (Figure 1). Thus monosilicic acid dissociates according to the reactions

$$Si(OH)_4 = SiO(OH)_3^- + H^+ \qquad K_1 \qquad (1)$$

and

$$Si(OH)_4 = SiO_2(OH)_2^{2-} + 2H^+ \qquad \beta_2 \qquad (2)$$

The formation of $SiO_3(OH)^{3-}$ and SiO_4^{4-} ions may be ignored so that $Si(OH)_4$ acts essentially as a diprotic acid (*e.g.* Baes and Mesmer, 1976; Grenthe *et al.*, 1992). Sodium ions and monosilicic acid will react to form a dissolved silicate complex according to

$$Na^+ + Si(OH)_4 = NaSiO(OH)_3^0 + H^+ \qquad K_{Na^0} \qquad (3)$$

and the formation of polysilicic acids may be expressed by the general overall reaction

$$x\,Si(OH)_4 = Si_xO_z(OH)_{4x+y-2z}^{y-} + y\,H^+ + (z-y)H_2O \qquad K_{xyz} \qquad (4)$$

where

$$K_{xyz} \supset \frac{\left[Si_xO_z(OH)_{4x\ \ y-2z}^{y-}\right] \cdot \left[H^+\right]^y}{\left[Si(OH)_4\right]^x} \qquad (5)$$

Magadiite and quartz, or amorphous silica, dissolve according to

$$NaSi_7O_{13}(OH)_3 \cdot 4H_2O + H^+ + 8H_2O = Na^+ + 7Si(OH)_4 \qquad K_{mag} \qquad (6)$$

$$K_{mag} \supset \frac{\left[Na^+\right] \cdot \left[Si(OH)_4\right]^7}{\left[H^+\right] \cdot \left[H_2O\right]^8} \qquad (7)$$

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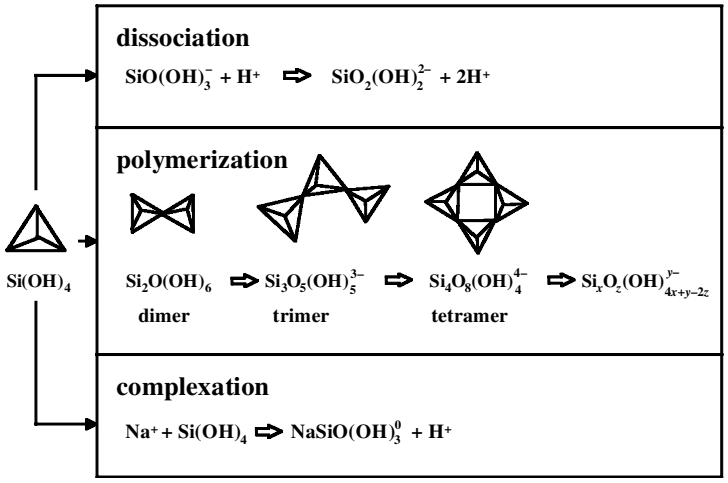

Figure 1. Dissolved silica species in aqueous solution for the system Na_2O-SiO_2-H_2O.

and

$$SiO_{2(s)} + 2H_2O = Si(OH)_4 \quad K_s \tag{8}$$

$$K_s = [Si(OH)_4] \tag{9}$$

where square brackets denote activities. From the above expressions it may be seen that the solubility products can be applied only if in a mixture of the various silica compounds the activity of $Si(OH)_4$ and Na are known. This is achieved using the mass balance

$$\begin{aligned}[SiO_2]_{total} = {} & [Si(OH)_4] + [SiO(OH)_3^-] + \\ & [SiO_2(OH)_2^{2-}] + [NaSiO(OH)_3^0] + \\ & [Si_2O_2(OH)_5^-] + [Si_2O_3(OH)_4^{2-}] + \\ & [Si_3O_5(OH)_5^{3-}] + [Si_4O_6(OH)_6^{2-}] + \\ & [Si_4O_7(OH)_5^{3-}] + [Si_4O_8(OH)_4^{4-}]\end{aligned} \tag{10}$$

and substituting the individual concentrations of the silica species by their stability constants at a given value for pH, $[SiO_2]_{total}$ and Na. Numerical results may be obtained using, *e.g.* the program MINEQL+ 4.06 by Schecher and McAvoy (1998). The constants are summarized in Table 1.

The temperature dependence of the dissociation constants of monosilicic acid was obtained from Grenthe *et al.* (1992) with $\Delta H_R^0(K_1)$ = 6.11±0.05 kcal mol^{-1} and $\Delta H_R^0(\beta_2)$ = 17.9±3.6 kcal mol^{-1}, respectively. The uncertainty of the $\Delta H_R^0(\beta_2)$ value was set comparatively high in order to account for the non-standard conditions to which the original value refers. For the formation of the Na silicate complex $\Delta H_R^0(K_{Na^0})$ = 5.35±0.06 kcal mol^{-1} is used (Arnorsson *et al.*, 1982),

Table 1. Stability constants in the system Na_2O-SiO_2-H_2O.

Reaction		pK (25°C)
$Si(OH)_4 = SiO(OH)_3^- + H^+$	K_1	9.81±0.02[1]
$Si(OH)_4 = SiO_2(OH)_2^{2-} + 2H^+$	β_2	23.14±0.09[1]
$2Si(OH)_4 = Si_2O_2(OH)_5^- + H^+ + H_2O$	K_{212}	8.1±0.3[2]
$2Si(OH)_4 = Si_2O_3(OH)_4^{2-} + 2H^+ + H_2O$	K_{223}	19.0±0.3[2]
$3Si(OH)_4 = Si_3O_5(OH)_5^{3-} + 3H^+ + 2H_2O$	K_{335}	27.5±0.3[2]
$4Si(OH)_4 = Si_4O_6(OH)_6^{2-} + 2H^+ + 4H_2O$	K_{426}	13.44±0.2[3]
$4Si(OH)_4 = Si_4O_7(OH)_5^{3-} + 3H^+ + 4H_2O$	K_{437}	25.5±0.3[2]
$4Si(OH)_4 = Si_4O_8(OH)_4^{4-} + 4H^+ + 4H_2O$	K_{448}	36.3±0.5[2]
$Na^+ + Si(OH)_4 = NaSiO(OH)_3^0 + H^+$	K_{Na^0}	8.66±0.05[4]
$Si(OH)_4 = SiO_{2(am.\,SiO_2)} + 2H_2O$	$K_{am.\,SiO_2}$	2.72±0.02[5]
$Si(OH)_4 = SiO_{2(quartz)} + 2H_2O$	K_{quartz}	3.74±0.1[6]

[1] Grenthe *et al.* (1992), extrapolation to I = 0 with values from Baes and Mesmer (1976), Busey and Mesmer (1977), and Sjöberg *et al.* (1981, 1983)
[2] Grenthe *et al.* (1992), correction to I = 0 with data published by Sjöberg *et al.* (1985) via ion interaction coefficients for phosphate species of corresponding charge
[3] Baes and Mesmer (1976) for I = 0
[4] Arnorsson *et al.* (1982), extrapolated to 25°C with data from Seward (1974)
[5] Rimstidt and Barnes (1980)
[6] Rimstidt (1997)

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which was obtained by interpolation of the experimental data of Seward (1974) at elevated temperatures. The temperature dependence of the dissociation of water is taken from Helgeson (1967) with $\Delta H^0_R(K_{H_2O})$ = 13.335 kcal mol^{-1}. For polymeric species, data exist only for 25°C. However, these species only become important beginning with pH ≈ 10.5, and it is generally agreed that this is true also for elevated temperatures. Thus polymeric species are ignored for experimental solutions with pH <10.2 at elevated temperatures. The temperature dependence of amorphous silica with $\Delta H^0_R(K_{am.\ SiO_2})$ = 3.43 kcal mol^{-1} is taken from Rimstidt and Barnes (1980).

EXPERIMENTAL

The solubility experiments were carried out in 250 and 100 mL polyethylene batch reactors containing 20 g of natural and synthesized magadiite, respectively. The continuously agitated suspensions were kept at constant temperature in a thermostat room (20°C; 250 mL) or in specially designed drying cabinets (40 to 80°C; 250 mL). At 100°C, a continuously shaken 100 mL teflon-coated steel autoclave with a separate heating system was used.

Each of the starting solutions was prepared with double-distilled water and analytical grade reagents. In some of the experiments, the pH of the solution was kept constant by small amounts of phosphate, borate or ammonia buffers. Their compositions are given in Table 2. Liquid samples were collected after defined time intervals via a polyethylene syringe and separating the solutions from solids by membrane filtration (0.1 μm). In the experiments at elevated temperatures, the solution was diluted immediately after sampling in order to avoid precipitation of amorphous silica upon cooling. The concentration of silicic acid was measured by the β-silico-molybdato-method (Dietzel and Usdowski, 1995). Sodium was analyzed by ICP-OES methods (Perkin Elmer 3300).

Natural magadiite

The natural samples were from Lake Magadi and consisted of well crystalline magadiite and some halite (NaCl). The material was re-suspended in double-distilled water several times until the solution was free of chloride. The infrared (IR) spectra and X-ray diffraction (XRD) patterns of the pretreated natural magadiite are shown in Figures 2 and 3. The molar SiO_2/Na_2O-ratio is 13.4, and the specific surface area is 22.1 m^2 g^{-1} (BET method).

Synthesis of magadiite

Magadiite was synthesized according to Lagaly *et al.* (1975). Quantities of 3 g NaOH, 12.5 g amorphous silica (13719, Riedel de Häen), and 50 mL double-distilled water were reacted in a teflon autoclave for 5 weeks at 100°C. The reaction product was separated from the liquid by centrifugation and was washed several times with double-distilled water until pH <8 was attained. The freeze-dried solids were analyzed by X-ray powder diffraction (goniometer type Philips PW 1130/1370) and

Table 2. Chemical composition of the experimental solutions at equilibrium with synthesized magadiite and with natural magadiite*. The concentrations shown in brackets are given in log(mol L^{-1}). (Na^+) and ($Si(OH)_4$) denote activities of Na^+ ions and silicic acid, respectively. $[SiO_2]_{total}$ represents the analytically obtained total silica concentration. pK_{mag} denotes the stability constant with respect to magadiite. *I* is the ionic strength of the solution.

	T (°C)	pH	$[Na^+]$	(Na^+)	$[SiO_2]_{total}$	$(Si(OH)_4)$	$[SiO(OH)_3^-]$	$[NaSiO(OH)_3^0]$	$[SiO_2(OH)_2^{2-}]$	pK_{mag}	*I*
1[1]	20	7.95	−2.51	−2.55	−2.88	−2.88	−4.77	−6.25	−10.20	14.76	0.010
2[2]	20	9.30	−2.46	−2.50	−2.95	−3.07	−3.63	−5.04	−7.72	14.69	0.007
3[3]	20	9.87	−2.36	−2.39	−2.79	−3.13	−3.12	−4.41	−6.64	14.43	0.003
4[4]	20	10.10	−2.24	−2.28	−2.70	−3.19	−2.93	−4.14	−6.18	14.51	0.010
5[5]	20	11.43	−2.14	−2.21	−1.52	−3.38	−1.80	−3.05	−3.67	14.44	0.027
*6[6]	20	8.72	−2.20	−2.30	−2.92	−2.96	−4.03	−5.37	−8.49	14.30	0.074
7[7]	20	9.92	−2.40	−2.46	−2.73	−3.12	−3.02	−4.44	−6.41	14.38	0.018
*8[6]	20	8.74	−2.30	−2.40	−2.89	−2.93	−3.98	−5.42	−8.42	14.17	0.074
9[7]	20	9.90	−2.56	−2.62	−2.71	−3.08	−3.01	−4.59	−6.41	14.28	0.018
10[3]	40	10.11	−2.02	−2.06	−2.42	−3.12	−2.58	−3.60	−5.29	13.79	0.006
11[3]	60	10.08	−1.63	−1.68	−2.16	−3.11	−2.31	−3.02	−4.46	13.37	0.014
12[3]	80	10.12	−1.37	−1.44	−1.83	−3.04	−1.98	−2.54	−3.64	12.60	0.027
13[3]	100	9.98	−1.03	−1.13	−1.57	−2.94	−1.77	−2.11	−3.08	11.73	0.056

[1] phosphate buffer (3 mmol K^+ L^{-1}, 2 mmol P_{total} L^{-1}, and 8 mmol Cl^- L^{-1})
[2] borate buffer (1.6 mmol K^+ L^{-1}, 2 mmol B_{total} L^{-1}, and 6 mmol Cl^- L^{-1})
[3] double distilled H_2O
[4] ammonia buffer (0.108 mol NH_4OH L^{-1}, 1.2 mmol NH_4^+ L^{-1}, and 20 mmol Cl^- L^{-1})
[5] potassium hydroxide solution
[6] ammonia buffer (0.013 mol NH_4OH L^{-1}, 0.077 mol NH_4^+ L^{-1}, and 0.074 mol Cl^- L^{-1})
[7] ammonia buffer (0.067 mol NH_4OH L^{-1}, 0.021 mol NH_4^+ L^{-1}, and 0.015 mol Cl^- L^{-1})

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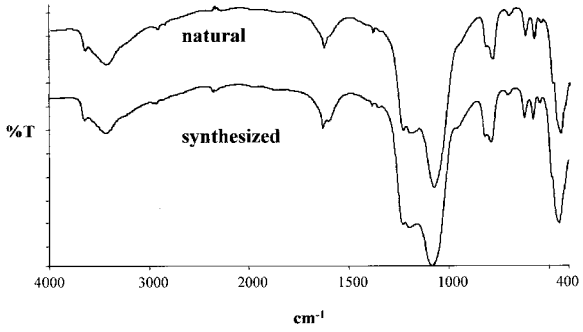

Figure 2. IR spectra of the pretreated synthetic and natural magadiite.

IR spectroscopy (Perkin Elmer FTIR 1600). Figures 2 and 3 display patterns that agree perfectly with magadiite as described by Scholzen *et al.* (1991). The chemical composition obtained by X-ray fluorescence (XRF) spectrometry (Philips PW 1480) yielded a molar SiO_2/Na_2O ratio of 13.7, which is very close to the ideal stoichiometry of magadiite (SiO_2/Na_2O = 14). The specific surface area of the synthesized magadiite according to BET-measurements was 12.2 $m^2\ g^{-1}$.

Transmission electron microscopy (TEM) was used before and after the dissolution experiment to see possible changes of the structure and habit of magadiite and the occurrence of a potential deposit of additional solids during the dissolution. The instrument used for TEM investigations was a Philips CM20/STEM microscope operated with a LaB_6 cathode at an acceleration voltage of 200 kV. The images were recorded with a multi-scan CCD camera and processed with Gatan's Digital Micrograph software. For TEM sample preparation the powder specimens were mounted on holey carbon grids.

In Figure 4 characteristic images are shown for magadiite at two resolution scales. The TEM image of the magadiite sample before the dissolution experiment shows 1 to 2 μm aggregates which consist of minute platy crystals with a near-orthogonal habit (Figure 4a). The crystals are equant and very thin. Magadiite belongs to the monoclinic crystal system (Brindley, 1969) and the minute platy crystals consist of layers representing the sheet structure of magadiite (Figure 4b). The basic structure is composed of duplicated Si–O tetrahedral sheets similar to clay minerals with no octahedral sheets and no Al (*e.g.* Kwon *et al.*, 1995). Vertical crystals exhibit an approximated thickness of ~5–10 nm. Thus the crystals may represent from 3 to 6 sheets considering the 00*l* X-ray reflections which correspond to a basal spacing of 1.57 nm (see Figure 3). The edges of the equant and well-oriented crystals are ~100±20 nm in size.

RESULTS

In Figure 5 the evolution of the concentration of total dissolved silica as a function of the reaction time for three typical experiments is shown. The concentration of silicic acid increases continuously until a constant value is reached. The results of all the experiments show that the concentrations of Na and silicic acid are constant after a reaction period of ~60–90 days within analytical error for all experiments (values at 90 days are given in Table 2). At pH 11.43 (experiment 5 in Table 2) the molar $[Na^+]/[SiO_2]_{total}$ ratio of the solution of ~0.2 is similar to the stoichiometry with respect to magadiite ($[Na^+]/[SiO_2]$ = 0.14). In the experimental solutions at lower pH, the ratios are in the range 1 to 5, within the same order of magnitude as that obtained by Bricker (1969) of ~2. This exhibits a rather congruent dissolution only at high OH^--activities which catalyzes the destruction of the Si–O–Si bonds. The analyses of the magadiite samples by XRD and IR spectroscopy before and after the experiments show no observable changes during the dissolution experiments. Nevertheless, it is obvious that the dissolution of magadiite in the slight alkaline solutions leads to a depletion of interlayered Na^+ which is balanced by a partial protonation of the primary magadiite (*e.g.* Lagaly *et al.*, 1975).

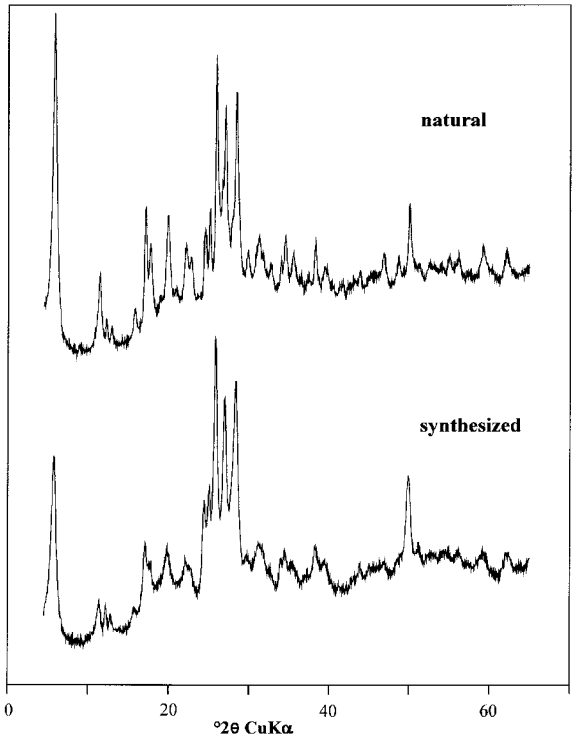

Figure 3. XRD pattern of the pretreated synthesized and natural magadiite (CuKα).

In Figure 4c,d, characteristic TEM images of the magadiite after the dissolution experiment are shown (experiment 12 at 80°C, see Table 2). The structures and size dimensions for the aggregates are similar to those of the untreated magadiite (Figure 4a,b). At high resolution, the near-orthogonal habit of the minute platy crystals is confirmed (Figure 4b,d). For several maga-

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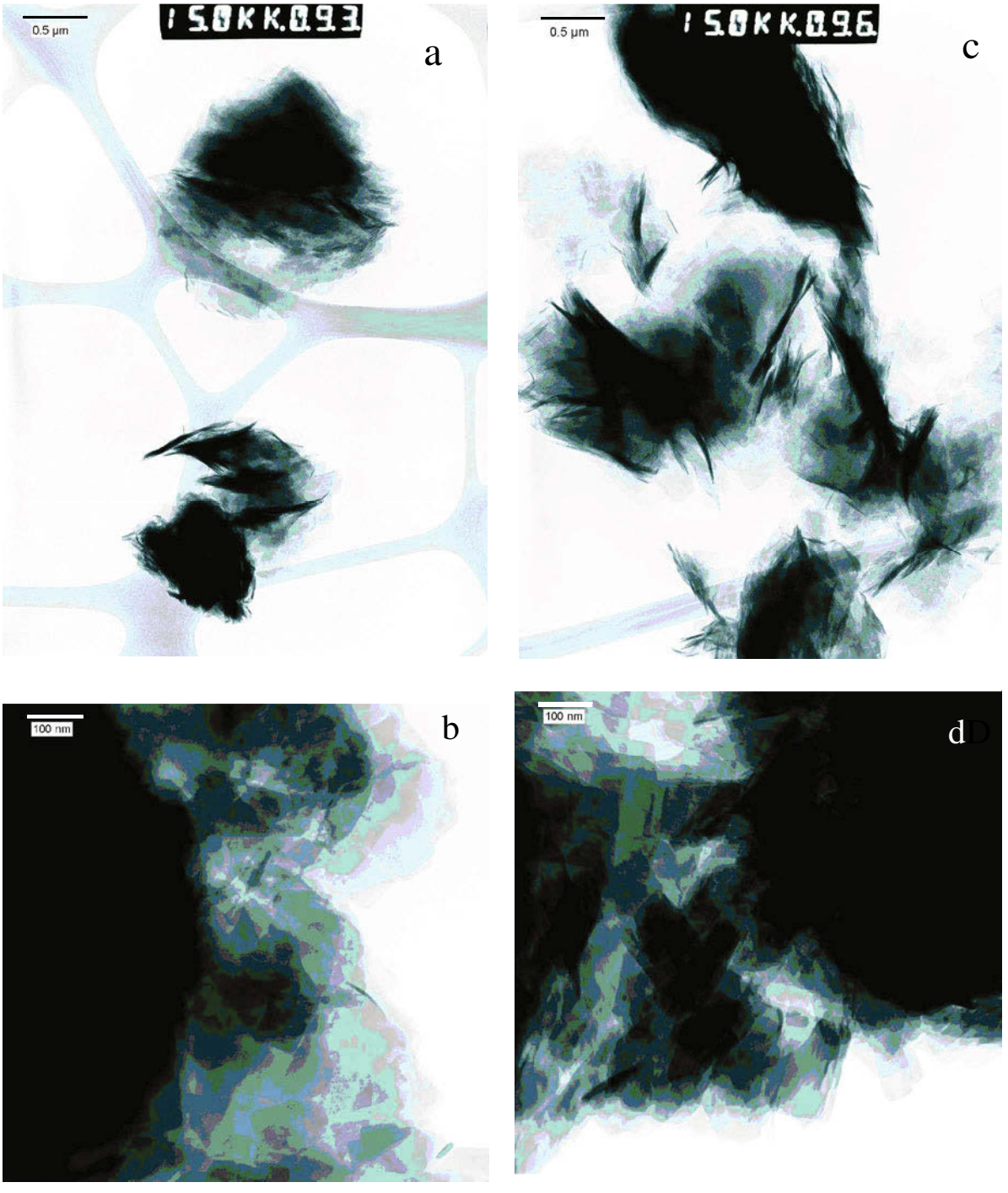

Figure 4. TEM images of the synthesized magadiite before (a and b) and after the dissolution experiment at 80°C (c and d) at two resolution scales each, respectively.

diite crystals, a partial dissolution may be documented by rather rough crystal edges, but no significant changes of the structure and habit of the aggregates or the minute magadiite crystals were obtained, and no precipitation of an additional solid-like amorphous silica was detected from the TEM images.

The experimental results for the various pH values and temperatures, as well as the distribution of species calculated from equation 10 are summarized in Table 2. The results show that the polysilicic acid contents may be ignored except at pH 11.43, where the silica fixed in polymers is ~44 mol % Si with respect to $[SiO_2]_{total}$. It

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may be seen that in alkaline solutions and at elevated temperatures, the concentration of the measured $[SiO_2]_{total}$ is significantly greater than the activity of $Si(OH)_4$. The $[SiO_2]_{total}$ values vary from $10^{-3.0}$ to $10^{-1.6}$ mol L^{-1}, whereas $(Si(OH)_4)$ displays a rather constant value from $10^{-3.4}$ to $10^{-2.9}$ mol L^{-1}. This is due to the additional amounts of deprotonated monosilicic acids, to the formation of the dissolved Na silicate complex, and to the formation of a quantity of polysilicic acids (pH >11).

For the stability constant of magadiite, K_{mag} (equation 7), the activity coefficient for Na^+ was obtained from the Davis equation and, as the ionic strengths of the experimental solution were low, that for water was taken as unity. The activity coefficient for $Si(OH)_4$ is based on an empirical relationship from Wolery (1992), which may be applied to electrically neutral and non-polar species.

The calculated values for the solubility constant for magadiite, K_{mag}, are independent of the pH of the solution. The experiments with respect to natural magadiite samples may indicate a rather low solubility (mean pK_{mag} value of 14.5 from experiments 6 and 8 in Table 2) compared to that of the synthesized samples (mean pK_{mag} value of 14.2). Nevertheless, the values lay within the overall deviation obtained of pK_{mag} = 14.4±0.2.

Table 2 shows that the stability constants increase over about two orders of magnitude from pK_{mag} = 14.4 at 20°C to pK_{mag} = 11.7 at 100°C. In Figure 6 the values of the constant are shown as a function of temperature according to the van't Hoff equation

$$\ln(K_{mag}) \supset -\frac{\Delta H^0_R(K_{mag})}{R \cdot T} \qquad (11)$$

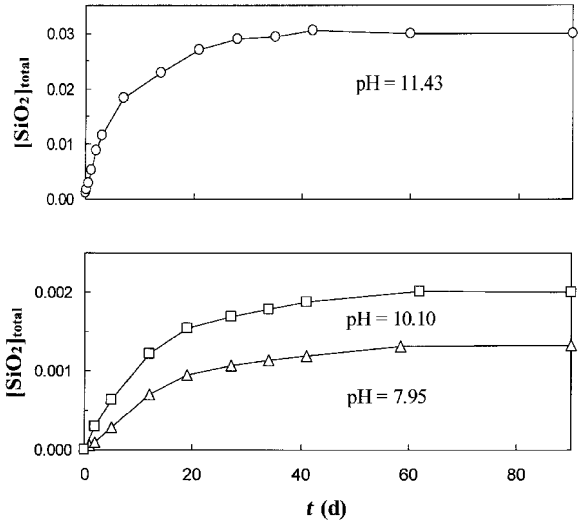

Figure 5. Evolution of total dissolved silica concentration in mol SiO_2 L^{-1} as a function of reaction time (see experiments 1, 4 and 5 in Table 2). Δ: pH 7.95, □: pH 10.10, ○: pH 11.43.

The slope of the regression line results is $\Delta H^0_R(K_{mag})$ = 16.2±0.4 kcal mol^{-1}. Interpolation to 25°C yields K_{mag} = $10^{-14.35}$ and $\Delta G^0_R(K_{mag})$ = 19.6±0.3 kcal mol^{-1}(ΔG^0_R = $-RT\ln K^0_R$). The free energy of formation of magadiite is calculated by the free energy $\Delta G^0_R(K_{mag})$ of reaction 6 according to the equation

$$\Delta G^0_R = \Delta G^0_{Na^+} + 7\Delta G^0_{Si(OH)_4} - \Delta G^0_{H^+} - 8\Delta G^0_{H_2O} - \Delta G^0_{mag} \qquad (12)$$

where $\Delta G^0_{Si(OH)_4}$ = −312.34 (Grenthe *et al.*, 1992), $\Delta G^0_{Na^+}$ = −62.55 and $\Delta G^0_{H_2O}$ = 56.63 kcal mol^{-1} (Lide, 1996). The ΔG^0_{mag} value of −1815.5 kcal mol^{-1} obtained for the present study is similar to the value of −1762.2 kcal mol^{-1} obtained by Bricker (1969).

DISCUSSION

Distribution of dissolved silica as a function of pH

The results of the dissolution experiments show that the values of the stability constants for the individual kind of dissolved silica species used in the present study may be realistic within the related errors (Table 1). This is documented by the calculated value for the solubility constant K_{mag} for magadiite which is independent of pH (Table 2). Following this, the distribution of dissolved compounds at equilibrium with magadiite may be calculated according to the mass balance equation 10 and the values of the stability constants in Table 1. The activity of $Si(OH)_4$ is obtained from the solubility product (expression 7).

Figure 7 shows the cumulative distribution of silica species at equilibrium with respect to magadiite in 0.1 M Na(OH,Cl) solution. The relative proportions are given with respect to the Si atoms fixed in the polymeric and monomeric molecules. The ionic strength is kept constant at I = 0.2. In this case monosilicic acid dissociates above pH ≈ 8, and polymeric silica exists above pH ≈ 10.5. The concentration of monosilicic acid

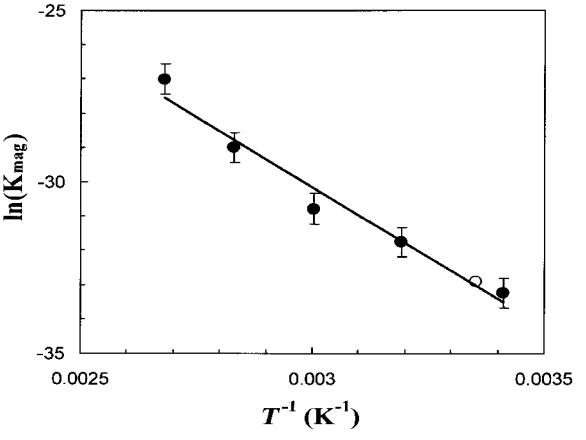

Figure 6. Stability constant with respect to magadiite (see equation 7) as a function of absolute temperature. ●: present study (Table 2), regression line: $\ln(K_{mag}) = -8146\ T^{-1} - 5.71$, correlation coefficient: 0.972; ○ : Bricker (1969).

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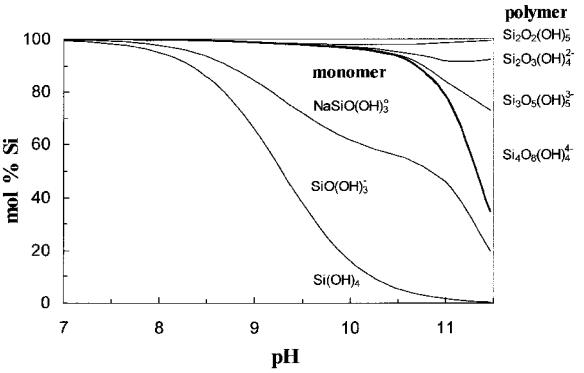

Figure 7. Cumulative distribution of silicic acids at equilibrium with magadiite in 0.1 mol Na(OH,Cl) L^{-1} at a constant ionic strength of 0.2. The molar proportions (mol % Si) refer to Si fixed in the specific molecules with respect to $[SiO_2]_{total}$.

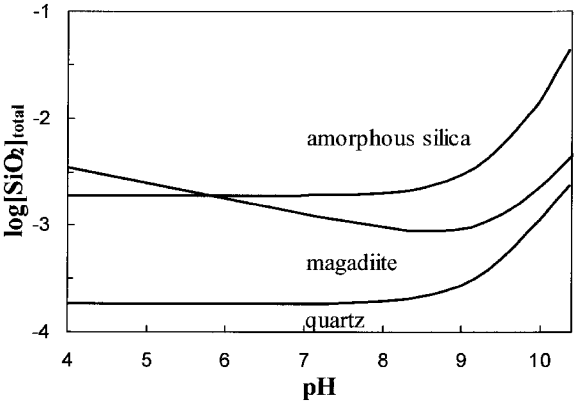

Figure 8. Concentration of $[SiO_2]_{total}$ at equilibrium with magadiite, amorphous silica and quartz (T = 25°C, 0.1mol Na(OH,Cl) L^{-1}, I = 0.2).

is related to complexation with Na^+ ions ($NaSiO(OH)_3^0$) and dissociation with respect to the first stage of deprotonation ($SiO(OH)_3^-$). At pH 11 the proportion of $Si(OH)_4$ with respect to $[SiO_2]_{total}$ is only ~2 mol % and decreases continuously in more alkaline solutions. This decrease is mostly related to the occurrence of additional silica species. Above this, the $[SiO_2]_{total}$ increases significantly in alkaline solutions. At pH 8 and 11 the SiO_2 concentration at equilibrium with respect to magadiite is $10^{-3.0}$ and $10^{-1.6}$ mol L^{-1}, respectively (0.1 mol Na^+ L^{-1}; I = 0.2; 25°C). At pH 11.3 ~68 mol % Si is apportioned to polymeric species. The polymeric silica consists of dimeric, trimeric and tetrameric species. Thus, polysilicic acids occur especially at high pH and high concentration of dissolved silica, indicated by equation 5.

Solubility of magadiite, quartz and amorphous silica as a function of pH at 25°C

The solubility of magadiite, quartz and amorphous silica can be displayed by $[SiO_2]_{total}$ concentration at constant chemical conditions, which relates to the values of the specific solubility constants. Figure 8 shows the total silica contents of the solutions at equilibrium with the above solids at 25°C, 0.1 mol Na^+ L^{-1}, and I = 0.2 as a function of pH. The concentration of silica exhibits a similar dissolution behaviour for both quartz and amorphous silica, which is related to an analogous dissolution equation 8 for both solids. The solubility increases as pH increases because of the formation of additional silica species as discussed above (see Figure 7 for magadiite). Lowest silica concentrations are observed with respect to quartz.

The SiO_2 contents at equilibrium with magadiite show a minimum value at pH $\approx$ 8.5 and follow a different dissolution pattern. At low pH the concentration of silica increases, as the result of the stoichiometry of equation 6 whereas in alkaline solution it increases due to additional dissolved species. Thus, the concentration of silica, at constant Na content, in a solution saturated with respect to magadiite is lowest in neutral to slightly alkaline solutions. Below pH 5.9, the intersection point of the magadiite and amorphous silica, magadiite exhibits a higher solubility than amorphous silica. Thus, at pH <5.9 magadiite will dissolve while amorphous silica precipitates.

Solubility of magadiite versus amorphous silica at 25 and 100°C

In Figure 9 the concentrations of $[SiO_2]_{total}$ at equilibrium with magadiite (solid lines) and amorphous silica (dashed lines) as a function of pH for 25 and 100°C are shown. The $[SiO_2]_{total}$ concentration increases for both solids as temperature increases. The minimum of $[SiO_2]_{total}$ concentration at equilibrium with magadiite shifts from pH 8.5 to 7.8 as temperature increases from 25 to 100°C. A similar shift is obtained with respect to amorphous silica. The concentration of $[SiO_2]_{total}$ increases strongly above pH 9 for 25°C and above pH 8 for 100°C. Moreover, the intersection of the lines shifts to lower pH values at elevated temperatures. At

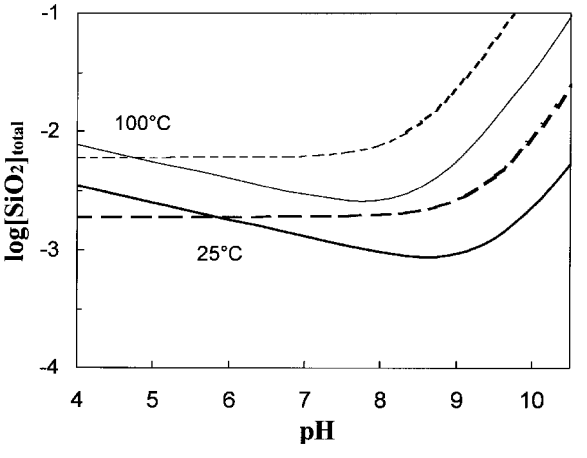

Figure 9. Concentration of $[SiO_2]_{total}$ at equilibrium with magadiite (solid lines) and amorphous silica (dashed lines) at 25 and 100°C (0.1 mol Na(OH,Cl) L^{-1}; I = 0.5).

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100°C the total SiO_2 concentrations at equilibrium with magadiite and amorphous silica are equal at pH 4.8. Thus, the stability of magadiite *vs.* that of amorphous silica is extended to lower pH values as the temperature increases.

Effect of Na concentration on magadiite solubility

Sodium ions may affect the solubility of magadiite according to the equation 7 and by the formation of the dissolved Na silicate complex ($NaSiO(OH)_3^0$). It is shown in Figure 10 that an increase of Na^+ ions in the solution causes a decrease of $[SiO_2]_{total}$ concentration at equilibrium with magadiite, especially for pH <9, whereas the effect on the formation of $NaSiO(OH)_3^0$, which may raise $[SiO_2]_{total}$ concentration, is comparatively small.

At constant concentrations of Na ions an increase of hydronium ions (pH <9) lead to an increase of the silica content of the solution (equation 7). In stronger alkaline solutions the dissociation of monosilicic acid and the formation of polysilicic acids surmount the effect of Na^+ and H_3O^+ ion concentrations on the solubility of magadiite.

Effect of ionic strength on magadiite solubility

In Figure 11 the concentrations of $[SiO_2]_{total}$ at equilibrium with magadiite as a function of pH at ionic strengths of 0.5, 0.1 and 0.001 are shown. The Na contents and the temperature are kept constant at 0.001 mol $Na^+ L^{-1}$ and 25°C, respectively. The effect of ionic strength on the solubility of magadiite is related to the values of the activity coefficients of the dissolved species. At pH <9 the SiO_2 concentration is almost independent of ionic strength due to the uncharged $Si(OH)_4$ species. However, in alkaline solutions solubility with respect to magadiite increases at high ionic strengths. In this case negatively-charged monomeric and polymeric species occur. Assuming a solution at pH 11 and an ionic strength of 0.001 at equilibrium with respect to magadiite, the $[SiO_2]_{total}$ is ~$10^{-1.9}$ mol L^{-1}. The concentration of $[SiO_2]_{total}$ may double if the ionic strength increases to 0.5 ($[SiO_2] = 10^{-1.6}$ mol L^{-1}).

CONCLUSIONS

The results show that the solubility product of magadiite increases in the range from 20 to 100°C according to the expression

$$\ln(K_{mag}) = -8146T^{-1} - 5.71 \quad (13)$$

with $\Delta H_R 0(K_{mag}) = 16.2 \pm 0.4$ kcal mol^{-1}. The validity of the K_{mag} value obtained is confirmed for magadiites of different genesis (natural and synthesized) and for various pH.

The stability of magadiite is mostly related to the chemical composition of the solutions. A sensitive chemical parameter of natural solutions is the pH. Most natural waters have pH values between 5 and 9 so that the predominant dissolved silica species is $Si(OH)_4$, the undissociated monomeric species (Hem, 1970). However, ionized monomeric species occur as stable in solutions at pH >8, and polysilicic acids exist at pH >10.5 and at high concentration of dissolved silica (*e.g.* Iler, 1979; Eikenberg, 1990; Grenthe *et al.*, 1992). Significant quantities of the sodium silicate complex $NaSiO(OH)_3^0$ occur at high Na content of the solutions.

In natural systems quartz always has the lowest $[SiO_2]_{total}$, whereas the $[SiO_2]_{total}$ for magadiite and amorphous silica are significantly higher (Figure 8). Figure 9 shows that the stability of magadiite *vs.* amorphous silica depends strongly on temperature and pH. At 25°C magadiite is stable relative to amorphous silica at pH >6 for the conditions of the present study. This is documented by the intercept of the concentration curves of $[SiO_2]_{total}$ in Figure 9. Thus, amorphous silica will dissolve at pH >6 while magadiite is formed. Moreover, the results in Figure 9 show that the range of the stability for magadiite *vs.* that of amorphous silica is extended to lower pH values at temperatures up to 100°C.

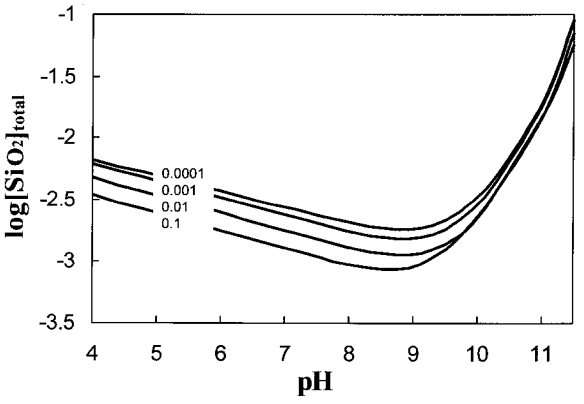

Figure 10. Concentration of $[SiO_2]_{total}$ at equilibrium with magadiite as a function of Na^+ ion concentration ($I = 0.1$; 25°C). The values in the diagram denote mol $Na^+ L^{-1}$.

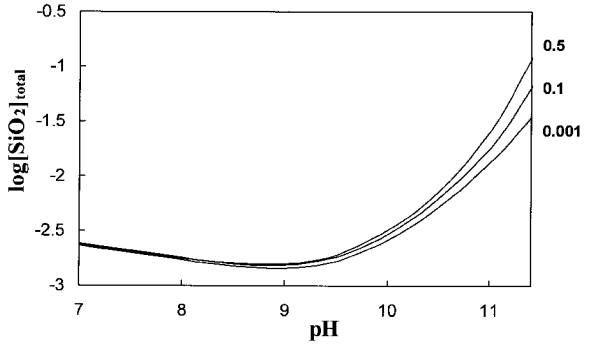

Figure 11. Concentration of $[SiO_2]_{total}$ at equilibrium with magadiite as a function of pH at ionic strengths of 0.5, 0.1 and 0.001 (0.001 mol $Na^+ L^{-1}$; 25°C).

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Furthermore, the solubility of magadiite depends on the concentration of Na^+ ions. Figure 10 shows that the higher the Na content of a solution the lower the $[SiO_2]_{total}$. Thus, increasing the Na^+ ion concentration of a solution by dissolution of highly-soluble Na salts (*e.g.* halite or sodium carbonates) or by mixing with Na-rich solutions will significantly reduce the solubility of magadiite.

The effect of ionic strengths on the solubility of magadiite depends strongly on pH (Figure 11). This effect is small at pH <9.5 and may be ignored at pH <8.5. However, ionic strength is relevant at pH >9.5, where negatively-charged species occur. Following this, *e.g.* the inflow of brines, which are rich in dissolved components, into a basin of alkaline solutions, which are rich in $[SiO_2]_{total}$, will increase the ionic strength of the alkaline solution favoring the dissolution of magadiite.

A scenario for the formation of magadiite from alkaline solutions may be due to a decrease of pH or temperature. At a constant chemical composition of a solution (pH 10.3, 0.1 mol Na^+ L^{-1}, and I = 0.2) a decrease from 100 to 25°C results in the $[SiO_2]_{total}$ changing from $10^{-1.21}$ to $10^{-2.42}$ mol L^{-1} (Figure 6). Thus, cooling may be one of the most important factors leading to magadiite precipitation from natural solutions. A decrease of pH, due to absorption of gaseous CO_2 into alkaline solutions or to an inflow of less alkaline or acidic solutions, increases the activity of $Si(OH)_4$ causing supersaturation with respect to magadiite (equation 7). In this situation the various dissolved silica compounds act as a reservoir, from which the uncharged monosilicic acid is obtained.

ACKNOWLEDGMENTS

The authors thank J. Amonette, D. Rimstidt, K. Kosuge and one anonymous reviewer for their comments.

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(*Received 27 August 2001; revised 29 April 2002; Ms. 572; A.E. James E. Amonette*)

https://doi.org/10.1346/000986002320679387 Published online by Cambridge University Press