Polymeric silicate complexing in aqueous fluids at high pressure and temperature, and its implications for water-rock interaction

C.E. Manning

Dept. of Earth & Space Sciences, University of California, Los Angeles, CA, USA

ABSTRACT: The solubility of silicate minerals in H_2O typically increases strongly as pressure (P) and temperature (T) rise along crustal geotherms. This simple observation has profound implications for material transfer in a wide range of geologic environments, but the controls on the P-T dependence of solubility remain poorly understood. New experimental studies suggest that solubility enhancement arises in large part from the increasing stability of silica-rich polymers at high P and T, e.g. $Si_2O(OH)_6$ dimers and $AlSi_2O_2(OH)_8^-$ and $NaAlSi_2O_2(OH)_8$ trimers. Although such complexes are well known in surface waters, their role in the aqueous solutions associated with magmatic and metamorphic processes is only now being appreciated. For example, SiO_2 dimers are abundant in quartz-saturated solutions in the system SiO_2-H_2O at >5 kbar and >500 °C. In more complex systems, silica multimers incorporate Al, alkalis, and, potentially, other rock-forming constituents. In the deep crust and mantle, these complexes may predominate relative to monomeric species and control the chemical interaction of fluids with crustal and mantle rocks. Silicate polymers increase chemical potential gradients, and therefore enhance mass transfer per unit fluid mass relative to polymer-free solutions. The abundance of silicate polymers also modifies the transport properties of dense aqueous fluids.

1 AQUEOUS SILICA POLYMERIZATION IN PURE H_2O

Silica polymers have long been recognized in aqueous solutions at low P and T. Early studies demonstrated their stability at high concentration in basic solutions or at strong quartz oversaturation (e.g. Lagerstrom 1959; Ingri 1959; Weill & Bottinga 1970; Busey & Mesmer 1977; Crerar et al. 1981; Cary et al. 1982; Alvarez & Sparks 1985). Nevertheless, thermodynamic analyses typically assumed that these complexes were not significant in equilibrium quartz-saturated H_2O at near-neutral pH because of lower aqueous silica concentration (e.g. Walther & Helgeson 1977). However, the concentration of aqueous silica in quartz-saturated H_2O increases dramatically with increasing P and T (Anderson & Burnham 1965; Manning 1994). Recent experimental studies show that this solubility enhancement is accompanied by increased extent of polymerization. Silica concentrations in equilibrium with quartz-undersaturated mineral assemblages at near-neutral pH are lower than predicted if monomers are the only silica species (Zhang & Frantz 2000; Newton & Manning 2002) and Raman spectroscopy of high-P-T quartz-saturated H_2O yields direct evidence for silica dimers (Zotov & Keppler 2000, 2002).

The identification of aqueous silica dimers is consistent with our knowledge of the structure and phase relations of hydrous silicate melts. In many silicate-H_2O systems at elevated P, the H_2O-saturated melt and the melt-saturated aqueous phase approach each other in composition with isobarically increasing T. The compositional difference between the two disappears along a critical curve, above which there is a single fluid whose composition varies without phase change from pure H_2O to relatively H_2O-poor, hydrous melt on the liquidus. In the system SiO_2-H_2O, the structure of supercritical hydrous SiO_2 melt is strongly polymerized at <10 wt% H_2O, such that bridging-oxygen rich species – Q_3 ($Si_2O_5^{2-}$) and Q_4 (SiO_2) – predominate (Farnan et al. 1987). Thus, in the supercritical region, an increase in SiO_2 concentration relative to H_2O is accommodated by the progressive increase in the abundance of Si-O-Si bonding; i.e. polymerization. The system SiO_2-H_2O has a second critical end point at ~10 kbar and 1060 °C (Kennedy et al. 1962). The comparatively low P and T of this feature indicate that there should be significant capacity for silica polymerization in fluids at geologically accessible conditions.

The significant equilibrium concentration of silica dimers in H_2O-rich solutions well below the hydrous melting temperature of quartz was not pre-

dicted by any theory of aqueous silica. This lack of prediction is in part attributable to a conceptual framework within which the thermodynamics of aqueous solutions are developed with reference to a state of infinite dilution. The analogy between hydrous melts and polymerized aqueous solutions implies that it is perhaps more useful to view the mixture of aqueous silica monomers and multimers at crustal metamorphic conditions as precursors to the polymerized hydrous melt produced at the water-saturated quartz solidus. Within such a framework, the structural chemistry of silicate melts (e.g. Hess 1971, 1995) will provide the best guide to speciation of dense aqueous fluids.

Initial steps toward developing new thermodynamic models of aqueous silica are under way. Newton & Manning (2003) investigated the thermodynamic properties of polymerized silicate solutions by constraining the activity coefficient of aqueous silica at 800 °C and 12 kbar through measurement of the concentration of total dissolved aqueous silica ($SiO_{2(t)}$) in H_2O in equilibrium with silica-buffering mineral assemblages. For the reaction 2 SiO_2 monomers (m) = 1 Si_2O_4 dimer (d), the equilibrium constant (K_{md}) is $K_{md} = X_d/X_m^2$, where X represents the mole fraction of $SiO_{2(t)}$ occurring as the subscripted species, and mixing is assumed to be ideal. This formulation is valid irrespective of the hydration states of the silica species because of the small silica concentration at these conditions (≤ 2.5 mol %). For a standard state of unit activity of the hypothetical pure-monomer solution at the P and T of interest, the monomer-dimer model leads to $\gamma_s = X_m/X_s$ and

$$K_{md} = \frac{(1-\gamma_s)}{2\gamma_s^2 X_s} \qquad (1)$$

where γ_s and X_s are the activity coefficient and mole fraction of total silica. The data yield $K_{md} = 155$ at 800 °C and 12 kbar, in excellent agreement with results from *in situ* Raman spectroscopy of a quartz-saturated solution at the same P-T (Zotov & Keppler 2002). Thermodynamic modeling indicates that higher polymers are unlikely to be significant at this P-T. In the system SiO_2-H_2O, a solution in equilibrium with quartz at 800 °C, 12 kbar, contains 2.5 mol % silica, of which 70 % occurs in dimers, and γ_s is small (0.30). Even at the low concentration (0.1 mol %), the activity coefficient is only 0.75 and the dissolved silica is substantially polymerized (25%).

2 Al AND Al-Si COMPLEXES

Like quartz, the solubility of corundum (Al_2O_3) and diaspore ($AlO(OH)$) in H_2O increase with P and T (Becker et al. 1983; Lin 2001; Tropper & Manning, in press). At 10 kbar, corundum solubility increases from 1 millimolal at 700 °C to 20 millimolal at 1100 °C. At all T, Al solubility in H_2O in equilibrium with diaspore or corundum at 10 kbar is at least ten times that at 1 kbar. Multimeric Al clusters have been observed in concentrated solutions at low P and T (e.g. Öhman & Sjoberg 1981; Bottero et al. 1987; Furrer et al. 1992, 2002; Boudot et al. 1996; Gérard et al. 2001). Though no direct observation has yet been made at elevated P and T, it is possible that, as with silica, the enhanced solubility of Al arises in part from increased stability of multinuclear Al clusters.

Aqueous fluids in the crust and mantle coexist with silicate minerals, so it is of fundamental importance to characterize solution and transport mechanisms of Al in Si-bearing solutions. Our experiments on the solubility of corundum (Al_2O_3) + kyanite (Al_2SiO_5) in H_2O at 700 °C, 10 kbar, yield higher Al solubility (6.17±0.55 mmol/kg H_2O) relative to corundum-only in H_2O at the same conditions. Because pH is near neutral, the elevation of Al concentration above that in the system corundum-H_2O implies formation of Al-Si multimers.

Al-Si complexing in aqueous solutions is a subject of some dispute. The formation of Al-Si complexes involving a bridging O may form in a wide variety of stoichiometries (e.g. Mueller et al. 1981). Browne & Driscoll (1992) reported that at 25 °C, 1 bar, 95% of aqueous Al and Si were bound in Al-Si complexes, primarily $AlOSi(OH)_3^{2+}$ formed via

$$Al^{3+} + H_4SiO_4 = AlOSi(OH)_3^{2+} + H^+ \qquad (2)$$

This result was challenged by Farmer & Lumsdon (1994), who found that minimal pH differences between Al solutions with and without Si were inconsistent with extensive Al-Si polymerization. Pokrovski et al. (1996) obtained a similar result at 25 °C. Significantly, however, Pokrovski et al. (1996) and Salvi et al. (1998) showed that $AlOSi(OH)_3^{2+}$ and other Al-Si complexes become progressively more stable with increasing T along the steam saturation curve. Thus, although Al-Si complexes are likely unimportant at equilibrium at 25 °C in natural waters, they may predominate in high-T environments such as hydrothermal systems. Combination of these observations with the new results on corundum-kyanite solubility suggests that enhanced stability of Al-Si complexes persists to the highest P and T yet studied, which represent deep crustal and mantle metasomatic environments.

3 Na-Al-Si COMPLEXES

A simple compositional model for the continental crust is feldspar + quartz. Thus, the extension of results in simple systems described above logically involves addition of alkalis. Antignano & Manning (2003) measured the solubility of albite+quartz in H_2O at 580°C, 5-12 kbar. Albite exhibited incongru-

ent dissolution, yielding a husk of paragonite ($NaAl_3Si_3O_{10}(OH)_2$) that mantles the albite grain. This is important because it produces a compositionally invariant solution at equilibrium and fixed P-T. The concentration of total dissolved solids (TDS) reaches 1.0 molal at 12 kbar. Si, Na, and Al solubilities all increase strongly with P, such that at 12 kbar molalities are: Si, 0.80; Na, 0.15; Al, 0.08. The aqueous Si concentrations in the albite-only experiments are higher than those in fluid equilibrated with quartz (Manning 1994) at the same conditions. This is consistent with the data of Anderson & Burnham (1983) on albite-H_2O at low P. Enhanced solubility of silica in the presence of albite+quartz, relative to quartz alone, suggests complexing of Si with Na and Al. Strong support for the formation of polymers lies in the fact that pH is near-neutral, so deprotonated silicic acid monomers are not abundant in these solutions. Formation of multimeric complexes involving Si, Al, and Na also explains the enhancement of Al solubility relative to that in equilibrium with corundum in H_2O. These complexes probably include a mixture of Na-Al, Na-Si, and Na-Al-Si molecules. Alkali-Al and Alkali-Si complexes are stable over a wide range of P and T, and may predominate under appropriate conditions (Anderson et al. 1987; Pascal & Anderson 1989; Anderson 1995; Pokrovskii & Helgeson 1995, 1997; Diakanov et al. 1996; Tanaka & Takahashi 1999). Na-Al-Si complexing has not been characterized in sufficient detail, but the stability of Si-Al trimers with associated Na^+ in aluminosilicate glasses and melts suggests that such structures are likely stable in aqueous solution as well (e.g. de Jong et al. 1981; Kubicki & Sykes 1995). In addition, the relatively low P and T of the albite-H_2O critical curve (Shen & Keppler 1997) are consistent with extensive Na-Al-Si complexing in the supercritical fluid phase.

4 IMPLICATIONS

The formation of polymeric silicate complexes in crustal and mantle fluids has important consequences for mass transfer and fluid properties. Viscosity and diffusivity will be significantly different in a polymer-bearing fluid than in a simple electrolyte solution. The large compositional dependence of silica polymerization (Newton & Manning 2003) yields a greater contrast in chemical potentials between different silica-buffering assemblages. For example, transport from silica-saturated to silica-undersaturated rocks (e.g. crustal to mantle lithologies in subduction zones) will require less fluid to attain the same compositional shift in the presence of polymers than in their absence (Newton & Manning 2002). The substantial enhancement of Al solubility through formation of Al-Si and Na-Al-Si complexes provides a simple explanation for the long-standing problem of precipitation of abundant aluminosilicate minerals from aqueous fluids in a wide range of metamorphic environments (e.g. Kerrick 1988; Widmer & Thompson 2001; Sepahi et al. 2004). A more general problem in crustal metamorphism is that many metamorphic rocks show evidence for significant compositional modification by flowing fluids (e.g. Ague 1997), but the fluid volumes required to produce the effect are often unreasonably high. Polymer formation could ameliorate this dilemma because it provides a mechanism for more efficient mass transfer. Thus, the recognition of polymeric silicate complexes represents an important step toward understanding water-rock interaction in metamorphic and igneous environments of the crust and mantle.

REFERENCES

Ague, J.J. 1997. Crustal mass transfer and index mineral growth in Barrow's garnet zone, northeast Scotland. *Geol.* 25: 73-76.

Alvarez, R. & Sparks, D.L. 1985. Polymerization of silicate anions in solutions at low concentrations. *Nature* 318: 649-651.

Anderson, G.M. 1995. Is there alkali-aluminum complexing at high temperatures and pressures? *Geochim. Cosmochim. Acta* 59: 2155-2161.

Anderson, G.M. & Burnham, C.W. 1965. The solubility of quartz in supercritical water. *Am. J. Sci.* 263: 494-511.

Anderson, G.M. & Burnham, C.W. 1983. Feldspar solubility and the transport of aluminum under metamorphic conditions. *Am. J. Sci.* 283-A: 283-297.

Anderson, G.M., Pascal, M.L. & Rao, J. 1987. Aluminum speciation in metamorphic fluids. In H.C. Helgeson (ed.), *Chemical Transport in Metasomatic Processes*: 297-321. Dordrecht: Reidel.

Antignano, A. & Manning, C. 2003. Solubility of albite + paragonite ± quartz in H_2O at 1 GPa, 580 °C: Implications for metamorphic fluids. *Eos* 84(46): Abstract V22D-0613.

Becker, K.H., Cemic, L. & Langer, K.E.O. 1983. Solubility of corundum in supercritical water. *Geochim. Cosmochim. Acta* 47: 1573-1578.

Bottero, J.-Y., Axelos, M., Tschoubar, D., Cases, J.-M., Fripiat, J.-J. & Fiessinger, F. 1987. Mechanism of formation of aluminum trihydroxide from Keggin Al_{13} polymers. *J. Colloid Interf. Sci.* 117: 47-57.

Boudot, J.-P., Maitat, O., Merlet, D. & Rouiller, J. 1996. Occurrence of non-monomeric species of aluminium in undersaturated soil and surface waters: consequences for the determination of mineral saturation indices. *J. Hydrol.* 177: 47-63.

Browne, B.A. & Driscoll, C.T. 1992. Soluble aluminum silicates: stoichiometry, stability, and implications for environmental geochemistry. *Science* 256: 1667-1670.

Cary, L.W., de Jong, B.H.W.S. & Dibble, W.E., Jr. 1982. A ^{29}Si NMR study of silica species in dilute aqueous solution. *Geochim. Cosmochim. Acta* 46: 1317-1320.

Busey, R.H. & Mesmer, R.E. 1977. Ionization equilibria of silicic acid and polysilicate formation in aqueous sodium chloride solution to 300°C. *Inorg. Chem.* 16: 2444-2450.

Crerar, D.A., Axtmann, E.V. & Axtmann, R.C. 1981. Growth and ripening of silica polymers in aqueous solutions. *Geochim. Cosmochim. Acta* 45: 1259-1266.

de Jong, B.H.W.S., Keefer, K.D., Brown, G.E. & Taylor, C.M. 1981. Polymerization of silicate and aluminate tetrahedral in glasses, melts, and aqueous solutions–III. Local silicon environments and internal nucleation in silicate glasses. *Geochim. Cosmochim. Acta* 45: 1291-1308.

Diakonov, O. Pokrovski, G., Schott, J., Castet, S. & Gout, R. 1996. An experimental and computational study of sodium-aluminum complexing in crustal fluids. *Geochim. Cosmochim. Acta* 60: 197-211.

Farmer, V.C. & Lumsdon, D.G. 1994. An assessment of complex formation between aluminum and silicic acid in acidic solutions. *Geochim. Cosmochim. Acta* 58: 3331-3334.

Farnan, I., Kohn, S.C. & Dupree, R. 1987. A study of the structural role of water in hydrous silica glass using cross-polarisation magic angle spinning NMR. *Geochim. Cosmochim. Acta* 51: 2869-2873.

Furrer, G., Trusch, B. & Müller, C. 1992. The formation of polynuclear Al_{13} under simulated natural conditions. *Geochim. Cosmochim. Acta* 56: 3831-3838.

Furrer, G., Phillips, B.L., Ulrich, K.-U., Pöthig, R. & Casey, W.H. 2002. The origin of aluminum flocs in polluted streams. *Science* 297: 2245-2247.

Gérard, F., Boudot, J.P. & Ranger, J. 2001. Consideration on the occurrence of the Al_{13} polycation in natural soil solutions and surface waters. *Appl. Geochem.* 16: 513-529.

Hess, P.C. 1971. Polymer model of silicate melts. *Geochim. Cosmochim. Acta* 35: 289-306

Hess, P.C. 1995. Structure, dynamics and properties of silicate melts. *Revs. Mineral.* 32: 145-189.

Ingri, N. 1959. Equilibrium studies of polyanions IV. Silicate ions in NaCl medium. *Acta Chem. Scand.* 13: 758-775.

Kennedy, G.C., Wasserburg, G.J., Heard, H.C. & Newton, R.C. 1962. The upper three-phase region in the system SiO_2-H_2O. *Am. J. Sci.* 260: 501-521.

Kerrick, D.M. 1988. Al_2SiO_5-bearing segregations in the Lepontine Alps, Switzerland: Aluminum mobility in metapelites. *Geol.* 16: 636-640.

Kubicki, J.D. & Sykes, S. 1995. Molecular orbital calculations on the vibrational spectra of Q^3-T(OH) species and the hydrolysis of a three-membered aluminosilicate ring. *Geochim. Cosmochim. Acta* 59: 4791-4797.

Lagerstrom, G. 1959. Equilibrium studies of polyanions III. Silicate ions in $NaClO_4$ medium. *Acta Chem. Scand.* 13: 722-736.

Lin, H.A. 2001. *Aqueous geochemistry at subduction zone conditions: experimental constraints.* Unpublished Ph.D. Thesis, University of California, Los Angeles, 247 p.

Manning, C.E. 1994. The solubility of quartz in H_2O in the lower crust and upper mantle. *Geochim. Cosmochim. Acta* 58: 4831-4839.

Mueller, D., Hoebbel, D. & Gessner, W. 1981. ^{27}Al NMR studies of aluminosilicate solutions. Influences of the second coordination sphere on the shielding of aluminum. *Chem. Phys. Lett.* 84: 25-29.

Newton, R.C. & Manning, C.E. 2002. Solubility of silica in equilibrium with enstatite, forsterite, and H_2O at deep crust/upper mantle pressures and temperatures and an activity-concentration model for polymerization of aqueous silica. *Geochim. Cosmochim. Acta* 66: 4165-4176.

Newton, R.C. & Manning, C.E. 2003. Activity coefficient and polymerization of aqueous silica at 800 °C, 12 kbar, from solubility measurements on SiO_2-buffering mineral assemblages. *Contrib. Mineral. Petrol.* 146: 135-143.

Öhman, L.-O. & Sjoberg, S. 1981. Equilibrium and structural studies of silicon(IV) and aluminum(III) in aqueous-solution. 1. The formation of ternary mononuclear and polynuclear complexes in the system Al^{3+}-gallic acid-OH⁻ - a potentiometric study in 0.6 m NaCl. *Acta Chem. Scand. Series A*: 201-212.

Pascal, M.L. & Anderson, G.M. 1989. Speciation of Al, Si and K in supercritical solutions: Experimental study and interpretation. *Geochim. Cosmochim. Acta* 53: 1843-1855.

Pokrovski, G.S., Schott, J., Harrichoury, J.-C. & Sergeyev, A.S. 1996. The stability of aluminum silicate complexes in acidic solutions from 25 to 150°C. *Geochim. Cosmochim. Acta* 60: 2495-2501.

Pokrovskii, V.A. & Helgeson, H.C. 1995. Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures: The system Al_2O_3-H_2O-NaCl. *Am. J. Sci.* 295: 1255-1342.

Pokrovskii, V.A. & Helgeson, H.C. 1997. Thermodynamic properties of aqueous species and the solubilities of minerals at high pressures and temperatures: the system Al_2O_3-H_2O-KOH. *Chem. Geol.* 137: 221-242.

Salvi, S., Pokrovski, G.S. & Schott, J. 1998. Experimental investigation of aluminum-silica aqueous complexing at 300 °C. *Chem. Geol.* 151: 51-67.

Sepahi, A.A., Whitney, D.L. & Baharifar, A.A. 2004. Petrogenesis of andalusite-kyanite-sillimanite veins and host rocks, Sanandaj-Sirjan metamorphic belt, Hamadan, Iran. *J. Metamorph. Geol.* 22: 119-134.

Shen, A. & Keppler, H. 1997. Direct observation of complete miscibility in the albite-H_2O system. *Nature* 385: 710-712.

Tanaka, M. & Takahashi, K. 1999. The identification of chemical species of silica in sodium hydroxide, potassium hydroxide and sodium chloride solutions by FAB-MS. *Anal. Sci.* 15: 1241-1250.

Tropper, P. & Manning, C.E. 2004. The solubility of rutile and corundum in H_2O at high P and T: constraints on Ti and Al mobility during high-P metamorphism. EMPG Conference Abstracts, in press.

Walther, J.V. & Helgeson, H.C. 1977. Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures. *Am. J. Sci.* 277: 1315-1351.

Weill, D. & Bottinga, Y. 1970. Thermodynamic analysis of quartz and cristobalite solubilities in water at saturation vapor pressure. *Contrib. Mineral. Petrol.* 25: 125-132.

Widmer, T. & Thompson, A.B. 2001. Local origin of high pressure vein material in eclogite facies rocks of the Zermatt-Saas zone, Switzerland. *Am. J. Sci.* 301: 627-656.

Zhang, Y.-G. & Frantz, J.D. 2000. Enstatite-forsterite-water equilibria at elevated temperatures and pressures. *Am. Mineral.* 85: 918-925.

Zotov, N. & Keppler, H. 2000. *In-situ* Raman spectra of dissolved silica species in aqueous fluids to 900 °C and 14 kbar. *Am. Mineral.* 85: 600-603.

Zotov, N. & Keppler, H. 2002. Silica speciation in aqueous fluids at high pressures and high temperatures. *Chem. Geol.* 184: 71-82.