Aluminosilicate polymerization in dense aqueous fluids: Implications for subduction-zone mass transfer

C.E. MANNING*, R.C. NEWTON, R. THOMAS,
J.D. HUNT* AND M CRUZ

University of California, Los Angeles., Los Angeles, CA 90095 USA (*correspondence: manning@ess.ucla.edu)

Aqueous fluids from basaltic, sedimentary or ultramafic rocks in subduction zones are dominated by polymeric solutes comprised of the major rock-forming oxides. High *P-T* study of mineral solubilities in model oxide-H_2O systems shows that SiO_2 is the most abundant solute in the aqueous phase. The system quartz-H_2O possesses a second critical end-point (CEP) on the melting curve at 0.98 GPa and 1180°C [1]. Polymerization – the progressive increase in bridging oxygens linking dissolved cations – proceeds with rising dissolved silica [2,3]. Within 200°C of the CEP, quartz solubility in H_2O at 1 GPa shows excess aqueous SiO_2 above that calculated for the monomer + dimer, signaling pre-melting SiO_2 oligomerization. Data at 1.5 GPa indicate that at a given *T*, extent of polymerization is even greater. At supercritical *P-T*, NaCl lowers quartz solubility, as at subcritical conditions [4], shifting the CEP to higher *T*. Addition of Al yields strong interactions with SiO_2 via polymerization. In the presence of kyanite, aqueous Si-Al oligomers carry most dissolved Al and enhance Si solubility at quartz saturation [5-7]. Addition of Na or K further promotes polymer formation, even at subcritical conditions. At 1 GPa within 100°C of the hydrothermal melting curves of alkali feldspar+mica+quartz, bulk solubilities rapidly increase from several wt% to >10 wt% via increase in polymerization as melting is approached from low *T*. Ca-bearing systems display similar effects [8]. Thus, polymeric aluminosilicates form a structural “backbone” of subduction-zone fluids, promoting critical mixing of H_2O and melt, enhancing solubility of trace elements [9], and influencing mass transfer.

[1] Newton & Manning (2008) *Earth Planet. Sci. Lett.* **274** 241-249; [2] Newton & Manning (2002) *Geochim. Cosmochim. Acta* **66** 4165-4176; [3] Newton & Manning (2003) *Contrib. Mineral. Petrol.* **146** 135-143; [4] Newton & Manning (2000) *Geochim. Cosmochim. Acta* **64** 2993-3005; [5] Manning (2007) *Geofluids* **7** 258-269; [6] Tropper & Manning (2007) *Chem. Geol.* **240** 54-60; [7] Newton & Manning (2008) *Chem. Geol.* **249** 250-261; [8] Newton & Manning (2007) *Geochim. Cosmochim. Acta* **71** 5191-5202; [9] Manning et al. (2008) *Earth Planet. Sci. Lett.* **272** 730-737.

PVTx properties of chloride-rich aqueous fluids at high P-T conditions

DAVIDE MANTEGAZZI[1]*, CARMEN SANCHEZ-VALLE[1]
AND THOMAS DRIESNER[2]

[1]Inst. for Mineralogy and Petrology, ETH Zurich, CH-8092 Zurich (*correspondence: davide.mantegazzi@erdw.ethz.ch, carmen.sanchez@erdw.ethz.ch)

[2]Inst. of Isotope Geochemistry and Mineral Resources, ETH Zurich, CH-8092 Zurich (thomas.driesner@erdw.ethz.ch)

Binary mixtures H_2O-NaCl are considered as good approximations of natural geological fluid in a wide range of processes in the Earth’s crust and mantle. Typical examples of such geological events are: metamorphic reactions, hydrothermal alteration of the seafloor, formation of ore deposits and magma production. Despite the key role of these fluids only few experimental data on the themodynamical properties of fluids other than pure H_2O [1-3] are available at high pressure and temperature conditions. For instance, the equations of state (EoS) for H_2O-NaCl mixtures are restricted to 0.5 GPa [4]. The knowledge of the thermodynamic properties of these fluids at geologically relevant P and T conditions is essential for the understanding and the quantitative modelling of fluid-mediated geological processes. Therefore more experimental data at high P-T conditions are needed.

In this contribution, we present PVTx properties of chlorinated aqueous fluids (namely H_2O-NaCl mixtures) with variable salinities determined from acoustic velocity measurements at high P-T conditions. Measurements were performed using Brillouin scattering spectroscopy in combination with externally heated diamond anvil cells (DAC). The EoS obtained from this work are further used to evaluate the P-T dependence of thermodynamic properties of chlorinated binary fluids, including thermal expansion coefficients, isothermal and adiabatic compressibilities and heat capacities. The results are combined with previous experimental and theoretical EoS of H_2O-NaCl mixtures [4] to provide an internally consistent dataset for the thermodynamical properties of the most relevant aqueous systems involved in fluid-mediated processes in the Earth’s crust and mantle.

[1] Wagner and Pruss (2002) *J. Phys. Chem. Ref. Data*, **31**, 387–535. [2] Abramson and Brown (2004) *GCA*, **68**, 1827-1835. [3] Sanchez-Valle and Bass (2007) *GCA*, **71**, A873-A873. [4] Driesner (2007) *GCA*, **71**, 4902-4919.