AMORPHOUS MATERIALS†

An experimental study of phosphorous and aluminosilicate speciation in and partitioning between aqueous fluids and silicate melts determined in-situ at high temperature and pressure

BJORN O. MYSEN*

Geophysical Laboratory, Carnegie Institution Washington, 5251 Broad Branch Road NW, Washington, D.C. 20015, U.S.A.

ABSTRACT

The structure of phosphorus-bearing, H2O-saturated silicate melts, silicate-saturated aqueous fluids, and silicate-rich single phase (supercritical) liquids has been characterized in situ to 800 °C and 1486 MPa in an Ir-gasketed hydrothermal diamond-anvil cell (HDAC) with the aid of both confocal microRaman and FTIR spectroscopy. Temperature and pressure in the HDAC were recorded with thermocouples (±1 °C uncertainty) and pressure- and temperature-dependent Raman shift of 13C diamonds (±40 MPa uncertainty). Starting materials were aluminum-free Na2O·4SiO2 (NS4) and with 10 mol% Al2O3 (NA10) substituting for SiO2, both with 5 mol% P2O5.

Aluminosilicate species of Q0, Q1, Q2, and Q3 type exist in coexisting fluid and melt and in single phase liquid together with phosphate species, PO4, P2O7, and QnP. In the QnP species, n O atoms bridge between Si4+ and P5+, whereas there is no Si-to-P linkage in the PO4 and P2O7 species. In melts, the abundance of the most depolymerized silicate species, Q0, is positively correlated with temperature and pressure, whereas that of the most polymerized species, Q3, decreases with temperature and pressure. In the silicate solute of aqueous fluids, the opposite relationship exists with Q0 abundance decreasing and Q3 (and Q1 and Q2) abundance increasing with increasing temperature and pressure. The silicate melts, therefore, become increasingly depolymerized and the silicate solute in aqueous fluids decreasingly depolymerized because increasing H2O solubility in melts causes melt depolymerization, whereas increasing silicate solute abundance in fluids results in silicate polymerization. The P2O7 and QnP are the dominant phosphate species in fluid, melt, and single phase liquid with orthophosphate, PO4, playing a subordinate role. The fluid/melt partition coefficients for P2O7 and QnP species are in the 0.15–0.7 range with that of QnP being greater than that of P2O7. The PO4 fluid/melt partition coefficients are <0.2. In all cases, the partition coefficients increase with increasing temperature and pressure. There is no clear influence of Al2O3 on partition coefficients. Hence, it appears that P-bearing complexes in fluids and melts are associated with Na+ that becomes available as silicate species polymerize. The mobility of phosphorus during metamorphic processes is principally governed by the availability of alkali metals (and perhaps alkaline earths).

Keywords: Phosphate solution, melt structure, aqueous fluid, fluid/melt partitioning

INTRODUCTION

Apatite is a common accessory mineral in metamorphic and magmatic rocks such that phosphorus solubility in melts equilibrated with apatite can be used to deduce petrogenetic processes (e.g., Watson 1979; Harrison and Watson 1984; Pichavant et al. 1992; Tollari et al. 2006; Antigniano and Manning 2008). Phosphorus solubility depends on melt composition (Harrison and Watson 1984; Pichavant et al. 1992; Wolf and London 1994; Tollari et al. 2006), which reflects how phosphate is dissolved in the melts. For example, vibrational and NMR spectroscopic data of quenched silicate melts (glasses) are consistent with structural interaction of phosphate groups that can form structural complexes containing Si4+ (Yang et al. 1986; Dupree et al. 1987, 1989; Yamashita et al. 2000; Cody et al. 2001), Al3+ (Gan and Hess 1992; Toplis and Schaller 1998; Cody et al. 2001), alkalis, and alkaline earths (Gan and Hess 1992; Schaller et al. 1999; Cody et al. 2001). Phosphate speciation in melts also depends on phosphorus concentration and temperature (Nelson and Tallant 1984, 1986; Mysen 1996; Reynard and Toplis 1997; Mysen and Cody 2001).

There is evidence of transport of phosphorus by H2O-rich fluids during high-pressure metasomatism (e.g., Silverstone et al. 1992; Bebout and Barton 1993). Phosphorus solubility data for aqueous fluids at high pressure and temperature are limited, and what exists may not be internally consistent (Ayers and Watson 1993; Antigniano and Manning 2008). Experimental information on P solution mechanisms in silicate-saturated aqueous fluids under pressure and temperature conditions of high-grade metamorphism or during melting in the deep crust and upper mantle

* E-mail: bmysen@ciw.edu
† The Amorphous Materials special section papers are presented as a group at http://www.minsocam.org/msa/ammin/toc/ and on GSW at http://ammin.geoscienceworld.org/misc/virtual_special_list.dtl.