

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

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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