The effect of temperature and bulk composition on the solution mechanism of phosphorus in peraluminous haplogranitic magma

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ABSTRACT

Solution mechanisms of P in peraluminous glasses and melts in the system CaO-Na2O-K2O-Al2O3-SiO2-P2O5 have been examined with in-situ microRaman spectroscopy from ambient temperature to near 1200 °C. The principal aim was to examine the relative stabilities of phosphate complexes as functions of P content, peraluminosity, and temperature. Increasing peraluminosity was accomplished by increasing the proportions of Al3+ and Ca2+ of constant SiO2 content. The molar ratio Al2O3/(CaO+Na2O+K2O) (A/CNK) ranged from ~1 to ~1.3.

In all compositions, P5+ is bonded to Al3+ to form AlPO4 complexes. In addition, there is evidence for pyrophosphate complexing (P2O7). In melts with the highest (Ca+Na+K)/P, there is probably also a small fraction of orthophosphate complexes present. The relative importance of AlPO4-like complexes is correlated positively with peraluminosity (A/CNK), P2O5 content, and increasing temperature at temperatures above that of the glass transition. These structural relationships among phosphate complexes are coupled with decreasing polymerization of the aluminosilicate melts.

INTRODUCTION

Phosphorus in igneous rocks is important for at least two main reasons. First, in the concentration range in natural magmas (<2–3 wt% P2O5), phosphorus strongly modifies both physical and chemical properties of the magmatic system. These properties include melt viscosity (Dingwell et al. 1993; Toplis et al. 1994), liquidus phase relations (Wylie and Tuttle 1964; Kushiro 1975; Ryerson 1985; London et al. 1993), redox equilibria of iron (e.g., Mysen 1992; Gwinn and Hess 1993; Toplis et al. 1994), and element partitioning (Watson 1976). Second, phosphate minerals (e.g., apatite and monazite) in some cases are abundant in highly evolved igneous systems (e.g., Pichavant et al. 1987; London 1987; London et al. 1990). Such minerals in equilibrium with a P-bearing magma can alter the trace-element patterns of the magma significantly without much impact on its major element composition (e.g., Watson 1980; Green and Watson 1982; Ghazot et al. 1996). Consequently, phosphorus solution mechanisms and their relations to saturation of phosphate minerals in aluminosilicate melts require characterization.

To characterize the behavior of P-bearing magmas and the crystallization behavior of phosphate minerals from such magmas, data on solubility and solubility mechanisms of P in the magmatic liquid are required. For subaluminous (A/CNK = 1) and peraluminous (A/CNK>1) glass, it has been suggested that the speciation of P is dominated by the presence of AlPO4-like units (Mysen et al. 1981; Kosinski et al. 1988; Dupree et al. 1989; Gan and Hess 1992; Toplis and Dingwell 1996; Mysen et al. 1997; Toplis and Schaller 1998). Complexing of P5+ with Al3+ in peraluminous aluminosilicate melts would account for the strong increase of apatite solubility with increasing A/CNK found experimentally (Pichavant et al. 1992; Wolf and London 1994). Formation of such Al-rich phosphate complexes in melts might also help explain the expansion of the quartz liquidus volume relative to that of feldspar in haplogranite systems (London et al. 1993).

These studies were, however, conducted on glasses at ambient temperature. The application of these structural data to that of their melt relies on assumptions of structural similarity between a melt and its glass. Recent data on melts in the system Na2O-Al2O3-SiO2-P2O5 have demonstrated, however, that phosphate and silicate speciation changes rapidly with increasing temperature across the glass transition (Mysen 1996, 1998a). Therefore, to provide structural data on melts obtained in-situ at magmatic temperatures, we present here Raman spectroscopic data on the solution mechanisms of P2O5 in peraluminous melts in the system SiO2-Al2O3-Na2O-K2O-CaO-P2O5 from room temperature to those above their liquidus. Data are reported for two series of melts, one with Ca/P = 5/3 (i.e., same as in apatite) and the other with Ca/P = 1, which enables us to test the possibility that P coordinates preferentially with Ca rather than with Al.

EXPERIMENTAL METHODS

Starting composition glasses (Table 1) were from the same batches as those for which Mysen et al. (1997) reported structural information of H2O-free and H2O-bearing glasses at 25 °C. Details of starting glass preparation and chemical analysis are