AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY†

Oxidation state of iron in hydrous phono-tephritic melts

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ABSTRACT

The oxidation state of Fe in hydrous ultrapotassic (phono-tephritic) melts coexisting with mixed H_2O-CO_2 fluids was studied experimentally at 1200 and 1250 °C and pressures from 50 to 500 MPa. The oxygen fugacity (f_{O_2}) varied from NNO–2.9 to NNO+2.6 in log f_{O_2}, relative to the Ni-NiO oxygen buffer (NNO), as imposed by external redox conditions in experimental vessels and internal variations in water activity from 0.05 to 1 inside the capsules. The Fe redox state of the quenched melts was determined by colorimetric wet-chemical analysis. This analytical method was optimized to measure the Fe^{2+}/ΣFe ratio of milligram-sized samples within ±0.03 (2σ). The accuracy and precision was tested with international reference materials and with standards analyzed by other methods. The Fe^{2+}/ΣFe ratio of the experimental glasses covered a range of 0.41 to 0.85. A small negative effect of dissolved water on Fe^{2+}/ΣFe at given f_{O_2} was found, consistent with the thermodynamic model of Moretti (2005). No effect of pressure and temperature on the redox state of Fe was resolvable in the investigated *P-T* range. Compared to hydrous ferrobasaltic melts that were studied previously under similar conditions, systematically lower Fe^{2+}/ΣFe ratios were found for the phono-tephritic melts, in particular at low oxygen fugacities. This effect is attributed to the much higher K_2O contents of the phono-tephrite (7.5 compared to 0.3 wt%), but the difference in FeO_T (7.8 wt% in the phono-tephrite and 12.9 wt% in the ferrobasalt) may have an influence as well. Comparison of the experimentally obtained relationship between log f_{O_2} and Fe^{3+}/Fe^{2+} for the studied hydrous ultrapotassic melts with commonly used empirical and thermodynamic models suggest that these models can be successfully applied to phono-tephritc melts, although such compositions were not implemented in the model calibrations. Furthermore, the new data can be used to improve the models with respect to the effects of compositional variables, such as H_2O or K_2O, on the redox state of Fe in silicate melts.

Keywords: Fe oxidation state, FeO determination, oxygen fugacity, water activity, phono-tephrite, ultrapotassic hydrous silicate melt, Alban Hills