
Stabilization of Silicate Melts through Polymerization Reactions, with Implications for the Redox State of the Mantle and Crust

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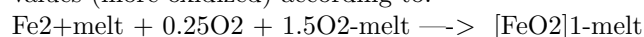
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Abstract

Melting of forsterite, fayalite, and numerous metasilicate crystals (e.g., pyroxenes, pseudowollastonite) produces melts appreciably more polymerized than their precursor crystals. Melting of forsterite, which is composed solely of Q0 species, produces melts in which Q1 and Q2 species dominate. Melting of fayalite also produces melts more polymerized than its precursor crystal and more polymerized than Mg₂SiO₄ melt. Q2 silicate crystals (e.g., pyroxenes) also produce melts more polymerized than their precursor crystals. The polymerization reactions stabilize the melts by buttressing them against the effects of extreme thermal agitation, by diminishing librational and rotational contributions to their heat capacities. In the absence of polymerization, melting temperatures of the most common silicate minerals would be appreciably greater than observed. Polymerization of Si tetrahedra in crystals and melts proceeds via nucleophilic reactions. Nucleophiles are produced by strong thermal agitation which causes dissociation of the bond between non-bridging oxygen (NBO) and a counter cation (M). Bond scission produces the negatively charged nucleophilic species Si-NBO⁻, which may attack and bond to Si centers of adjacent tetrahedra leading to melts more polymerized than their precursor crystals. All polymerization reactions produce free oxygen (O²⁻ or oxide ion). Melting of forsterite, for example, yields a minimum of ~6 mol% O²⁻ and still greater amounts of O²⁻ are produced during melting of fayalite. Melting of Q2 crystals produces ~1-5 mol% O²⁻, thus melting of olivine and pyroxenes in the mantle should produce O²⁻ at the mol% level. This strong base is likely to partition strongly into the melt rather than into the residual crystals. With accumulation in the melt, the chemical state, including redox states, will be affected by driving the melt toward greater Fe³⁺/Fe²⁺ values (more oxidized) according to:



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