

Polymerization during melting of ortho- and meta-silicates: Effects on Q species stability, heats of fusion, and redox state of mid-ocean range basalts (MORBs)

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ABSTRACT

²⁹Si NMR and Raman spectroscopic studies demonstrate that fusion of crystalline orthosilicates and metasilicates produces melts more polymerized than their precursor crystals. Forsterite, for example, consists of 100% Q⁰ species, whereas its melt consists of ~50 mol% of Q¹ species (Q = a Si tetrahedron and the superscript indicates the number of bridging oxygen atoms in the tetrahedron). Polymerization during melting can be rationalized from an energetics perspective. Si-NBO-M moieties of Q species are more susceptible to librational, rotational, and vibrational modes than are Si-BO-Si moieties (NBO = non-bridging oxygen; BO = bridging oxygen; M = counter cation). Thermal agitation activates these additional modes, thus increasing the C_p and free energy of melts. The reaction of Qⁿ to Qⁿ⁺¹ species during melting eliminates Si-NBO-M moieties and produces Si-O-Si moieties that are less susceptible to the additional modes, thereby minimizing the C_p of melts. By decreasing the abundances of Q⁰, Q¹, and Q² species in favor of Q³ and Q⁴ species, melts become more stable. In the absence of polymerization, melting temperatures of minerals would be appreciably greater than observed.

Polymerization involves formation of Si-O bonds, which are strongly endothermic (Si-O bond dissociation is ~798 kJ/mol). The large heats of fusion (ΔH_f) of orthosilicates result primarily from polymerization reactions during melting (ΔH_f of forsterite, fayalite, and tephroite are ~142, ~92, and ~90 kJ/mol). The fusion of metasilicates and sorosilicates (e.g., pyroxenes and melilites) involves endothermic polymerization *and* exothermic depolymerization reactions, although the former dominates. These reactions tend to negate each other during melting, yielding less positive ΔH_f values than observed for orthosilicate fusion (e.g., ΔH_f of enstatite, diopside, pseudowollastonite, and åkermanite are ~73, ~69, ~57, and ~62 kJ/mol). Where polymerization and depolymerization reactions are absent ΔH_f is low and is due mostly to disordering during melting (e.g., ΔH_f of cristobalite is ~8.9 kJ/mol).

Experimental evidence indicates that ferric iron is present as a *negatively charged* oxy-anionic complex in melts (e.g., [FeO₂]¹⁻) so that oxidation of Fe²⁺ should proceed according to: $4\text{Fe}_{\text{melt}}^{2+} + 1\text{O}_2 + 6\text{O}_{\text{melt}}^{2-} \rightarrow 4[\text{FeO}_2]_{\text{melt}}^{1-}$.

Free oxygen (O²⁻), a by-product of polymerization reactions, drives the reaction to the right. Mid-ocean ridge basalts (MORBs) consequently should be more oxidized than their source (e.g., lherzolites) or their residues (e.g., harzburgites). Extraction of melt from the upper mantle and deposition in the crust should produce a crust more oxidized than its upper mantle source. Production of O²⁻ during melting and its presence in alkali-rich magmas also explains the *alkali-ferric iron effect*.

Keywords: Silicate melting, mantle melting, Q species energetics, heats of fusion, polymerization reactions, MORB redox reactions