

Computational and experimental studies of iron-bearing carbonates and silicate glasses at lower mantle pressures

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Decomposition of carbonates may be responsible for creating silicate melts within the lower mantle by lowering the melting temperature of surrounding rock. Identifying and characterizing the stability of carbonate phases is therefore a necessary step towards understanding the transport and storage of carbon in Earth's interior. Dolomite is one of the major mineral forms in which carbon is subducted into the Earth's mantle. Although iron-free dolomite is expected to break down upon compression into single-cation carbonates, high-pressure polymorphs of iron-bearing dolomite may resist decomposition. Using a genetic algorithm that predicts crystal structures, we have found a monoclinic phase with space group $C2/c$ that has a lower energy than all previously reported dolomite structures at pressures above 15 GPa, where the substitution of iron for magnesium stabilizes monoclinic dolomite with respect to decomposition at certain pressures of the lower mantle. Thus, an iron-bearing dolomite polymorph may be an important carbon carrier in regions of Earth's lower mantle.

The depth at which carbonates will decompose is dependent on the age, temperature and density of the subducting slab. Decarbonation reactions may lower the melting temperature of surrounding rocks to produce silicate melts. In regions of the mantle where silicate melts may exist, it is important to understand the physical properties and dynamic behavior of the melts because they affect the chemical and thermal evolution of its interior. Composition, degree of polymerization, and iron's spin state affect such properties. The behavior of iron in silicate melts is poorly understood but, in some cases, may be approximated by iron-bearing glasses. We measured the hyperfine parameters of iron-bearing rhyolitic and basaltic glasses up to ~120 GPa and ~90 GPa, respectively, in a neon pressure medium using time-domain synchrotron Mössbauer spectroscopy. The spectra for rhyolitic and basaltic glasses are well explained by three high-spin Fe^{2+} -like sites with distinct quadrupole splittings, reflecting the influence of evolving coordination environments with pressure. With the assumption that coordination environments in silicate glasses may serve as a good indicator for those in a melt, this study suggests that ferrous iron in chemically-complex silicate melts likely exists in a high-spin state throughout most of Earth's mantle.