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The crystal chemistry of aluminous perovskite may cause precipitation of metallic Fe in the lower mantle

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Aluminous silicate perovskite, the major phase of Earth's lower mantle, accommodates significant amounts of Fe³⁺. High-pressure experiments on starting materials (simplified FMAS-CFMAS and complex peridotitic compositions) where iron is present as Fe²⁺, were carried out at variable oxygen fugacities, using sample capsules of Re, C and Fe. The crystal chemical tendency of aluminous perovskite to incorporate ferric iron, drives the redox reaction: 3FeO = Fe + Fe₂O₃. In the experiments with Fe- and C-capsules, metallic Fe is precipitated within and next to the perovskite crystals.

Perovskites with 0.07-0.25 Fe_{total} and 0.03-0.12 Al per formula unit of 2 cations have Fe³⁺/Fe_{total} ratios of 0.3 to 0.8 in equilibrium with Fe²⁺-dominated ferropericlase. For an 8-cation formula, the most essential end members of aluminous perovskites may be expressed as M₄Si₄O₁₂, M₃Al₂Si₃O₁₂, M₃Fe³⁺AlSi₃O₁₂ and M₄Al₂Si₂O₁₁, where M denotes divalent cations in cubic coordination. The oxygen-vacancy- and Fe³⁺-Al-components give 10-30 and 10-50 mol%, whereas the pyrope component is generally less than 5 mole%. Strong positive correlations between the total Al-content and the Fe³⁺-Al- and O-vacancy components and weak positive correlations between Fe_{total} and these components are observed. The perovskite crystal chemistry appears to be independent of the oxygen fugacity of the experiments.

For typical mantle compositions, more than 60% of Fe in perovskite will be ferric. This implies that the bulk Fe³⁺ content of the lower mantle is more than ten times that of the upper mantle. Perovskite must therefore sequester oxygen by the reduction of ferrous iron to metallic iron, unless the lower mantle is strongly enriched in oxygen relative to the upper mantle. For a significant material transport between the upper and lower mantle, the lower mantle should contain about 1 wt% Fe-dominated metal, forming as material enters the perovskite stability field. If minor amounts of the Fe-metal have segregated to the core since the lower mantle formed, the oxygen content of the mantle may have increased, from a reduced state at the end of core separation, to the level of the present upper mantle. Although a minor metal phase will not significantly influence the elastic properties of the lower mantle, the substitution mechanism of Al and Fe³⁺ is likely to have a strong influence on the elastic properties of perovskite. A metal phase present in the lower mantle has also important consequences for the siderophile element budget.

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Trace element partitioning and defects in perovskites

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We have recently been determining the trace element partitioning relationships between CaSiO₃ perovskite and melt, (Mg,Fe)SiO₃ perovskite and melt and CaTiO₃ perovskite and melt. These show unusual patterns indicating that cation vacancies are important. The implications are that perovskites in the lower mantle can dissolve large amounts of 4+ ions such as U⁴⁺ and Th⁴⁺ in the A-site.

The first observation is that all 3 of the perovskites we have studied have higher partition coefficients for 4+ and 3+ ions replacing Ca and Mg than for Ca and Mg themselves. This is quite different from upper mantle minerals such as clinopyroxene, orthopyroxene and olivine where the major 2+ ions (Ca, Mg, Fe²⁺) partition more readily into the crystal than ions of other charge. By varying the concentrations of potential charge coupling ions, such as Al³⁺ for Si⁴⁺ we find that coupled substitution does not have an important effect on partition coefficients.

Varying melt composition has a profound effect on Th⁴⁺ and Pr³⁺ partitioning into Ca-perovskites. In particular, the partition coefficients are strong functions of CaO content of the melt. This is not, however, an effect to be empirically attributed to some parameter such as NBO/T. It is due to the effect of Ca activity on the concentration of cation vacancies in the perovskite. The effect can be seen clearly in both CaTiO₃ and CaSiO₃ perovskites. Thus, we find that the low energy substitution mechanism of Th⁴⁺ for Ca²⁺ is (Th⁴⁺+V_{Ca}) replacing 2Ca²⁺, where V refers to a vacancy on the calcium site.

The implications of the ready substitution of 3+ and 4+ ions for 2+ ions in perovskites are that lower mantle CaSiO₃ has high U/Pb, Lu/Hf and Sm/Nd ratios while (Mg,Fe)SiO₃ has low U/Pb and Lu/Hf with high Sm/Nd