# Crystal chemistry of $Fe^{3+}$ in $(Mg,Fe)SiO_3$ perovskite and implications for lower mantle properties

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Recent work on Fe-bearing silicate perovskites indicates that $Fe^{3+}$ may be an important cation in mantle perovskites, [1,2] and the behavior of $Fe^{3+}$-bearing perovskite therefore has important implications for the composition and dynamics of the lower mantle. In order to understand the effect of $Fe^{3+}$ on the perovskite structure, we carried out multi-anvil syntheses of $Fe^{3+}$-bearing $(Mg,Fe)SiO_3$ (with and without Al) from a starting mixture of oxides, using $Fe_2O_3$ as the exclusive source of iron. To maintain a $Fe^{3+}/\Sigma Fe$ ratio close to 1 in the final run product, the sample capsule was surrounded by an oxidizing layer of $Fe_2O_3$.

Synthesis products were characterized using electron microscopy, electron microprobe, X-ray diffraction, and Mossbauer spectroscopy. Microprobe and Mossbauer measurements indicate that the synthesized perovskites contain no $Fe^{2+}$ within detection limits, but as much as 7.4 mol% $Fe^{3+}$. Although evidence of $Fe^{3+}$ in both crystallographic sites was observed in all samples, results suggest that $Fe^{3+}$ preferentially occupies the octahedral site. The presence of $Fe^{3+}$ in the octahedral site of $(Mg,Fe^{3+})SiO_3$ causes a substantially larger molar volume than that of $(Mg,Fe^{2+})SiO_3$ with the same Fe content (in which $Fe^{2+}$ substitutes exclusively into the dodecahedral site). $Fe^{3+}$ greatly increases the b/a axial ratio, potentially enhancing the seismic anisotropy of the lower mantle. Changes in the crystal chemistry of $Fe^{3+}$-bearing perovskite with depth may also complicate the nature of the spin transition zone, since octahedral $Fe^{3+}$ becomes low spin at much lower pressures than does dodecahedral $Fe^{3+}$. [3]

[1] McCammon (1997) *Nature* **387**, 694-696. [2] Frost *et al* (2004) *Nature* **428**, 409-412. [3] Catalli *et al* (2010) *Earth Plan. Sci. Lett.* **289**, 68-75.

# Agricultural impact on P and metal availability in stream sediments

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Intensive commercial agriculture is associated with significant applications of phosphorus fertilizers for crops and trace metals (e.g., Zn, Cu) for animal production. Excess amounts of these elements are often found in nearby aquatic systems. This is of particular concern as high P levels cause stream eutrophication. Therefore, analytical protocols are needed to assess the impact of agricultural pollution. Sequential extraction (SE) schemes have been developed to determine the availability of contaminants for aquatic systems in relation to their chemical bonding within the sediment. While most SE schemes consider P and metals separately, we provide an assessment of a SE scheme for both categories (modified after the method of Tiessen and Moir [1] for P).

Our study focused on the Sumas River watershed, an intensive agricultural region in British Columbia (Canada) strongly affected by nutrient and metal pollution. To quantify agricultural impacts, we collected river bed sediment samples from headwaters (no anthropogenic disturbance) to the intensively managed agricultural region downstream, over the length of 35 km. We examined trends in concentrations (e.g., P, Zn, Cu, and Pb) for different geochemical fractions of these stream sediments. Both concentrations and Pb isotopic compositions are used to trace natural (e.g. serpentinites present in headwater region) and anthropogenic sources, and to corroborate the utility of the SE scheme.

Our results show increasing contaminant concentrations towards downstream, e.g., from 33 to 5,479 ppm for P, from 24 to 167 ppm for Zn, from 9 to 60 ppm for Cu, and from 0.9 to 21 ppm for Pb. The most effective extractants were found to be 0.1 M NaOH (for labile P and Cu) and 1 M HCl for other metals. An increase of labile P with increasing agriculture intensity suggests that sediment source is important for contaminant availability, with anthropogenically-introduced contaminants often accumulating in more labile fractions. For sediments, the $^{206}Pb/^{207}Pb$ ratio decreases from headwaters (1.20373) to downstream (1.17631), consistent with increasing contributions of anthropogenic origin.

[1] Tiessen, H. and Moir, J. (1993), *Soil Sampling and Methods of Analysis, CSSS, Lewis Publ.*,75-86.