

## Grain-boundary enrichment of iron on magnesium silicate perovskite

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**Abstract:** We present a combined experimental and numerical simulations study of grain boundaries in (Fe, Mg)SiO<sub>3</sub> perovskite. TEM observations of grain boundaries in a well equilibrated perovskite sample consistently show small but significant enrichments of Fe. This result is in good agreement with classical potentials simulations of grain boundary structures in MgSiO<sub>3</sub> perovskite which predict substitution of iron onto grain boundaries to be energetically favourable over iron substitution in the bulk perovskite structure.

**Key-words:** grain boundary structure, grain-boundary enrichment, (Mg, Fe)SiO<sub>3</sub> perovskite, high-pressure studies, TEM studies.

### Introduction

Rocks consist of two components: grains (of one or more mineral types) and the interfaces between these grains, or grain-boundaries. The bulk properties of rocks and their constituent grains have been extensively studied but grain boundary properties are much less well understood. It is clear, however, that when grain boundaries become a volumetrically significant component of a system, in rocks with a small grain size for example, grain-boundary effects can dominate its physical (*e.g.*, strength, anelasticity, transport properties: Coble, 1962; Karato *et al.*, 1986; Jackson *et al.*, 2002; Roe & Shulka, 1981), and chemical (reaction-rates, partitioning: Helgeson *et al.*, 1984; Drury, 1996), properties. At low pressures, grain boundaries can be very loosely bonded with significant void space; sedimentary rocks for instance can have very high porosities (Athy, 1930) and even well sintered volcanic and metamorphic rocks show dilational behaviour under uniaxial compression corresponding to the opening of cracks at grain boundaries (Sellers & Napier, 2004). Under increasing pressure, the void space accommodated at grain boundaries reduces and the bonding between grains becomes stronger. At mantle pressures grain boundaries (between grains of the same composition) can be considered as planar defects with the miss-match between the lattices of neighbouring grains a function of their geometric relations (Liao *et al.*, 2007; Luzzi *et al.*, 1991). Even at high pressure, the lattice mismatch that occurs between grains contacting at an arbitrary angle can result in channels of void spaces (at an atomic level) which may accommodate incompatible elements and produce enhanced chemical diffusivity in certain directions. Recently Hiraga *et al.* (2003)

observed grain-boundary enrichment of several trace elements in natural and synthetic olivine aggregates and suggested that this might explain the origin of certain exotic mantle-derived magmas. Lower mantle silicates take the perovskite structure which is known to have a rich defect chemistry, readily accepting heterovalent as well as aliovalent cation substitutions. One might expect, therefore, that the grain-boundary chemistry of lower-mantle assemblages is simple compared to upper mantle assemblages. Here we present a transmission electron microscope (TEM) study of a polycrystalline (Mg, Fe)SiO<sub>3</sub> perovskite sample and a numerical (lattice static) simulation of one possible grain-boundary orientation. The results of both these studies show an enrichment of iron on the grain boundaries.

### Experimental methods

A perovskite sample was taken from the iron-rich side of diffusion couple C76 from the study of Holzapfel *et al.* (2005). The perovskite was synthesized from a natural bronzite with an [Fe]/([Fe] + [Mg]) of 0.136, and containing traces of Al (850 ppm) and Ca (2200 ppm). Synthesis conditions were 25 GPa and 2073 K, in a Re capsule. The recovered perovskite sample was subsequently packed in NiO in a Ni capsule, and re-annealed as a diffusion couple with iron-free perovskite at 26 GPa and 1976 K for 570 min. The long annealing duration ensured that the sample was close to chemical and textural equilibrium.

A region far from the interface of the diffusion couple was chosen for the present study and prepared for analysis by analytical transmission electron microscope (TEM). The sample was prepared for the TEM by mechanical thinning