

Is a cation ordering transition of the Mg-Fe olivine phase in the mantle responsible for the shallow mantle seismic discontinuity beneath the Indian Craton?

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[1] We use first-principles molecular dynamics simulations to study the behavior of cation ordering in the non-equivalent octahedral sites of Mg-Fe olivine solid solutions. Our theoretical calculations confirm the previous experimental finding that Mg²⁺ and Fe²⁺ can invert their octahedral site occupancy at a critical temperature. Assuming that the site preference of Fe changes discontinuously between two states in which it is completely restricted to either M1 or M2 sites, we have calculated the transition temperature, T_t , between the two extreme states. Under ambient pressure T_t is calculated to be 520°C that agrees fairly with the experimental finding in which, however, the ordering state changed discontinuously over a much smaller range of the site occupancy of Fe. T_t is found to be pressure sensitive, showing an increase by 30 to 100°C per unit GPa, depending upon the iron content. Using the Indian continental geotherm, we estimate a depth of around 75 Km corresponding to the calculated transition pressure and temperature of cation ordering, which matches well with the depth for the Hales discontinuity marked by a jump of shear wave velocity by ~4%. For olivine solid solutions with 12.5% iron, the ordering transition increases V_s from 4.5 to 4.7 Km/s. Both the inferences, viz. depth of discontinuity and magnitude of velocity increase find support from the modeling of teleseismic earthquake waveforms recorded over broadband seismographs on the Dharwar Craton. This leads us to infer that the cation ordering transition in ferromagnesian olivine might be a potential factor for the Hales discontinuity.

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1. Introduction

[2] Intracrystalline cation ordering is a phenomenon of great interest in mineral physics. Olivine phase (space group: *Pbnm*) shows the ordering of divalent cations, Mg²⁺ and Fe²⁺ in two geometrically non-equivalent octahedral sites, called M1 (**4a** with point symmetry 1) and M2 (**4c** with point symmetry *m*) [Deer *et al.*, 1982]. M1 octahedra are smaller in size, and more regular, as compared to M2 sites. Several workers have used a partitioning coefficient, K_D (where $K_D = \text{Fe}_{\text{M1}} \cdot \text{Mg}_{\text{M2}} / \text{Fe}_{\text{M2}} \cdot \text{Mg}_{\text{M1}}$), to express the degree of cation ordering [Ghose and Ganguly, 1982; Artioli *et al.*, 1995]. $K_D = 1$ implies a completely disordered state, and its departures from unity indicates an ordered state of cations. $K_D > 1$ means an ordering with Fe²⁺ preference to M1, while Mg²⁺ to M2, and vice versa when $K_D < 1$.

[3] Cation partitioning data of natural olivines show wide variations in the K_D values, ranging from far less than 1 to greater than 1. The K_D data suggest that Fe²⁺ cations can be partitioned preferentially either to M2 [Burns, 1970; Wenk and Raymond, 1973; Ganguly, 1982; Ghose and Ganguly, 1982; Brown, 1982; Khisina *et al.*, 1985] or M1 [Finger, 1971; Brown and Prewitt, 1973; Ottonello *et al.*, 1990]. Unlike other Mg-Fe silicates, e.g., pyroxene, the olivine phase, however, has weak geometrical contrasts of its non-equivalent octahedral sites, which do not support such a strong site preference for Mg²⁺ and Fe²⁺. The mechanism of cation ordering, especially its transition behavior (i.e., $K_D > 1$ to $K_D < 1$) is unresolved. Earlier workers reported olivines with $K_D > 1$ from plutonic and metamorphic rocks, and those with $K_D < 1$ from volcanic rocks [Shinno *et al.*, 1974]. Based on these findings, the thermal history of rocks has been suggested a potential factor to influence the cation partitioning process. A number of alternative explanations prevail in the literature. Burns [1970] proposed that higher crystal field split energy (CFSE) can favor Fe²⁺ partitioning into M1 due to smaller M-O distances. Also, experimental studies suggest the valence state of iron as a controlling factor [Hazen, 1977]. Olivine buffered with lower oxidation conditions resulted to low K_D values, implying partitioning

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