

An electrochemical cell across the core-mantle boundary

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The electrical conductivity of the lower mantle reaches ~100 S/m near the bottom of the lower mantle [1], and is likely to increase substantially over the bottom few km due to the temperature jump across the thermal boundary layer at the core-mantle boundary. The main mineral of the lower mantle is MgSiO₃-rich perovskite (MSPv), containing also Fe²⁺, Fe³⁺ and Al. There is an increasing body of evidence that MSPv is a mixed electrical conductor, with charge-hopping between Fe²⁺ and Fe³⁺ predominating at low temperature, but O²⁻ conductivity becoming important at high T [2].

The core and lower mantle are expected to be out of equilibrium with respect to the chemical potential of oxygen (μO₂), whether due to heterogenous accretion of the Earth, or metal/silicate segregation at different P-T conditions from those at the CMB [3]. There will also be a thermoelectric potential due to cooling of the mantle relative to the core over geologic time. Both ΔμO₂ and ΔT set up an electrochemical cell across the CMB; the presence of two modes of conduction allows current to flow, the flux of O²⁻ being balanced by the flow of electrons via Fe²⁺/Fe³⁺ charge-hopping in MSPv, perhaps also in magnesiowüstite.

Assuming a conductivity of 100 S/m at the CMB implies D_O of ~10⁻⁹ m²/s (Nernst-Einstein relation), hence a characteristic length $x=(Dt)^{1/2}$ of only 12 km over 4.5.10⁹ years. In a static mantle, therefore, the effect would be of minor importance. However, plume theory postulates that material from the lower mantle is processed by focussed flow through the bottom few km of the thermal boundary layer at the CMB. This is the advective mode that cools the core. The constant replenishment of material at the CMB greatly increases the flux of O²⁻ across the CMB. For a global plume flux of 3.10¹⁴ kg/a [4], and a velocity boundary layer at the CMB of 30 km [5], we calculate that ~10% of available oxygen would be coulometrically titrated from mantle to core. If "available oxygen" is identified with the Fe³⁺ content of the mantle, the flux of O²⁻ across the CMB of is ~10⁴ moles/s, corresponding to a current of ~2.10⁹ Amps. The amount of O transferred to the core over geological time is trivial (<0.1% of the mass of the core), but the effect may be locally important in altering the redox state of the mantle.

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Natural and Experimental Mass Fractionation of Transition Metal Isotopes

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Natural variations in the stable isotope abundances of Ti, Fe, Cu and Zn are now well-documented in both terrestrial and extraterrestrial materials (Zhu et al., 2000a, b; 2001; 2002a, b). Three isotope plots for Fe isotopes (ε⁵⁷Fe vs ε⁵⁶Fe) show that Fe in terrestrial biological and non-biological samples and in meteoritic material has isotope variations consistent with formation by mass fractionation of a single isotopically homogeneous Fe source of Fe formed at or before the time of chondrule formation.

Natural variations in Fe, Cu and Zn isotopes in biological materials, including metalloproteins from cultured yeast and bacteria demonstrate unequivocally that fractionations as large as 20ε units in Fe and Cu occur within a single cell.

Experiments carried out in aqueous solution at 25°C show that redox speciation reactions on Cu(I) – Cu(II) and Fe(II) – Fe(III) produces effects up to 40ε units. These inorganic mass fractionation are large, and the considerable variations observed in ε⁶⁵Cu and ε⁵⁷Fe in black smoker deposits are therefore not unexpected.

At the temperatures of silicate and Fe melt formation differences in ε⁶⁷Fe between silicate and metal of ca. 3ε units have been documented. Similar variations are also observed between olivine and pyroxene in spinel lherzolite xenoliths.

Experimental constraints on transition metal isotope fractionation at low temperatures in inorganic and biological systems now starts to produce a framework within which natural variations can be understood. The existence of measurable isotope effects at higher (ca. 1000°C) temperatures offers new opportunities in studies of igneous petrology and planetary differentiation.

Reference

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