Material transfer across earth's core/mantle boundary: Recent perceptions

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The singular geochemistry displayed by several ocean–island basalts, picrites, komatiites, and peridotites, believed to be plume-delivered from deep down earth's mantle, has prompted geochemists to visualize the existence of a unique zone near earth's core/mantle boundary (CMB) having noble metals and other siderophiles as well as rare-gases in amounts quite anomalous to the mantle composition. Several views on how such a zone could have developed have been published. An early explanation, attributed this to the heterogeneous nature of the accreting bodies, the late-accreting ones being more oxidized than their predecessors. This trend had resulted in the oxidation of all metallic iron in the early melt reservoir and consequently all the 'iron loving' siderophiles were retained within the lower mantle itself. However, current understanding of cosmochemical processes doubts such temporal changes in the accreting materials. Another view considered earth's core formation was inefficient allowing accumulation of metals, sulphides and siderophiles, in the lower mantle, while according to a model developed six years ago, such an anomalous zone arose from the introduction of noble metals via 'late veneer' of accreting bodies[1].

A very recent, though speculative model[2] on the above subject, a variation of the 'late veneer' concept, postulates that the giant moon-forming impact[3] (~4540 Ma ago) was followed by prolonged accretion (till about 3900 Ma) of smaller bodies, fragments, particles, dust, from near-earth orbits, some of them chondritic in composition and rich in iron and solar-wind implanted rare-gases. Their impact triggered melting of early-formed basaltic crust, followed by metal segregation and degassing. The resultant crust, now rich in incompatible elements, subducted and stabilized on top of the earth's core/mantle interface[2]. Such a model supported by Pu–U–I–Xe isotope systematics is claimed to meet the geochemical requirements, answer siderophile anomalies and problems of earth's heat budget and inventory of incompatible elements.

In recent years, the possibility of materials from the earth's core entering into the adjoining mantle is receiving attention from several workers. The idea of some fluid outer core flux crossing over the core/mantle interface by capillary action had earlier been put forward[4] and the present spurt in interest on core contribution follows the discovery of elevated Os-isotope ratios $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ in certain plume-derived samples – picrites from Hawaii, komatiites from Gorgona Island (Colombia) and Kostomuksha greenstone belt in the Baltic shield and alloy grains from Oregon, USA[5–7]. The presence of these coupled Os-isotopes implies entry of core component in their source region since Os-isotope is a fractionation product of the core-residing and highly siderophile Pt–Re–Os system[8]. The separation of the inner core from the outer core preferentially removed Os from the latter leaving it enriched in Pt and Re relative to Os and exhibiting Re/Os and Pt/Os ratios higher than chondritic values (suprachondritic). Now ^{187}Re and ^{190}Pt decay to form ^{187}Os and ^{186}Os (non-radiogenic isotopes of Os are ^{188}Os and ^{189}Os) and with progressive inner core formation, the $^{187}Os/^{188}Os$ and $^{186}Os/^{188}Os$ isotope ratio in the outer core would tend to be suprachondritic. Assuming the values in several types of chondrite meteorites as comparable to the terrestrial systems, the coupled $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ ratios have been calculated to show enrichments of >7% and >0.01% respectively, relative to other Os isotopes[8]. This is claimed to result from small additions from the outer core making the adjacent mantle region suprachondritic with respect to $^{186}Os/^{188}Os$. The coupled Os-isotope ratios observed in the samples from Hawaii and other places are thus claimed to be good fingerprints reflecting entry of core flux into the CMB region. However, despite the strong geochemical basis, the reliability of the Os-isotope ratios as signature for this purpose is now considered weak in view of its changing parent–daughter fractionation[9].

In their quest for alternate isotopic systems, which could unequivocally reveal core contribution to mantle plumes, geochemists experimented with short lived isotope system (moderate and highly siderophile elements), such as ^{182}Hf–^{182}W (refs 9, 10). During core formation, Hf, a lithophile element, is retained in the silicate mantle, while almost all W, a siderophile element, is drawn into the core. Also, whenever there is partial melting in the mantle, W always enters the melt fraction further depleting the mantle. Mantle is, therefore, the place where all the ^{182}Hf stays and radioactively decays with a half-life of ~8 million years to ^{182}W. This decay is completed in the first 60 million years of earth history, long after the core had formed in the first 30 million years[11,12]. By this time most of the W would have been partitioned into the core with no mantle ^{182}Hf left to yield ^{182}W. Hence, this would impart suprachondritic abundance of ^{182}W (estimated to be 2 parts in 10,000) in the mantle whereas the core will be depleted in ^{182}W and showing only chondritic amount or 2 parts in 10,000 lower than in the mantle[9]. Now, even if a small exchange of material from such a core takes place across the CMB, then the rocks from such a mantle would show depleted ^{182}W relative to bulk silicate mantle, a feature that could serve as an unequivocal fingerprint to identify core material transfer. A recent re-examination[9] of the same Hawaiian picrites and South African kimberlites studied earlier revealed no correlation in the ^{186}Os and no variation in ^{182}W values relative to silicate earth, thus ruling out core contribution in them. Instead, it is surmised that the observed $^{186}Os/^{188}Os$ anomalies may have come from subducted crustal rocks having high Pt/Os and low Re/Os ratios, such as manganese nodules[9], though a very recent correlation study using Tl-isotope of these picrites has ruled out such a sedimentary origin for the Os-isotope variations[13].

During prolonged cooling of the earth and core solidification, the unsettled physics and chemistry of the core/mantle interface is conceived to initiate solubility changes, electromagnetic disturbances from core's magnetic field and changes in electric potential[10]. These lead to the precipitation and accumulation of buoyant (with respect to liquid outer core) oxide crystals, oxide immiscible liquids, sulphide liquid and crystals, carbides and hydrides of the siderophile elements, all of which can escape by 'oxidative exsolution' into the lower mantle[10]. Another transfer mode is through 'oxidative titration' or external injection of oxygen-rich material into the outer core. For example, the subducted oxidized slabs, stagnating over long geological periods at the CMB, get digested here and recycled back into the mantle by oxidative exsolution. In the early earth scenario, with poor oxygen in the atmosphere, the flourishing photosynthesizing organisms could have provided the oxygen for the oxidation of these slabs, or as recently suggesed[14], the materials subducted 2.8–1.8 billion years ago may represent relics of banded iron formations whose production is linked to such organisms. Core to mantle transfer can also be brought about by changes in earth's magnetic field taking place in time and space as these induce shifts in the electric potential favouring electrochemical fractionation and transfer of materials across the CMB with time. The fractionation of platinum group elements, which otherwise does not take place, occurs here under these conditions[10].

In spite of a spate of reports during the last fifteen years or so on the chemistry of the lowermost mantle, the siderophile anomaly in this region still remains a major issue. The proposed entry of core materials to confer the special chemistry to this region has not yet been clearly demonstrated in the samples suspected, even though the entry of some outer core flux could be feasible considering that the core/mantle interface has remained at very high temperature for hundreds of millions of years juxtaposed with fluid outer core. Also there is the unending debate about the existence of deep-sourced plumes themselves and about their capability to transport melt against a maze of physico-chemical impediments for the ascent, all the way from the CMB to the surface of earth. Unless the existence of an uninterrupted conduit is established, as has been shown for the Hawaiian plume recently[15], conclusions favouring core components in some of the plume-delivered rocks will continue to be much discussed.

1. Sankaran, A. V., *Curr. Sci.*, 2001, **80**, 120–122.
2. Tolstikhin, I. and Hofmann, A. W., *Phys. Earth Planet. Int.*, 2005, **148**, 109–130.
3. Sankaran, A. V., *Curr. Sci.*, 2002, **82**, 389–391.
4. Jeanloz., R., *Annu. Rev. Earth Planet. Sci.*, 1990, **18**, 357–386.
5. Brandon, A. D., Walker, R. J., Puchtel, I. S., Becker, H., Humayun, M. and Revillon, S., *Earth Planet. Sci. Lett.*, 2003, **206**, 411–426.
6. Brandon, A. D., Norman, M. D., Walker, R. J. and Morgan, J. W., *Earth Planet. Sci. Lett.*, 1999, **174**, 25–42.
7. Puchtel, I. S., Brandon, A. D., Humayun, M. and Walker, R. J., *Earth Planet. Sci. Lett.*, 2005, **237**, 118–134.
8. Walker, R. J., Morgan, J. W. and Horan, M. F., *Science*, 1995, **269**, 819–822.
9. Scherstén, A., Elliot, T., Hawkesworth, C. and Norman M., *Nature*, 2004, **427**, 234–237.
10. Walker, D., *Can. Mineral.*, 2005, **43**, 1553–1564.
11. Kleine, T., Münker, C., Mezger, K. and Palme, H, *Nature*, 2002, **418**, 952–955.
12. Yin, Q., Jacobsen, S. B., Yamashita, K., Blicher-Toft, J., Télouk, P. and Albarède, F., *Nature*, 2002, **418**, 949–952.
13. Nielsen, S. G., Rehkämper, M., Norman, M. D., Halliday, A. N. and Harrison, D., *Nature*, 2006, **439**, 314–317.
14. Dobson, D. B. and Brodholt, J. P., *Nature*, 2005, **434**, 372–374.
15. Lei, J. and Zhao, D., *Earth Planet. Sci. Lett.*, 2006, **241**, 438–453.

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