

Siderophile anomalies – A vexed problem in mantle geochemistry

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Whenever earthly explanations to some of the unresolved geological issues are unsatisfactory, earth scientists have discovered, often with success, a cosmic connection to these problems. Whether these issues pertained to the unique aspects of earth–moon pair or to the origin of life on earth or to the bouts of evolution and extinction, climatic shifts, sea level changes, wandering poles and continents, the influence of extraterrestrial agencies has been perceived. This approach to solutions appears logical since earth itself was formed by the coming together (accretion) of several planetessimals and hence the possible role of cosmic impactors cannot be overlooked in the production of the puzzling features, not only in earth's early history when meteorite collisions were very frequent, but also during later periods when the impacts continued, though less frequently, millions of years apart. One of the topics of geochemistry, much discussed presently, is about the anomalous distribution of certain metal groups during earth's chemical evolution. For over two decades, scientists have been trying to solve this issue through examination of mantle derived samples supposedly formed during those early earth times. But these samples are found to have departed from their original chemistry over time and memories of earlier processes that shaped them, erased or altered. Now, after a series of investigations including experimental studies backed by highly improved instrumentation, they have once again delved into earth's roots in the solar system and identified certain types of extraterrestrial impactors for producing this anomaly.

The much-debated anomaly in earth's mantle is about a group of elements called *siderophiles*. During earth's chemical evolution, segregation of various elements into silicate, metallic, sulphide or atmospheric phases that developed was controlled by certain fundamental properties of the elements. As early as 1922, the great geochemist, V. M. Goldschmidt had recognized this

and classified the elements according to their chemical affinities into *siderophiles* (affinity for metallic iron), *chalcophiles* (affinity for sulphur), *lithophiles* (affinity for silicates and oxygen) and *atmosphiles* (affinity for the gaseous atmosphere), Table 1. However, these properties are not fixed but are known to change under oxidizing or reducing conditions; besides, some of the siderophile elements like Ni, Co, Mo, W and P are moderately siderophile, while a few like Ga, Cu, P, Sn are volatile moderately siderophile and the noble metals Os, Ir, Pt, Au, Rh, Ru, Re, Pd, are highly siderophile¹.

Existing ideas about the chemical constitution of earth are derived from the study of meteorites called chondrites, which are among the most primitive members of the solar system. The chondrites are stony meteorites, mostly composed of silicates and classified as carbonaceous, ordinary and enstatite varieties according to their diminishing degree of oxidation. The CI type carbonaceous chondrites are completely oxidized and their composition is considered identical to solar nebula out of which planets including earth were formed. These meteorites are undifferentiated preserving the original solar abundance of various elements (with exception of a few volatile elements), which the primitive molten earth inherited and geochemists always refer to chondrite composition while tracing

earth's chemical evolution to form metallic core and silicate mantle.

The siderophile elements, particularly the noble metals, were supposed to have been removed with iron when the latter separated to form earth's core. This segregation should, therefore, have left the early mantle, depleted in these elements relative to the chondritic abundance. However, several studies have revealed that they were orders of magnitude higher than should be present^{2–12}, a feature that has been widely discussed as the 'siderophile anomaly'. For example, Mn, V, Cr and Ga are present almost or slightly below chondritic abundance; P, W, Co, Ni, Sb, As, Ge, Mo depleted to levels ~0.1 to 0.02 chondritic abundance whereas Au, Re, and Ir are depleted ~0.01 to 0.001 of chondritic values and Co/Ni, Au, Ir, Re/Ir show near chondritic ratios whereas Pd/Ir, Pt/Ir and Rh/Ir, exhibit higher chondritic ratios⁹. To understand these anomalies, geochemists have performed experiments under physical and chemical conditions existing in a growing earth and these have led to quantifying important properties that control metal extraction processes in molten earth, essentially metal-silicate partition coefficients (between solid metal, sulphur-bearing metallic liquid and silicate liquid), which depend on temperature, pressure and oxygen fugacity as well as composition of metal-silicate phases, particularly in relation to those existing

Table 1. Goldschmidt's classification of elements

Siderophile	Chalcophile	Lithophile	Atmosphile
Fe, Co, Ni	Cu, Ag	Li, Na, K, Rb, Cs	H, N, (C), (O)
Ru, Rh, Pd	Zn, Cd, Hg	Be, Mg, Ca, Sr, Ba	He, Ne, Ar, Kr,
Os, Ir, Pt	Ga, In, Tl	B, Al, Sc, Y	Xe, Rn
Au, Re, Mo	(Ge), (Sn), Pb	Rare earths	
Ge, Sn	As, Sb, Bi	(C), Si, Ti, Zr, Hf, Th,	
C, P	S, Se, Te	P, V, Nb, Ta	
(Pb), (As), (W)	(Fe), (Mo), (Cr)	O, Cr, W, U,	
		(H), F, Cl, Br, I,	
		(Tl), (Ga), (Ge)	
		(Fe), Mn	

Note: Elements shown in brackets exhibit secondary affinity to the group in which they are shown.

during core formation. Current views consider that our planet was partly or completely molten while the accretionary phase continued^{13,14} and among the mechanisms that could have exercised control on the siderophile elements in mantle, heterogeneous accretion, inefficient core formation and metal-silicate equilibrium have received much attention in the past, but a number of other mechanisms have also been postulated subsequently.

According to the heterogeneous accretion hypothesis¹⁵, the incoming accreting materials had variable metal contents and the early ones which formed 80 to 90 per cent of earth, were essentially reducing. They initiated large-scale removal of all siderophile elements (except a few with lithophile tendencies) into the core. In the next phase, the accreting materials were more oxidizing and except for some noble metals, more of the remaining highly siderophile elements (HSE) were again removed into the core. In the final stage, when earth had aged presumably some 50–90? million years¹⁶, the accreting materials were so oxidizing that they inhibited existence of metallic iron thus forcing the few stranded siderophiles to remain in the mantle and later get homogeneously distributed as seen in present day mantle^{13,15}. This view failed to justify the excess Ga which like Ni should have been depleted during core formation¹⁷ and also the less than expected abundance of sulphur in the mantle. The latter feature is now explained as either due to volatilization during high temperature accretion and/or separation into the core with Fe-alloy¹⁸. Also, known geochemical or cosmochemical processes¹³ do not explain the supposed changes in the nature of accreting materials with time. The weaknesses in the heterogeneous accretion hypothesis led to the suggestion that core formation, like many other natural processes was inefficient leading to stagnation of small amounts of metal and sulphides in the mantle and that no current hypothesis could explain the distribution of siderophiles in earth's mantle¹⁷.

The third model explains the distribution of siderophile elements as the outcome of core-mantle differentiation of a 'deep magma ocean' that was created by the enormous kinetic energy released by large-sized bodies impacting early

earth^{13,19,20}. Iron, sinking gravitationally, possibly assisted by shear stresses^{20,21}, carried the siderophile elements into the core. This is thought to have continued at progressively higher temperature 2500–4500 K and pressure as the size of proto-earth increased with time⁹. However, high-pressure experimental investigations^{13,18,22} concluded that temperature effects alone cannot bring about the observed siderophile distribution (e.g. Ni and Co partitioning is not proved between molten alloy and silicate^{11,18}). Increasing pressure, irrespective of varying oxygen fugacity or sulphur content, decreased their siderophile behaviour, as evidenced by the near chondritic Ni to Co ratio in the mantle^{11,18,23}. A recent approach explains abundance of several siderophiles in the mantle by two-step equilibration with significant quantities of the metal in the core inherited from preterrestrially differentiated planetessimals at low temperature and pressure and later in the earth at high temperature and pressure^{9,24}.

Among the siderophiles, the anomalous abundance of the noble metals – Os, Ir, Pt, Au, Ru, Rh, Pd and Re happen to be well studied. Though almost 99 per cent of these metals must have gone into the core with the metallic phase, several mantle-derived samples like Iherzolites and peridotites show excess amounts. Unlike the moderately siderophile elements like Ni, Co which show lithophile tendency under pressure and remain in the silicate mantle¹⁸, Pd, Pt retain their strong siderophile nature, even at high pressure^{2,25}. Their excess in the mantle is now postulated to be introduced by late accreting materials – the 'late veneer', that arrived after core formation²⁵. Some doubt this possibility on basis of incompatibility of data on Os/Ir, Ru/Ir, Pt/Ir and Rh/Ir ratios with respect to various types of CI chondrites⁶. Instead, influx of outer core materials known to be rich in Re, Ru, Pt, Pd, back into the mantle reproducing the observed abundance pattern is suggested^{6,26}. Especially in the 'early Archaean era such materials from outer core would have a C-chondritic noble metal signature unlike the present day outer core which will have a fractionated pattern'⁶. The presumed formation of the moon as a result of a single collision of a large-sized body with early earth²⁷ is also considered likely cause

for excess siderophile, if ~3–4% of the impactor's core carrying siderophiles were mixed into earth's mantle²⁸. Deep recycling of continental and oceanic crusts has also been considered for the observed excess noble metals but at the extremely low levels of these metals in the crustal rocks, unimaginably large amounts of such segments are required to produce the observed levels in the mantle^{6,29}.

Researchers during last three years have shown that the HSE abundance may after all be the result of normal petrogenetic processes in the mantle^{2,8}. One of these recent studies was carried out on small sulphide grains in the mantle samples instead of whole rock, since the HSE noble metals are usually concentrated in the sulphides (where they are present in the lattice² rather than as irregularly disseminated clusters as conceived by some⁷) and in co-existing silicates^{2,26,30}. The studies noted that HSE contents varied in the two generations of sulphides generally observed in peridotites and Iherzolites, viz. as enclosures in silicate phases (olivines) and as interstitial grains (enclosures in chalcopyrite/pentlandite). Whereas the silicates are residues of melting processes, interstitial sulphides are products of sulphide-bearing metasomatic fluids². According to this view, the observed non-chondritic relative abundance in some of these mantle-derived samples is due to sulphide differentiation within the mantle by partial melting and sulphide addition through melt/rock reaction. In other words, the near chondritic noble metal abundance observed in the whole rock upper mantle samples from different places may represent mixtures of two types of sulphides and are unlikely to result from additions from the outer core or from distinct late veneer meteorite populations². Earlier studies^{7,8} carried out on different sources of peridotites indicated that distribution of noble metals in the mantle was heterogeneous on a small scale but homogeneous on a large scale and the process that generated its distribution is more complex than simple *in situ* extraction⁸ since the platinum group of elements (except for Pt and Au) reside in mantle sulphides as melt-resistant atomic clusters or micro-alloys⁷.

The mantle distribution of siderophile elements have, no doubt, roused several

possible mechanisms, some of them advanced after experiments under realistic conditions and precise analytical studies. Though each one of the envisaged mechanisms is not completely satisfying, nor applicable for all time and for all elements, they may have, nonetheless operated, perhaps briefly, as demanded by the changing physical and chemical scenario in the planet's evolutionary stages. After more than twenty years of speculation and geochemical studies by several research groups, opinion now seems to be veering towards a hybrid mechanism of metal/silicate equilibrium and heterogeneous accretion¹³. That the materials accreting have been heterogeneous is obvious from the assorted meteorites falling on earth and if the assumed 'late veneer' was added when the magma ocean was metal-free, efficient mixing of such highly oxidized chondrites could indeed have brought about the observed siderophile abundances¹³. Though various models have, undoubtedly, narrowed down areas of speculative interpretations and assumptions, only more experimental work on metal-silicate interactions and understanding of core-mantle evolution of early earth, can lead to better explanation of the observed siderophile patterns.

1. Righter, K. and Drake, M. J., *Geochim. Cosmochim. Acta*, 2000, **64**, 3581–3597.

2. Allard, D., Griffin, W. L., Lorand, J. P., Jackson, S. E. and O'Reilly, S. Y., *Nature*, 2000, **407**, 891–894.
3. Drake, M. J., *J. Geophys. Res.*, 1987, **92**, 377–384.
4. Newsom, H. E., in *Origin of Earth* (eds Newsom, H. E. and Jones, J. H.), Oxford University Press, New York, 1990, pp. 273–288.
5. Newsom, H. E. and Sims, K. W. W., *Science*, 1991, **252**, 926–933.
6. Snow, J. E. and Schmidt, G., *Nature*, 1998, **391**, 166–169.
7. Lorand, J. P., Pattou, L. and Gros, M., *J. Petrol.*, 1999, **40**, 951–987.
8. Rehkämper, M., Halliday, A. N., Alt, J., Fitton, J. G., Zipfel, J. and Takazawa, E., *Earth Planet. Sci. Lett.*, 1999, **172**, 65–81.
9. Rama Murthy, V., *Science*, 1991, **253**, 303–306.
10. Morgan, J. W., Wandless, G. A., Petrie, R. K. and Irving A. J., *Tectonophysics*, 1981, **75**, 47–67.
11. Thibault, Y. and Walter, M. J., *Geochim. Cosmochim. Acta*, 1995, **59**, 991–1002.
12. Hilgren, V. J., Drake, M. J. and Rubie, D. C., *Science*, 1994, **264**, 1442–1445.
13. Drake, M. J., *Geochim. Cosmochim. Acta*, 2000, **64**, 2363–2370.
14. Stevenson, D. J., *Science*, 1981, **214**, 611–619.
15. Wänke, H., *Philos. Trans. R. Soc. London*, 1981, **303**, 287–302.
16. Shearer, C. K. and Newsom, H. E., *Geochim. Cosmochim. Acta*, 2000, **64**, 3599–3613.
17. Jones, J. H. and Drake, M. J., *Nature*, 1986, **322**, 221–228.
18. Li, J. and Agee, C. B., *Nature*, 1996, **381**, 686–689.
19. Wetherill, G. W., *Science*, 1985, **228**, 877–879.
20. Sankaran, A. V., *Curr. Sci.*, 2000, **79**, 790–793.
21. Bruhn, D., Groebner, V. and Kohstedt, D. L., *Nature*, 2000, **403**, 883–886.
22. Righter, K., Drake, M. J. and Yaxley, G., *Phys. Earth Planet Inter.*, 1997, **100**, 115–134.
23. Peach, C. L. and Martinez, E. A., *Geochim. Cosmochim. Acta*, 1993, **57**, 3013–3031.
24. Rama Murthy, V. and Karato, S., *Phys. Earth Planet Inter.*, 1997, **100**, 81–95.
25. Holzheid, A., Sylvester, P., O'Neil, H. St. C., Rubie, D. C. and Palme, H., *Nature*, 2000, **406**, 396–399.
26. Pattou, L., Lorand, J. P. and Gros, M., *Nature*, 1996, **379**, 712–715.
27. Cameron, A. G. W. and Ward, W. R., *Lunar Sci.*, 1976, **7**, 120–122.
28. Newsom, H. E. and Taylor, S. R., *Nature*, 1989, **338**, 29–34.
29. Fryer, B. J. and Greenough, J. D., *Can. J. Earth Sci.*, 1992, **29**, 2329–2340.
30. Mitchell, R. H. and Keays, R. R., *Geochim. Cosmochim. Acta*, 1981, **45**, 2425–2445.

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