THE ABUNDANCES OF VOLATILE TRACE ELEMENTS IN THE EARTH'S MANTLE: NEW EVIDENCE FROM ANALYSES OF MANTLE XENOLITHS.
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Introduction: Volatile elements are depleted in the Earth's mantle. Volatile siderophile and volatile chalcophile elements were extracted into the core, while volatile lithophile elements define a depletion trend probably reflecting primary nebular depletion in the Earth making material. We demonstrate here that In, Cd, and Sn behave as lithophile elements in the Earths' mantle and that their Earth mantle abundances can be reliably derived from analyses of upper mantle rocks. Indium is one of the most volatile trace elements, judging from the condensation temperature, but its abundance is significantly higher than that of other lithophile volatile elements, with higher condensation temperatures, such as Zn, Sn and Cd.

Mantle xenolith samples: This study includes (a) anhydrous lherzolites (15-18 % cpx) representing the rare most "fertile" end members of coherent xenolith suites from worldwide intra-plate volcanic fields (SW-US, Mexico, Mongolia, Germany) and (b) depleted anhydrous and hydrous lherzolites and harzburgites (2-13 % cpx) from the Eifel (Germany), which are well-equilibrated with respect to lithophile trace elements [1]. The xenoliths equilibrated at temperatures from 850 to 1250 °C and at depths between about 30 to 80 km in the subcontinental mantle. They are composed of clinopyroxene (cpx), orthopyroxene (opx), olivine (ol), and spinel (sp). Metasomatized Eifel xenoliths contain additional pargasitic amphibole (amph) in textural and chemical equilibrium with the other phases. The majority of the samples is free of visible sulfides, except for the "fertile" xenoliths from Kilbourne Hole (SW-US) which carry Fe-Ni-Cu-sulfides (up to 0.07 % modal abundance) as discrete intergranular grains (up to 150 μm in diameter) and smaller inclusions in silicates.

The REE patterns in cpxs of the most "fertile" xenoliths are flat from the heavy rare earth elements (REE) to the middle REE, and slightly to moderately depleted in light REE (LREE). Such patterns are expected for residues of a "primitive" source that lost only an extremely small partial melt fraction. No evidence for secondary enrichment of the "fertile" xenoliths is recognized, even highly incompatible trace elements like La, U, and Th are homogeneously distributed within single clinopyroxene grains. Some of these "fertile" xenoliths provide evidence for Proterozoic model ages (1.6-2.0 Ga) for small-degree melting [2, 3].

Analytical procedure: The abundances of Cd, In, Sn, As, Sb, Bi, and Te were measured in the minerals on polished thin sections by LA-ICP-MS (RSES, ANU, Canberra). Ablation was performed in a He atmosphere by an ArF Excimer laser (193 nm, 86 μm laser spot size). ^{29}Si (for cpx, opx, and ol), ^{27}Al (for sp), and ^{57}Fe (for sulfide) were used as internal standards, based on the electron-microprobe analyses. Silicate glass reference material NIST SRM612 and the basalt glass standard USGS BCR-2G were measured before and after ten analysis of xenolith minerals.

Results and discussion: Only Cd, In, Sn, and As abundances are above the detection limit in the main minerals of the xenoliths. The main host phases for these elements are cpx and amph, except for As which is in sulfides in the sulfide-bearing Kilbourne Hole xenoliths (As sulfide/cpx > 100). In contrast the In, Cd and Sn contents of these sulfides are so low (sulfide/cpx < 5) that the contribution of sulfides to the bulk rock abundances of these elements is negligible, demonstrating the lithophile behaviour of these elements within the subcontinental lithospheric mantle.
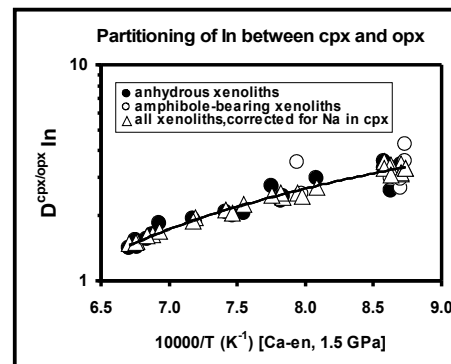
Figure 1.

Temperature-dependent inter-crystalline subsolidus partitioning of Sn, In, Cd and As: All xenoliths record temperature dependent systematic distributions of In, As, Cd and Sn between clinopyroxene and orthopyroxene ($D^{cpx/opx}$) as well as between clinopyroxene and olivine. The partition coefficients decrease with increasing temperature and also with increasing Na contents in cpx. The correlations (Fig. 1) indicate that inter-crystalline chemical equilibrium between the co-existing mineral phases is achieved. The $1/T-lnD^{cpx/opx}$

trends of In, As and Sn are similar to those of Ga, V and Ti indicating substitution of the elements into the same site of the pyroxene structure (M1).

Upper mantle abundances of In, Sn, and Cd: Mantle abundances of these three elements were calculated by combining the contents in the minerals and the modal compositions of the peridotites. Compared to whole rock analysis, this method has the advantage that the estimated element budgets are without modification by recent secondary alteration processes. The average of nine "fertile" xenoliths with slightly depleted LREE patterns and bulk major element compositions close to that proposed for the primitive mantle (PM) is given in Table 1. In addition, the xenoliths define linear trends of In, Cd and Sn with bulk rock CaO (Fig. 2). Using a CaO content of 3.65 % [5] for PM, these correlations yield the same abundances for In, Sn, and Cd as derived from the "fertile" xenoliths (Table 1).
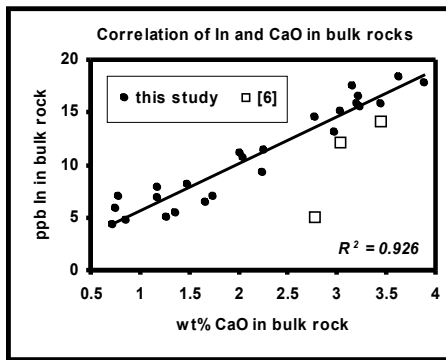

Correlation of In and CaO in bulk rocks

Figure 2.

(ppb)	In	Sn	Cd	Zn
PM [4]	11	130	40	50
PM [5]	13	138	64	53.5
PM [7]	14		18	
PM, this study: av. 9 "fertile" xenoliths	17 ± 3	90 ± 21	35 ± 6	
PM, this study: CaO = 3.65 wt%	17	89	34	
PM/C1, Mg = 1	0.095	0.036	0.022	0.072

Table 1.

Significance of the high In abundance:

In Fig 3 decreasing mantle abundances of lithophile elements vs. 50% condensation temperatures should reflect the primary nebular signature of Earth accreting material [9]. The high In abundance, which is now well established, does not fit the trend. Indium is much more volatile than the elements Zn or Sn with higher condensation temperatures.

A possible explanation that ultimately requires experimental confirmation is outlined here. Siderophile and chalcophile elements were affected by core formation in the Earth. Highly siderophile elements, Te, S and Se

were quantitatively extracted from the mantle into the core. Other chalcophile elements (Cu, Zn, Sn, Cd, Pb, Tl, Bi) were less efficiently extracted while In was not affected at all. The present Te, S and Se abundances in the Earth's mantle are a result of a volatility fractionated late veneer [10], added after the end of core formation. The contribution of the late veneer to In, Zn etc. (Fig 3) is minor. The high In abundance would then indicate that In is less chalcophile than the other elements with similar condensation temperatures and In would reflect the abundance level of very volatile lithophile elements in the Earth mantle. This could be important for the abundances of other highly volatile elements, such as rare gases or water. The decrease in abundance from Mg to Zn and the flat extension of this trend to lower condensation temperatures would qualitatively fit with abundance patterns in carbonaceous chondrites, although at a higher abundance level [11]. Thermodynamic data provide some support for the strongly lithophile behavior of In. At given oxygen and sulfur fugacities In is much more lithophile than chalcophile when compared to Zn, Bi, Cd and Sn. The low abundances of the halogens Br and I, need a separate explanation. A final decision on the validity of this model requires experimental evidence.
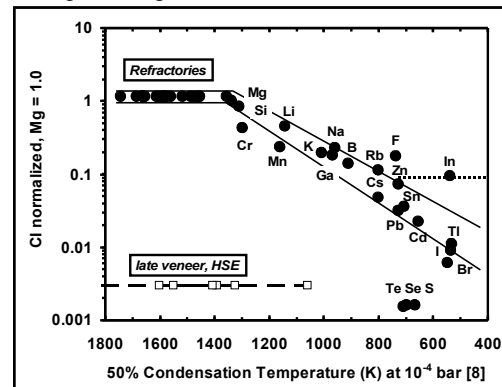

Figure 3.

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