

**ACCRETION OF VOLATILE ELEMENTS TO THE EARTH AND MOON.** D. C. Rubie<sup>1</sup>, D. J. Frost<sup>1</sup>, F. Nimmo<sup>2</sup>, D. P. O'Brien<sup>3</sup>, U. Mann<sup>4</sup> and H. Palme<sup>5</sup>, <sup>1</sup>Bayerisches Geoinstitut, University of Bayreuth, D-95440 Bayreuth, Germany, dave.rubie@uni-bayreuth.de, <sup>2</sup>Department of Earth and Planetary Sciences, University of California Santa Cruz, Santa Cruz, CA 95064, <sup>3</sup>Planetary Science Institute 1700 E. Ft. Lowell Rd., Tucson, AZ 85719-2395, <sup>4</sup>ETH-Zürich, Institut für Mineralogie und Petrologie, CH-8094 Zürich, Switzerland, <sup>5</sup>Forschungsinstitut und Naturmuseum Senckenberg, Senckenberganlage 25, D-60325 Frankfurt am Main, Germany

**Introduction:** Our recent work on modeling accretion and core-mantle differentiation of the Earth has shown that the bulk composition of the Earth can be represented by solar-system (C1 chondritic) relative abundances of non-volatile elements but with an enhancement of the concentrations of the refractory elements Ca, Al, Nb, W, Ta etc. by ~22% and V by ~11% [1]. This suggests that the material that accreted to form the Earth was, on average, enriched in an early-condensing refractory component. Volatile elements, in contrast, are strongly depleted in the Earth's mantle relative to C1 abundances by factors of 5-10 (Fig. 1).

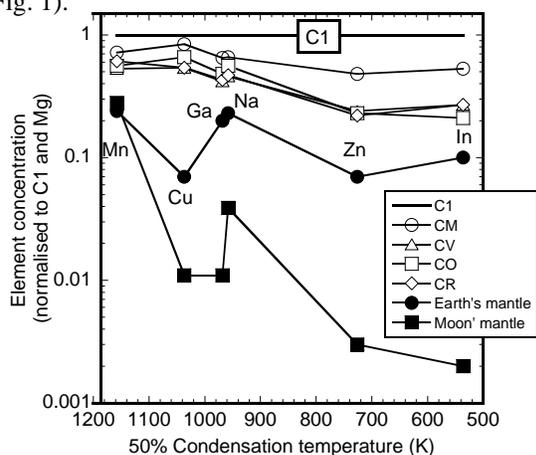


Fig. 1. Concentrations of some volatile elements Mn, Cu, Ga, Na, Zn and In in carbonaceous chondrites (groups CM, CV, CO, and CR) and the mantles of the Earth and Moon, based on [2]. Element concentrations normalized to C1 abundances and Mg are plotted against their 50% condensation temperatures – which decrease with increasing volatility.

The elements Mn, Cu, Ga, Na, Zn and In are depleted in the various types of carbonaceous chondrites relative to C1 abundances (Fig. 1). The degree of depletion generally increases with decreasing condensation temperature (i.e. with increasing volatility). Differentiation processes such as planetary core formation clearly cannot explain this trend. With the exception of Cu, the depletion pattern in Earth's mantle is very similar to the carbonaceous chondrite trends, which

strongly suggests that the volatile elements have been accreted to the Earth in material that compositionally resembled carbonaceous chondrites, as suggested earlier [3]. There are, however, differences in the isotopic composition of some elements between carbonaceous chondrites and the Earth which excludes carbonaceous chondrites as Earth parental material, e.g. Cr [4]. One element in the Earth's mantle that does not fit into the depletion trend is Cu (Fig. 1). But Cu is a siderophile (metal-loving) element [5] and its depletion in the Earth's mantle must therefore be affected by metal-silicate segregation during core formation. Thus the depletions of Cu and other siderophile volatile elements show that volatile elements were accreted to the Earth before core formation was complete, which is contrary to the conclusion of [6].

In order to better understand the depletion trends in the Earth and Moon and how volatile siderophile elements are affected by core-mantle differentiation, we have investigated metal-silicate partition coefficients for these elements at high pressure.

**Experimental:** The partitioning of Mn, Ga, Zn and In between liquid Fe-alloy and peridotitic silicate liquid has been investigated at 2-24 GPa 2023-2873 K using multianvil apparatus [7]. Results for Mn and Ga, based on our study and data from the literature, are shown in Fig. 2 as  $\log K_D$  versus  $1/T$ , over the pressure range 2-25 GPa.  $K_D$ , which is nominally independent of oxygen fugacity, is defined as:

$$K_D = \frac{[a_M^{metal}][a_{FeO}^{silicate}]^{n/2}}{[a_{MO_{n/2}}^{silicate}][a_{Fe}^{metal}]^{n/2}}$$

where  $M$  is the element of interest,  $a$  is the activity of each component in either metal or silicate and  $n$  is the valence of  $M$ .

Results show that Mn is lithophile over the range of experimental conditions and only becomes weakly siderophile under highly reducing conditions (e.g. IW-5). Pressure has a weak effect on partitioning and makes Mn more siderophile (Fig. 2). In contrast, Ga is siderophile at low pressure (e.g. 2 GPa) but becomes lithophile at very high pressures. The opposing effects of pressure on the partitioning of Mn and Ga places critical constraints on the time of their accretion.

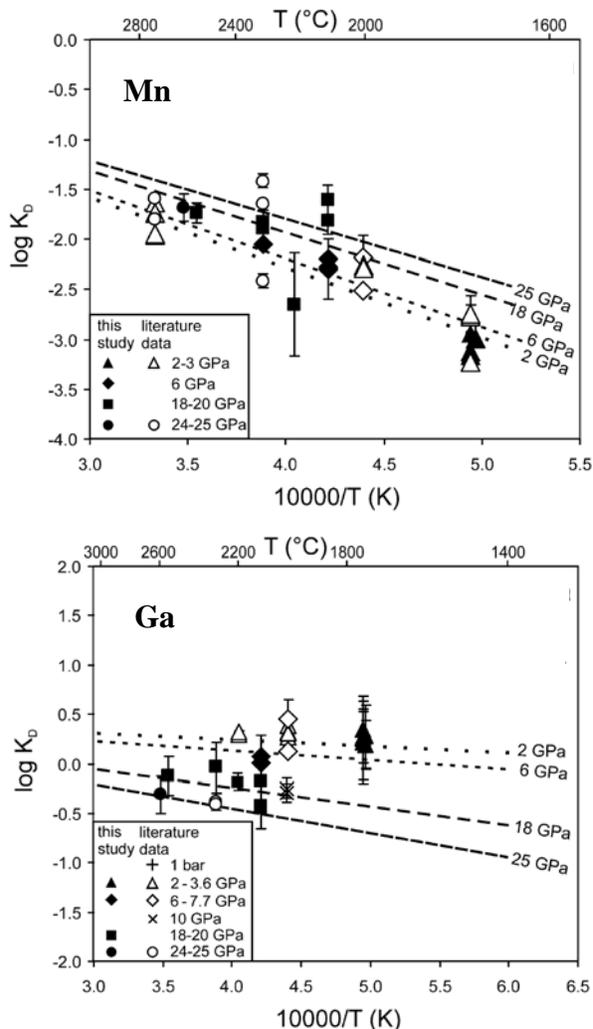


Fig. 2.  $\log K_D$  as a function of inverse temperature for Mn (top) and Ga (bottom). See [7] for further details. (After [7].)

The results for Zn and In are comparable to those for Mn and Ga. In is siderophile at low pressure but becomes lithophile at very high pressures, whereas Zn is lithophile over the entire pressure range of interest [7].

**Discussion:** The similarity of the depletion patterns of Mn, Ga, Zn and In in the Earth and carbonaceous chondrites (Fig. 1) indicates that these elements were not fractionated by core formation in the Earth. As described above, at low pressures (e.g.  $<2$  GPa),  $D(\text{Ga}) \gg D(\text{Mn})$  and  $D(\text{In}) \gg D(\text{Zn})$ , where the metal-silicate partition coefficient  $D = (\text{concentration in metal}/\text{concentration in silicate})$ . Under such conditions, Ga would have been depleted relative to Mn and In relative to Zn, which is not observed. The lack of fractionation of these elements in Earth's mantle implies conditions where  $D(\text{Ga}) \approx D(\text{Mn})$  and  $D(\text{In}) \approx D(\text{Zn})$ , which, based on our experiments, requires pressures of at least 40-60 GPa [7]. This means that the volatile

elements were added to the Earth at a late stage of accretion because otherwise metal-silicate equilibration pressures would have been too low.

The Moon also formed late in the Earth's accretion history as the result of a giant impact between the Earth and a Mars-sized planet. This raises the question of the timing of volatile element addition relative to the timing of the Moon-forming giant impact. Concentrations of volatile elements in the Moon's mantle are on average 1-2 orders of magnitude below those in the Earth's mantle. An exception is Mn, the concentration of which is very similar in Earth and Moon. In contrast to the Earth, Ga is strongly depleted in the Moon relative to Mn and In is depleted relative to Zn – depletions that could be a consequence of core formation in the Moon at low pressure.

The similar depletions of Mn in both bodies has been used to argue that the Moon formed mostly out of Earth mantle material [8, 9], a view that is supported by isotopic similarities. This conclusion contrasts with the findings from numerical impact simulations [10] that the Moon should consist mostly of impactor material. Because most elements more volatile than Mn are uniformly depleted in the Moon, the complete devolatilization of a major fraction of the Moon may have occurred. This would explain the lack of isotopic fractionation of K [11]. The lack of additional Mn depletion in the Moon may be a consequence of Mn being the least volatile element. As a compatible element Mn is sited in the larger mineral grains, such as olivine and pyroxene, and evaporative loss would require diffusion through such minerals. Loss of Na in lunar material may indicate destruction of Na-rich plagioclase grains, which would occur at a temperature where Mn-rich, FeO-poor Mg-silicates are still stable.

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