Combining experimental and numerical studies of lunar differentiation

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The lunar magma ocean (LMO) model [1,2] remains the starting point for most models of early lunar differentiation. Petrologists have studied LMO crystallisation sequences [3,4], and numerical thermochemical convection models have been developed to study the evolution of layered cumulate piles formed during MO crystallisation [5-7]. These models generally take into account changes during differentiation in major element composition and density of the minerals involved.

Here, we give an overview of our recent progress on combining mineral and melt density measurements [8-10], experimental studies of the distribution of trace elements during and after LMO crystallisation, and numerical models of lunar interior thermal evolution. Recent experimentally determined mineral-melt partitioning data [11,12] show that the interior distribution of the main heat-producing elements K, U and Th is highly heterogeneous in the aftermath of LMO crystallisation and differentiation. This has significant effects on the thermal evolution of the lunar interior after solidification - effects that are missed if partitioning of heat-producing elements is ignored.

In the Moon, K, U and Th are concentrated in late-crystallising, dense ilmenite/cpx-rich cumulates. Thermochemical convection models show that sinking of these cumulates towards the lunar core, and increased levels of heat production associated with their trace element chemistry lead to (a) the formation of a thermal blanket on the core which could play a role in the recently proposed extreme longevity of lunar dynamo activity [13] (b) prolonged interior mantle dynamics consistent with the young ages of some surface lava flows derived from crater density analysis [14]. These results illustrate the value of combining experimental and numerical approaches to planetary interior evolution.

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Isotopic tracers of metal cycling in the oceans and sediments

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The emerging isotopic systems of the transition metals potentially have much to tell us about sources of metals to the oceans, their biogeochemical cycling within the oceans, and the nature of the output processes to sediment. With respect to the latter, it has been the redox-sensitivity of the outputs, and the variability of the isotopic fractionations involved in different output pathways, that has attracted most attention. For example, the isotopic composition of Mo in marine sediments has already been used as a monitor of ancient water-column redox conditions. Here, we introduce the isotopic systems of other transition metals (Cu, Zn, Ni), systems that are much less developed, and assess their potential for providing complementary paleoceanographic information to Mo.

Isotopic data for seawater and Fe-Mn crusts reveal that the light isotope of Cu, as with Mo, is preferentially removed from the seawater solution under fully oxic conditions. In contrast, Zn isotopic compositions of Fe-Mn crusts are heavier than Zn in the dissolved phase in the deep ocean, by about 0.5 ‰ for $^{66}Zn/^{64}Zn$. Sorption experiments for Cu to Mn oxide reproduce the sense of the natural fractionation, but the magnitude of the latter is slightly greater than in the experiments. For Zn, by contrast, the fractionation seen in the Mn oxide experiments is opposite to that in nature. This could be due to complexing of Zn in the natural seawater solution, or to the superimposition of other biological effects on Zn isotopes in the oceans.

In contrast to the oxic output discussed above, and in a developing picture that looks qualitatively very similar to Mo, it appears that both Cu and Zn undergo little or no isotopic fractionation as a result of removal from seawater solution under anoxic conditions. For example, in the most euxinic sediments from the Black Sea and Cariaco Basin, enrichments of Cu and Zn are associated with isotopic compositions that are identical to (Zn) or likely very close to (Cu) the local deep ocean.

We are at an earlier stage in the development of Ni isotopes. It is clear that seawater is homogeneous at $\delta^{60/58}Ni_{SRM986} = 1.44\pm0.1$ ‰. In common with both Cu and Mo this is distinctly heavier than the riverine input (at about 0.8 ‰ based on the discharge-weighted mean of 7 large and small rivers), while rivers themselves, again in common with Cu and Mo, are heavier than rocks (0.1-0.2 ‰). These observations imply fractionation of Ni isotopes in both the weathering and marine environment. In the case of Ni it appears that it is not the oxic sink that removes the light isotope to push seawater to heavy values, as analyses of Fe-Mn crusts suggest that they are significantly heavier than seawater at 1.7-1.9 ‰.