

The Cl isotope composition of the mantle revisited

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Published estimates for the $\delta^{37}\text{Cl}$ value of the mantle range from less than -3‰ to $+5.7\text{‰}$. We combine new data from mantle-derived materials with new chondritic and lunar data to refine the $\delta^{37}\text{Cl}$ value of the mantle to between -0.5 and 0.0‰ (SMOC). Samples include basalts from Hawaii, Iceland and New Mexico ($\delta^{37}\text{Cl} = -0.15 \pm 0.15\text{‰}$, $n=7$), peridotites from Balmuccia, Italy ($-0.25 \pm 0.16\text{‰}$, $n=5$), and Cl-bearing diamonds from Canada (-0.05‰). The $\delta^{37}\text{Cl}$ values of our new and previously published data (Sharp *et al.* Nature, 2007; Science, 2010) average $-0.15 \pm 0.35\text{‰}$ ($n = 26$), indistinguishable from the lowest lunar sample ($\delta^{37}\text{Cl} = -0.7\text{‰}$), the average of type 3 chondrites ($\delta^{37}\text{Cl} = -0.5\text{‰}$; Mercer *et al.* LPSC 2011) and evaporites ($\sim 0\text{‰}$).

Although Cl isotope variations do exist in contaminated mantle (John *et al.* EPSL, 2010), the large published range for the primitive mantle is explained by analytical artefacts. Published TIMS data are unreliable, yielding high $\delta^{37}\text{Cl}$ values (Nakamura *et al.* LPSC 2011). A published SIMS value for 'archived' MORB ($< -3\text{‰}$, Layne *et al.* Geol. 2009) has a Cl content an order of magnitude lower than corresponding standards, explaining the anomalously low value. Low mantle estimates from gas source mass spectrometry (Bonifacie *et al.* Science, 2008) are also likely artefacts of small sample size; their observed systematic decrease in $\delta^{37}\text{Cl}$ value with size is not seen in our work, presumably because we use a more sensitive continuous-flow method. We do see a sharp drop off to $\delta^{37}\text{Cl}$ values of $< -3\text{‰}$ for peak areas less than 200mV sec, but larger replicates of the same mantle samples always give $\delta^{37}\text{Cl}$ values close to 0‰ . The similarity of the crustal and mantle reservoirs explains the lack of secular variation in crustal samples, obviates the need for a fractionation mechanism between mantle and crust and defines a homogeneous inner solar system reservoir.

The Cl isotope composition of the Moon and Mars

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The bulk Earth and the least altered carbonaceous chondrites have Cl isotope compositions ($\delta^{37}\text{Cl}$ values) close to 0‰ (Sharp *et al.* Nature, 2007; Mercer *et al.* LPSC, 2011). In contrast, Cl isotope variations on Mars, and especially the Moon, are extreme – Apollo samples range from near 0‰ (the Earth value) up to 24‰ (Sharp *et al.* Science, 2010 and unpublished). We interpret the high $\delta^{37}\text{Cl}$ values as a result of degassing of metal chlorides. On Earth, Cl volatilizes from basaltic melts as HCl (g) with no apparent Cl isotope fractionation. In the absence of H_2O , Cl volatilizes as metal chlorides, which leads to the preferential loss of ^{35}Cl , and an ever-increasing $\delta^{37}\text{Cl}$ value of the residual Cl in the melt. The $\delta^{37}\text{Cl}$ value is a function of both the H/Cl ratio and total Cl content. The lowest and Earth-like $\delta^{37}\text{Cl}$ value is found as surface coatings of lunar glass beads which have the highest H- and lowest Cl-contents (Saal *et al.* Nature, 2007) of all measured samples. The highest $\delta^{37}\text{Cl}$ values are found in KREEP basalts (McCubbin *et al.* GCA in press), which formed in melts with high Cl contents. These results are consistent with a chemical divide between H and Cl. Cl is lost by HCl volatilization until either Cl or H is consumed, leaving the other element in excess. The low $\delta^{37}\text{Cl}$ samples (74002, 36) fall on the high H/Cl side of the chemical divide, the high $\delta^{37}\text{Cl}$ value samples lie on the low H/Cl side. If initial Cl contents are low, Cl vaporization will be minimal because Cl saturation of the melt may be only slightly overstepped. We conclude that the Moon was generally anhydrous (10s of ppb H), but anomalous eruptive samples (lunar glass beads) with high H- and low Cl-contents existed and are manifest as low $\delta^{37}\text{Cl}$ samples.

In contrast to the Moon, Martian meteorites range from -3‰ to $+2\text{‰}$ ($n=8$). All shergottites have negative $\delta^{37}\text{Cl}$ value and all cumulates have positive $\delta^{37}\text{Cl}$ values. Only near-surface effects are known to fractionate Cl isotopes. The different Cl isotope compositions of Martian samples are explained by near-surface contamination or volatile loss.