Oxygen isotopes and water in bulk matrix of CM2 Murchison as an analog for Ryugu matrix

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Introduction: Fine-grained phyllosilicates like serpentine and saponite form a dominant component in CM and CI chondrites. The triple oxygen isotope composition of the matrix phases in carbonaceous chondrites (CC) is poorly characterised due to their small grain size and the unavailability of suitable standards for SIMS analysis. CM chondrites may be considered as a good analog for the materials from the C-type asteroid Ryugu [1]. Since Ryugu samples are observed to be almost entirely made of matrix material like CI chondrites, it is essential to characterise in situ bulk matrix isotope composition using SIMS in Ryugu and the matrix-rich CCs.

Samples and methodology: We measured triple oxygen isotopes and water in the 'bulk' matrix of CM2 Murchison using the Sensitive High Resolution Ion Microprobe Stable Isotope (SHRIMP SI) at RSES, Australian National University. A chip of the rock was mounted in Bi-Sn alloy, a new mounting technique developed to measure trace amounts of water in nominally anhydrous minerals (NAMs). In this case it is also useful in the measurement of oxygen isotopes to avoid contamination from epoxy in the porous CC matrix in high-precision analyses. $^{16}O^-$, $^{17}O^-$ and $^{18}O^-$ ions were measured in multi-collection mode using Faraday cups followed by $^{16}O^1H$ peak characterisation from automated mass scans on the same spots. A spot size of 30 µm was used. The measurements were referenced to San Carlos Olivine (SCO). An antigorite serpentine reference material was also analysed to establish any issues with the $OH^–$ peak tailing under $^{17}O^–$.

Results: Triple oxygen isotope analysis in 27 spots from Murchison matrix were acquired. The observed range in the isotope ratios are $\Delta^{17}O \approx +1$ to +7‰ (mean 2SE at 95% confidence ≈ 0.21‰), $\delta^{17}O \approx +2$ to +7‰ (mean 2SE ≈ 0.5‰), $\delta^{18}O \approx -3$ to +5‰ (mean 2SE ≈ 0.25‰). External reproducibility of $\Delta^{17}O_{SCO}$ was ≈ 1‰. Any instrumental mass fractionation effects are expected to affect $\delta^{17}O$ and $\delta^{18}O$ but not $\Delta^{17}O$. The water abundance ($^{16}O^1H/^{16}O$ ratios) ranges from 0.025 to 0.06, and so is significantly larger than $^{17}O^-$. Figure 1a shows the plot of $^{16}O^1H/^{16}O$ vs $\Delta^{17}O$.

We also measured water in olivine grains scattered in the Murchison matrix. The apparent $^{16}O^1H/^{16}O$ ratios in the Murchison olivines vary from 6×10^{-6} to 9×10^{-6}. Additionally, the $^{16}O^1H/^{16}O$ ratios in SCO span the same range of ~6×10^{-6} to 9×10^{-6}. Calibration using multiple reference materials shows a water concentration of ~10-15 ppm in Murchison olivines as well as SCO [2].

Discussion: There is a distinct lack of studies characterising in situ CC matrix oxygen isotope compositions. One analysis of isolated Murchison matrix fraction using BrF_5-catalysed extraction of oxygen from silicates has yielded $\delta^{18}O$ = 12.70‰, $\delta^{17}O$ = 4.72‰, $\Delta^{17}O$ = -1.88‰ [3]. This analysis is isotopically 'heavier' than the whole-rock values for Murchison but lies on the same 2-component mixing line as the host rock. The $\Delta^{17}O$ range observed in this work is ≈ 2 to 8‰ higher than the analysis reported in [3]. This disparity may be potentially related to the tailing of the OH^- peak under $^{17}O^-$ peak due to their similar mass [4]. A 100 µm collector slit on SHRIMP SI and optimum peak tuning ensures good separation of the two ion species seen in figure 1b. However, in case of an interference, OH counts/sec should be proportional to the tailing effects, i.e., a rise in $\delta^{17}O$. Compared to the R^2 = 0.82 value for $^{16}O^1H/^{16}O$ vs $\Delta^{17}O$ in figure 1a, correlation with $\delta^{17}O$ shows $R^2 \approx 0.3$. Can the positive $\Delta^{17}O$ values be trusted? The covariation seen in water vs $\Delta^{17}O$ agrees with the two-

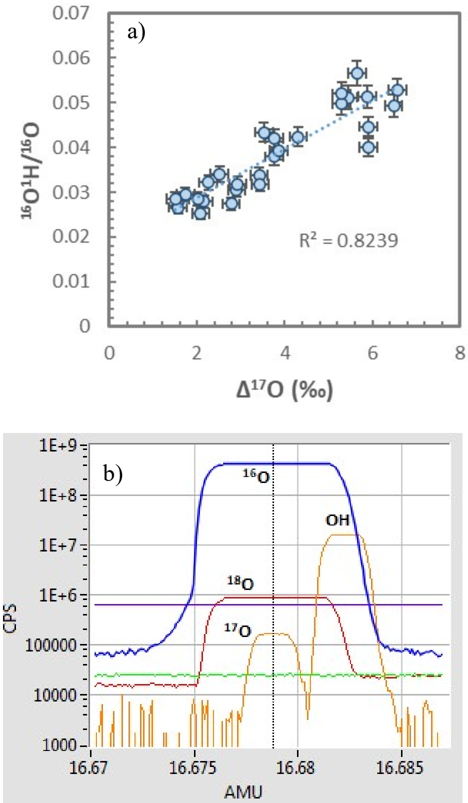

Figure 1: a) Plot of $^{16}O^1H/^{16}O$ vs $\Delta^{17}O$ in Murchison matrix. 10% uncertainty is assumed for the water ratios; b) Mass scan in Murchison matrix showing well-resolved $^{17}O^-$ and $^{16}OH^-$ peaks. Vertical line through the peaks is the position of the magnet during data acquisition.

component mixing model between a solar reservoir and heavy water reservoir for variable water : rock ratios [3]. More work is underway to constrain the nature of these in situ measurements and ascertain any instrumental artefacts.

The water observed in the Murchison olivines stands in contrast to the elevated water concentrations from chondrule olivines in CM chondrites reported in recent studies, and the difference is likely due to different sample preparation methods [5,6]. Water in olivines from different meteorites and Ryugu would be crucial to constrain the formation conditions of the olivines that make up a majority of the chondrules and are scattered throughout the CC matrix.

Conclusions: CM Murchison matrix should be a good analog for the matrix from Ryugu samples. In situ bulk matrix analysis of CM Murchison using SHRIMP SI yield a $\Delta^{17}O$ range of +1 to +7‰, which is at least 2‰ higher than the whole-rock isotope composition range for CM chondrites. There is good covariation between the water content measured in the 27 spots and the $\Delta^{17}O$ values. If there is any interference of the OH^- ion species into $^{17}O^-$, the covariation should be strong for $\delta^{17}O$ values too. However, that is not the case. A more robust dataset measuring matrix from other hydrous CCs like CI and CR chondrites is needed to constrain the nature of these in situ bulk matrix measurements. Moreover, water in the NAM olivine from Murchison chondrules and matrix show ~10-15 ppm water which is in contrast to recent studies and has implications on the formation and evolution of their host components.

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