

WATER IN OLIVINES FROM CM2 AND CV3 CHONDRITES USING SIMS: IMPORTANCE OF SAMPLE PREPARATION. A. Patkar¹, T. Ireland², J. Avila², S. Turner³. ¹Research School of Earth Sciences, Australian National University, Acton ACT 0200, Australia (aditya.patkar@anu.edu.au); ²School of Earth and Environmental Sciences, University of Queensland, St Lucia QLD 4067, Australia; ³School of Natural Sciences, Macquarie University, NSW 2109 Australia

Introduction: Characterizing H₂O contents in meteorites can help to constrain the origin and source(s) of water on their asteroidal parent bodies. Since carbonaceous chondrites (CC) are one of the major potential sources of water to Earth [1], measuring the water concentrations in their various components is essential. Although the water content in the hydrated CC matrix has been well characterized, water in the nominally anhydrous minerals (NAMs) from chondrules remains debated. Recent studies have attempted to quantify water concentrations in nominally anhydrous minerals (NAMs) like olivine and pyroxene using SIMS, e.g.: [2,3]. A wide range of ~10 ppm to ~12000 ppm (1.2 wt%) has been reported from CC olivines [3,4]

The primary difference between the various studies is the sample mounting and preparation protocols observed for analysis. For instance, [2] and [3] have employed epoxy (resin) mounts for the in-situ SIMS analysis for water in olivines. Other studies like [5] have employed the use of Indium mounts. Some have also used thin sections to measure water contents in NAMs [4]. In this report, we focus on the water concentration in olivines from CM and CV chondrites and the importance of sample preparation and mounting media in these analyses of water in NAMs using SIMS.

Samples and methodology: Four CCs- Murchison (CM2), Murray (CM2), Bali (CV3) and Allende (CV3) were studied. Small chips of Murchison and Allende were crushed and olivines were isolated and mounted in Bi-Sn alloy, a new mounting method developed for trace water measurements in NAMs. Although this removes any spatial context, it helps to minimize contamination from the surrounding matrix during water measurements. The mounts were polished using diamond paste without introducing any water during the process. We also mounted chips of Murchison and Allende in epoxy for comparison. Thin section of CM2 Murray was obtained from the Australian National University meteorite collection while that of CV3 Bali was loaned from NMNH, Smithsonian Institution.

In situ water contents were measured with the Sensitive High Resolution Ion Microprobe Stable Isotope (SHRIMP SI) at the RSES, ANU. Cs⁺ primary ion source and an electron gun were used to sputter

~25 µm spots in the olivines and to acquire ¹⁶O⁻ and ¹⁶O¹H⁻ secondary ion species. They were collected simultaneously in multi-collection mode using Faraday cups equipped with a resistor (¹⁶O⁻) and a capacitor (¹⁶O¹H⁻). A 100 µm collector slit was used for adequate resolution of ¹⁶O¹H⁻ from ¹⁷O⁻ species (M/ΔM ≈ 4500). Samples were stored in vacuum for a week and gold-coated before analysis. Qualitative chemical analysis was performed using a JEOL JSM-6610A SEM at RSES, ANU prior to SHRIMP SI analysis to identify target areas for analysis.

Raw ¹⁶O¹H/¹⁶O ratios were converted to water abundances using multiple reference materials: Suprasil Glass (SUP, 1 ppm water, obtained from Heraeus Quarzglas), San Carlos Olivine (SCO, 15±2 ppm), Russian Cr-diopside (100±10 ppm) and ND70 basaltic glass (9980±100 ppm) [6]. Each sample mount (BiSn and epoxy) had a SUP and SCO to account for any sample-related effects during measurement.

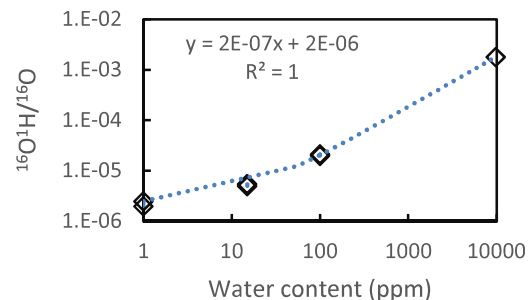


Figure 1: ¹⁶O¹H/¹⁶O vs water content (ppm) calibration using four reference materials with their water contents mentioned above. SUP is used to monitor water background at ¹⁶O¹H/¹⁶O ≈ 2 × 10⁻⁶.

Results and Discussion: 44 olivine grains were isolated from Murchison ranging from 30 to 250 µm on their longest axis. Qualitative analysis shows FeO_t content varying from ~0.5 wt% to ~40 wt% which roughly encompasses the entire compositional range seen in olivines from Murchison. We also measured triple oxygen isotopes on these grains to confirm the entire isotopic range seen from Murchison olivines. The Δ¹⁷O range was observed at -6‰ to -4‰ for the Mg-rich olivines (FeO_t < 5 wt%) and -3‰ to -2‰ for

the more fayalitic olivines ($\text{FeO}_t > 10$ wt%) which shows a representative population of olivines from the meteorite after physical separation. The olivines have sampled a variety of type I and II chondrules and likely isolated olivine grains (IOGs) scattered around the matrix which are proposed to have originated from the chondrules [7]. Similarly, olivines from Allende were observed to have typical oxygen isotope compositions as seen in chondrules. However, the Allende olivines are more commonly seen as broken chondrules with a mixture of olivines and mesostasis rather than solitary olivine grains.

H_2O concentrations measured using the $^{16}\text{O}^1\text{H}^-$ ions in Murchison and Allende olivines isolates mounted in BiSn show ~ 10 -30 ppm water (~ 70 spots across 44 isolated olivine grains in Murchison and ~ 45 spots across 9 isolated olivine grains in Allende) using the linear calibration method in fig. 1. However, it should be noted that the $^{16}\text{O}^1\text{H}^-/^{16}\text{O}$ variation seen is the same as that in SCO (~ 40 spots across 4 grains). This wide range is likely due to minor sample chamber pressure fluctuations leading to variable $^{16}\text{O}^1\text{H}^-$ contributions from the vacuum. This variability is reflected in the $^{16}\text{O}^1\text{H}^-/^{16}\text{O}$ ratios from SUP which is used to monitor the water background. The changes observed in the water background are reflected in the SCO and CC olivines. After correcting for these fluctuations, these CC olivines show water content similar to SCO.

CM2 Murray and CV3 Bali thin sections yielded a wide range of water concentrations with Murray olivines having ~ 70 to 200 ppm water (27 spots across 15 grains) while Bali olivines with ~ 1000 to 1500 ppm water (15 spots across 8 grains). The physical characteristics, chemical compositional and oxygen isotopic range of olivines from these two chondrites are like the ones found in Murchison and Allende.

The epoxy mount with a chip of Murchison and Allende each yielded a water concentration of ~ 800 to 1000 ppm (~ 10 spots across 5 grains each). The observed water background from SUP was $^{16}\text{O}^1\text{H}^-/^{16}\text{O} \approx 1 \times 10^{-4}$, up from 2×10^{-6} seen in the BiSn mount session. Figure 2 shows the water measurements across different chondrites and mounting media.

There is considerable difference between the water measurements from BiSn mounts and thin sections/epoxy. Epoxy is known to constantly outgas in vacuum and is likely to be the major contributor to the $^{16}\text{O}^1\text{H}^-$ counts from the CC olivines and the reference materials. The outgassing is also reflected in the pressure in the sample chamber which rose by a factor of ~ 2 after introducing the epoxy mounts/thin sections (from 7.5×10^{-9} to 1.5×10^{-8} mbar). The nature of the outgassing is not well-constrained, and the water background is also raised considerably as seen in SUP

$^{16}\text{O}^1\text{H}^-/^{16}\text{O}$ ratios. Murray and Bali thin sections show variable measurements likely due to the outgassing nature of the thin sections. Murray section outgassed less and thus showed a lower background than Bali, which showed a water background similar to the epoxy mount. Thin sections particularly do not have standards on them normally and make it difficult to constrain any sample-related effects.

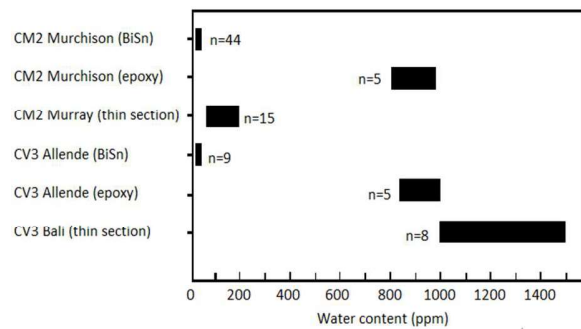


Figure 2: Water concentration in ppm from different chondrite olivines mounted in BiSn, epoxy and thin sections. The number represents the grains that exhibit the range of water content.

Conclusions: CM2 Murchison and CV3 Allende olivines hold water comparable to SCO in their structure, i.e., $\sim 15 \pm 2$ ppm. This low concentration of water contrasts with previous studies [2,3] and it is likely due to different sample preparation and mounting protocols.

Our results indicate that thin sections and epoxy (resin) mounts show much higher water concentrations than metal mounts like Indium and BiSn in NAMs and make it difficult to resolve between low level water concentrations. Different thin sections made using variable methods and gluing media can further complicate analyses. Epoxy outgassing is the primary contaminant in these analyses.

The low concentration of water in the olivines from CM and CV chondrites have major implications on their volatile inventory and provides constraints on the formation and subsequent alteration conditions in the early solar system.

References: [1] Alexander C'MOD. (2017) *Phil. Trans. Royal Soc.*, 375(2094). [2] Stephant A. et al. (2017) *GCA*, 199, 75-90. [3] Azevedo-Vannson S. et al. (2021) *LPSC 52*, Abstract #2548. [4] Jin Z and Bose M (2019), *Sci. Adv.*, 5. [5] Shimizu K. (2021) *GCA*, 301, 230-258. [6] Turner M. et al. (2015), *JAAS*, 30, 1706-1722 [7] Jacquet E. et al. (2021), *MAPS*, 56, 13-33.