METEORITIC CARBONATES – THE KEY TO SAMPLING EXTRATERRESTRIAL FLUIDS?

P. A. B. Krizan[1], Q. H. S. Chan[1], M. E. Zolensky[2], R. J. Bodnar[3], D. Papineau[4,5,6], C. Bays[1], and I. Standen[1]
[1]Department of Earth Sciences, Royal Holloway University of London, Egham, TW20 0EX, Surrey, United Kingdom, [2]NASA Johnson Space Centre, Houston, Texas, 77058, United States of America, [3]Department of Geoscience, Virginia Tech, Blacksburg, Virginia 24061, United States of America, [4]Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, United Kingdom, [5]London Centre for Nanotechnology, 17-19 Gordon Street, London, WC1H 0AH, United Kingdom, [6]Centre for Planetary Sciences, London, Gower Street, London WC1E 6BT, United Kingdom

Introduction: Fluid inclusions are naturally occurring mineral features that preserve trapped fluid phases inside a solid phase. These cavities exist as a closed system, recording the environmental conditions present during entrapment – both physical and chemical [1]. As a result, fluid inclusions are great candidates for directly studying past fluid activity on extraterrestrial bodies within the Solar System. On Earth, fluid inclusions are abundant as they occur within numerous host minerals. They are a powerful tool for accurately and directly understanding aqueous processes in various geological environments. In contrast, extraterrestrial fluid inclusions have only been positively identified on three separate occasions within host materials ranging from ordinary chondrites to C/B-type asteroid mission return samples [2, 3, 4]. The possibility of directly studying the fluids involved in aqueous alteration and accurately constraining their heliocentric distances drives the hunt for these elusive capsules [5].

Our goals are to locate new fluid inclusion candidates (hereon referred to as candidates) and assess whether fluid inclusions are a common feature within meteoritic carbonates and why they may have eluded detection for so long. We also aim to characterize the host grain's mineralogical properties and assess the potentially preferential conditions for fluid entrapment on the asteroid parent body.

Samples & Methods: 18 meteorite specimens were examined: **CI1s**: Ivuna & Orgueil; **CM2s**: ALH 84029, Cochabamba, LON 94101, LON 94102, Mighei, Murchison, Santa Cruz, Sayama; **C-ung**: Bells & Sutter's Mill; **Cba**: Bencubbin; **L/LL4**: Bjübole; **L/LL6**: Holbrook; **ordinary chondrites:** Zag (H3-6) & Jilin (H5); and a diogenite **ALHA 77256.**

Where possible, to avoid introducing and misidentifying artifact inclusions as candidates resulting from sample preparation, we prepared new thin sections using a specially designed anhydrous preparation technique specifically formulated for studying fluid inclusions [6]. Candidates were identified based on particular selection criteria: a negative crystal shape, irregular or sub-spherical shape, mid to high transparency of the trapped fluid, some resemblance of facets, and possession of a freely moving vapor bubble (the latter is not a strict requirement but provides strong evidence for fluid inclusions).

Candidates within petrographic thin sections were located and imaged using a Nikon LV100ND Eclipse microscope system. Compositional analyses of the trapped fluids and their associated host mineral grains were performed using a series of confocal Raman spectrometer instruments (Renishaw, JY Horiba, and Witec models).

Results and Discussion: Candidates were successfully identified in 4 CM2s (**ALH 84029, LON 94101, Mighei, Sayama**), 2 CI1s (**Ivuna & Orgueil**), and 2 C-ungrouped meteorites (**Bells & Sutter's Mill**). All candidates were less than 10 µm in diameter and had a mean maximum size of ~ 3.5 µm. Submicron-sized candidates dominated the candidate population in each host carbonate grain. Our observations agree with previously reported dominant fluid inclusion sizes within meteoritic carbonates [2, 3]. Fluid inclusions were positively found in both Ca and Ca/Mg carbonates (Figure 1).

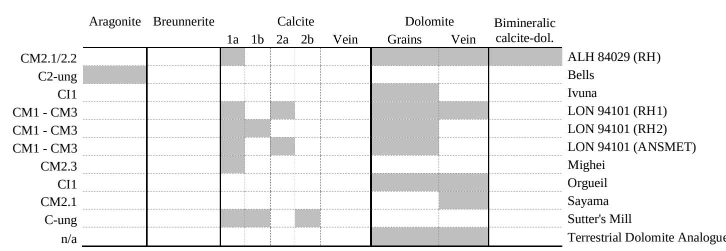

Figure 1. Summary of the fluid inclusion-bearing carbonate host grain compositions determined by Raman spectroscopy within each meteorite specimen.

At room temperature, a maximum of 1-2 candidates in some carbonates per sample presented a visible moving vapor bubble. Only ~ 25% of each sample's total host carbonate grains hosted a candidate with a vapor phase. Most of the observed candidates presented a single-phase fluid system during petrographic observations. However, it was difficult to accurately interpret the phase states of the fluid inclusions using optical microscopy due to their predominant submicron sizes. Therefore, the candidates' fluid phase system interpretation is likely subject to bias toward larger-sized vapor bubbles [3].

Based on previous studies of aqueous extraterrestrial fluid inclusions and their minimum formational temperatures of aqueous fluid inclusions [2], we infer that the majority (~80%) of our observed candidates likely had a low formational temperature (50 – 100 ^{O}C) due to their failure to demonstrate a visible vapor bubble at room temperature. The absence of a vapor bubble could also be attributed to a void, which at this scale would be hard to distinguish from a single-phase fluid inclusion using a petrographic microscope.

Compositional analyses of trapped fluids were inconclusive due to overshadowing fluorescence within the higher wavelength of the Raman spectra. Aqueous fluids have a wide range for their Raman-active symmetric stretching vibration between ~ 2750 - 3900 cm^{-1}. We focused our compositional analyses on the most viable candidate within the ANSMET LON 94101 sample, with a feret diameter of ~3.79 µm located ~ 3 microns below the sample surface, which fitted all the specified candidate selection criteria.

Raman spectra show that all the meteoritic candidate hosting grains are more crystalline when compared to terrestrial analogs. This implies a relatively slow mineral growth during aqueous alteration on the parent body, which may, in turn, explain the preference for smaller-sized candidates in carbonates. The high crystallinity of all host grains suggests that fluid entrapment in carbonates occurs within a specific range of conditions. Furthermore, we propose that the paired analysis of the organo-carbonate relationship and the shift within the carbonate Raman modes can be used to infer the relative conditions and paragenesis experienced by the inclusion-hosting grain.

Conclusions: Our observations clearly show that viable candidates are abundant within a wide range of meteoritic carbonates. Nonetheless, significant doubt over their validity as indigenous fluid inclusions still exists due to the inability of traditional approaches to determine the composition of the trapped fluids at a submicron scale. Therefore, it is clear that the traditional use of petrographic thin sections may be inappropriate for the carbonate-hosted study of fluid inclusions in carbonaceous chondrites – primarily due to the high risks of induction of artifact inclusions during sample preparation [2]. Ideally, future studies should seek a more accurate and reliable approach that avoids the exposure of the sample to any fluids and can assess samples in their raw grain format. High-resolution analyses via TOF-SIMS are planned for the candidate within the ANSMET LON 94101 thin section (Figure 2) to confirm the composition of the two-phase, low-viscosity fluid.

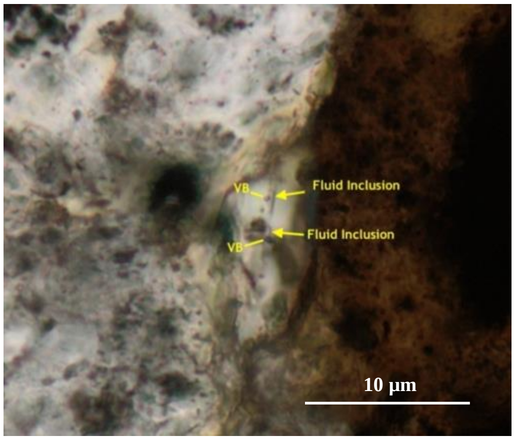

Figure 2. A photomicrograph of two-phase candidates (arrowed) within a dolomite grain within the ANSMET LON 94101 polished thin section. Vapor bubbles are labeled VB.

Our petrographic observations of the candidates and the Raman spectra of the host carbonate grains imply that the entrapment of fluids on the parent body occurs within a specific range of conditions and differs considerably from those of their terrestrial counterparts. However, additional compositional analyses are required to confirm these interpretations. Impact stresses also likely impede the survival/preservation of larger candidates during delivery [7], especially within carbonates where their cubic cleavage may also negatively contribute.

Acknowledgments: We would like to thank the Natural History Museum in London for loaning us the Murchison, Zag, Ivuna, and Bencubbin samples; the Vatican Observatory for loaning us Orgueil, Holbrook, Bjurböle, and Mighei samples; and ANSMET for lending us the LON 94101 & 94102, ALH 84029, ALHA 77256 samples. Furthermore, thank you to Dr. Zolensky for suggesting and loaning us the Santa Cruz, Cochabamba, Ivuna, Sayama, Jilin, Sutter's Mill, Mighei, and Bells samples used in this research.

References: [1] Chi, G., et al., (2020) 11(1), 7 [2] Zolensky, M. E., et al., (2017) Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 375(2094) [3] Tsuchiyama, A., et al., (2021) Science Advances, 7(17) [4] Nakamura, T., et al., (2022) Science, eabn8671 [5] Yurimoto, H., et al., (2014) Geochemical Journal, 48(6), 549-560 [6] Bodnar, R.J. and Zolensky M. E. (2000) Meteoritics & Planetary Sci. 35, A29-30 [7] Madden, M. E. E., Horz, F., & Bodnar, R. J. (2004) The Canadian Mineralogist, 42(5)