ACCRETION AND CIRCULATION OF ^{16}O-POOR WATER IN THE ACFER 094 PARENT BODY

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Introduction: Since its discovery in Algeria in 1990, the Acfer 094 ungrouped carbonaceous chondrite has been considered one of the most primitive chondrites in our meteorite collection. It contains abundant presolar grains and has undergone almost no thermal metamorphism [1, 2]. A notable feature of Acfer 094 is the occurrence of aggregates of extremely ^{16}O-poor magnetite-pentlandite (Δ^{17}O $\approx$ 85‰ [3]) named cosmic symplectite (COS) [4]. COS is the best candidate among all known planetary materials to represent an extremely ^{16}O-poor water reservoir in the solar nebula, which is invoked, for example, to explain the evolution of ^{16}O-poor planetary materials from the ^{16}O-rich Sun (e.g. [5]). CO self-shielding models predict that this heavy water reservoir resides in the outer solar nebula [e.g., 6].

How did the Acfer 094 parent body (A094-PB) accrete the signature of this outer nebula water reservoir? There are two likely scenarios: Scenario 1) COS formed in the solar nebula and A094-PB later accreted this phase [3]. Scenario 2) A094-PB accreted in the outer Solar System with isotopically heavy water ice incorporated into its matrix [7], then COS formed after melting of this ice. In this study we distinguish between these two hypotheses by petrographic and O isotope studies of Acfer 094 COS and matrix.

Methods: Petrographic observations and SEM-EDS analyses of an Acfer 094 thin section (USNM 72337) were performed using a Tescan Mira3 FEG-SEM. Oxygen isotopes of COS grains were measured with the Wash U NanoSIMS using a ~1 pA primary beam focused to ~100 nm. We acquired 3x3 µm scanning ion images of ^{16}O$^-$, ^{17}O$^-$, and ^{18}O$^-$ using EMs. Oxygen isotope ratios of COS were normalized to magnetite grains found in a dark inclusion of Acfer 094, assumed to be $\delta^{17,18}$O $\approx 5 \pm 4$‰ [8]. Other analytical conditions are similar to [9]. Oxygen isotopes of Acfer 094 matrix were measured on the University of Hawai‘i Cameca ims 1280 ion probe using a <3 pA primary Cs$^+$ beam focused to ∼300 nm. We acquired 128×128 pixel, 20×20 µm scanning ion images in monocollection mode for ^{16}O$^-$, ^{17}O$^-$, ^{18}O$^-$, ^{16}OH$^-$, ^{24}Mg^{16}O$^-$, ^{27}Al^{16}O$^-$, and ^{56}Fe^{16}O$^-$ on the mono-EM. Other analytical conditions are similar to [10].

Results and Discussion: COS grains are dispersed throughout the matrix and show elongated shapes of ~10−30 µm in length and ~5−10 µm in width (Fig. 1a). They are associated with fractures and are occasionally surrounded by a rim of fibrous sulfide (Fig. 1b). We measured δ^{18}O and δ^{17}O values ranging from 160 to 210‰, mostly consistent with previous measurements [3] (Fig. 2).

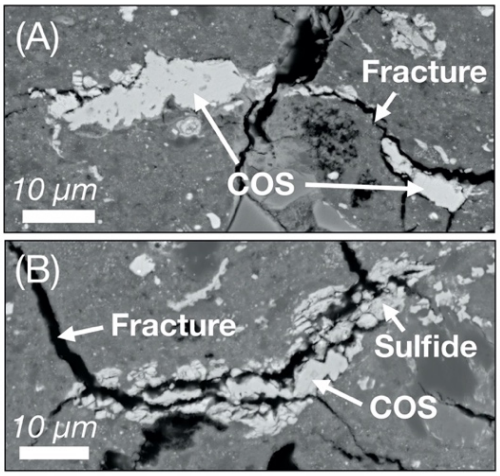

Figure 1. *BSE images of elongated COS grains within Acfer 094 matrix (A) free of sulfide and (B) surrounded by a rim of fibrous sulfide. Most of the COS are associated with fractures.*

The occurrence of elongated COS and sulfide associated with fractures is comparable to fracture filling veins of secondary assemblages (e.g., carbonate or sulfide) previously reported in aqueous altered CM chondrites and CM1-like clasts from the Kaidun meteorite, respectively [11]. These veins are considered to be strong evidence of Ca- and (Fe, S)-bearing fluid circulation on the asteroidal parent body. We thus infer a similar mechanism for the formation of COS, with S originating from S-bearing phases accreted by A094-PB. Since Acfer 094 contains ultra-porous lithologies, similar in structure to cometary IDPs [7], A094-PB may have contained H_2S ice (which is observed in comets [12]).

O-isotopic compositions of secondary minerals in altered chondrites (e.g., CM chondrites) suggests that aqueous alteration occurs essentially in a closed system, with ^{16}O-poor fluid interacting with ^{16}O-rich anhydrous silicates [13]. If aqueous alteration took place in Acfer 094, then the O-isotopic compositions of its hydrated matrix may have recorded a reaction path between (i) heavy water and (ii) the ^{16}O-rich matrix silicates. This reaction is expected to lie along a mixing line between these two reservoirs (presumably the slope-1 line), but small shifts toward ^{17,18}O−rich values can result from equilibrium partitioning between matrix silicates and water at varying temperatures [14].

However, it appears that temperature variations having a minor effect on determining the isotopic composition of hydrated chondrites [13].

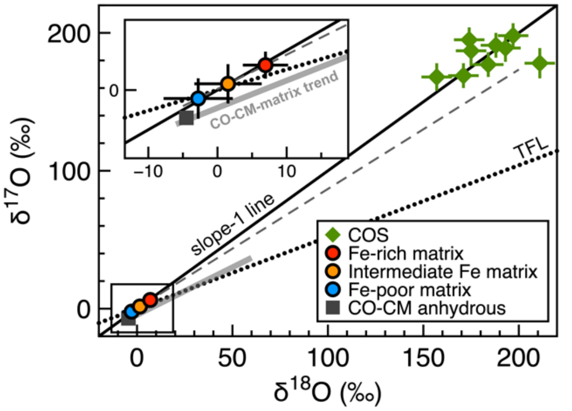

Figure 2. *Three oxygen isotope diagram showing the composition of the COS and the matrix determined in this study. They both fall along the slope-1 line suggesting a genetic relationship between matrix and heavy water (COS). The gray line is the bulk CO, CM and CM-matrix trend reported in [13]. Bulk CO-CM anhydrous value is taken from [15]. The grey dashed line represents the extrapolated linear correlation of the matrix. Errors are 2σ.*

Our Fe-Mg-Al scanning ion map (Fig. 3) reveals that the Acfer 094's matrix is a mostly mixture of Fe-rich and Mg-rich silicates (Fig. 3). Since Fe content in the matrix is an indicator of aqueous alteration in the least altered carbonaceous chondrites [16], we grouped each pixel by its Fe content and calculated the O isotopic composition of Fe-poor, intermediate, and Fe-rich matrix (Fig. 2). Our SIMS analyses show that the Acfer 094's matrices do not plot along the bulk CO−CM−matrix line (i.e., $\delta^{17}O = 0.69 \times \delta^{18}O - 4$ [13]) established by isotopic partitioning between CO or CM water and anhydrous silicates, convolved with mixing of two distinct isotopic reservoirs. Instead, they fall along a slope-1 line, which extrapolates to near the COS composition (Fig. 2). This result suggests that increasing aqueous alteration of the matrix correlates with increasing contribution of COS-like heavy O isotopes. Instrumental mass fractionation corrections were not applied, but would increase the $\delta^{17,18}O$ values of Fe-rich matrix and decrease the $\delta^{17,18}O$ values of Fe-poor matrix in a mass-dependent way by a few per mil [17], decreasing the slope of the correlation.

Together, our petrographic and isotopic results demonstrate that A094-PB accreted a significant proportion of ^{16}O-poor water ice (supported by the recent discovery of ultra-porous lithologies in Acfer 094 [7]) with O-isotopic composition probably close to that of COS. We propose that, due to an increase of temperature in A094-PB, accreted ice in this body melted, leading to S-bearing fluid circulation and precipitation of ^{16}O-poor magnetite and sulfide at temperature likely below 100°C [4]. In order to preserve the extreme isotopic composition of the COS, the interaction between the heavy fluid and the anhydrous matrix should be minimal. Then, the remaining fluid reacted with ^{16}O-rich fine-grained silicates, increasing the $\delta^{17,18}O$ values of these grains.

The work presented here implies that A094-PB accreted isotopically heavy water ice in the outer Solar System (Scenario 2). But the presence of pentlandite within COS suggests that A094-PB may also have accreted a significant proportion of S-bearing ice (H_2S or SO_2) from the outer Solar System. Thus, like for oxygen isotopes, sulfides in COS may carry the particular isotopic signature of an outer Solar System sulfur reservoir which may have undergone photochemical processing [18].

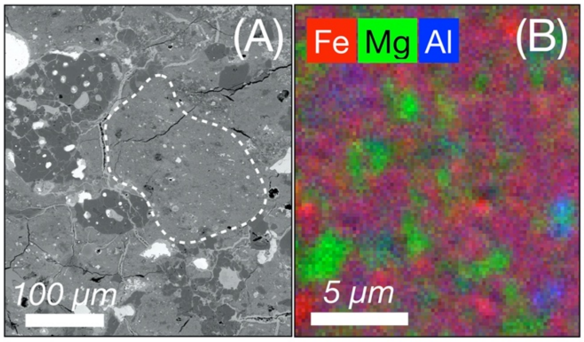

Figure 3. (A) *BSE image of an area of Acfer 094 showing a matrix region (dashed line) which contains both Fe-rich and Fe-poor grains. The dashed area delimited the approximate location where matrix has been measured by SIMS. (B) Fe-Mg-Al elemental map acquired by SIMS of the analyzed matrix area.*

References: [1] Nguyen A. N. et al. (2007) *APJ 656,* 1223–1240. [2] Kimura M. et al. (2008) *MAPS 43,* 1161–1177. [3] Sakamoto N. et al. (2007) *Science 317,* 231–233. [4] Seto Y. et al. (2008) *GCA 72*, 2723−2734. [5] Clayton R. N. (2002) *Nature 415*, 860−861. [6] Lyons J. R. and Young E. D. (2005) *Nature 435*, 317−320. [7] Matsumoto M. et al. (2019) *Science Advances* 5, eaax5078. [8] Rowe M. W. et al. (1994) *GCA* 58, 5341−5347. [9] Vacher L. G. et al. (2019) *82nd METSOC* abstract #2157. [10] Ogliore R. et al. (2009) *MAPS 44*, 1675−1681. [11] Zolensky M. E. et al. (1996) *MAPS 31*, 484−493. [12] Calmonte U. et al. (2016) *MNRAS 462*, S253−S273. [13] Marrocchi Y. et al. (2018) *EPSL* 482, 23−32. [14] Clayton R. N. and Mayeda T. K. (1999) *GCA 63*, 2089−2104. [15] Piralla M. et al. (2020) *GCA* 269, 451−454. [16] Leroux H. et al. (2015) *GCA 170*, 247−265. [17] Valley J. W. and Kita N. T. (2009) *MAC short course 41*, 19−63. [18] Chakraborty S. et al. (2013) PNAS 110, 17650−17655.