

OXYGEN ISOTOPE SYSTEMATICS OF ALLENDE FUN CAI CMS-1. C. D. Williams¹, T. Ushikubo², G. J. MacPherson³, E. S. Bullock³, N. T. Kita² and M. Wadhwa¹, ¹School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404, USA, curtis.williams@asu.edu, ²WiscSIMS, Department of Geoscience, University of Wisconsin, Madison, WI 53706, USA, ³Smithsonian Institution, Washington D. C. 20560, USA.

Introduction: The oxygen isotopic composition of calcium-aluminum-rich inclusions (CAIs) from the Allende CV chondrite form an array on a three-isotope diagram with a slope of ~ 1.0 , designated the carbonaceous chondrite anhydrous minerals (CCAM) mixing line [1,2]. Within CAIs, the typical sequence of ^{16}O -enrichment for individual phases is spinel \geq pyroxene $>$ olivine $>$ anorthite $>$ melilite. The trend defined by these minerals is indicative of two-component mixing and commonly interpreted as reaction and isotopic exchange of ^{16}O -rich primary phases with a ^{16}O -poor gas [2].

The oxygen isotopic composition of CAIs with Fractionation and Unidentified Nuclear (FUN) effects do not fall along the CCAM line. The oxygen isotopic composition of FUN CAIs display both large mass-dependent fractionation leading to an enrichment in ^{18}O as well as subsequent mixing between ^{16}O -rich and ^{16}O -poor reservoirs [2-8]. The mass-dependent fractionation line defined by individual phases from FUN CAIs projects back towards the ^{16}O -rich end of the CCAM mixing line.

Recently, we reported on the titanium, silicon and magnesium isotopic compositions of a new FUN CAI (designated CMS-1) identified in the Allende CV chondrite [9]. CMS-1 is characterized by nucleosynthetic anomalies in titanium ($\epsilon^{46}\text{Ti} = -13.9 \pm 1.7$, $\epsilon^{48}\text{Ti} = 1.0 \pm 1.1$, and $\epsilon^{50}\text{Ti} = -51.3 \pm 6.9$) as well as large mass-dependent fractionation of silicon and magnesium ($f_{\text{Si}} = 16.3 \pm 0.5\%$ and $f_{\text{Mg}} = 37.5 \pm 2.5\%$). The magnitude of these isotopic anomalies are similar to previously identified FUN CAIs [2,3,6-8,10-19]. Experimental data predict complementary fractionation in oxygen isotopes [20]. Here we report on the oxygen isotopic composition of the primary phases (spinel, melilite, fassaite) that comprise CMS-1.

Analytical Technique: Oxygen isotope ratios were collected using the Cameca IMS 1280 at the WiscSIMS laboratory, University of Wisconsin-Madison. Analytical conditions are similar to those reported in [21]. A focused Cs^+ beam was tuned to produce a $15\mu\text{m}$ diameter spot with a primary ion intensity of 3nA . Secondary ions of $^{16}\text{O}^-$, $^{17}\text{O}^-$ and $^{18}\text{O}^-$ were detected simultaneously using three Faraday cups, with typical count rates of $^{17}\text{O}^-$ of 1.3×10^6 cps. The mass resolving power was set to ~ 2200 for $^{16}\text{O}^-$ and $^{18}\text{O}^-$ using two detectors on the multi-collection array and ~ 5000 for $^{17}\text{O}^-$ using the axial detector at a

fixed position. After each analysis, $^{16}\text{OH}^-$ was measured to determine its contribution to the $^{17}\text{O}^-$ signal. The estimated $^{16}\text{OH}^-$ contribution to $^{17}\text{O}^-$ was always less than 0.03% . Following oxygen isotope analyses, SEM images were taken of all spot analyses to ensure there was no significant overlap of pits, cracks, inclusions or phases.

Measured $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ ratios are reported relative to VSMOW. San Carlos olivine ($\delta^{18}\text{O} = 5.32\%$; [22]) was measured periodically throughout the session to correct for instrumental mass bias and to determine the external reproducibility. The external reproducibility (2SD) for $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ is 0.22 , 0.50 and 0.53% , respectively. Potential matrix effects were corrected by establishing calibrations using åkermanite and gehlenite for melilite and spinel, as well as diopside and two synthetic fassaite glasses with 5 and 10 wt.% TiO_2 respectively for Ti-Al-rich pyroxene.

Results: CMS-1 is an irregularly shaped compact Type A inclusion (Fig. 1). The primary mineralogy of CMS-1 is composed of Ti-Al-rich pyroxene and melilite with abundant inclusions of spinel. Ti-Al-rich pyroxene ranges in TiO_2 content from 3.8 to 12.6wt.%, while melilite has a restricted compositional range, 17.9 to 48.0 mole % Åk. Although most of the interior spinel is nearly pure MgAl_2O_4 , many grains have FeO ranging up to 16.8 wt.%; this is unusual for spinel that is not part of a Wark-Lovering rim sequence.

The oxygen isotopic compositions of the primary phases are distinct from one another as shown on the three-isotope diagram (Fig. 2). Spinel is uniformly ^{16}O -enriched and defines a slope- $1/2$ mass-fractionation line, with some primitive compositions close to the point where the spinel mass-dependent fractionation line would intersect the CCAM line at the ^{16}O -rich end ($\delta^{17}\text{O} \sim -49\%$, $\delta^{18}\text{O} \sim -48\%$). Other spinel grains are highly fractionated and plot close to where the spinel mass-dependent fractionation line intersects the mixing line defined by pyroxene ($\delta^{17}\text{O} = -15.40\%$, $\delta^{18}\text{O} = -32.17\%$). Pyroxene plots exclusively on the mixing line and has a large range in its isotopic composition ($\Delta^{17}\text{O} = -12.45\%$ to -23.96%). Melilite is entirely ^{16}O -poor and plots at the top of the mixing line defined by the pyroxene, but somewhat below the terrestrial mass-dependent fraction line ($\Delta^{17}\text{O} = -2.77$ to -7.57%).

Discussion: The oxygen isotopic composition of CMS-1 suggests a formation history that involved at

least three stages of evolution. First, the bulk composition of CMS-1 is typical of Compact Type A CAIs, and an equivalent melt would have the predicted crystallization sequence spinel – melilite – pyroxene, which is consistent with the textures of this inclusion. The initial oxygen isotopic composition of this melt would then be best constrained by the first phase to crystallize (i.e. spinel). The most primitive spinel identified from CMS-1 is characterized by ^{16}O -rich oxygen isotopic compositions, suggesting that the oxygen isotopic composition of the parental melt originated near intersection of these spinel with the CCAM line ($\delta^{17}\text{O} \sim -49\%$, $\delta^{18}\text{O} \sim -48\%$).

A second melting event resulted in evaporation and mass-dependent fractionation. Relict spinel (i.e. grains that did not completely melt) retained their original isotopic compositions. However, new spinel that crystallized from the evaporating and isotopically evolving melt defines a mass-dependent fractionation line similar to that characterized by refractory phases measured in other FUN CAIs [e.g., 3,4,8]. This melting event also resulted in the mass-dependent fractionation of fassaite and melilite whose oxygen isotopic compositions, upon complete crystallization, were at the “bend” in the array observed in figure 2 ($\delta^{17}\text{O} \sim -31\%$, $\delta^{18}\text{O} \sim -14\%$). The degree of fractionation observed in pyroxene and melilite, and the most extremely fractionated spinel, ($\sim 26\%$ in ^{18}O) is consistent with predicted values based on the mass-dependent fractionation of magnesium and silicon isotopes [20].

Recently, [23] suggested that reaction between melilite and perovskite may be responsible for the variable oxygen isotopic compositions observed in pyroxene. In this scenario, a uniformly ^{16}O -rich CMS-1 would contain spinel, melilite and perovskite. Perovskite would subsequently exchange oxygen with a ^{16}O -poor nebular reservoir, while the other phases did not due to the slower diffusivity of oxygen in spinel and melilite [24]. If pyroxene were to grow at the expense of (^{16}O -poor) perovskite and (^{16}O -rich) melilite [24-26], the first pyroxene to crystallize would inherit the composition of the ^{16}O -poor perovskite becoming more enriched in ^{16}O (and depleted in TiO_2) as the reaction proceeded and the isotopic reservoir of melilite began to dominate the system. This is consistent with the observed correlations between oxygen isotopic composition of CMS-1 pyroxene and their TiO_2 content, where $\Delta^{17}\text{O}$ increases with decreasing TiO_2 content. Following this process, melilite itself would exchange its oxygen with a ^{16}O -poor reservoir.

References: [1] Clayton R. N. et al. (1973) *Science* 182, 485-488. [2] Clayton R. N. et al. (1977) *EPSL* 34, 209-224. [3] Davis A. M. et al. (2000) *M&PS* 35, A47. [4] Krot A. N. et al. (2008) *LPSC XXXIX* 2162. [5] Lee T. et al.

(1980) *GRL* 7, 493-496. [6] Marin-Carbonne J. et al. (2011) *LPSC XXXXII* #2764. [7] Marin-Carbonne J. et al. (2012) *LPSC XXXXIII* #1687. [8] Thrane K. et al. (2008) *ApJ* 680, L141-L144. [9] Williams C. D. et al. (2012) *MetSoc* # 5102. [10] Esat T. M. et al. (1978) *GRL* 5, 807-810. [11] Lee T. et al. (1976) *GRL* 3, 109-112. [12] Loss R. D. et al. (1994) *ApJ* 436, L193-L196. [13] McKeegan K. D. et al. (2005) *LPSC XXXVI* #2077. [14] Niederer F. R. et al. (1985) *GCA* 49, 835-851. [15] Niederer F. R. et al. (1981) *GCA* 45, 1017-1031. [16] Niederer F. R. et al. (1980) *ApJ* 240, L73-L77. [17] Papanastassiou D. A. and Brigham C. A. (1989) *ApJ* 338, L37-L40. [18] Srinivasani G. et al. (2000) *M&PS* 35, 1333-1354. [19] Wasserburg G. J. et al. (1977) *GRL* 4, 299-302. [20] Davis A. M. et al. (1990) *Nature* 347, 655-658. [21] Kita N. T. et al. (2009) *Chemical Geology* 264, 43-57. [22] Kita N. T. et al. (2010) *GCA* 74, 6610-6635. [23] MacPherson G. J. et al. (2012) *LPSC XXXXIII* #2415. [24] Dobson D. P. et al. (2008) *EPSL* 270, 125-129. [25] Han J. and Brearley A. J. (2011) *MetSoc* #5388. [26] Yang H.-Y. (1975) *Proc. Geol. Soc. China* 18, 48-58.

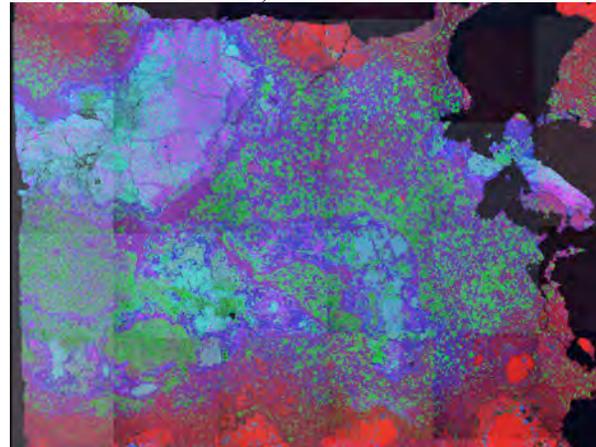


Figure 1 Ca-Al-Mg X-ray map for CMS-1. sky blue = melilite, magenta = spinel, grayish brown = Ti-Al-rich pyroxene, red = magnesium-rich phases in matrix and chondrules, green = Ca-Fe silicates in accretionary rim.

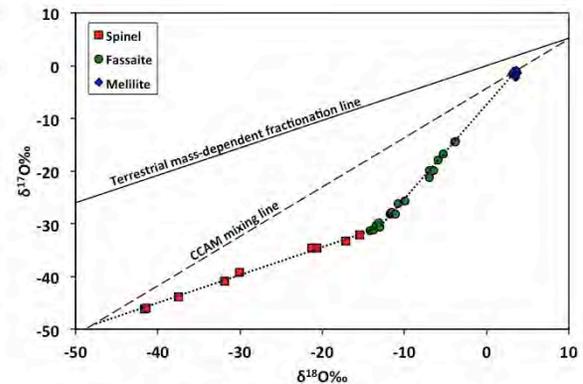


Figure 2 Oxygen isotopic composition of individual phases from Allende FUN CAI CMS-1. Spinel (red squares), Ti-Al-rich pyroxene (green circles) and melilite (blue diamonds).