GROSSITE-RICH REFRACTORY INCLUSIONS IN CARBONACEOUS CHONDRITES: EVIDENCE FOR EARLY GENERATION OF DIFFERENT O-ISOTOPE RESERVOIRS IN THE PROTOPLANETARY DISK AND O-ISOTOPE EXCHANGE DURING FLUID–ROCK INTERACTION.

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Introduction: The oxygen isotopic composition of the Sun inferred from the measurements of the solar wind returned by the Genesis spacecraft [1] is ^{16}O-enriched ($\Delta^{17}O = -28.4\pm3.6$‰) relative to the whole-rock O-isotope compositions of chondrites and achondrites, and chondrule phenocrysts, which all plot close to the terrestrial fractionation line ($\Delta^{17}O \sim \pm5$‰). Vast majority of refractory inclusions (CAIs and AOAs) in carbonaceous chondrites of petrologic types 2–3.0 are isotopically uniform and have solar-like $\Delta^{17}O$ [2–5]. In contrast, CAIs and AOAs in metamorphosed CV and CO chondrites are isotopically heterogeneous with melilite, anorthite, perovskite, Zr- and Sc-rich oxides and silicates, and occasionally Al,Ti-diopside being ^{16}O-depleted relative to hibonite, spinel, Al-diopside, and forsterite [6–10]. The timing of generation of different O-isotope reservoirs and the nature of O-isotope heterogeneity in refractory inclusions in CO3 and CV3 chondrites are poorly known. Grossite ($CaAl_4O_7$) is one of the first minerals predicted to condense from a gas of solar composition [11] and therefore it could have recorded isotopic compositions of reservoirs during the earliest stages of the Solar System evolution. Here we report on O-isotope compositions of grossite-rich CAIs in CH3 and CO3 chondrites measured *in situ* with the UH Cameca ims-1280. For analytical procedures see [9].

Results and Discussion: Oxygen isotopic compositions of the grossite-rich CAIs from the Acfer 182/214 (CH3.0) chondrites are shown in Fig. 1; each column in Fig. 1b corresponds to an individual CAI. Most CAIs, including a relict grossite CAI rimmed by spinel inside a porphyritic pyroxene chondrule, are isotopically uniform. However, there is a large range of $\Delta^{17}O$ among CH CAIs, from ~ −40 to ~ −10‰. About 85% of grossite-rich CH CAIs have no resolvable excess of radiogenic ^{26}Mg [13,14], suggesting formation prior to injection and homogenization of ^{26}Al in the protoplanetary disk (PPD) [15]. We infer that the oxygen isotopic compositions of grossite-rich CH CAIs are primary and that they recorded the existence of different O-isotope reservoirs during the earliest stages of the PPD evolution.

Oxygen isotopic compositions of the grossite-rich CAIs from the DOM 08006 (CO3.0), Y-81020 (CO3.05), and DOM 08004 (CO3.1) chondrites are shown in Fig. 2. In DOM 08006, the CAIs have rather uniform, within uncertainties of our measurements (2σ ~

±2.5‰), ^{16}O-rich compositions ($\Delta^{17}O \sim -25$ to −20‰). In Y-81020 and DOM 08004, the CAIs measured are isotopically heterogeneous. The heterogeneity is mineralogically-controlled: grossite, krotite, melilite, and perovskite are ^{16}O-depleted to various degrees ($\Delta^{17}O$ range from −23 to 0‰) relative to hibonite, spinel, and Al-diopside, which are compositionally similar to the DOM 08006 CAIs. In the DOM 08004 CAIs, grossite is cross-cut by veins of an unidentified Na-bearing Fe,Al-rich phase (Fig. 3). In a CAI from Y-81020 (Fig. 4), grossite
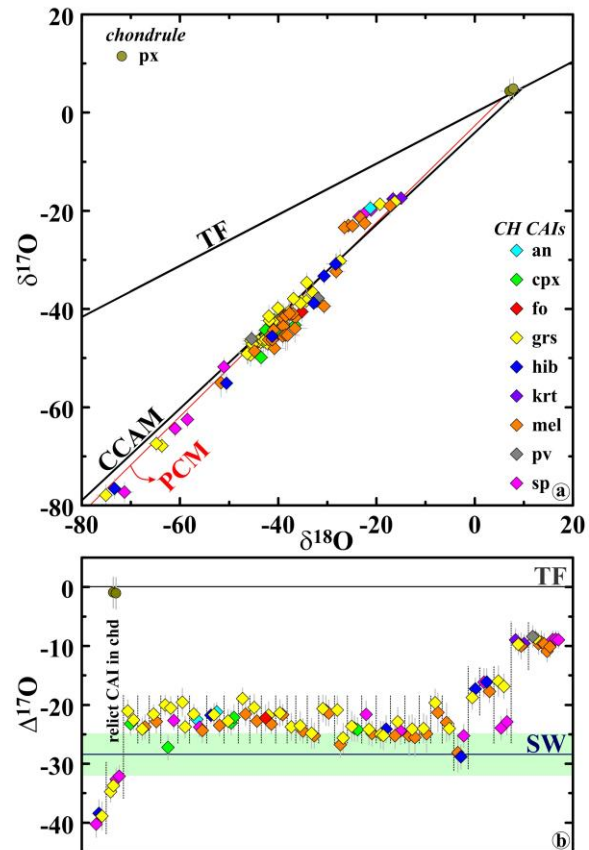

Fig. 1. (a) $\delta^{17}O$ *vs.* $\delta^{18}O$ and (b) $\Delta^{17}O$ (bottom) of the grossite-rich CAIs from the Acfer 182/214 (CH3.0) chondrites. Each column in "b" corresponds to an individual inclusion. Most CAIs are isotopically uniform. Abbreviations here and in Figs. 2–4: an = anorthite; cor = corundum; cpx = Al,Ti-diopside (in CAIs) or high-Ca pyroxene (in chondrules); fo = forsterite; grs = grossite; hib = hibonite; krt = krotite; mel = melilite; pl = plagioclase; pv = perovskite; px = low-Ca pyroxene; sp = spinel; CCAM = carbonaceous chondrite anhydrous mineral line; PCM = primitive chondrule mineral line [12]; SW = solar wind [1]; TF = terrestrial fractionation line.
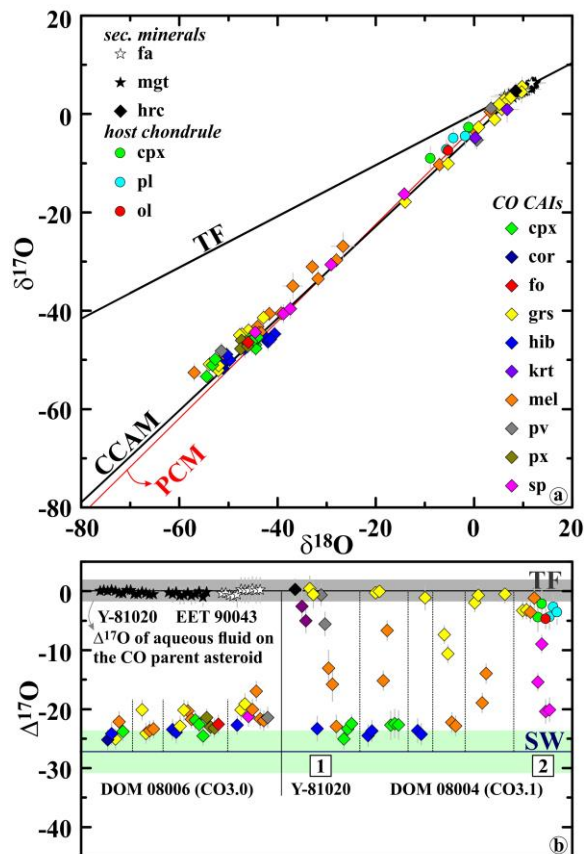
Fig. 2. (a) $\delta^{17}O$ *vs.* $\delta^{18}O$ and (b) $\Delta^{17}O$ of the grossite-rich CAIs from DOM 08006 (CO3.0), Y-81020 (CO3.05), and DOM 08004 (CO3.1), and of the aqueously-formed magnetite (mgt), fayalite (fa) and Zn-bearing hercynite (hrc) from Y-81020 and EET 90043 (CO3.1) chondrites. In DOM 08006, the grossite-rich CAIs have nearly uniform ^{16}O-rich compositions; in Y-81020 and DOM 08004, they are isotopically heterogeneous. ol = Fe,M-olivine; pl = plagioclase.

and krotite are replaced by Zn-bearing hercynite and troilite. Replacement of $CaAl_2O_4$ and grossite by Zn-bearing hercynite has been previously described in CAIs from Vigarano (CV3) [16,17] and NWA 1934 (CV3) [18]. Possible hydrothermal reactions involved in the formation of Zn-bearing hercynite are: (1) $CaAl_2O_{4(s)}$ + $0.5Fe_{aq}$ + $0.5Zn_{aq}$ = $(Fe,Zn)Al_2O_{4(s)}$ + Ca_{aq} and (2) $CaAl_4O_{7(s)}$ + Fe_{aq} + Zn_{aq} + H_2O = $2(Fe,Zn)Al_2O_{4(s)}$ + Ca_{aq} + H_2. In the isotopically heterogeneous grossite-rich CO CAIs, $\Delta^{17}O$ of grossite, krotite, perovskite, and melilite approach those of aqueously-formed magnetite, fayalite, and Zn-hercynite in Y-81020 and EET 90043 (CO3.1). Since $\Delta^{17}O$ of these aqueously formed minerals correspond to $\Delta^{17}O$ of an aqueous fluid on the CO parent asteroid, we infer that the observed O-isotope heterogeneity in the grossite-rich CAIs from DOM 08004 and Y-81020 resulted from the fluid–rock interaction. Based on the ^{53}Mn-^{53}Cr dating of the MAC 88107 (CO3.1) fayalites [19], O-isotope exchange in the grossite-rich CO

CAIs could have occurred > 3−5 Myr after CV CAIs. This exchange, however, has not affected Al-Mg isotope systematics of the grossite-rich CAIs: the internal ^{26}Al-^{26}Mg isochrons in these CAIs are undisturbed [8].

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Fig. 3. BSE image of a relict grossite-rich CAI in a porphyritic pyroxene chondrule from DOM 08004 (CO3.1). In Fig. 2b, it is labelled as 2. Cr-sp = Cr-bearing spinel; mes = mesostasis; sec = unidentified secondary phase(s). Holes are SIMS spots.
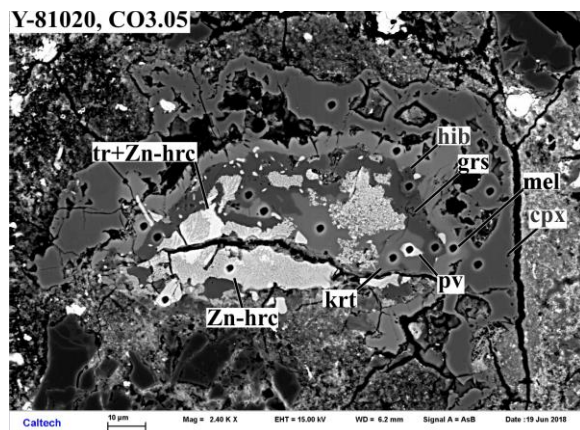

Fig. 4. BSE image of a grossite-rich CAI from Y-81020 (CO3.05). Grossite and krotite are partially replaced by Zn-bearing hercynite (Zn-hrc) and troilite (tr). In Fig. 2b, this CAI is labelled as 1. Small holes are SIMS spots.