MINERALOGY, PETROGRAPHY, OXYGEN AND MAGNESIUM ISOTOPIC COMPOSITIONS AND FORMATION AGE OF GROSSULAR-BEARING ASSEMBLAGES IN THE ALLENDE CAIS.

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Introduction: Grossular (*grs*) is one of the major secondary minerals in the Allende CAIs. It is commonly associated with secondary monticellite (*mnl*), wollastonite (*wol*), forsterite (*fo*), anorthite (*an*), nepheline (*nph*), sodalite (*sod*), wadalite (*wdl*), Al-rich, Ti-poor/free pyroxene (*Al-px*), and Na-rich, Mg-poor/free melilite (*Na-mel*) [1−6; this study]. *Wdl* shows a large excess in ^{36}S that is correlated with ^{35}Cl/^{34}S ratio, indicating for *in situ* decay of ^{36}Cl ($t_{1/2}$ ~ 0.3 Myr) [6]. The *grs-wdl* paragenesis can potentially provide an opportunity for correlated studies of ^{26}Al-^{26}Mg and ^{36}Cl-^{36}S systematics, as well as a clue for O-isotopic heterogeneity of the Allende CAIs and disturbance of their ^{26}Al-^{26}Mg systematics. Time (early *vs.* late) and place (solar nebula *vs.* parent body) of grossular formation, however, are controversial. Recent study of the ^{26}Al-^{26}Mg systematics in *grs* yielded $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0$ ranging from ~5×10^{-5} to <3×10^{-6} [3]. These observations were interpreted as evidence for prolonged duration of *grs* formation that started almost contemporaneously with crystallization of CAIs and lasted > 3 My [3]. This interpretation has been questioned by [4−7], who suggested *grs*-bearing assemblages formed during late-stage fluid-assisted thermal metamorphism on the CV parent asteroid. In order to understand the origin of secondary mineralization in the Allende CAIs, we initiated a combined (mineralogy, petrology, isotope chemistry) study of Allende CAIs using SEM, FE-EPMA, FIB+STEM, SIMS and NanoSIMS. Here we report mineralogy, petrography, O- and Mg-isotopic compositions of *grs*-bearing assemblages in coarse-grained igneous (Type B, C and compact Type A) CAIs from Allende.

Analytical Techniques: The mineralogy and petrography of Allende CAIs were studied using JEOL JXA-8500F FE-EPMA. O-isotopic compositions were measured with the UH Cameca ims-1280 ion microprobe by combination of multicollection and peak-jumping: $^{16}O^-$ and $^{17}O^-$ were measured simultaneously using multicollection FC and monocollection EM, respectively; subsequently, ^{18}O was measured with monocollection EM. Mg-isotopic compositions of *grs* and *mel* were measured in monocollection, peak-jumping mode (using EM & FC) and multicollection mode (using 4 FCs), respectively.

Results and Discussion: There are three main textural occurrences of *grs* in Allende coarse-grained CAIs: **(*i*)** *Mel* with abundant *an* inclusions in Type C CAIs (lacy melilite) are pseudomorphed by a porous aggregate of *grs*, *mnl*, *fo* and *Na-mel* (up to 3 wt% Na_2O) [4]. *Grs*, *mel* and *an* are ^{16}O-depleted to varying degrees (Δ^{17}O = −10‰ to −5‰) compared to *sp* and *Al,Ti-px* (Δ^{17}O ~ −25‰) [7]. $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0$ in *grs* have not been measured yet. **(*ii*)** In cores of Type B and CTA CAIs (*AJEF*, *TS21*, *TS23*, *TS34*, *Big-All*, *3529-Z*), Åk-rich *mel* and *an* are replaced by coarse *grs*, *mnl*, *wol*, *wdl*, *Al-px*, and *Na-mel* (up to 7 wt% Na_2O), and crosscut by veins composed of *grs*, *Na-mel*, *Al-px*, and *wdl* (Fig. 1). The coarse *grs* coexisting with *mnl* has high ^{27}Al/^{24}Mg ratio (~50−100) and shows no resolvable excess of ^{26}Mg (^{26}Mg*) ($(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0 < 3.9\times10^{-6}$, Fig. 2). **(*iii*)** In outer portions of Type B1 CAIs *TS23*, *TS34* and *Big-All*, *grs* occurs in veins crosscutting Åk-poor *mel* mantles and extending into the coarse-grained *grs-mnl-wdl±wol* assemblages in the CAI cores. The veins show mineralogical zoning correlated with composition of *mel* they crosscut (rim → core): *an+grs* → *grs±Al-px* → *grs+Al-px+mnl+wdl*. *Grs* grains in veins crosscutting the outermost portions of *mel* mantle contain up to 3 wt% of MgO and have ^{27}Al/^{24}Mg ratios similar to those in mantle *mel* (5−10). These *grs* grains show resolvable ^{26}Mg* that on the Al-Mg isochron diagram plot along a line corresponding $^{26}\mathrm{Al}/^{27}\mathrm{Al} = (5.4\pm0.3)\times10^{-5}$ defined by Mg-isotopic compositions of *mel* (Fig. 2). Primary *mel* in mantle of *TS34* and secondary *grs* in veins crosscutting *mel* are characterized by isotopically heavy Mg (Δ^{25}Mg ~ 6‰ and 5‰, respectively).

These observations suggest Mg-isotopic compositions of *grs*, including ^{26}Mg*, were inherited from *mel* following nearly complete ^{26}Al decay.

In CTA and Type B CAIs, *sp* and *Al,Ti-px* retained original ^{16}O-rich compositions (Δ^{17}O ~ −23‰), whereas primary *mel* and *an* are ^{16}O-depleted to a level found in *grs* and *sod* (Δ^{17}O ~ −3‰ to −6‰) (Fig. 3). These observations suggest O-isotopic exchange in *mel* and *an* either predated formation of secondary *grs* and *sod* or both processes occurred contemporaneously.

We infer that *grs*, *wol*, *fo*, and *Na-mel* pseudomorphically replacing *mel+an* in Type C CAIs resulted from closed-system metamorphic reactions between *mel* and *an*, most likely on the Allende parent asteroid. Mass-balance calculations using the chemical compositions of primary and secondary minerals in CTA and Type B CAIs indicate that during alteration Cl, Na, and Si were added to, whereas Ca was removed from CAIs [8,9]. Because these elements have different volatilities [10] but exhibit similar behavior in aqueous solutions [11], we infer they were transported by a fluid. The presence of aureoles of secondary Ca-rich minerals (hedenbergite, andradite, *wol*) around most CAIs [12] and dark inclusions in Allende [13] suggests redistribution of Ca was localized and alteration occurred *in situ*, after accretion of the Allende parent asteroid [9,12,13].

The Na- and/or Cl-bearing secondary minerals, *nph*, *sod*, and *wdl*, show zoned distribution in CTA and Type B CAIs. *Nph* and *sod* occur preferentially in the outermost portions of the CAIs, whereas *wdl* is found exclusively in the CAI cores. The observed differences in spatial distribution of *nph*, *sod*, and *wdl* may suggest their formation was controlled by local chemistry, e.g., by the activity of Na, Cl, Ca, and SiO_2 in the fluid. The inferred origin of *grs*-*wdl* paragenesis in Allende CAIs during fluid-assisted thermal metamorphism is consistent with the absence of *grs* in CAIs from less metamorphosed and altered CV chondrites Leoville, Efremovka, and Kaba, as well as from primitive meteorites in other chondrite groups (e.g., CR2, CO3.0, Acfer 094, Adelaide).

References: [1] Hutcheon I. D. & Newton R. 1981. LPSC 12, 491. [2] Davis A. M. et al. 1994. LPS 25, 315. [3] Fagan T. J. et al. 2007. MAPS 42: 1221. [4] Krot A. N. et al. 2008. GCA 72: 2534. [5] Ishii H. et al. 2008. LPSC 39, #1989. [6] Jacobsen B. et al. 2009. LPSC 40, #2553. [7] Krot A. N. et al. 2009. MAPS 44: A116. [8] Hashimoto A. & Grossman, L. 1987. GCA 51: 1685. [9] Krot A. N. et al. 1998. MAPS 33: 1065. [10] Lodders K. 2003. ApJ 591: 1220. [11] Brearley A. J. 2003. In *Treatise on Geochemistry*, H. D. Holland, K. K. Turekian, Eds. (Elsevier Press, 2003), vol. 1, 247. [12] Ford R. L. & Brearley A. J. 2008. LPSC 39: 2399. [13] Krot A. N. et al. 2001. Geochem. Internat. 36: 351. This work was supported by

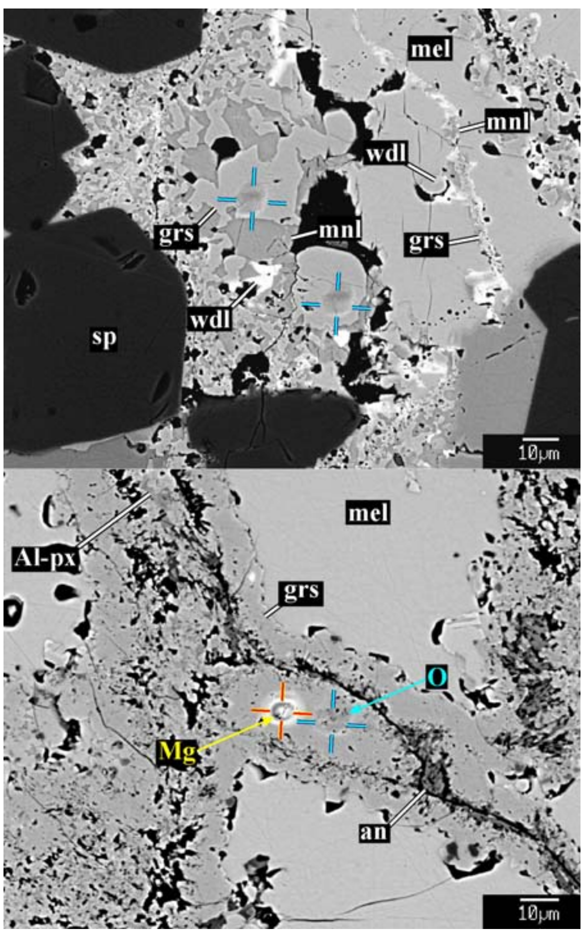

Fig. 1. Backscattered electron images of *grs*-bearing assemblages in the Allende Type B1 CAI *TS34*. Coarse-grained *grs*, *mnl*, and *wdl* replace Åk-rich *mel* in the CAI core. *Grs-an* vein with minor *Al-px* crosscuts Åk-poor *mel* mantle. Ion probe spots for O- and Mg-isotopic measurements are indicated by color lines.

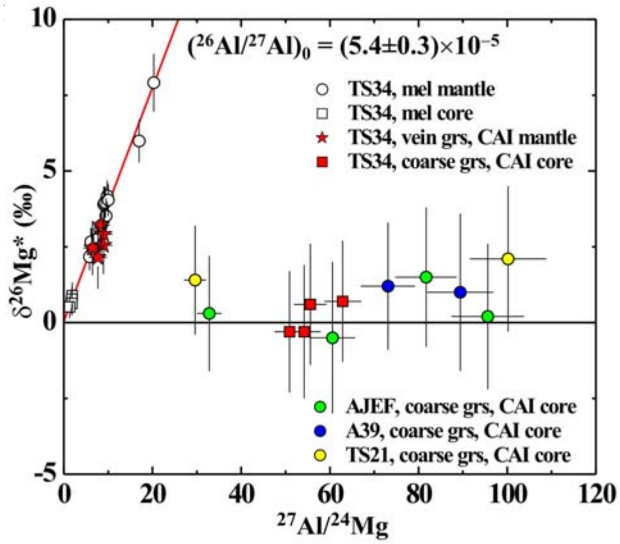

Fig. 2. Al-Mg isochron diagram of *mel* and *grs* in Allende Type B CAIs *TS34*, *TS21*, *A39*, and *AJEF*. Coarse *grs* replacing Åk-rich *mel* in CAI cores and coexisting with *mnl* have high $^{27}Al/^{24}Mg$ ratio and show no resolvable $^{26}Mg^*$; their Mg-isotopic compositions are similar to those of Åk-rich *mel*. *Grs* in veins crosscutting Åk-poor *mel* mantle in *TS34* have low $^{27}Al/^{24}Mg$ ratio and show $^{26}Mg^*$ corresponding to the initial ($^{26}Al/^{27}Al$) of $(5.4\pm0.3)\times10^{-5}$ defined by Mg-isotopic compositions of *mel* in *TS34*. We infer $^{26}Mg^*$ in *grs* was inherited from *mel* following complete ^{26}Al decay. Contrary to the conclusion of [3], the observed $^{26}Mg^*$ in *grs* does not require its early formation. Both textural occurrences of *grs* formed contemporaneously, possibly during fluid-assisted thermal metamorphism on the Allende parent asteroid.

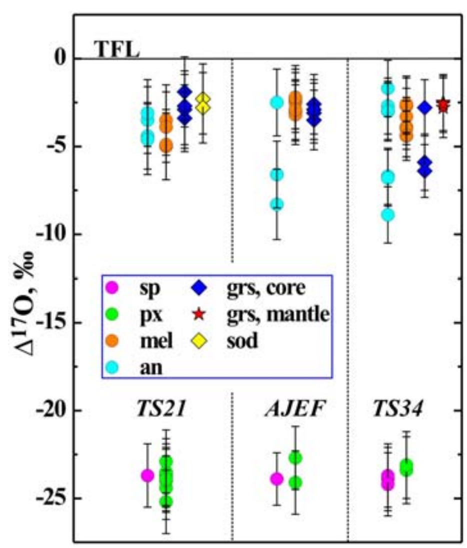

Fig. 3. O-isotopic compositions of individual minerals in Allende Type B CAIs *TS21*, *AJEF*, and *TS34* plotted as $\Delta^{17}O$. *Sp* and *Al,Ti-px* retained original ^{16}O-rich compositions ($\Delta^{17}O \sim -23‰$); *mel* and *an* are ^{16}O-depleted to a level observed in secondary *grs* and *sod* ($\Delta^{17}O \sim -3‰$). These observations suggest O-isotopic exchange in *mel* and *an* either predated formation of secondary *grs* and *sod* or both processes occurred contemporaneously.