

ALTERATION OF ALLENDE TYPE B1 CAIs: WHEN, WHERE AND HOW; Andrew M. Davis¹, Steven B. Simon² and Lawrence Grossman^{1,2}. ¹Enrico Fermi Institute, ²Department of the Geophysical Sciences, University of Chicago, Chicago, IL 60637.

Abstract. We have undertaken a detailed petrologic, chemical and isotopic investigation of secondary alteration of the Allende Type B1 CAIs TS23 and TS34. ²⁶Al-²⁶Mg systematics show that alteration occurred at least 2.4 m.y. after crystallization of primary anorthite. Textural evidence shows that alteration occurred prior to incorporation of the CAIs into Allende. Trace element abundances and textures show that alteration is dominated by reaction of Mg-rich melilite with nebular SiO₂. Reaction between melilite and anorthite also occurred, as did loss of Sr and gain of volatiles.

Introduction. Although the crystallization history of Type B CAIs is becoming well-constrained by experimental petrology [1,2,3] and by detailed studies of trace element zonation [4,5,6,7], the very last stages of crystallization and the alteration that followed are not well understood. Phase equilibria [1] show that the last liquid should crystallize spinel + melilite + fassaite + anorthite. Ion microprobe analyses show that fassaite that crystallized late in Type B CAIs is enriched in LIL trace elements relative to early-formed fassaite, because they are incompatible in all crystallizing phases [6]. Application of partitioning data to REE abundances in CAI anorthite also indicates that this phase crystallized from a late, REE-rich liquid [8]. No mesostasis has ever been observed in a CAI, but the report of extremely REE-rich alteration products with chondrite-normalized abundances like that of very late fassaite (~1000 × CI) in the Allende Type B1 inclusion TS23 [6] led us to consider the possibility that fassaite or REE-rich mesostasis was altered, rather than melilite [9] or melilite and anorthite [10] as is commonly assumed. To investigate the extent to which melilite, anorthite, fassaite or mesostasis were altered, and to assess whether REE and other trace elements were internally redistributed, or lost or introduced during alteration, we have undertaken a detailed SEM, electron microprobe and ion microprobe study of alteration products in the Allende Type B1 CAIs TS23 and TS34.

Petrography. Both of these inclusions have melilite-rich mantles and spinel-, fassaite-rich cores. They also contain melilite with reversely-zoned bands, indicating that pyroxene crystallized before anorthite and making the latter the last major phase to join the crystallization sequence [2]. Mantle melilite is only lightly altered, with alteration products (predominantly grossular) present mainly along veins, whereas in the interior, patches of alteration products ~100 μm across are present. These patches mainly consist of 10–20 μm anhedral grains of wollastonite and monticellite and anhedral to nearly euhedral grossular. Point-counting of b.s.e. images of two such areas give ~50 wt% grossular, ~40 wt% monticellite and ~10 wt% wollastonite. All three alteration minerals are very close to end-member compositions. These intensely altered zones generally occur between ragged (partially altered) grains of anorthite and Mg-rich melilite (typically Ak₇₂₋₇₆) and clean, unaltered grains of fassaite and spinel.

Mg isotopes. Mg isotopic measurements on TS23 and TS34 show that most anorthite contains excess ²⁶Mg consistent with the canonical early solar system ²⁶Al/²⁷Al ratio of 4–5 × 10⁻⁵, but some anorthite in altered zones of TS34 shows evidence of later disturbance, at least 3.3 × 10⁵ years after formation of primary anorthite. Grossular is the only secondary phase with high Al/Mg. One fairly clean grossular spot in TS34 contains no excess ²⁶Mg and must have crystallized at least 4.6 × 10⁵ years after primary anorthite. Hutcheon and Newton [10] reported a clean grossular spot in TS23 with no excess ²⁶Mg that must have formed at least 2.4 × 10⁶ years after primary anorthite.

In the previous discussion, we assumed that the ²⁶Al-²⁶Mg system can be used as a chronometer. Another possible explanation of the Mg isotopic data is that open system alteration occurred shortly after primary mineral crystallization in a region of the solar nebula with no ²⁶Al. If grossular formed at essentially the same time as anorthite, the ²⁶Al/²⁷Al ratio in it must have been diluted by at least a factor of ten compared to the reservoir from which the primary phases of TS23 and TS34 crystallized. Mass balance considerations require that most of the Al from breakdown was lost from the CAI and that most of the Al now in grossular was introduced from the ²⁶Al-free reservoir in which alteration occurred. Trace element data (below) do not suggest wholesale exchange of components with a reservoir external to these CAIs during alteration.

Trace elements. We measured major and trace elements in several profiles across alteration zones in the heavily altered interiors of TS23 and TS34. Alteration zones are light REE-enriched, with La enriched relative to CI chondrites by 20–100 times. The REE patterns resemble those of adjacent late-crystallized melilite. The altered zones are enriched in B, F, Na, K, Cl and Pb relative to adjacent primary phases and strongly depleted in elements that occur primarily in fassaite, Ti, Sc and Zr. Alteration zones are fairly high in Sr, Ba and Eu, like adjacent melilite and anorthite. A plot of chondrite-normalized Eu/Sr vs. Ba/Sr shows several interesting features. Fassaite and anorthite

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have constant Eu/Sr, but variable Ba/Sr. Early-crystallized melilite has $\text{Eu/Sr} \times \text{CI}$ values of ~ 1 , but Eu/Sr and Ba/Sr drop for late-crystallized melilite. Alteration zones show a good correlation between Eu/Sr and Ba/Sr, with the trend line passing through the melilite points. Alteration zones appear to have inherited their trace element abundances from melilite; Sr was lost in varying amounts relative to Ba and Eu.

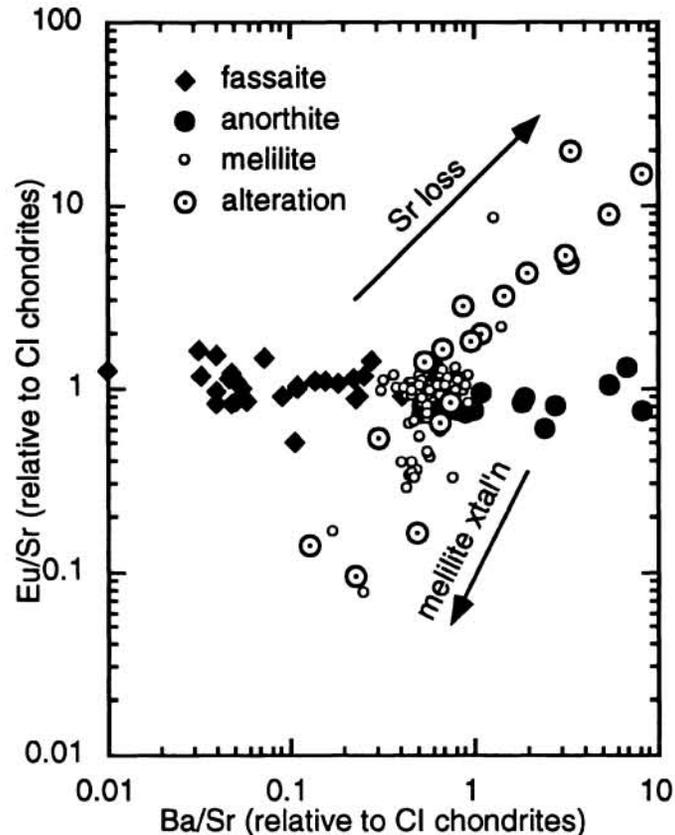
Discussion. It has long been assumed that most of the alteration products observed in CAIs were derived from melilite [9,11]. Our petrographic and trace element studies show that the precursor was largely Mg-rich melilite, but there is textural evidence that some alteration of primary anorthite also occurred. In addition, the partial resetting of the ^{26}Al - ^{26}Mg system in anorthite adjacent to an altered area in TS34 suggests that some elemental exchange can occur in primary anorthite. Hutcheon and Newton [10] proposed that melilite and anorthite reacted to form grossular + monticellite, based on the association of the former phases with intensely altered patches, but our data (Fig.) indicate little contribution from anorthite, and the bulk alteration products are more SiO_2 -rich than melilite + anorthite. We conclude that the alteration products were derived from Mg-rich melilite by reaction with a SiO_2 -, alkali-bearing fluid. The intense alteration in the interior of the inclusions vs. the light alteration of the gehlenitic mantles further suggests that Mg-rich melilite is more easily altered than gehlenitic melilite. The fact that altered zones do not have the high REE contents expected for the liquid from which primary fassaite and anorthite grew indicates that there was essentially no late-stage, residual mesostasis in Type B1 CAIs prior to alteration.

When? ^{26}Al - ^{26}Mg systematics indicate that alteration occurred at least 2.4 m.y. after crystallization of the primary minerals of Type B1 CAIs. The only way to accommodate a substantially shorter nebular lifetime is to have alteration occur in an ^{26}Al -free reservoir with wholesale exchange between ^{26}Al -free Al in the reservoir and ^{26}Al -rich Al released from breakdown of primary minerals.

Where? Textural evidence shows that alteration occurred prior to incorporation of the CAIs into the Allende parent body, presumably while the inclusions were still in the solar nebula.

How? Alteration occurred by reaction of nebular SiO_2 with åkermanite-rich melilite, but with some reaction between melilite and anorthite. LIL abundance patterns of altered zones were inherited from melilite with no exchange of these elements with an external reservoir. There is no evidence for alteration of fassaite, spinel or mesostasis. During alteration, SiO_2 and volatile elements were introduced and Sr was lost.

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