IN SITU TRACE ELEMENT ANALYSIS OF AN ALLENDE TYPE B1 CAI: EK-459-5-1.

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Introduction: Variations in refractory major and trace element composition of calcium, aluminum-rich inclusions (CAIs) provide constraints on physical and chemical conditions and processes in the earliest stages of the Solar System. Previous work indicates that CAIs have experienced complex histories involving, in many cases, multiple episodes of condensation, evaporation, and partial melting [1]. We have analyzed major and trace element abundances in two core to rim transects of the melilite mantle as well as interior major phases of a Type B1 CAI (EK-459-5-1) from Allende by electron probe micro-analyzer (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to investigate the behavior of key trace elements with a primary focus on the REEs Tm and Yb.

Materials and Methods: BSE and X-Ray elemental maps were collected at NASA-JSC on a JEOL 7600F SEM equipped with a SSD EDS. EPMA major and minor element compositions were analyzed at NASA-JSC on a Cameca SX100 electron microprobe. LA-ICP-MS trace element concentrations were analyzed on the University of Houston Varian 810 ICP-MS coupled with a Photon Machines Analyte 193 eximer laser-ablation system.

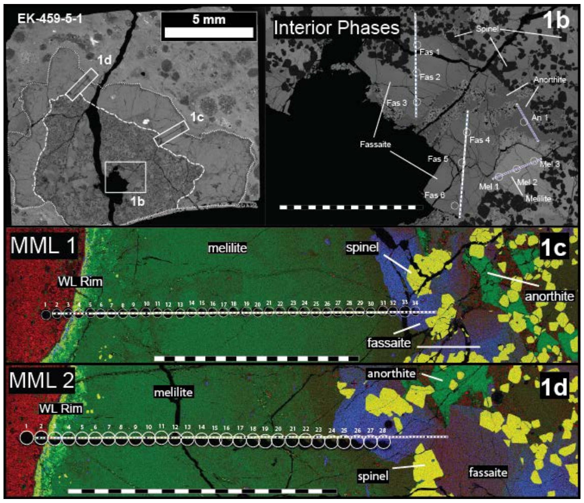

Figure 1: (a) BSE Image of the CAI with locations of (b), (c), and (d). (b) BSE image of the interior of the CAI. (c) X-Ray Mg(R)-Al(G)-Ti(B) of the mantle transect 1 with locations of analyses. (d) X-Ray Mg(R)-Al(G)-Ti(B) of the mantle transect 2 with locations of analyses.

Results: *Petrographic Descriptions*: EK-459-5-1 is a Type B-1 calcium aluminum-rich inclusion from the Allende CV3 carbonaceous chondrite (Fig. 1a) approximately 1-1.5 cm in diameter consisting of a coarse-grained interior-core portion (Fig. 1b) of melilite, fassaite, spinel and anorthite surrounded by a nearly monomineralic mantle of melilite. The melilite mantle (1-3 mm thick; Figs. 1c and 1d) is composed of coarse-grained melilite with minor abundances of fassaite throughout and minor spinel occurrences near the exterior of the CAI. The CAI exterior consists of Wark-Lovering (WL) rim of approximately 20-30 μm thickness consisting of layers of anorthite, spinel, melilite, perovskite ± sodalite.

Trace Element Chemistry: Fassaite REE patterns (Fig. 2) display a gradual increase in element abundance with increasing atomic number, large negative Eu anomalies and smaller negative anomalies in Tm and Yb. Melilite REE patterns (Fig. 2) are flat with positive Eu anomalies and negative Tm- and Yb-anomalies with the melilite in the core of the CAI showing a slight enrichment in the LREEs. Anorthite REE patterns (Fig. 2) displays a general decrease in concentration with an increasing atomic number, large positive Eu anomalies and a serriform HREE pattern. Coexisting negative Tm- and Yb-anomalies are present in fassaite and melilite for the phases analyzed in both the core and in the melilite rim. While Tm and Yb anomalies are not uncommon in refractory inclusions, the coexistence of negative Tm and Yb in the same CAI is rare but has been observed [2]. Rim-to-core melilite mantle transects display no variation in Tm-anomalies (Fig. 3a), elevated Yb-anomalies for MML1 near the core (Fig. 3b), and elevated REE and Y concentrations near the core for MML2 (Fig. 3c). An oscillatory zone in the compositions of melilite with respect to Al, Mg, and Si also occurs in the melilite mantle near the core-mantle boundary.

Discussion: *Rim-to-Core Transects*: Marked differences in major and trace element behavior in the melilite mantle near the core-mantle boundary indicate that there may be up to three distinct zones in the CAI: 1) the core with elevated REE compositions for fassaite and LREE enriched melilite patterns; 2) an oscillatory zone marked by oscillations in Al, Mg, and Si, low Yb-anomalies for MML1, and REE and Y enrichment for MML2, and 3) an outer rim composed of massive melilite with gradual increasing Åk-number towards the rim.

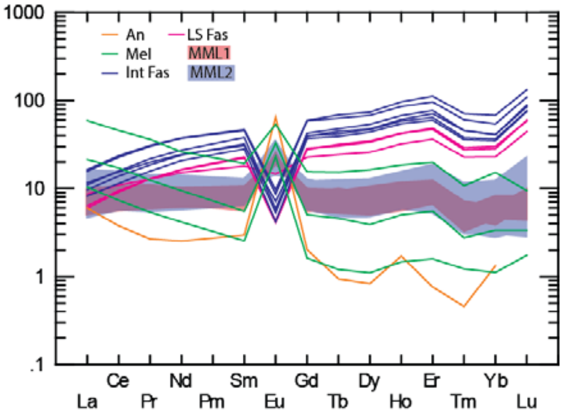

Figure 2: REE patterns for individual phases in EK-459-5-1 normalized to CI chondrites. MML fields are all mantle melilite analyses in the two mantle transects.

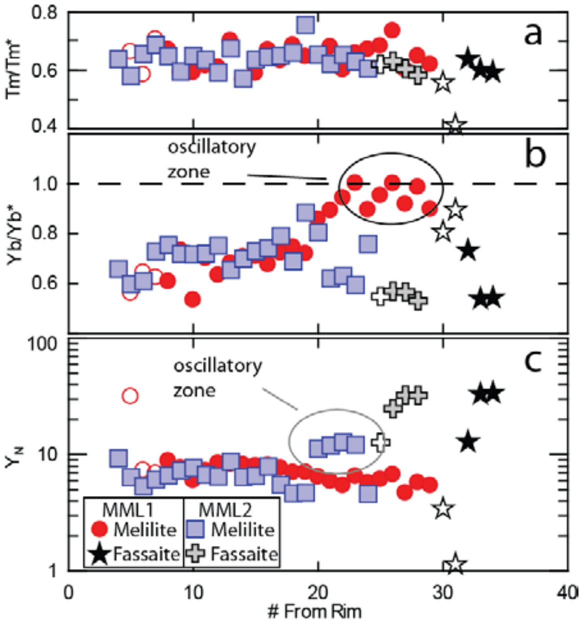

Figure 3: Rim (left) to core (right) mantle transects for (a) Tm-anomaly, (b) Yb-anomaly, and (c) Y compositions for the melilite. Open symbols are analyses suspected of alteration or mixed phases.

REE Anomalies. Europium anomalies are the result of Eu existing as a divalent cation. Strong correlations between Eu and the alkaline earth elements Ba, Sr and Ca indicate Eu anomalies indicate the presence of Eu^{2+}.

Fractionation of the trivalent REEs in CAIs may be caused by differences in condensation temperature, reduction potential, compatibility and abundance or availability of the REE in the reservoir from which the CAI is crystallizing. Thulium is one of the first REEs predicted to condense at 1650 K and the order of calculated condensation temperatures [3] is Nd>Sm>La>Yb>Ce>Eu for the REEs with condensation temperatures below 1650 K. If fractionation of Tm and Yb is solely due to differences in condensation, anomalies in Nd, Sm, and La should be present, but these are not observed.

Conditions in the H-rich gasses of the early Solar Nebula were highly reducing and that may have led to the reduction of some key REEs. The order of relative reduction potential for the most easily reduced REEs is Eu>Yb>Sm>Tm [4]. Though uncommon, coexisting negative Eu, Yb, and Sm anomalies have been observed in some chondrules [5] and their occurrences attributed to formation from precursor material that formed in a highly reducing environment. Under extremely reducing conditions present in the Solar Nebula, it is possible that negative Eu, Yb, Sm and Tm anomalies could occur. However, if the observed negative Tm and Yb anomalies were only controlled by changes in volatility due to reduction to the divalent state, then anomalies in Sm should be present, but these are not observed.

It is clear that no one factor is controlling the behavior of the REEs in CAIs. It has been hypothesized that Type B1 CAIs formed by the amalgamation and remelting of previously formed CAI material [1]. Therefore, it is possible that some combination of refractory material possessing individual REE anomalies may have contributed to the formation of the Type B1 CAI, EK-459-5-1.

References: [1] Rubin,A.E. (2012) *Meteoritics and Planet. Sci.*, 47, 6, 1062-1074. [2] Srinivasan, G. (2000) *Meteoritics and Planet. Sci.*, 35, 1333-1354. [3] Lodders et al. (2009) *Lanbolt Börnstein, New Series*, VI/4B, 4.4, 560-630. [4] Morss, L. R. (1976) *Chemical Reviews*, 76, 6, 827-840. [5] Pack, A., et al. (2004) *Science*, 303, 5660, 997-1000.