ATOM PROBE TOMOGRAPHY OF OPAQUE ASSEMBLAGE IN ALLENDE CAI S. Parman[1], S. Jacobsen[2], M. Petaev[2], A. Akey[3]. [1]DEEPS, Brown University, Providence, RI 02912, USA, [2]EAPS, Harvard University, Cambridge, MA 02138, USA, [3]CNS, Harvard University, Harvard University, Cambridge, MA 02138, USA.

Introduction: Calcium-Aluminum-rich inclusions (CAI) in chondritic meteorites represent some of the earliest material to form in the Solar System [1]. Their compositions, and the compositions of phases found within them, are fundamental to understanding conditions and condensation/evaporation/alteration processes within the early nebula. Isotopic anomalies within the CAI also provide clues to compositional heterogeneity within the nebula, and can be used to determine the ultimate origins of the building blocks of the solar system [2].

A persistent hurdle to studying CAIs is that chemical and isotopic heterogeneities are often micron to nanometer in size. These heterogeneities include metal and sulfide-rich opaque assemblages (OA), or fremlinge [1,3]. OA themselves often contain submicron refractory metal nuggets (RMN). While the origin of RMN is actively debated [3,4], they may represent some of the earliest material to condense from the nebula, or may even be presolar in origin [5].

Laser-assisted atom probe tomography (APT) is a relatively new analytical method that provides a unique combination of sub-nanometer spatial resolution with ppm-level detection limits. It has been used successfully on both terrestrial [6] and meteoritic refractory metals [5]. Here we apply APT to analyze phases in an OA in a type B CAI from the Allende meteorite.

Methods: A 20 micron long lift-out was extracted from the OA using a focused ion beam (FIB), from which five needles were cut and shaped (see refs 4 and 5 for descriptions of APT sample preparation methods). All needles were analyzed with the LEAP 4000HR at the Center for Nanoscale Systems at Harvard.

Results:

Tip 1 - Primarily consists of a homogeneous troilite grain, within which there is 1) a Ca-rich inclusion ~20 nm in diameter and 2) 2-3 Ru-rich inclusions ~10 nm in diameter

Tip 2 - The tip contains a grain boundary between taenite and spinel (Figure 1). The phases are homogeneous and contain no inclusions.

Tip 3 - Primarily consists of V-rich magnetite (Figure 2). Within the magnetite is a grain boundary which is enriched in a number of elements, including Mg, Na, P, Se, Br, Cu and Al. The magnetite contains at least two types of inclusions: 1) a Ru-rich RMN ~ 20nm in diameter and 2) an unidentified phase rich in Mg and Na. Both of these are spatially associated with the grain boundary.

Tip 4 - Primarily consists of taenite. A small (~5 nm) Cd-rich inclusion/area was detected. It did not evaporate cleanly, so its composition and dimensions are uncertain.

Tip 5 - Primarily consists of taenite. A small (~5 nm) Ge- and N-rich inclusion was detected. It did not evaporate cleanly, so its composition and dimensions are uncertain.

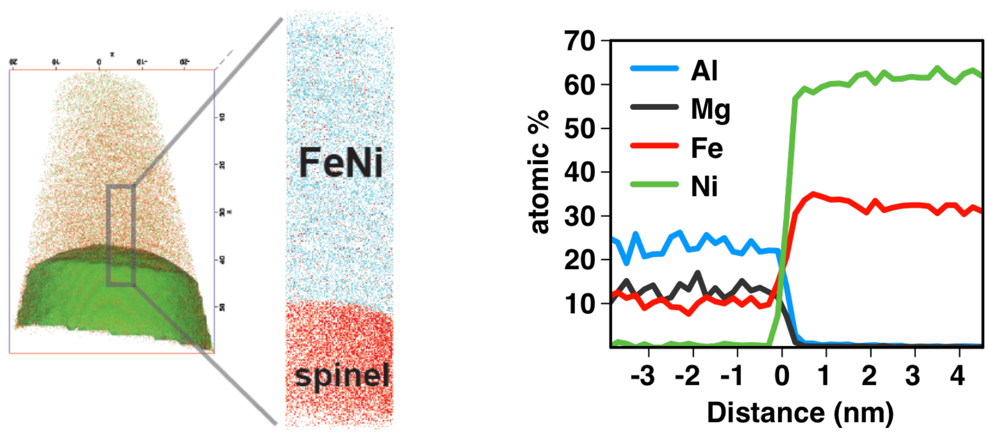

Figure 1. *Atom probe reconstruction of taenite-spinel phase boundary in Allende OA.* ***Left*** *– Lower half of tip is spinel (outlined in green). Upper half is taenite. Gray box shows area of expanded view (**middle** image, red – Al atoms, blue – Ni atoms). Curvature of the boundary is an artifact of the reconstruction method.* ***Right*** *– Compositional profile across the phase boundary. Concentrations were calculated perpendicular to the boundary (proxigram) through the central portion of the needle. The change in composition is sharp, occurring over less than 2 nm for all elements, indicating some low-temperature re-equilibration between these two phases has occurred.*

Discussion: The primary result of the APT analyses is the detection of a variety of nm-scale compositional heterogeneities in the OA. APT successfully imaged these down to a spatial resolution of ~1 nm in both metals and oxides. The small enrichments of elements along the 5 nm-wide magnetite grain boundary in tip 3 is a good example of a feature that would be difficult to measure by any other method. In the largest tip, with 99 million atoms, concentrations in the 5-10 ppm range are detectable above background. Isotopic anomalies that have been measured in CAI (e.g. ^{26}Al, ^{50}Ti, ^{41,48}Ca, ^{54}Cr, ^{58}Fe, ^{64}Ni, $^{92-100}$Mo, $^{96-104}$Ru, ^{10}Be …[4]) are too small to be detected in our analyses at this time, due to a combination of the small sample size (<100 million atoms per tip) and numerous mass interferences (particularly in the oxides).

Equilibration temperatures and timescales – Compositional gradients across the taenite-spinel boundary in tip 2 can be extracted from the APT reconstruction (Fig. 1). This analysis shows that the boundary is less than 1 nm thick in the spinel, but is ~2 nm in the taenite (enriched in Fe, depleted in Ni). This suggests some low temperature re-equilibration occurred between the two minerals. Nevertheless, the very short diffusion length scales suggests the pair cooled extremely rapidly (perhaps minutes to hours), if they formed at high temperatures (>1400°C). Alternatively, they could have formed at low temperatures (~500°C), as has been suggested by Blum et al [3]. This would be more likely to preserve such sharp phase boundaries.

Alteration – Allende is well known to have experienced significant alteration [1]. The grain boundary in tip 3 shows that this alteration produced heterogeneities down to the nm scale, and introduced a range of elements into otherwise pristine minerals.

Origin of RMN – The Ru-rich RMN in tip 3 is heterogeneous in a number of elements, most notably Os. Given its small size, these compositional gradients would not survive long at high temperatures. It is also notable that the RMN is found on a grain boundary with clear signs of aqueous alteration. Could the RMN in this case be the product of alteration? Again, this may be consistent with the hypothesis of Blum et al [3], that the OA and RMN formed during low temperature metamorphism involving oxidation and/or sulfidizing conditions.

References: [1] MacPherson, G.J. (2003) Treatise E.A. Geochem. Vol 1:210-246. [2] Dauphas N. and Schauble (2016) Ann. Rev. Planet. Sci. 44: 709-783. [3] Blum J.D. et al (1989), GCA 53: 543-556. [4] Schwander D. et al (2015) Met. Planet Sci 50: 893-903. [5] Daly L. et al (2017) Geology 45: 847-850. [6] Parman S.W. et al (2015) Amer Min 100: 852-860.

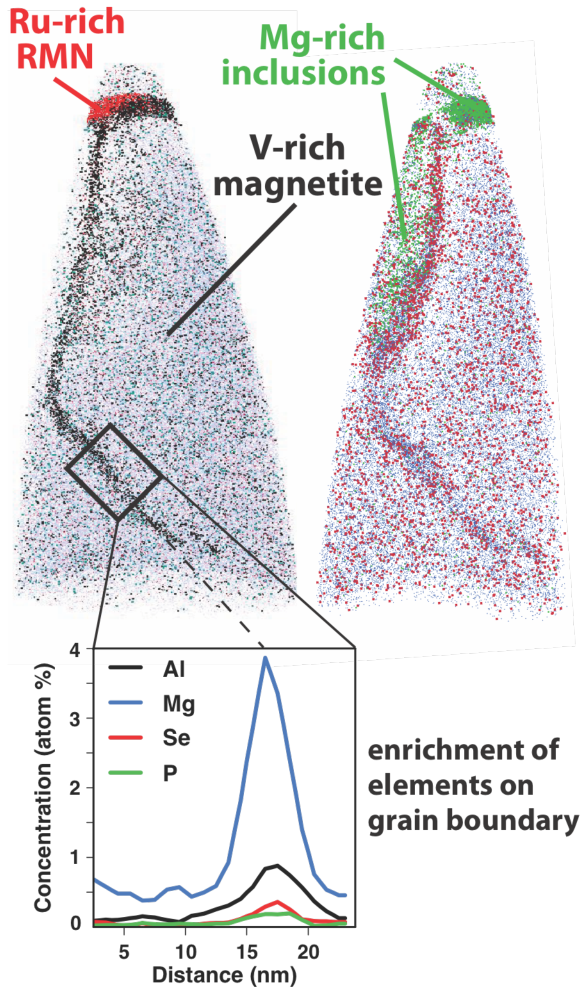

Figure 2. *Atom probe reconstructions of V-rich magnetite that contains a grain boundary, an Ru-rich RMN and two Mg-Na-rich inclusions. Each dot represents the position of a single atom: Mg-black, Ru-red, Na-green, P-magenta Image is ~100nm tall.* ***Left*** *– A grain boundary is clearly outlined by Mg atoms. A Ru-rich RMN lies along the grain boundary and is spatially correlated with two Mg-Na-rich inclusions.* ***Right*** *– Same reconstruction, emphasizing the Mg-Na-rich inclusions.* ***Bottom -*** *Concentration profiles (proxigrams) across the grain boundary (black rectangle). Note x-axis is in nanometers. Enrichments in fluid-mobile elements, like P, Se, Br and Cu, suggest they were introduced by low-temperature aqueous alteration, though this would not explain the enrichment in Al, which has low solubility in aqueous fluids. Whether the grain boundary predates the alteration or was produced by the alteration is not clear*