

TEM/SEM EVIDENCE FOR RESIDUAL MELT INCLUSIONS IN TYPE B1 CAIs. J. M. Paque¹, A. Toppani^{2,3}, D. S. Burnett¹, N. Teslich³, W. Moberlychan³, Z. R. Dai³ and J. P. Bradley³. ¹California Institute of Technology, MS 100-23, Pasadena, CA 91125, (julie@paque.com), ²Centre Spect. Nucleaire Spect. De Masse, Bat. 104, 91405, Orsay Campus, France, ³LLNL, 7000, East Avenue, L-413, Livermore, CA, 94550.

Introduction: Ca-Al-rich Inclusions (CAIs) are objects encompassing a rich diversity of bulk and phase compositions reflecting various processes, environments, and times, and as probably the oldest igneous rocks in the solar system, they have been studied in considerable detail. The melting events have received a great deal of attention because of their potential for constraining physical processes and high temperature environments in the primitive solar nebula. Although the extensive study of the Type B1 inclusions should in principle make these the best understood of all igneous rocks, new analytical capabilities inevitably reveal new insights.

In order to further constrain the late stages of crystallization and/or alteration events, we have examined the spinel/melilite interface of 4 spinels in Leoville and Allende CAIs. TEM sections were prepared using the Focused Ion Beam (FIB) technique [1] as it allows high spatial resolution observation of an object already characterized for mineralogy, petrology or isotopic compositions. Mineralogical and chemical studies at the nm to μm scale (e.g., chemical composition of individual sub- μm minerals, microtextures of each mineral layer or crystallographic relationships between the mineral layers) provide information about crystallization and alteration of CAIs. Previous SEM studies [2] revealed the presence of ubiquitous "boundary clinopyroxenes" at the interface between spinel and melilite. This is unexpected for rim/mantle spinels, as the rims are widely accepted as being formed prior to the appearance of clinopyroxene in the crystallization sequence.

Sample preparation: Leoville USNM 3537-2 is a coarse-grained spherical type B1 CAI of about 7 mm in diameter with a flat type I REE pattern [3]. Allende TS34 is a large spherical CAI, showing a moderate degree of secondary alteration. Based on electron microprobe and SEM data the interface between spinel and melilite in four areas has been chosen for TEM examination. In Leoville and TS34 one spinel from the core and one from the mantle were selected.

The thin sections of the interface have been prepared using the 30 keV focused Gallium Ion Beam at the Lawrence Livermore National Laboratory (LLNL). Deposition of a 2-3 μm thick Pt-strip protecting the chosen location was followed by the ion beam trenching of about 0.5-1 μm thick section. The section was then extracted from the bulk material using an in-situ method that results in the section being welded to the

TEM grid using Pt [4]. Sections were then thinned in situ down to 100 nm. Under similar experimental conditions, fragile phases such as phyllosilicates, glass, or even organic material were left undamaged, suggesting that our final TEM sections were not damaged during their preparation.

Results: Fig. 1 shows a typical example of boundary clinopyroxene on a spinel from TS34. Here the clinopyroxene are discontinuous blebs, but in other cases a continuous rim up to roughly 5 microns thick is observed. Spinel free of boundary clinopyroxene are very rare in both inclusions studied, and allowing for sampling effects in a section view, it is likely that *all* spinel have boundary clinopyroxene. A region of alteration occurs at the upper right hand corner of Fig. 1, but there is no correlation of the boundary clinopyroxene and alteration in TS34. More importantly, Leoville 3537-2 is an unaltered inclusion.

Three out of the 4 TEM sections have additional phases between the spinel and rim. One section, from the core of Allende TS34 was selected to see if a section of the spinel boundary that showed no boundary clinopyroxene on the SEM scale would still reveal a thin layer in the TEM. However, the section shows a clean, sharp interface between the spinel and melilite. Thus, the discontinuities seen in Fig. 1 are real, and are not just thickness variations in a continuous clinopyroxene rim. The other Allende section, from the mantle of TS34 shows a thin clinopyroxene rim between the spinel and melilite, but no other phases.

The simplicity of the Allende boundaries is in contrast to those for both Leoville TEM sections (one each from the core and mantle). These have very complicated interfaces, including amorphous material, between the spinel and melilite.

The interface between spinel Leo2 and melilite (core) has been well characterized (Fig. 2). Immediately adjacent to the spinel is a continuous rim of fassaite with a smooth interface to the spinel. Outside the clinopyroxene a layer of glass is observed. The interface between the glass and melilite is irregular and has many embayments and fingers of melilite extending into the glass. The glass is very deficient in CaO, and also contains an excess of oxygen, possibly due to H_2O .

The spinel Leo1 (mantle) is similar to that shown on Figure 2; however it is also surrounded by several calcite veins. The FIB section was chosen to intersect both the spinel/melilite interface and a calcite vein.

Calcite, Ti-fassaite, perovskite and glass are all present along the interface. Both calcite and fassaite are in contact with spinel, while glass is adjacent to the melilite.

Discussion: Several possibilities exist to explain the spinel/melilite interface mineralogy: crystallization, remelting, subsolidus diffusion, or alteration. The presence of glass makes subsolidus diffusion unlikely. Similarly, glass is not going to be produced through low temperature alteration. It is easier to understand the glass and the boundary clinopyroxene in general as igneous in origin. The low Ca content of the glass, calcite, and the possible hydrous nature of the glass would need to be explained by high mobility during aqueous/CO₂ fluid alteration.

Remelting of a spinel-melilite interface during a secondary heating event should not lead to clinopyroxene, so residual melt from the primary crystallization phase is indicated. However, the observation of glass does not rule out remelting events.

The observed difference between the Allende and Leoville boundaries is surprising. It might have been expected that the glass observed in Leoville would have been converted to alteration phases in the Allende CAI. The lack of glass in the Allende TEM sections allows the possibility of a shock origin for the glass in Leoville, but there is no obvious way to explain the boundary clinopyroxenes with shock.

Pockets of liquid associated with spinel in large melilite crystals are commonly seen in experimental samples (Fig. 3) under a wide range of crystallization condition. However, the melilite adjacent to the glass always showed an increase in akermanite content, due to continuation of crystallization from the residual liquid as temperature decreased. The FIB sections never show this increase in akermanite adjacent to the glass.

Conclusion: The boundary clinopyroxene and glass (at least in the Leoville sections) are best explained as a residue of the primary melting event which formed Type B1 CAIs. The presence of melt inclusions may set a previously unavailable lower limit on the cooling rate of these inclusions. Comparison with glass inclusions in experimental samples may lead to improved primary cooling rate estimates. A mild, previously unrecognized alteration event in Leoville CAIs may be required to explain the presence of calcite and the possible observed water in the Leoville glass.

References: [1] Heaney, J. H. et al. (2001) *American Mineralogist* **86**, 1094-1099. [2] Paque J. M. et al. (2005) *Lunar Planet. Sci. XXXVI*. #1809. [3] Sylvester, P. J. et al. (1992) *Geochem. Cosmochim. Acta*, **56**, 1343-1363. [4] Smith, J. B. et al. (2005) *LPSC XXXVI*, #1003

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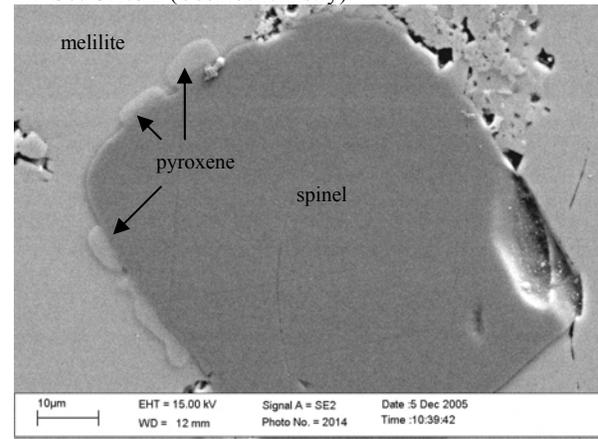


Fig. 1. Blebs of pyroxene rim spinel in Allende TS34.

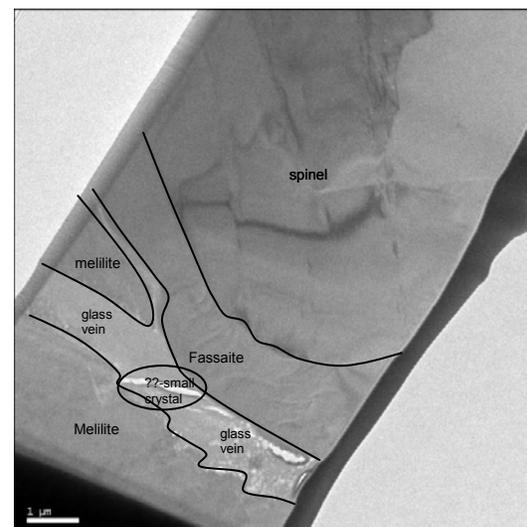


Fig. 2. TEM image of section of Leo2. Contrast the smooth interface between the glass vein and fassaite with the ragged interface between the glass and melilite.

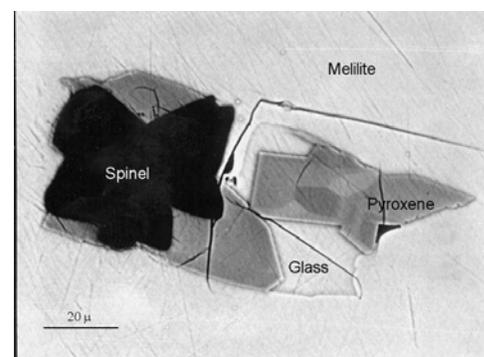


Fig. 3. Experimental sample (98-53) from Type A/B1 analog (maximum temperature=1500°C, cooling rate=2°C/hr, quench temperature=1167°C). Melt plus spinel is trapped in the large melilite crystal and eventually crystallizes pyroxene.