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Abstract- We used focused ion beam thin section preparation and scanning transmission electron microscopy (FIB/STEM) to examine the interfacial region between spinel and host melilite for three spinel grains, two from the mantle and one from the core of an Allende type B1 inclusion, and a second pair of spinel grains from a type B1 inclusion from the Leoville carbonaceous chondrite. The compositions of boundary clinopyroxenes decorating spinel surfaces are generally consistent with those of coarser clinopyroxenes from the same region of the inclusion, suggesting little movement of spinels between mantle and core regions after the formation of boundary clinopyroxenes. The host melilite displays no anomalous compositions near the interface, and anorthite or other late-stage minerals are not observed, suggesting that crystallization of residual liquid was not responsible for the formation of boundary clinopyroxenes.

Allende spinels display either direct spinel-melilite contact or an intervening boundary clinopyroxene between the two phases. In the core, boundary clinopyroxene is mantled by a thin (1-2 μm thick) layer of normally zoned (X_{Ak} increasing away from the melilite-clinopyroxene contact) melilite with X_{Ak} matching that of the host melilite at the melilite-melilite contact. In the mantle, X_{Ak} near boundary spinels is constant. Spinels in a Leoville type B1 inclusion are more complex with boundary clinopyroxene, as observed in Allende, but also variable amounts of glass (~1 μm width), secondary calcite, perovskite, and an unknown Mg-, Al-, OH-rich and Ca-, Si-poor crystalline phase that may be a layered double hydrate. Glass compositions are consistent to first order with a precursor consisting mostly of Mg-carpholite or sudoite with some aluminous diopside. One possible scenario of formation for the glass veins is that open system alteration of melilite produced a porous, hydrated aggregate of Mg-carpholite or sudoite + aluminous diopside that was shock melted and quenched to a glass. The unknown crystalline phase may be a shocked remnant of the precursor phase assemblage but is more likely to have formed later by alteration of the glass. Calcite appears to be an opportunistic fracture filling that postdated all major shock events.

Boundary clinopyroxenes probably share a common origin with coarser-grained pyroxenes from the same region of the inclusion. In the mantle, these crystals may represent clinopyroxene crystallized in Ti-rich liquids caused by the direct dissolution of perovskite and an associated Sc-Zr-rich phase or as a reaction product between dissolving perovskite and liquid (i.e., indirect dissolution of perovskite). In the core, any perovskite and associated Ti-enriched liquids that may have originally been present disappeared before the growth of boundary clinopyroxene.

INTRODUCTION

There are two fundamentally different classes of Ca-Al-rich inclusions (CAIs), those that partially or completely melted, sometimes more than once, and those (e.g., "fluffy type A") that never melted at all. This divergence in thermal processing implies nebular processes and environments of variable intensity and/or locality and the objective of much research on these objects is to connect the observed phase assemblages and compositions to the conditions and time scales that produced them. This simple goal is complicated by the fact that many processes, such as volatilization from, and condensation onto, partially molten droplets, crystallization, diffusive relaxation, and low-temperature alteration may all have been important and may have happened more than once. Since observations obtained from any given technique likely bear an imprint from more than one of these processes, the development of new approaches to characterize CAIs and their components is highly desirable. In this study, we use focused ion beam thin section preparation and scanning transmission electron microscopy (FIB/STEM) techniques to obtain a detailed view of the interface between spinel crystals in type B1 CAIs and their host melilites on a much smaller spatial scale than previously attainable**.** This opens a potential new window into the igneous events that affected these objects and their subsequent evolution.

Type B1 inclusions are classic examples of CAIs thought to have passed through a partially molten stage. The basic igneous mineral assemblage is disarmingly simple: spinel (essentially $MgAl_2O_4$), a binary melilite (åkermanite (Åk: $Ca_2MgSi_2O_7$) – gehlenite ($Ca_2Al_2SiO_7$)), anorthite (essentially $CaAl_2Si_2O_8$), and a Ti-Al-bearing clinopyroxene with the bulk composition encompassed almost entirely within the system CaO-MgO-Al_2O_3-SiO_2-TiO_x. Type B1 inclusions are characterized by a melilite-rich, clinopyroxene-poor mantle surrounding a core, also containing melilite, but with substantial amounts of clinopyroxene and sometimes anorthite. Spinel occurs both in the mantle and core; anorthite, only in the core.

Experimental studies focused on type B inclusions have established the order of crystallization, appearance temperatures, liquid lines of descent, major element compositions of solid solutions, and trace element partitioning produced during cooling from high temperatures under various conditions (Beckett et al., 1990; Connolly and Burnett, 2003; Lundstrom et al., 2006; MacPherson et al., 1984; Paque et al., 1994; Peters et al., 1995; Stolper, 1982; Stolper and Paque, 1986) and several recent studies have emphasized the role of volatilization (Mendybaev et al., 2006; Richter, 2004; Richter et al., 2002; Richter et al., 2006). These works have yielded useful constraints on the temperature, redox conditions, pressure of the ambient vapor and time scales for melting, but a common thread is the use of bulk compositions, liquids whose presence and compositions are inferred, not observed, and/or coarse-grained crystals of one or more of the four major crystalline phases. With the exception of opaque assemblages or Fremdlinge (Armstrong et al., 1985; Blum et al., 1989a, b; Campbell et al., 2003; El Goresy et al., 1978; Palme et al., 1994) and the unusual silicate "UNK" (Barber et al., 1994; Paque et al., 1994), the possible utilization of minor or very fine-grained phases in type B inclusions to infer igneous conditions of formation has been largely neglected.

There are good reasons for this. Minor phases often form extremely fine-grained, multi-phase assemblages that are very difficult to characterize using standard scanning electron microscopy (SEM) or electron probe microanalysis (EPMA) techniques. For example, Paque et al. (2007a) noted the common occurrence of thin rinds and blebs of clinopyroxene along grain boundaries of spinel with melilite in TS-34, a type B1 inclusion from Allende that is also part of this study, but they were unable to undertake a detailed characterization because of the fine grain size. Similarly, Connolly and Burnett (1999) observed thin "halos" of undetermined mineralogical nature around spinel in anorthite from Leoville 3537-2, one of the inclusion we studied, and in TS-23, another Allende type B1 inclusion. These halos were also too thin to evaluate using the techniques available to the authors. Thus, the potential archive of information contained within these grains, which may well be even greater than for the more commonly studied coarse-grained major phases, cannot be fully realized using standard scanning electron microscopy (SEM)- and electron probe microanalysis (EPMA)-based analytical and imaging techniques.

In this study, we use SEM and EPMA to provide a basic petrographic context at the scale of a few μm and larger but then use FIB/STEM to characterize small scale features, a few μm to a few nm across, with an emphasis on the interfacial region between spinel in two type B1 CAIs and their host melilites. FIB/STEM is well posed for imaging and phase characterization of features a few microns across or less (Giannuzzi and Stevie, 1999; Heaney et al., 2001; Overwijk et al., 1993), and the technique is advantageous in allowing the observation of specific sites in an object already characterized for mineralogy, petrology and/or isotopic compositions by other analytical techniques (e.g., Bradley et al., 2005; Floss et al., 2004). Thus, mineralogical and chemical studies can be conducted at the nm to μm scale (e.g., identity and semi-quantitative chemical compositions of individual sub-μm minerals and crystallographic relationships between adjacent minerals) to potentially constrain the nature of crystallization and alteration in CAIs. Phase identification was made by electron diffraction, X-ray spectra, and electron energy loss spectra (EELS).

There is a relatively extensive literature on the TEM characterization of presolar grains in meteorites (e.g., Bernatowicz et al., 1991; Croat et al., 2005; Daulton et al., 2002, 2003; Nguyen et al., 2007; Stroud et al., 2004). Previous applications of TEM techniques to Allende and Leoville CAIs (e.g., Barber et al., 1984; Keller and Buseck, 1991, 1994; Müller, 1978; Müller and Wlotzka, 1982), however, mostly involved the use of Ar ion milling, which is not capable of targeting specific small-scale features. These CAI studies have nevertheless led to important constraints on the shock histories of the inclusions, insights into defect and dislocation densities of the constituent phases, and to the conclusion that hydrated phases, while quite rare, do occur in Allende CAIs. FIB/STEM has been used to study SNC meteorites (Bleiner et al., 2006; Heaney et al., 2001), the terrestrial alteration of ordinary chondrites (Lee et al., 2003) and, more recently, CAIs (Ford and Brearley, 2007; Paque et al., 2007c; Toppani et al., 2006). In this study, we emphasize the application of FIB/STEM techniques to boundary clinopyroxenes, blebs and rinds of clinopyroxene found on spinel grains included in melilite from type B1 inclusions, and to associated phases. Preliminary accounts of this work were presented by Paque et al. (2007b; 2007c).

EXPERIMENTAL AND ANALYTICAL TECHNIQUES

Analytical Techniques

Initial characterization of meteoritic samples was obtained using a LEO 1550 VP field emission scanning electron microscope and the JEOL 733 and JEOL JXA-8200 electron microprobes at Caltech. The experimental run product was analyzed using the JEOL 733. Analytical conditions for the electron probe included an accelerating voltage of 15 kV, a beam current of 20 to 40 nA, and a beam diameter of ~1 μm. Synthetic and natural minerals were used as standards and data reduction was done through a CITZAF correction procedure (Armstrong, 1988).

Electron-transparent thin sections of spinel-melilite interface regions were prepared at Lawrence Livermore National Laboratory (LLNL) using an FEI Nova NanoLab 600 dual-beam focused ion beam instrument (FIB). The FIB has an electron and an ion column (30 kV Ga^+) with Pt and C deposition capabilities, in-chamber manipulators for *in situ* section liftout and an EDAX energy dispersive spectrometer. STEM analysis was performed at LLNL using a 200 kV FEI Tecnai20 G2 monochromated (S)TEM, equipped with a high angle annular dark field detector, Gatan high-resolution imaging filter, and EDAX Si(Li) energy-dispersive spectrometer. EELS were acquired at the O K edge with 5.6 mrad collection angle and 0.05 eV/channel dispersion. The energy loss was calibrated by the zero loss peak after each spectra. Due to sample sensitivity to beam damage, a low intensity beam (spot size 6 and ~0.5 μm diameter) was applied to the measurement regions for long (several minute) acquisition times. EELS energy resolution is on the order of 1 eV.

Experimental Techniques

We conducted a dynamic crystallization experiment on a melilite-rich CAI-like bulk composition (“98”) using techniques described in Stolper and Paque (1986). The bulk composition, which is most relevant to type A inclusions and the mantles of type B1s, and a summary of additional isothermal and dynamic crystallization experiments on this bulk composition are given by Paque and Stolper (1984). Briefly, a slurry of powdered glass starting material in polyvinyl alcohol was placed on a Pt loop, air dried, and then suspended in air in a Deltech DT-31 vertical gas mixing furnace. The sample was held at an initial temperature of 1500°C for 3 hours, cooled at 2°C/hr to 1167°C and drop quenched into deionized water. The run product was polished as a thin section and characterized using the SEM and electron microprobe.

Meteoritic Samples and FIB Procedures

We studied two type B1 inclusions. Allende TS-34 is a large spherical type B1 inclusion showing a moderate degree of secondary alteration and has been the subject of numerous studies (e.g., Beckett et al., 2000; Clayton et al., 1977; Connolly et al., 2003; Paque et al., 2007a; Simon et al., 1991). Leoville USNM 3537-2 is a coarse-grained spherical type B1 CAI of about 7 mm diameter (Caillet et al., 1993; Connolly and Burnett, 1999). Both inclusions are interpreted to be igneous objects that partially or completely melted and cooled under reducing conditions. In the course of studying minor element concentrations in TS-34 spinels, Paque and coworkers noted the common occurrence of clinopyroxene on spinel inclusions in melilite. These grains were generally too thin to fully characterize and, therefore, the interface regions between spinel and melilite in five areas were chosen for more detailed FIB/STEM examination. Three of these grains, A2, E2 (mantle) and B2 (core) from TS-34, were previously studied by Paque et al. (2007a). Two additional spinel grains, one each from the mantle (Leo1) and core (Leo2), were selected from Leoville 3537-2.

Electron-transparent sections of the interface region between spinel and melilite were prepared using the FIB at LLNL. The chosen location was first protected from amorphization and ion implantation by chemical vapor deposition of a 2-3 μm thick, ~15 to 20 μm long Pt-strap through interaction of a locally injected organometallic gas with the electron or ion beam. This was followed by ion beam milling of trenches on both sides and channels at the edges to produce a ~1-2 μm thick section (Giannuzzi et al., 1998; Giannuzzi and Stevie, 1999; Heaney et al., 2001; Overwijk et al., 1993) nearly free from the surrounding material and connected only at one corner. This preliminary section is thicker than most examples cited in the literature to further reduce the concentrations of implanted Ga and redeposited material in the final thinned section. The thick section was extracted from the bulk material by "welding" it using Pt deposition to a tungsten needle controlled by micromanipulator and severing the final connection to the surrounding material using the ion beam. In a similar fashion, the section was "welded" to a specially-designed TEM grid and the connection to the tungsten needle severed. Sections were ion beam thinned *in situ* to ~100 nm for electron beam transparency. Although the precise thickness of surface structural damage caused by the sample preparation is sensitive to both the material and ion milling parameters (Giannuzzi and Stevie, 1999; Prenitzer et al., 2003), extremely fragile samples such as clays, phyllosilicates, and even organic material, can be studied using the FIB procedures of this study (Lee et al., 2003; Obst et al., 2005).

RESULTS

Experimental Results

The run product for dynamic crystallization experiment 98-53 produced euhedral melilite enclosing spinel. In some cases, spinel plus liquid was trapped in the growing melilite crystal (Fig. 1a) from which clinopyroxene crystallized at lower temperatures along with a more magnesian (i.e., higher Åk) melilite on the walls of the melt inclusion.

Figure 1b shows an example of melilite compositions in dynamic crystallization experiment 98-53 as a function of distance from the interface with glass or clinopyroxene. A total of seven such profiles have been obtaineed. All of the melilite is zoned but, as some interfaces with glass are approached, the melilite becomes unusually åkermanitic (magnesian). While the glass compositions are homogeneous, Åk contents of the melilite along one traverse shown in Fig. 1b increases by ~30 mole % within 10 μm of the interface; based on regional variations in melilite composition, negligible variations in Åk would be expected. Similarly, melilite at some, but not all, clinopyroxene-melilite contacts show Åk enrichments. We have observed similar behavior for other unpublished experiments conducted over a broad range of liquid compositions and run conditions. Not every direction extending from glass-melilite contacts will show these anomalous increases in Åk but some invariably do. Thus, the expectation based on experiment is that trapped liquids in melilite are associated with crystallization of additional melilite from the trapped liquid that is unusually åkermanitic near the interface with glass or clinopyroxene (i.e., at least some of the melilite will have an excursion to high-Åk near the interface). It is also important to note that, due to differences in the direction of crystallization of the melt inclusion relative to the plane of the polished section, glass-melilite or clinopyroxene-melilite boundaries without such Åk enrichments are also observed. Hence, multiple determinations of near-interface melilite compositions are required to establish whether or not a particular clinopyroxene is or is not associated with anomalous zoning of the adjacent melilite.

SEM Petrography of Meteoritic CAIs

Figure 2 is a backscattered electron (BSE) photomicrograph showing well developed examples of boundary clinopyroxene on melilite-hosted spinels from the mantle region of Allende type B1 inclusion TS-34. Clinopyroxene occurs both as a continuous or nearly continuous rim or “rind” up to ~5 μm thick, extending over tens of μm along a crystal edge (Fig. 2a) and as discontinuous blebs less than 1 to as much as 8 μm in maximum thickness (typically 1 - 3 μm thick; Fig. 2b). The melilite in TS-34, like other Allende CAIs, is variably altered to fine-grained mixtures of grossularite, monticellite, and wollastonite (Davis et al., 1994) but we observed no correlation between the presence or absence of boundary clinopyroxene and areas of alteration in TS-34.

Close examination of the interfacial region between spinel and melilite in TS-34 shows that ten of the eleven TS-34 spinel grains and clusters studied by Paque et al. (2007a) have boundary clinopyroxenes. Of the eight mantle melilites they analyzed, six have clinopyroxene rinds, one is associated with blebs, and one has both a rind and blebs. No core spinels in melilite were found to have clinopyroxene rinds but two of three have associated blebs. Thus, spinels in this population of grains that are free of boundary clinopyroxene in the plane of the section appear to be rare, and allowing that some sections through spinel crystals with blebs may miss all of them, it is possible that all eleven spinel occurrences described by Paque et al. (2007a) have boundary clinopyroxene.

Since Paque et al. (2007a) selected relatively large grains for their minor element mapping, we also made a systematic survey of small spinels from a ~300 x 700 μm relatively spinel-rich melilite from the core of TS-34 (Fig. 3a) and from a similarly sized portion of a melilite crystal from the mantle (Fig. 3b). All of the spinel grains in the mantle test area that lack boundary clinopyroxenes are relatively small, but overall, most of the small spinels have boundary clinopyroxenes, suggesting that the presence of blebs or rinds is endemic among spinel grains of all sizes. In an area of similar size in the core (Fig. 3a), spinel grains lacking boundary clinopyroxenes lie mostly along a central swath through the test area; there may be two populations of spinels, not size related, one of which lacks boundary clinopyroxenes. Based on semi-quantitative EDS analyses, Ti contents from the core of spinel grains shown in Fig. 3a are similar for both and typical of those of core spinels. Thus, the presence or absence of boundary clinopyroxenes is not reflected in the spinel composition. Moreover, since compositions of mantle and core spinels are distinct (Connolly et al., 2003; Paque et al., 2005), the boundary clinopyroxene-free cluster in Fig. 3a is not a group of spinel grains originally located in the inclusion mantle that was later transported into the core.

Leoville 3537-2 spinels also have boundary clinopyroxenes but the textural relationships are more complex than in TS-34 even at the SEM level. Figure 4 shows BSE photomicrographs of spinel grains included in melilite from Leoville 3537-2. Each has one or more phases present on the grain boundary between spinel and melilite. As with TS-34, both continuous (rinds) and discontinuous (blebs) boundary phases are observed. Clinopyroxene is evidently among the phases present, based on semi-quantitative analyses, but it was not possible through SEM examination to establish the identity of other phases except that calcite is observed filling fractures in melilite near one of the spinel grains, Leo2, that we consider in detail below. Since Leoville 3537-2 is a nominally unaltered inclusion, the complexity is not simply a consequence of differences in alteration processes for the two inclusions although we revisit this inference below.

In both TS-34 and 3537-2, boundary clinopyroxenes are generally too small for quantitative electron microprobe analyses but EDS analysis of relatively thick examples demonstrates that the boundary clinopyroxene compositions are similar to coarse-grained mantle clinopyroxenes (i.e., high in Ti and Al) for TS-34 analyzed in this study**,** by Simon et al. (1991), and Simon and Grossman (2006) and that boundary clinopyroxenes on core spinels are typical of core clinopyroxene (i.e., lower in Ti and Al). We also analyzed a relatively coarse-grained, isolated (in the plane of the section) mantle clinopyroxene and found, as have others (Lin et al., 2003; Simon et al., 1991), that Sc concentrations are often fairly high (up to 0.3 wt% Sc_2O_3). Scandium zoning is somewhat patchy but the lowest concentrations (<0.15 wt %) are restricted to outer portions of the crystal.

While the boundary clinopyroxenes are generally thin and difficult to analyze using SEM/EPMA techniques, melilite compositions around the spinel grains are readily analyzed, although spatial resolution is poor within ~5 μm of the interface. Figure 1b shows that crystallization of melilite from a melt inclusion results in a large Åk gradients decreasing away from some but not all clinopyroxene or glass interfaces. Thus, any search for Åk gradients in natural CAIs adjacent to boundary clinopyroxene ascribable to melt inclusions must have a good statistical basis. Primarily using 2-dimensional melilite composition maps (2 - 8 μm step size) centered on mantle spinel grains with located boundary clinopyroxene, we extracted those analyses which define Åk profiles approximately normal to melilite - boundary clinopyroxene or melilite - spinel interfaces. Melilite compositional variations adjacent to the boundary were almost always observed (33 profiles near four spinel grains), but these were relatively small (change in Åk less than 6) and some of this could be due to secondary fluorescence of Mg from the spinel. For melilite in the region around spinel grain A2, Åk oscillations between Åk22 and Åk25 are observed at distances large compared to the thickness of the boundary clinopyroxene, with occasional "hot spot" excursions to Åk30-36. It is probably inevitable that, whatever the origin of the boundary clinopyroxene, there will be some accompanying perturbation in the composition of the adjacent melilite. It is likely significant that the Åk variation around boundary clinopyroxene in TS-34 are much smaller than those observed from the crystallization of the synthetic melt inclusion (Fig. 1b). The issue of Åk gradients near spinel-melilite interfaces is also addressed below based on a higher spatial resolution examination of the FIB section profiles.

In summary, based on SEM/EPMA results, boundary phases on spinel-melilite interfaces are quite common in both Allende TS-34 and Leoville 3537-2. These boundaries appear to be dominated by clinopyroxene in TS-34 but may involve additional phases in 3537-2.

FIB/STEM Studies

Based on SEM imaging, five spinel grain interfaces were selected for FIB/STEM analysis. Figure 5a shows one of these, spinel grain A2 from the mantle of TS-34, along with the location of the FIB section eventually removed (marked by a protective Pt strap). We selected A2 and the specific location of the section to study a thin clinopyroxene rim between the spinel and melilite, which was inferred to be present based on Ti hot spots in the Ti maps obtained by Paque et al. (2007a) but not well resolved by SEM imaging. SEM EDS analyses of melilite composition in the region around the trench show Åk20 to Å25, typical of values in other areas of melilite adjacent to A2. An SEM image of this boundary on the FIB section prior to final thinning (Figure 5b) confirms clinopyroxene with no other phases present. On a submicron scale, the clinopyroxene rim is constructed from clinopyroxene crystals parallel to the spinel surface that vary in thickness, one portion ~ 0.1 to 0.2 μm thick and a second, considerably thicker region, ~0.7 μm. Near the base of the section and near the junction between the two large clinopyroxenes, there appear to be clusters of small clinopyroxene crystals that extend into the melilite. Thus, the spinel side of the contact is relatively smooth and the melilite side more irregular, although the clinopyroxene-melilite interface appears smooth at any particular point. Unfortunately, the FIB section for A2 did not survive final thinning to electron-transparency for TEM analyses and we were therefore unable to further characterize it.

FIB/STEM section E2, was taken across a spinel-melilite interface in the mantle of TS-34 and Fig. 6a shows an SEM image of the section together with a traverse across the interface. There is no significant variation in the melilite chemistry, which contrasts with Fig. 1b. Note that SEM spatial resolution is considerably higher in Fig. 6a than can be obtained on a traditional thick section because the sample is only 1.5 μm thick. Figure 6b shows a low-magnification conventional brightfield TEM image of the interface region. Clinopyroxene – spinel and clinopyroxene – melilite interfaces are sharp with no additional phases present but high-resolution examination reveals that melilite and spinel are separated by a ~150 nm thick boundary phase. This may be an alteration mineral but we have not established its identity.

FIB section B2-1 was made at a location on core spinel grain B2, which had no Ti hot spots in the Ti map obtained by Paque et al. (2007a) and no obvious boundary clinopyroxene under SEM examination. This location was selected to see if a FIB/STEM section of a melilite-spinel boundary showing no boundary clinopyroxene on the μm scale was also devoid of clinopyroxene at the nm scale. This issue is important because clinopyroxene or some other phase *always* separating spinel from melilite would hint at a reaction between melilite or liquid and spinel or some universal process by which clinopyroxene invariably forms on spinel but is never subjected to a process that could remove an extremely thin layer. The FIB/STEM section, however, shows a clean, sharp interface between the spinel and melilite. It is clear from Allende spinel grain A2 (Fig. 5b) that the thickness of clinopyroxene rinds can vary significantly but extremely thin layers of clinopyroxene <~0.1μm are not observed. Section B2-1 demonstrates that direct contact of spinel with melilite does occur even at the scale of a few nm and that clinopyroxene-decorated spinel surfaces, while extremely common, are not universal.

A second FIB section was prepared from core spinel grain B2 at a location where boundary clinopyroxene was indicated in the SEM maps. Figure 7a shows the spinel interface regions for the FIB section B2-2. This section is characterized by two blebs of boundary clinopyroxene in contact with spinel and a third similarly sized and, apparently, isolated clinopyroxene grain ~10 μm away. The host melilite for B2 is ~Åk50, typical of core melilite in TS-34. Four SEM line scans (~0.8μm beam width) on the FIB section were obtained, two of which are shown in Fig. 7b. Data for the other two line scans are similar. Because these data were obtained from a sample 1.5 μm thick, the SEM spatial resolution is higher than obtained on a traditional infinitely-thick section. All three clinopyroxenes are rimmed with melilite ~2 μm thick that becomes more åkermanitic with distance from the clinopyroxene-melilite interface until it matches the composition of the host melilite. The linescans are semi-quantitative but based on spot analyses in or near the traverses, the range in Åk in Fig. 7b is a few mole % and the average near the clinopyroxene-melilite interfaces is ~Åk45.

Two spinel grains from Leoville 3537-2 were selected for FIB/STEM study. Spinel grain Leo2, from the core, is shown in Fig. 8 with the location of the FIB section. This section slices across an unusually thick continuous boundary clinopyroxene that lies along one side of the spinel grain in the SEM photomicrograph. An electron microprobe measurement of the melilite composition in the vicinity of the FIB section gives $Åk_{51}$, typical of core melilite compositions in this inclusion. Figure 9, a brightfield TEM photomicrograph provides an overview of the interface region and higher resolution images are shown in Figs. 10 - 12. A clinopyroxene rim of variable thickness from 0.5 to 2 μm is in contact with the spinel with a smooth interface between them (Fig. 9). Multiple spinel crystals are evident in the FIB section through spinel grain Leo2. Polycrystalline spinel was not observed in any of the other FIB sections although this could reflect smaller portions of excavated spinel. Unlike TS-34 spinels, the boundary clinopyroxene on spinel is not in direct contact with the host melilite, being separated by a vein of mostly glassy material, generally ~ 1 μm across, showing no electron diffraction pattern. Where this glassy layer is in contact with clinopyroxene, the interface is smooth but melilite-glass interfaces are rough, typical of corrosion (Fig. 11a), with apparent intrusion into the melilite along cracks or cleavage traces. This is true both of the "island" of melilite, a portion of which can be seen in Fig. 9, and the host melilite. A typical glass composition is 18 wt. % MgO, 36% Al_2O_3, 48 % SiO_2, and 6% CaO with < 1 wt.% FeO, TiO_2 or Na_2O, a composition which is Mg-, Si-rich and Ca-poor relative to the coarse-grained igneous silicates. In the central portion of the glassy layer in Fig. 9, there is an Mg-, Al-rich, Ca-, Si-poor unidentified crystalline material (it can also be in contact with clinopyroxene). Based on electron diffraction patterns (e.g., Fig. 10 inset) and high-resolution imaging, this is a single-phase mineral with a layer lattice structure.

Figure 12 shows a low-magnification conventional brightfield TEM image of the glass vein with unidentified crystals and surrounding mineral phases. The locations of oxygen electron energy loss spectra (EELS) for regions containing glass only, crystals plus some glass, clinopyroxene and spinel are indicated. Both the glass and unidentified crystals are electron beam sensitive and it was therefore necessary to obtain the EELS spectra using a broad beam and low intensity. These are inset in the image. A pre-peak is visible about 8 eV below the main peak in the O-K edge absorption spectra from both the glass and unidentified crystals (with included glass) regions. The nominally anhydrous minerals spinel and clinopyroxene show no pre-peak. In hydrated minerals, the pre-peak is indicative of OH^- groups and the ratio of the pre-peak to main peak heights scale with the concentration of OH^- (Wirth, 1997). The glass-only region shows a pre-peak to main peak height ratio of 0.2 similar to hydroxyl-bearing minerals like talc and indicative of the presence of OH^-. The concentration of OH^- is, however, indeterminate, as quantitative data of Wirth (1997) refer to crystalline phases. Based on speciation studies (e.g., Silver et al., 1990), molecular water is also likely to be present in the glass, possibly exceeding the H present as OH^-. We are not aware of previous reports of hydrated glasses in CAIs. Wlotzka and Wark (1982), however, reported zeolites in a Leoville CAI which would be consistent with the presence of hydrated phases, possibly pre-terrestrial, in 3537-2.

In the unidentified crystal. the pre-peak to main peak ratio for a mixture of ~1/3 glass and ~2/3 crystal is even higher, >0.35 (Fig. 12), than it is for the glass (~0.2; i.e., the ratio in the unidentified crystal probably exceeds 0.4). From the data of Wirth (1997), OH computed as H_2O for this phase exceeds ~20 wt%. The crystals show an elongated fibrous texture in high magnification imaging and a diffraction pattern typical of layered hydrated mineral phases (Fig. 10). Local composition measurements indicate an Mg-, Al-rich, Ca-, Si-poor phase with Mg/Al >1.6. Given the very high OH^- content of the crystal, its Mg-Al rich composition, high Mg/Al ratio, and layered structure, we speculate that this is a layered double hydroxide (Rives, 2001) with Mg/Al~2, similar to meixnerite but with a lower Mg/Al.

The Leoville 3537-2 mantle spinel Leo1 (Fig. 13) is surficially similar to other Leoville spinels shown in Figs. 4 and 8 in having a thin discontinuous rim of clinopyroxene and other phases on the surface of the grain. Leo1 was selected for FIB/STEM because there are also several veins in melilite in the vicinity of the spinel whose mineralogical characteristics could not be established unequivocally through SEM examination although compositions were consistent with calcite as the predominant phase. These veins inhabit cracks in melilite that reach, but do not crosscut, the spinel. In contrast to other FIB sections, which were oriented perpendicular to the spinel surface, the FIB section for Leo2 was deliberately oriented at a lower angle in order to simultaneously sample both the spinel/melilite interface and a section of vein in the host melilite. Figure 13 shows the location of the extracted FIB section. The vein in the host melilite, which is shown in a high magnification TEM image in Fig. 14, is calcite, ~0.5 to 1 μm in thickness, which crosscuts the host melilite, as shown in the inset. Calcite is the only phase identified within the vein in this area, and it does not appear to have affected the melilite composition, which is the same (~$Åk_{23}$) on both sides of the calcite vein. We infer that other veins in Fig. 13 are also composed of calcite. Calcite has been reported previously in Leoville (Abreu and Brearley, 2005; Ash et al., 2002; Caillet and Buseck, 1992; Komorowski Caillet et al., 2007; Sylvester et al., 1993), generally as a minor isolated phase or in veins.

As shown in Fig. 13, the calcite vein crosscuts the boundary clinopyroxene but terminates at the spinel. Figure 15, the spinel-melilite interface for Leo1 at the other end of the FIB section from the calcite vein, shows that calcite also occupies the interface region with spinel where it forms contacts with spinel, glass, clinopyroxene, and perovskite. In other areas near the interface, not shown on Figure 15, calcite lies between spinel and melilite. Since the calcite veining is prominent in the melilite (Figs. 13-14), we interpret this to mean that calcite precipitated opportunistically along existing fractures and that fracturing in the interface region was predominately, but not exclusively, along the spinel-clinopyroxene contact. Perovskite is occasionally inferred from the spinel Ti maps (Paque et al., 2007a), and Caillet et al. (1993) noted that spinels in Leoville 3537-2 are frequently decorated by perovskites. In Leo1, both calcite and clinopyroxene are in contact with spinel, while glass is adjacent to the melilite. Note that glass-melilite contacts are irregular (i.e., rough interface boundaries), but calcite-spinel contacts are smooth. The glass composition for the interface region of spinel grain Leo1 is similar to that of the glass in Leo2 (17 wt. % MgO, 36% Al_2O_3, 41% SiO_2, and 7 % CaO).

DISCUSSION

We order this discussion largely in reverse of the chronological order that created the interfacial regions between spinel and melilite, saving for last an analysis of boundary clinopyroxenes, which occur in both Allende TS-34 and Leoville 3537-2. We begin by first considering the significance of calcite veining in melilite near the spinel grain Leo1, which we infer to have been a late fracture filling event that generally had little effect on the compositions of other phases present. We then evaluate the possible influence of melilite alteration events and the significance of glass veins and the associated hydrated crystalline phase around Leoville spinels. Our principle objective here is to answer two simple questions: How did the glasses form and what was the nature of the precursor? Finally, we address the origin of boundary clinopyroxenes, their relationship to coarser-grained pyroxenes, and their significance for thermal processing of type B1 inclusions.

Calcite

Calcite in meteorites is a secondary phase that can be produced in both terrestrial and extraterrestrial environments. In Leoville, which is a lightly weathered find, some of the calcite is unambiguously terrestrial because it forms veins crosscutting the fusion crust, which formed during passage through the Earth's atmosphere long after any possible parent body alteration (Abreu and Brearley, 2005). On the other hand, Caillet and Buseck (1992) argued that calcite partially replacing wollastonite in a Leoville CAI, a process that appears to have pre-dated the mechanical deformation events, was in fact pre-terrrestrial. The thin ~ 1 μm thick veins of calcite we observed around spinel grain Leo 1, and occasionally other localities in the inclusion, fill polygonally fractured melilite but are not observed to reach the Wark-Lovering rim or to cross the inclusion boundary into the matrix. The veins are not associated with additional alteration phases that might hint at the point of origin and, in contrast to the glass veins discussed below, they do not appear to corrode melilite at calcite-melilite contacts. Thus, while it is possible that the calcite we observe in Leoville 3537-2 is pre-terrestrial, we exclude it from a consideration of conditions in the Leoville parent body or in the primitive solar nebula. Its importance lies in possible effects of the altering medium, whether asteroidal, nebular, or terrestrial, on the compositions of previously existing phases. The lack of additional phases in the veins (Figs. 13-14) is consistent with precipitation in fractures from relatively low temperature aqueous fluids without significant dissolution or precipitation of other crystalline phases**.** It is also possible that water, which appears to be present in the interfacial glass and the unidentified Mg-, Al-, OH-rich crystals in Leoville 3537-2, as discussed above, is a product of the same event. Calcium could have been leached from the glass to form calcite, but the area of calcite in the general vicinity of Leo1 greatly exceeds the area of glass, and we therefore infer that Ca in the calcite is more likely to have been brought in with the fluid from an external source. Moreover, we see no evidence for dissolution of melilite in contact with calcite or of the precipitation of additional phases on the melilite (Fig. 14). Melilite in contact with glass in the interface region appears corroded (Fig. 15); areas in contact with calcite are generally smooth. In addition, we show below that compositions of glass associated with Leo1 and Leo2 are consistent with no significant loss or gain of Ca postdating glass formation. Thus, we infer that the alteration event involving the calcite around Leo2 postdated formation of the other phases and that it had no significant effect on the compositions of the previously existing phases with the caveat that hydration of the glass may have occurred during the same event.

Formation of Leoville Glass Veins

Both Leo1 and Leo2 have glass veins between melilite and pyroxene or spinel. Other CAIs or Ca-Al-rich fragments in matrix in carbonaceous chondrites are known to have glass (El Goresy et al., 2002; Gray et al., 1973; Ireland et al., 1991; Kurat, 1975; Marvin et al., 1970; Reid et al., 1974), but their compositions are strikingly different. In Figure 16a, a "Stolper" projection (Stolper, 1982), CAI glass compositions are projected from $MgAl_2O_4$ spinel onto the plane formed by the compositions of gehlenite ($Ca_2Al_2SiO_7$), anorthite ($CaAl_2Si_2O_8$), and forsterite (Mg_2SiO_4). Glass compositions from CAIs taken from the literature form an arc in this projection anchored by the anorthite and gehlenite vertices (for a discussion on the application of projections to CAIs, see Beckett et al., 2006). Most are glass-rich objects, perhaps originally crystals or inclusions melted in high velocity impacts in the primitive nebula as discussed by Stolper (1982), but there are also examples of glass as a minor constituent in type A and B inclusions (El Goresy et al., 2002; Gray et al., 1973). The composition of glass from experiment 98-53, which is also shown in Fig. 16a, plots within this arc near the clinopyroxene – spinel – anorthite – melilite invariant point. Note that the 98-53 glass was a trapped liquid produced through fractional crystallization of melilite, and its composition plots close to the equilibrium saturation surface for melilite + spinel (see also Stolper and Paque, 1986). We infer that residual liquids trapped by crystallizing melilite should plot near a melilite-saturated phase field or a short extension of it. Failure of a stable phase to nucleate can lead to continued metastable crystallization of an already crystallizing phase. However, even allowing for the uncertainties in the TEM EDS analyses, glass compositions for the veins around Leo1 and Leo2, are far away from the arc for literature CAI glasses in Fig. 16a or its extensions and well away from the spinel + melilite multiply saturated liquidus phase field. The possible incorporation of melilite or clinopyroxene into the analyzed volume would move the projected compositions towards the spinel + melilite liquidus phase field, not away from it. Incorporation of spinel in the analysis volume would raise the "elevation" of the composition but have little effect on the projected position. It is likely that either a different process produced the Leoville glasses or that precursors to the Leoville glasses were very different from those of glasses from CAIs previously described in the literature.

As noted in the previous paragraph, the Leoville glass compositions are well removed from the melilite-saturated liquidus surface, which would be odd for a liquid nominally produced as a residual liquid during crystallization of melilite. In this brief section, we therefore undertake a formal assessment of fractional crystallization sequences of the Leoville glasses. If this material is derived from melt inclusions in melilite, then melilite should appear somewhere in the crystallization sequence. Figure 16b, which is a spinel projection onto the plane formed by the compositions of forsterite (Mg_2SiO_4), anorthite ($CaAl_2Si_2O_8$), and silica (SiO_2), is designed for more silica-rich compositions than Stolper's (1982) diagram and is therefore more suitable for a discussion of phase equilibria relevant to the Leoville glasses. Both phase diagrams share the plane anorthite – forsterite – spinel, which in projection plots as a line. Both are projected from $MgAl_2O_4$ spinel, which means that variable amounts of spinel component in the bulk composition have no effect on the projected composition. Figure 16b also shows the spinel-saturated liquidus surface after Sheng et al. (1991) and Sheng (1992) (also shown in Beckett et al. (2006)), contoured in wt.% spinel component. Spinel is the liquidus phase for bulk compositions with wt. % spinel component greater than on the surface in the same projected position, and some other phase is on the liquidus for lower amounts of spinel. The compositions of Leo1 and Leo2 glasses are 15-20 wt.% spinel component above the saturation surface and, therefore, spinel is the liquidus phase. Figure 16b can be used to infer crystallization sequences for spinel-saturated liquids that plot on the diagram and compositions of their residual liquids (see Beckett et al. (2006) for a discussion). For the Leo1 glass, the fractional crystallization sequence would be spinel → anorthite → cordierite → olivine and, for the Leo2 glass, spinel → cordierite → anorthite → olivine; crystallization paths for residual liquids derived from crystallization of both glasses are shown in gray.

A fundamental observation comes from an examination of the crystallization sequences for the Leoville glasses. Even when allowance is made for the uncertainties in the TEM EDS analyses and possible contamination by other phases in the analyzed volume, all of which would either have no effect (spinel) or pull the composition towards the melilite field. (melilite, clinopyroxene), melilite is completely absent from the crystallization sequence. It would be extremely odd for a trapped liquid around a spinel inclusion incorporated into a crystallizing melilite to be undersaturated with respect to the host phase. At the time a melt inclusion is incorporated into a crystal, the liquid is generally saturated or even supersaturated with respect to the host phase, and it invariably crystallizes on the walls of the melt inclusion (cf., Gaetani and Watson, 2000; Streck and Wacaster, 2006) as is observed for the run product 98-53 described above. Thus, if the Leoville glasses are residual liquids from melt inclusions captured by melilite, we would expect melilite to appear in the crystallization sequence. Yet this is not the case for either of the Leoville glasses. Both glass compositions plot on the silica-rich side of the anorthite – forsterite - spinel join, which is a thermal divide for spinel-saturated liquids. Compositions close to, but on the silica-poor side of this join, will evolve towards melilite-saturated melts (e.g., olivine or anorthite crystallization of liquids near to, but on the silica-poor side of the join, will move them away from the join) and ultimately, the residual liquids will approach the spinel-saturated clinopyroxene and melilite stability fields (Fig. 16a). Similarly, olivine or anorthite crystallization from liquids near to, but on the silica-rich side of the join, will move residual liquid compositions further away from the join and, in particular, further away from the melilite-saturated phase field. Both of the Leoville glasses are well to the silica-poor side of the thermal divide (Fig. 16b). Neither will produce a residual liquid composition on the other side of the join through fractional or equilibrium crystallization and, therefore, neither of them is a residual liquid from the melilite-rich side of the thermal divide. Indeed, the glass compositions can be described in terms of positive amounts of anorthite, forsterite, spinel and cordierite, which is consistent with the anorthite - forsterite – cordierite – spinel – liquid invariant point being a eutectic composition. The compositions of Leo1 and Leo2 glasses are in the general vicinity of this invariant point in Fig. 16b but the spinel contents are well above the saturation surface and there is no evidence for the presence of cordierite in Leoville 3537-2 or of igneous olivine for that matter (i.e., these are not near-eutectic liquids).

The absence of anomalies in melilite composition near the glass veins is also inconsistent with a partially crystallized residual liquid. Had the glass been a quenched residual liquid, extraordinary zoning would have been expected near the interface with the glass as is seen in experimentally produced synthetic glass. Such zoning is not observed in the Leoville glasses.

The Leoville glasses are not residual liquids produced through fractional crystallization and, in particular, they are not residual liquids produced during the crystallization of melilite.

In the preceding paragraphs, we used a phase diagram to infer crystallization sequences for the Leoville glasses. The saturation surface can also be contoured in temperature and this leads to the conclusion that high temperatures would be needed to melt anhydrous precursor materials of the Leoville glasses, >~1325°C. We can also use Berman's (1983) thermodynamic model to estimate the liquidus temperatures as 1541°C (Leo2) and 1611°C (Leo1), spinel being the liquidus phase in both cases. All of these temperatures are quite high and if the entire inclusion had been subjected to them, most or all of it would have melted. This implies an event that was extremely local in its thermal effects and did not involve the bulk of the inclusion. If, however, the glass precursor was hydrated, relevant temperatures may have been substantially lower and the requirement of high peak temperatures correspondingly relaxed.

Based on the above discussion, we infer that glasses from Leoville 3537-2 are not quenched remnants of residual liquids produced during crystallization of the host melilite, so we remain with the two simple questions posed at the beginning of the Discussion: How did the glasses form and what was the nature of the precursors? A possible answer to the first question is that the Leoville glasses are the product of a locally enhanced pressure regime formed during a shock event whose peak pressure in the major phases was too low to cause significant heating effects. Leoville has a well defined foliation with deformation of chondrules and inclusions (e.g., Cain et al., 1986), but inferred peak pressures for the bulk meteorite are <20 GPa (Nakamura et al., 1992), which would not be expected to lead to widespread melting. Shock waves are, however, notorious for producing local melting along grain boundaries and highly heterogeneous effects in heterogeneous, especially porous, materials (e.g., Kieffer et al., 1976; Sharp and DeCarli, 2006; Stöffler et al., 1988). Where a shock wave passes through a porous material, or through a grain boundary between two dissimilar materials, considerable increases in peak pressures may be attained relative to ambient values nearby due to compaction effects and differences in the impedance of materials at the grain boundary (e.g., Sharp and DeCarli, 2006). We envision the precursor to a glass vein as a thin porous layer of alteration material, possibly hydrated, that was shocked to a peak pressure enhanced relative to pressures achieved in the other phases in the inclusion. On pressure release, the waste heat produced by shock in the vein region led to a large temperature increase with melting of the phases present. After shock heating, the ~1 μm thick veins cooled nearly instantaneously, leaving the observed glass. If the alteration assemblage was anhydrous, rather high local temperatures, ≥1550-1650°C would have been required and probably quite large enhancements in peak pressure. If the phase assemblage were hydrous, required melting temperatures would have been lower, and possibly much lower, and required enhancements in peak pressures relative to those achieved in melilite correspondingly less. We can place some constraints on the nature of the precursor material through an analysis of the glass compositions shown in Fig. 16b. One endmember is likely to be a composition that projects to or near the silica vertex in Fig. 16b. Candidates include sudoite ($Mg_2Al_4Si_3O_{10}(OH)_8$), Mg-carpholite ($MgAl_2Si_2O_6(OH)_4$), chloritoid ($MgAl_2SiO_5(OH)_2$), and cordierite ($Mg_2Al_4Si_5O_{18}$), which plot at the silica vertex (i.e., Ca-free phases with molar Mg:Al = 2:1) and zeolites (Wlotzka and Wark, 1982), sapphirine ($(Mg,Al)_8(Al,Si)_6O_{20}$), and clinochlore ($Mg_5Al_2Si_3O_{10}(OH)_8$), which plot along the base of the triangle in Fig. 16b, ~15 - ~30 % of the way towards the forsterite vertex. The weight ratio of the silica to spinel components in the glasses allows a more specific assessment for potential endmembers plotting at the silica vertex. The Leo1 and Leo2 glasses yield 0.62 and 0.81 for this ratio, close to the values for the chlorite endmember sudoite (0.63) and the chain silicate Mg-carpholite (0.84). Cordierite (1.22) would be less consistent with the glass compositions; chloritoid (0.422) is possible but would require additional and substantial spinel content. The silica-poor endmember appears to be consistent with an aluminous diopside. Clinochlore and sapphirine are inconsistent with pyroxene or melilite dominating at the silica-poor end of a mixture although other phases might be possible. Wlotzka and

Wark's (1982) zeolite is a possible endmember but it would require large amounts of spinel (~40 wt.%), which is quite refractory and negative amounts of Ca-Tschermak's molecule ($CaAl_2SiO_6$) in the pyroxene. Compositions of the Leo1 and Leo2 glasses can, however, be described in terms of positive amounts of Mg-carpholite, spinel, Ca-Tschermak's, molecule and diopside. Replacing Mg-carpholite by sudoite requires negative amounts of Ca-Tschermak's molecule for Leo1 glass but probably within error of zero. Thus, mass balance suggests that Mg-carpholite or sudoite and an aluminous diopside are consistent to first order with the glass compositions. These phases could be produced through the alteration of melilite in the interface region between spinel and melilite with cracks providing access, and this would be consistent with the observed corroded contacts between Leoville glasses and melilite. Both Mg-carpholite and sudoite are low-temperature phases, restricting the alteration process to temperatures <~400°C (Fransolet and Schreyer, 1984; Vidal et al., 2001; Wei and Powell, 2006). Assuming Al to be immobile, this process would have required the loss of ~1/3 of the original Ca from the melilite (~Åk25) being altered with ~1/3 of Mg and Si in the alteration products being introduced from outside the interface region. If either Mg-carpholite or sudoite was, in fact, the Si-rich endmember, then the assemblage was hydrated, which as noted above could have important consequences in a shock event and also imply a significant partial pressure of H_2O. The alteration process would probably require the gain of Mg, Si, and water, presumably through transport in a vapor or aqueous solution along cracks. If this scenario is correct, then preterrestrial alteration of Leoville CAIs did occur although, based on the spatially limited glass, the extent was very modest. It was a shock subsequent to this alteration event that led to melting in the vein due to the anvil effect of the melilite - spinel contact region, the porous nature of the alteration material and the presence of water, which could have greatly reduced the required peak pressure for melting. A fundamental implication of our analysis is that the Leoville glass is not recording an igneous event in which the major igneous phases in the inclusion were participating. Although Allende CAIs are more altered overall, Leoville spinel-melilite contact regions are more complex than those of Allende because of processes that occurred after the formation of the boundary clinopyroxenes. This suggests that the process(es) producing boundary clinopyroxenes may have been the same in both Allende and Leoville type B1 inclusions and that the origin of boundary clinopyroxene may be better constrained via Allende CAIs where alteration and shock effects along the boundaries with spinel appear to be absent.

Unidentified Crystal

The glass vein around spinel grain Leo1 contains an Mg-, Al-, OH-rich crystalline phase. If as supposed above, this is a layered double hydroxide, it seems likely that the phase formed after the shock event that produced the glass. Otherwise, one would have to postulate that this extremely water-rich phase survived a shock event intact while the precursor phase(s) to the glass was completely vitrified. It is possible that the unidentified phase crystallized from the glass or condensed from a vapor during cooling following the shock; an alternative, perhaps the most likely one, is that this phase is a terrestrial alteration product of the glass. Although the origin of the unidentified crystal remains to be determined, it formed after the completion of all igneous processing.

Boundary Clinopyroxenes

In a previous subsection, we rejected the possibility that glass veins in Leoville are a product of residual liquids produced during crystallization of melilite but the idea that boundary clinopyroxenes crystallized from residual liquids (i.e., from melt inclusions along spinel-melilite boundaries) also needs to be carefully considered. In this section, we first evaluate the possible crystallization of boundary clinopyroxenes from residual liquids and then briefly consider shock melting. We believe that these processes were not responsible for boundary clinopyroxenes, in Allende TS-34 or Leoville 3537-2. We then evaluate two alternatives we believe to be more plausible and suggest that both may have been operative. The first is that some boundary clinopyroxenes are a consequence of either direct dissolution of perovskite (clinopyroxene later crystallized in regions of melt with enhanced concentration of Ti produced by the dissolution of perovskite) or indirect dissolution of perovskite (clinopyroxene formed a reaction rind between perovskite and liquid). The second is that some boundary clinopyroxenes are relict crystals relative to the most recent melting event.

There are several reasons why it is unlikely that boundary clinopyroxenes generally formed from residual liquids within melt inclusions, including the following:

(1) As discussed in the Results section, careful analytical searches in the vicinity of spinel grains with boundary clinopyroxene show small gradients in melilite composition both on melilite-spinel and on melilite-boundary clinopyroxene contacts. Similarly the FIB/SEM data in Figure 7b show a thin rind of zoned melilite between boundary clinopyroxene in the core of the inclusion and host melilite. For crystallization of melt inclusions around spinel grains in TS-34 mantle melilite of composition Åk22 to Åk35, frequent observations of high Åk values (Åk40 to Åk60) should have occurred, but these were never observed. Independent of boundary clinopyroxene, the presence of spinel is associated with small perturbations in the composition of the surrounding melilite These small changes contrast with compositions of melilite in the experimental run product, which are characterized by large increases in Åk content near glass - melilite or clinopyroxene – melilite contacts (Fig. 1b). Although conceivably important (as well as high Åk "hot spots" observed within apparently pure melilite regions), we conclude that these small Åk variations of unknown origin in melilite adjacent to

boundary clinopyroxene do not support the origin of the boundary clinopyroxene by crystallization of a melt inclusion. Whatever the origin of the boundary clinopyroxene, it is likely that there would be some small compositional perturbations in the surrounding melilite

For spinel inclusions in *core* melilite, where large clinopyroxene crystals are co-crystallizing, small spinel-melilite boundary clinopyroxene may be plausible as the last drops of the original liquid with pyroxene-like compositions but here the adjacent melilite might be expected to have unusually high Åk values, which is not observed. Moreever, given the fact that pyroxene was crystallizing elsewhere, a simpler explanation is that the boundary pyroxene nucleated ont eh spinel and was then incorporated sans melt inclusion into crystallizaing melilite. In any case, as emphasized below, the boundary clinopyroxenes on spinel inclusions in mantle melilite represent the largest interpretational challenge because they are enclosed in aluminous, presumably early crystallizing melilite with liquid compositions greatly undersaturated with respect to clinopyoxene.

(2) Even if the issue of melilite zoning is ignored, residual liquid compositions produced by fractional crystallization of melilite in type B CAIs are not exactly equivalent to melilite + clinopyroxene ± spinel. This is shown in the residual glass compositions from the present experimental study. We would therefore expect to at least occasionally encounter additional phases that co-crystallized with the boundary clinopyroxenes and, aside from the occasional perovskite crystal, which doesn’t solve the mass balance discrepancy, we never do. This is particularly true of boundary clinopyroxenes in the *mantle*, for which potential melt inclusions would be expected to have compositions well removed from those of the pyroxene. Yet, glass or additional crystalline igneous phases such as anorthite are

not observed. The absence of anorthite is especially significant, as this phase is present in essentially all Type B CAIs. It is widely accepted that anorthite nucleation is delayed in crystallization of Type B CAI compositions, but late is not never, and some boundary anorthite should have been found along with clinopyroxene if these formed by crystallization of melt inclusions in melilite.

(3) For spinel inclusions in *mantle* melilite, primary crystallization cannot explain the presence of the Ti-rich boundary clinopyroxenes unless present ideas on the equilibrium crystallization sequence of Type B CAIs are incorrect, because clinopyroxene appears late in the fractional crystallization sequence after the Ti content of the melt has been enhanced by considerable fractional crystallization of the low Ti phases**,** spinel and melilite (e.g., Stolper, 1982). The same problem exists for larger mantle clinopyroxene, not obviously associated with spinel. One could appeal to clinopyroxene crystallization following failure of melilite (as well as anorthite) to nucleate, but there is no evidence for this in a large number of dynamic crystallization experiments conducted for a broad range of bulk compositions and run conditions (Beckett et al., 1990; Beckett and Stolper, 2000; MacPherson et al., 1984; Maharaj and Hewins, 1995, 1997; Paque and Stolper, 1984; Stolper and Paque, 1986; J.M. Paque, unpublished data). Supercooling followed by rapid disequilibrium growth of mantle melilite might be possible and indeed apatite crystals attributed to this effect are occasionally observed in terrestrial rocks (Bacon, 1989), but it is not obvious that the boundary layer liquid would be depleted in melilite components to the extent that clinopyroxene crystallization would result**;** moreover, at least in the mantle, this would require very large enhancements in the Ti concentration of the liquid at the interface, for which there is no experimental evidence. An alternative of enhanced Ti contents in the outer portions of type B1 inclusions (e.g., Kennedy et al., 1997) is also

difficult to reconcile with crystallization of mantle clinopyroxenes because bulk enhancements of Ti in the mantle of type B1 inclusions are quite low. Most of the Ti budget for the inclusion is in the core where most of the clinopyroxene for the inclusion resides.

In the preceding subsection, we argue against the formation of boundary clinopyroxenes through crystallization of trapped liquids. Shock melting also appears unlikely given the similarity in composition between the boundary clinopyroxenes and coarser-grained pyroxenes in the same region of the inclusion and the absence of sufficient Ti near spinel-melilite interfaces to produce the clinopyroxene. Shock melting of a spinel-melilite interface could never provide the high Ti seen in the boundary clinopyroxenes. Even if one were to presuppose that shock melting somehow led to the formation of the boundary clinopyroxenes, this would fail to explain, especially in the mantle, essentially equivalent, and in many cases larger, clinopyroxenes not associated with any spinel, which would therefore have had a different and presumably lower peak pressure.

An alternative scenario for the formation of boundary clinopyroxenes, particularly in the mantle, is that perovskite dissolution led to the crystallization of clinopyroxene. If perovskite underwent "direct dissolution," it would have bled Ti into the melt, with the locally enhanced Ti concentrations leading to later crystallization of clinopyroxene during cooling before the melt homogenized with nearby Ti-poor liquid. An alternative is "indirect dissolution", which occurs when a phase reacts with a liquid to form one or more intermediate phases between the dissolving phase and liquid. In this case, clinopyroxene would be viewed as a reaction product between perovskite and spinel plus liquid. Moreover, since the Ti necessary for growth of these Ti-rich pyroxenes would be limited to a small volume of melt in the immediate vicinity of the dissolving or dissolved perovskite seed, the size of any resulting clinopyroxene grain would be limited by the supply of dissolving perovskite. Taking the limiting case of all Ti in the perovskite being retained by the clinopyroxene, the volume of product clinopyroxene would be ~ 4 – 6 times that of the original perovskite. Thus, a 1 μm perovskite grain could produce a ~5 μm clinopyroxene, which is consistent with observed dimensions of perovskite crystals and boundary clinopyroxenes. Moreover, if such a grain of clinopyroxene, having grown in the locally Ti-enhanced liquid, were to continue to be exposed to the surrounding, progressively less saturated melt, it would ultimately dissolve away unless the temperature lowered sufficiently to stabilize clinopyroxene or it was captured by a crystallizing melilite (more likely, at least in the mantle). It is worth noting that mantle clinopyroxenes don't show crystal terminations even though nearby crystals are unlikely to have impeded growth prior to incorporation into melilite. Both the isolated**,** sometimes large, spinel-free clinopyroxenes and the boundary clinopyroxenes in the mantle are generally rounded/resorbed, consistent with partial dissolution (Simon and Grossman, 2006; Simon et al., 1991). Kennedy et al. (1997) appealed to a perovskite dissolution mechanism to explain low REE concentrations in mantle melilites of an Allende type B1 inclusion USNM 3655A. Their idea was that perovskite sequestered much of the REE budget for the inclusion during the initial stages of melilite crystallization and that as perovskite dissolved into the liquid, REE concentrations in the liquid rose. Kennedy et al. (1997) observed perovskite in the mantle of 3655A, and they commonly decorate spinel crystals in the mantle of Leoville 3537-2 (Caillet et al., 1993; Connolly and Burnett, 1999). Ti-rich clinopyroxenes rimming rounded perovskite grains are relatively common in compact type A (CTA; very melilite-rich) inclusions and, indeed, both El Goresy et al. (2002) and Lin et al. (2003) interpreted such grains as having grown on dissolving perovskite cores. It is worth noting that compositions of mantle clinopyroxenes in type B1 inclusions are very similar to those in type A inclusions, and it is not unreasonable to surmise that a similar process may have produced both. The difference for mantles of type B1 inclusions may be that the perovskite, which was present initially, dissolved completely or nearly completely prior to the nucleation of clinopyroxene due either to smaller average perovskite grain sizes than in type A inclusions or to more intense heating. The arguments given above apply specifically to mantle clinopyroxenes and, given the relatively low Ti contents of boundary clinopyroxenes in the core, the similarity of their compositions to nearby coarse-grained clinopyroxenes, the differences in composition relative to clinopyroxenes from the mantle, and the rarity of perovskite decorating spinel in the core compared to the mantle, it seems unlikely that perovskite dissolution can account for both.

In detail, the chemistries of perovskite and mantle clinopyroxenes are probably inconsistent with a scenario that produces mantle clinopyroxenes solely through crystallization around a dissolving or completely dissolved perovskite. At least in compact type A inclusions (El Goresy et al., 2002; Fahey et al., 1987), perovskite, the presumed precursor, has generally lower Sc/Ti (0.001-0.015 vs. 0.001-0.11) and Sc/Zr (0.03-0.5 vs. 0.6-2.1) and higher Y/Sc (0.8-17 vs. 0.004-0.21) and Y/Zr (0.2-1.3 vs. 0.02-0.15) than does clinopyroxene in CTAs (Simon et al., 1999) or the mantle of TS-34 (Simon et al., 1991). We would not expect an exact match as the clinopyroxene must partition elements from the liquid and, as the trace elements are released from the perovskite, they diffuse at different rates in the melt. However, neither variable diffusion rates (faster for trivalent cations than for tetravalent cations) nor differences in apparent partition coefficients for clinopyroxene-liquid (Simon et al., 1991) seem likely to account for the differences in concentration ratios of elements between perovskite and mantle pyroxene. This suggests in the context of a perovskite dissolution model, that an additional now generally absent Sc-Zr-rich, Y-poor phase or phases was involved. Weber and Bischoff (1994; also Ma Chi, 2008, personal communication) described a mineral (approximately $Sc_4Zr_3O_{12}$) that has the right characteristics (high Sc and Zr with low Y). Such a phase would also be expected to have low REE contents, consistent with low enrichments of the REE in the mantle clinopyroxenes of TS-34 (Simon et al., 1991).

Thus, dissolution of perovskite, either rimmed by or intimately associated with a Sc-Zr-rich oxide could explain the observed chemistries of clinopyroxene surrounding perovskite in CTAs and of isolated clinopyroxenes in the mantles of type B1 inclusions.

There is mounting evidence that type B inclusions often experienced more than one melting event (Beckett and Stolper, 2000; Connolly et al., 2003; Ito et al., 2004; Lin and Kimura, 2000; MacPherson and Davis, 1993; Simon et al., 2005), and it is important to consider how this may have influenced boundary clinopyroxenes. Simon and Grossman (2006) showed that compositions of clinopyroxenes in the core and mantle of type B1 inclusions are distinctive**,** with clinopyroxenes in the mantle generally Mg-poor and often Ti-rich relative to those in the core. We noted above that compositions of boundary clinopyroxenes in Allende TS-34 and Leoville 3537-2 are consistent with those of coarse-grained clinopyroxenes from the same portion of the inclusion. This suggests first that boundary clinopyroxenes and spinel-free coarser clinopyroxenes from the mantle share a common origin. The same may be true for the core, but processes in the two venues differed. We suggested above that boundary clinopyroxenes in the mantle were derived from crystallization in the wake of dissolving perovskite grains. In the core, perovskite decorating spinels were generally destroyed before influencing the kinetics of pyroxene nucleation though spinel may still have provided a favorable nucleation site. Patchy zoned clinopyroxenes thought to represent multiple heating/cooling events are observed in some type B1 inclusions (Davis et al., 1998; Paque, 1990; although we note that complex zoning in pyroxene can be produced during simple single stage cooling as shown in Fig. 1a) and core clinopyroxenes frequently have resorbed textures (MacPherson et al., 1989), which is consistent with other lines of evidence for multiple melting events. These observations hint at complex thermal histories in which pyroxenes in the core were periodically exposed to temperatures high enough to cause partial resorption. Based on phase equilibria (Stolper, 1982), temperatures of 1250-1300°C would have been sufficient to provoke wide-scale partial melting in the core without strongly affecting the mantle. Any clinopyroxene not armored by aluminous melilite would have potentially been exposed to the melt and partially-to-completely dissolved. Mantle clinopyroxenes, which are included in refractory melilite grains, would not have been exposed to these new liquids during these events and would therefore have retained the signature of an earlier melting event.

There are both difference and similarities between boundary clinopyroxene and the large spinel-free clinopyroxenes in the mantle. Simon et al. (1991) report unusually high Åk melilite adjacent to a large mantle clinopyroxene grains in TS-34, and we observed a gradient of decreasing melilite Åk with distance away from one of the two large mantle clinopyroxene grains in our TS-34 section. In contrast, we found no high Åk melilite adjacent to boundary clinopyroxenes despite extensive search, and in the case of the FIB/STEM section for spinel grain Leo2, the lack of an anomalous composition gradient is observed on a 1-3 μm scale. Simon et al. (1991) interpreted a large mantle clinopyroxene in TS-34 as a relict grain surrounded by a melt inclusion (to explain the high Åk melilite adjacent to the mantle clinopyroxene). Our interpretation is only slightly different. We regard the large mantle clinopyroxene as forming from collections of relict perovskite ± spinel, not clinopyroxene. Moreover, we think that the Åk gradients with distance away from these large mantle clinopyroxenes are naturally produced as melilite crystallizes around a large clinopyroxene that is dissolving in the liquid. The same process was operative near the spinel-melilite boundary clinopyroxenes, possibly accounting for the small Åk gradients observed in our SEM/EPMA analyses or in FIB section B2-2 (Fig. 7).

CONCLUSIONS

We characterized the interfacial region between spinel and host melilite in type B1 inclusions from the Allende and Leoville carbonaceous chondrites using FIB/STEM techniques. Boundary clinopyroxenes, both blebs and rinds, are common in both inclusions studied**,** but the Leoville occurrences are more complex with glass veins, possibly hydrated, between the melilite and pyroxene or spinel. Calcite, perovskite, and an unknown phase may also be present.

The Leoville glasses have compositions consistent with a precursor phase assemblage containing an aluminous diopside and Mg-carpholite or sudoite, and inconsistent with residual melt compositions derived from fractional crystallization of melilite. We infer that the glass formed by shock melting of an alteration phase assemblage concentrated in the interface region between spinel and melilite. It is quite striking that in this study the evidence for alteration effects near spinel - melilite interfaces comes from the Leoville sample and not from the Allende FIB/STEM sections. This may be a matter of sampling in part, but it is clear that to regard Leoville, and presumably CAIs from other reduced CV3 meteorites, as completely unaltered is an oversimplification. It is just the style and extent of alteration that differs among the various CAIs.

Boundary clinopyroxenes did not crystallize from residual melt pools trapped in melilite as they lack anomalous melilite compositions near the interface and additional phases that might be expected for late-stage crystallization are not observed. Moreover, the compositions of boundary clinopyroxenes are similar to those of coarse-grained clinopyroxenes from the same region of the inclusion. The divergence of phase compositions in mantle versus core extends from spinel and melilite compositions to clinopyroxenes. In the mantle, clinopyroxene may have either crystallized in local Ti-enriched melts generated by direct perovskite dissolution with a preference for nucleation on spinels because perovskite often decorates the surface of these grains or formed as a reaction product between perovskite and melt (indirect dissolution of perovskite).

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FIGURE CAPTIONS

Fig. 1. Run product from dynamic crystallization experiment 98-53 (conducted in air, initially at 1500°C for 3 hours followed by cooling at 2°C/hr to 1167°C). (a) Back scatter electron photomicrograph of a spinel – clinopyroxene – glass inclusion in melilite. Scale bar is 20 μm. (b) Mole % åkermanite in melilite as a function of distance to an interface with melilite. The upper panel shows the regional pattern of zoning in the melilite in the general vicinity of the spinel inclusion. There is a slight (~2 mole %) decrease in Åk over a distance of 250 μm. The lower panel shows zoning in the immediate vicinity of the inclusion. There is a ~30 mole % increase in Åk in the 10 μm closest to the glass adjacent ot the spinel.

Fig. 2. Backscattered electron photomicrographs of examples of boundary clinopyroxene from Allende TS-34. (a) Clinopyroxene rind decorating a cluster of spinel crystals in the mantle. A larger scale view of this area is given in Fig. 4b (grain E2) of Paque et al. (2007a). (b) Clinopyroxene blebs on spinel in core melilite (grain B2 of Paque et al. (2007a)). Scale bars are shown at the base of each panel.

Fig. 3. Backscatter electron photomicrographs of spinels included in (a) core and (b) mantle melilite. Spinel grains decorated by boundary clinopyroxenes are indicated by black circles and those lacking boundary clinopyroxenes by white squares. Scale bars are 100 μm.

Fig. 4. Backscattered electron photomicrographs of spinels in host melilite from Leoville 3537-2. (a) Leo4; scale bar 10 μm. (b) Leo3; scale bar 10 μm. (c) Leo5; scale bar 20 μm. (d) Leo8; scale bar 10 μm.

Fig. 5. (a) Backscattered electron photomicrographs of Allende TS-34 mantle spinel grain A2, centered in the image, with an inset detailing the location of the FIB/STEM cross-section sample (after deposition of a protective Pt strap but prior to FIB trench milling). The bright object above spinel grain A2 in the main panel is an opaque

assemblage. Scale bar for the main panel is 100 μm. (b) SEM images of a FIB-thinned section of the interface between spinel and melilite for Allende TS-34 spinel grain A2 obtained in the FIB on a FIB section mounted on a TEM grid. The section is mounted on a TEM grid (right) by a ~1 μm thick layer of Pt and protected from ion implantation by a Pt layer (top). A nearly continuous layer of 0.2 - 0.8 μm thick clinopyroxene resides between the melilite and spinel. Toward the bottom of the section, a cluster of small pyroxene crystals lie on the melilite side of the boundary. Dark spots are voids. Scale bar is 5 μm. Abbreviations are sp (spinel), cpx (clinopyroxene), and mel (melilite).

Fig. 6. Mantle spinel grain E2. (a) Backscattered electron photomicrograph with traverses indicated and a corresponding EDS linescan. (b) Low magnification brightfield TEM image of interface region between spinel and melilite.

Fig. 7. Isolated (in the plane of the section; i-cpx) and boundary (b-cpx) clinopyroxene in FIB section B2-2 of core spinel grain “B2” from Allende TS-34. (a) Backscattered electron photomicrograph with traverses indicated. (b) EDS linescans across the isolated and a boundary clinopyroxene into adjacent melilite are also shown.

Fig. 8. Backscattered electron photomicrograph of spinel grain Leo2 from core melilite of Leoville 3537-2. The location of the FIB section is indicated by the double-headed arrow. Scale bar is 10 μm.

Fig. 9. Low magnification brightfield TEM image of the interface region between spinel and melilite in Leo2 from Leoville 3537-2. Melilite is separated from spinel by both clinopyroxene and glass. The elongated white regions in the glass vein are cracks. A crystalline phase lines the longest crack. Scale bar is 1 μm.

Fig. 10. High magnification brightfield TEM image of the interface between glass and unidentified crystal in spinel Leo2 from Leoville 3537-2 with electron diffraction patterns inset. The dense rim at the edge of the crack is caused by redeposition during ion milling. Scale bar is 5 nm.

Fig. 11. High magnification brightfield TEM image of interface region between glass and other phases around spinel Leo2 from Leoville 3537-2. (a) Glass-melilite interface with island melilite. Scale bar is 10 nm. (b) Interface between boundary clinopyroxene and unknown crystal. Scale bars are 10 (left panel) and 5 nm.

Fig. 12. Brightfield TEM image of the glass vein containing unidentified crystals and surrounding phases that border the core spinel Leo2 from Leoville 3537-2. Inset are oxygen K absorption edge electron energy loss spectra (EELS) from indicated regions containing a) spinel, b) clinopyroxene, c) the unidentified crystal phase plus some of the surrounding glass (approximately 30% by area) and d) glass in the vein. A pre-peak indicative of OH-groups in hydrated phases (Wirth, 1997) is visible about 8 eV below the main peak in the O edge of spectra for the unidentified crystal and glass (c, d) but not in clinopyroxene or spinel (a, b).

Fig. 13. Backscattered electron photomicrograph of mantle spinel Leo1 from Leoville 3537-2. The location of the FIB section is indicated by the arrowed line segment. Scale bar is 10 μm.

Fig. 14. Darkfield STEM image across calcite vein in melilite near Leoville 3537-2 spinel. The location of the TEM image is indicated by the circle on the electron image. Scale bar is 10 μm in the upper left image and 1 μm in the lower right.

Fig. 15. Darkfield STEM image of spinel-melilite interface region of Leoville 3537-2 spinel Leo2. Scale bar is 500 nm. Perovskite (pv). Other abbreviations as in the caption to Fig. 6.

Fig. 16. Composition relationships of glass veins in Leoville. (a) Projection of glass compositions from $MgAl_2O_4$ spinel onto the plane formed by the compositions of gehlenite ($Ca_2Al_2SiO_7$), anorthite ($CaAl_2Si_2O_8$) and forsterite (Mg_2SiO_4). Also shown are Al-rich glass compositions from the literature (El Goresy et al., 2002; Gray et al., 1973; Ireland et al., 1991; Kurat, 1975; Marvin et al., 1970; Reid et al., 1974), projected composition volumes for clinopyroxene (Cpx), melilite (Mel), and olivine (Ol), and

spinel-saturated multiply-saturated boundary curves after Stolper (1982). An arc is drawn through the projected glass compositions as a visual aid. Note that the black Leo 1 and Leo 2 squares enclosed in an ellipse in the upper right portion of the diagram are data points, not part of a legend. (b) Projection of Leoville glass compositions from $MgAl_2O_4$ spinel onto the plane formed by forsterite (Mg_2SiO_4), anorthite ($CaAl_2Si_2O_8$), and silica (SiO_2). Also shown is the spinel-saturated liquidus surface after Sheng (1992) contoured in wt. % spinel component with spinel-saturated liquidus phase fields for olivine (Ol), anorthite (An), corundum (Cor), mullite (Mull), cordierite (Cd), and sapphirine (Sap). Projected compositions of residual liquids produced on fractional crystallization of Leo1 and Leo2 glasses are shown in gray.

Figure 1a.

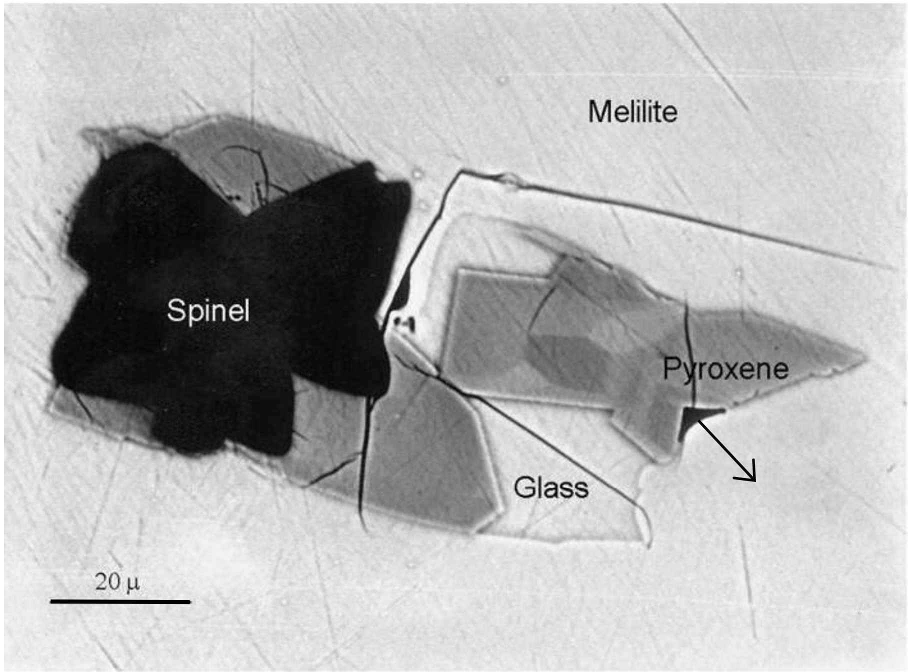
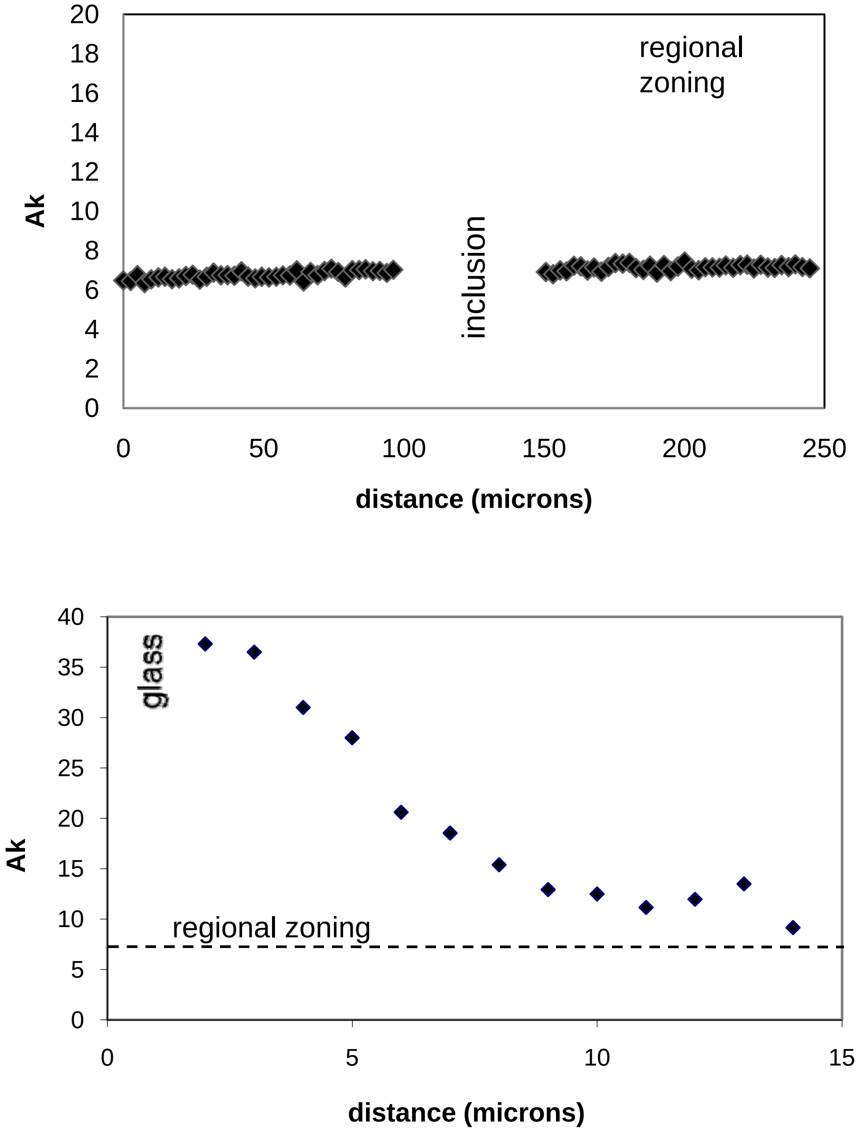


Figure 1b.



20
18
16
14
12
10
8
6
4
2
0
Ak
regional zoning
inclusion
0
50
100
150
200
250
distance (microns)
40
35
30
25
20
15
10
5
0
Ak
glass
regional zoning
0
5
10
15
distance (microns)

Figure 2.

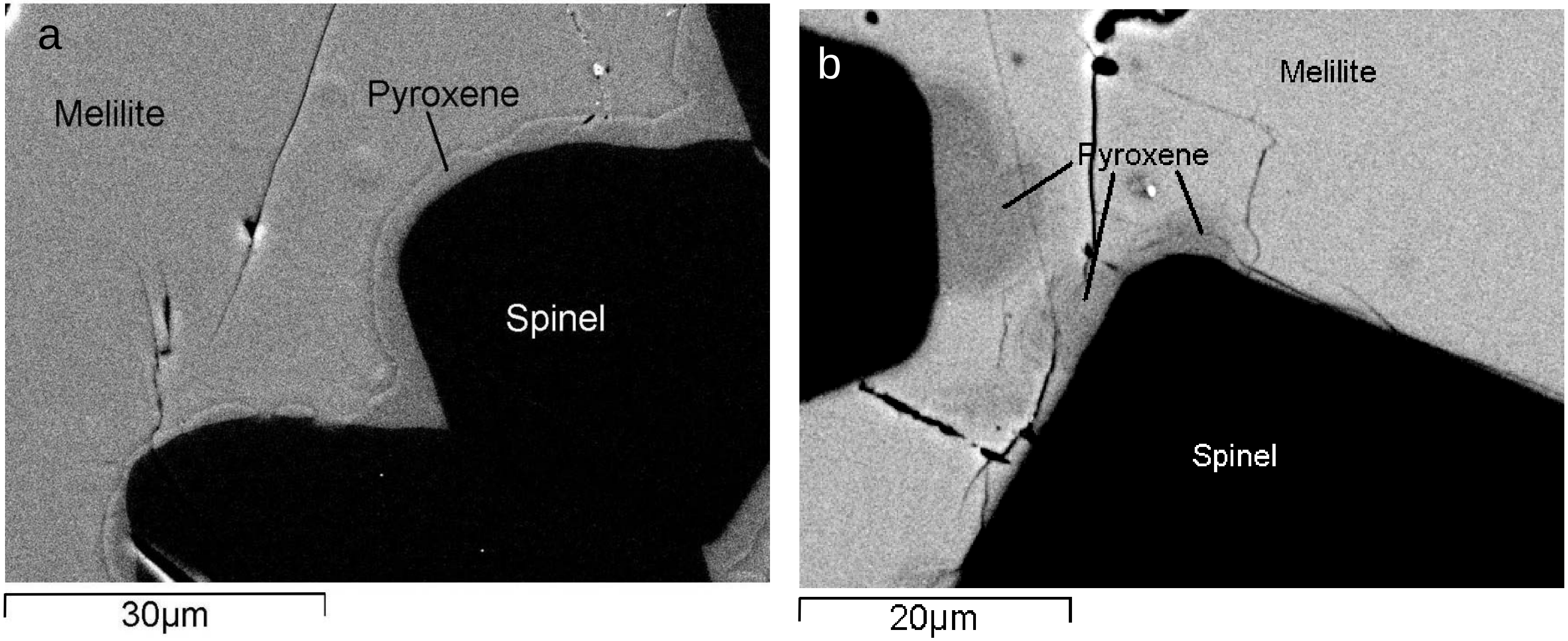

a
Melilite
Pyroxene
Spinel
30µm
b
Melilite
Pyroxene
Spinel
20µm

Figure 3.

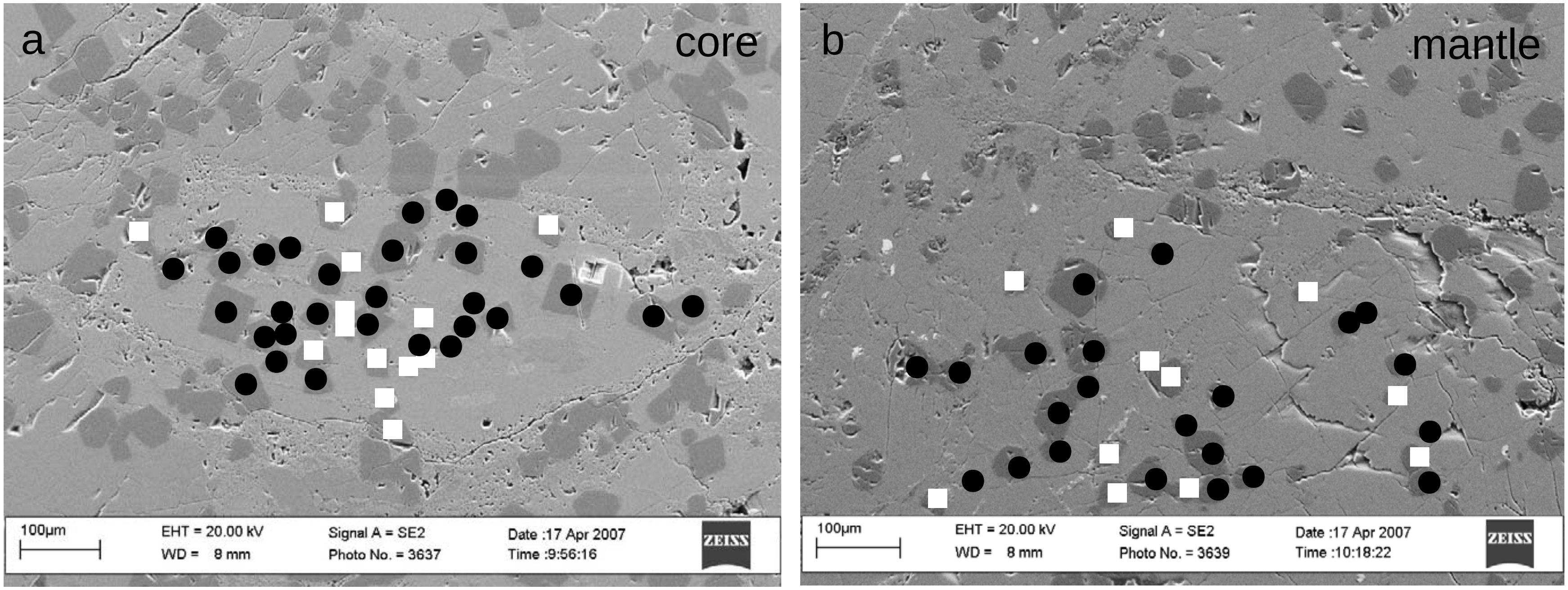
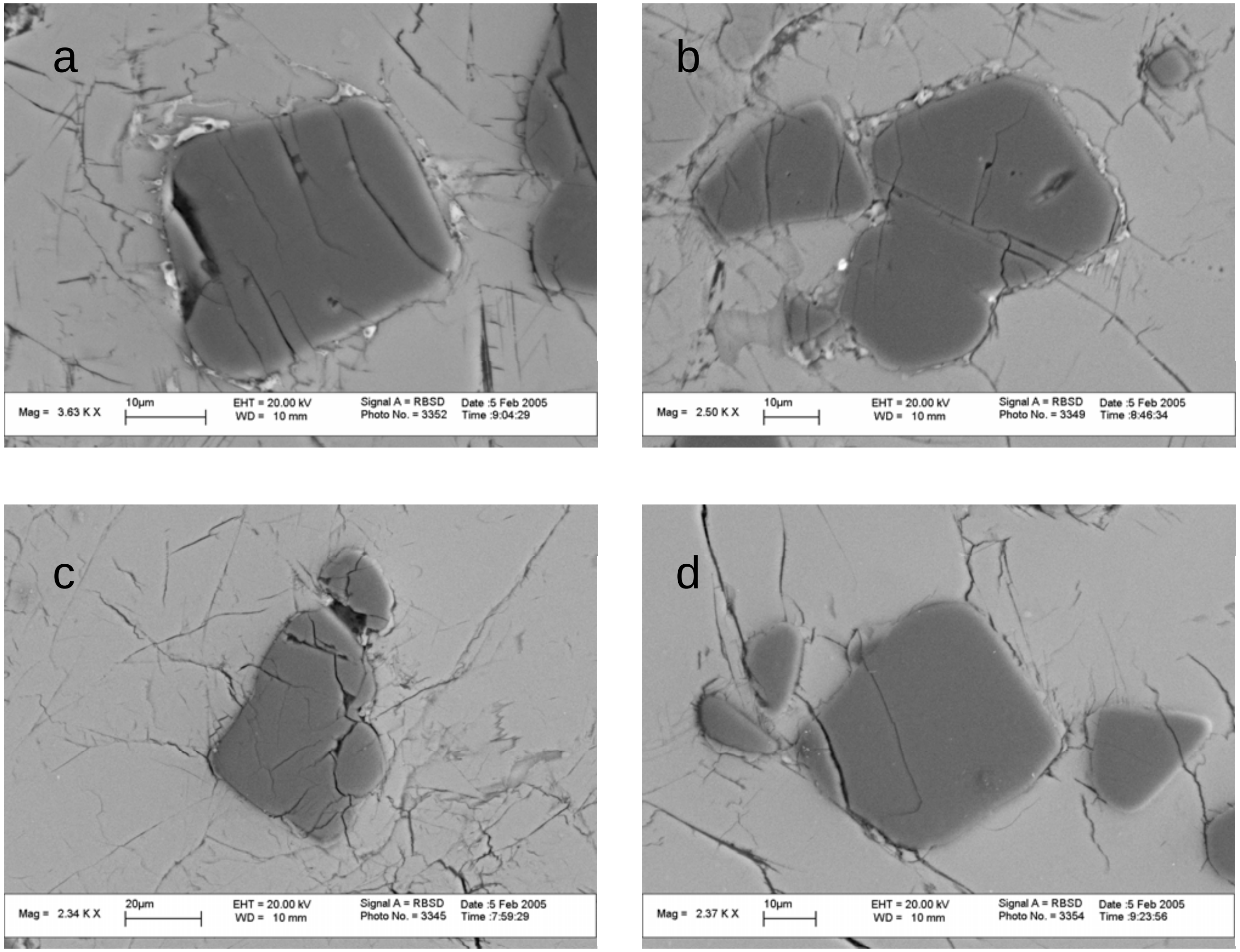

a
core
100µm
EHT = 20.00 kV
WD = 8 mm
Signal A = SE2
Photo No. = 3637
Date :17 Apr 2007
Time :9:56:16
b
mantle
100µm
EHT = 20.00 kV
WD = 8 mm
Signal A = SE2
Photo No. = 3639
Date :17 Apr 2007
Time :10:18:22

Figure 4.


a
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10µm
EHT = 20.00 kV
WD = 10 mm
Signal A = RBSD
Photo No. = 3352
Date :5 Feb 2005
Time :9:04:29
b
Mag = 2.50 K X
10µm
EHT = 20.00 kV
WD = 10 mm
Signal A = RBSD
Photo No. = 3349
Date :5 Feb 2005
Time :8:46:34
c
Mag = 2.34 K X
20µm
EHT = 20.00 kV
WD = 10 mm
Signal A = RBSD
Photo No. = 3345
Date :5 Feb 2005
Time :7:59:29
d
Mag = 2.37 K X
10µm
EHT = 20.00 kV
WD = 10 mm
Signal A = RBSD
Photo No. = 3354
Date :5 Feb 2005
Time :9:23:56

Figure 5a.

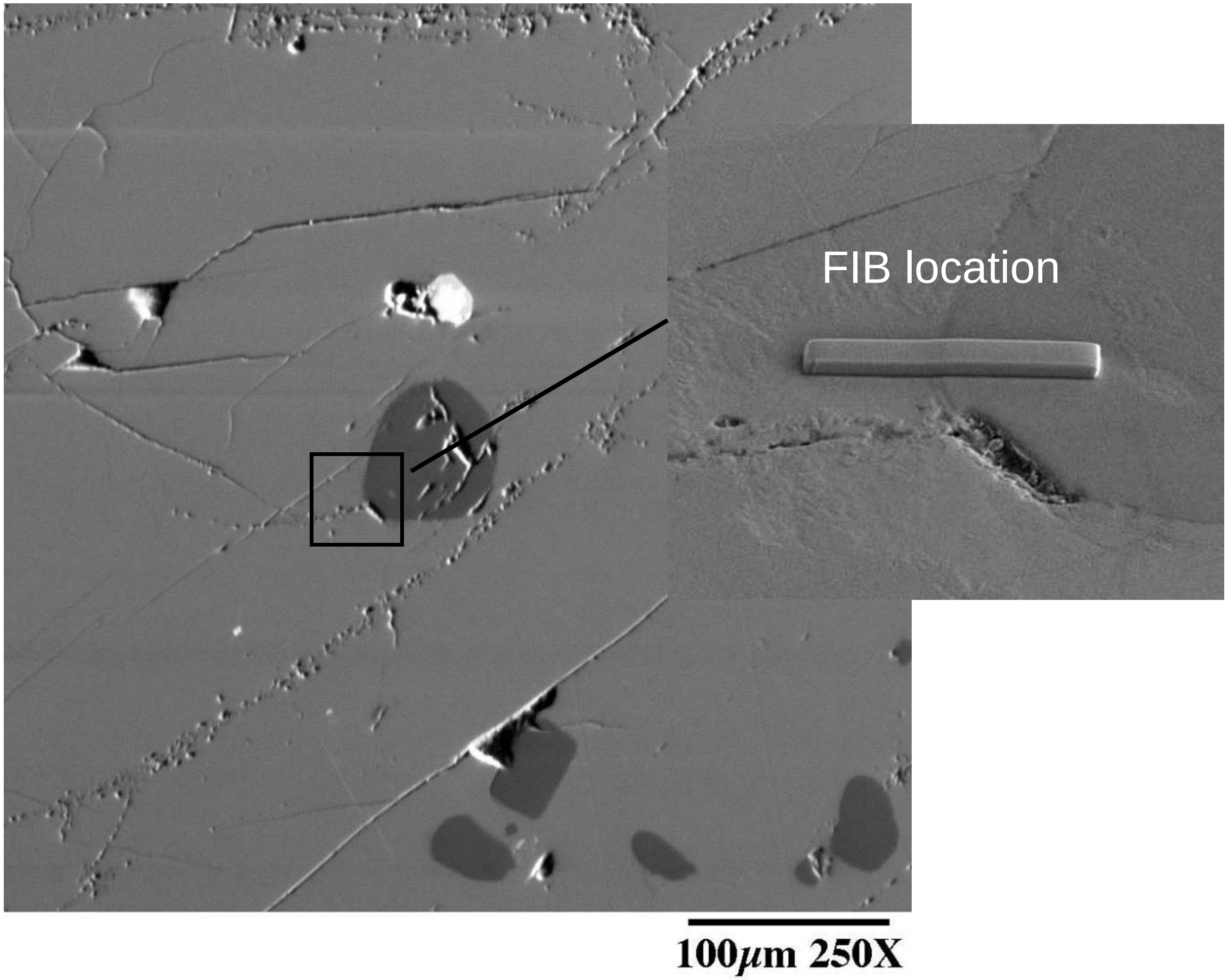


Figure 5b.

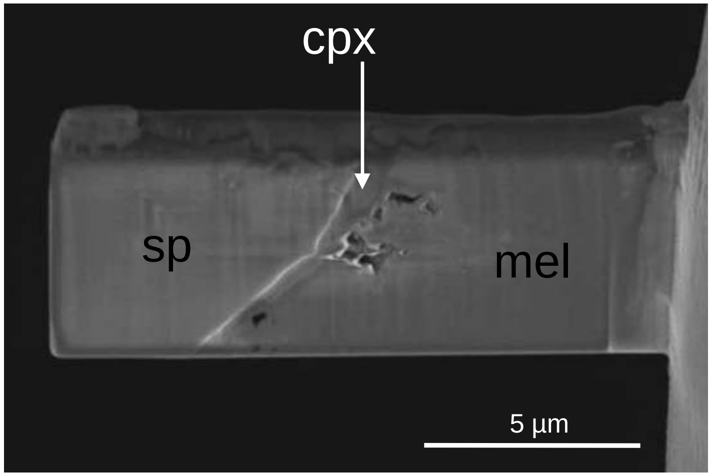


Figure 6a-1.

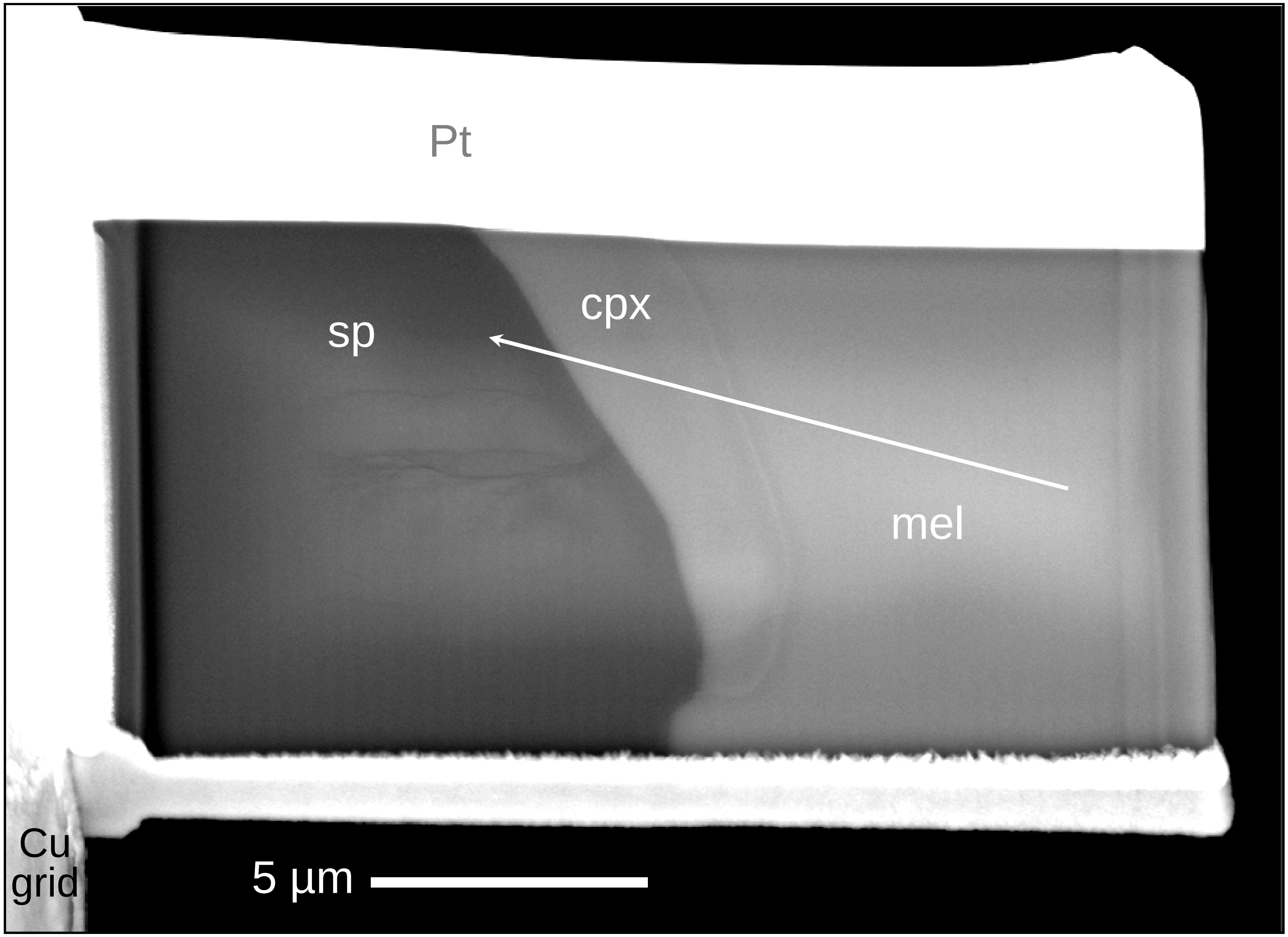
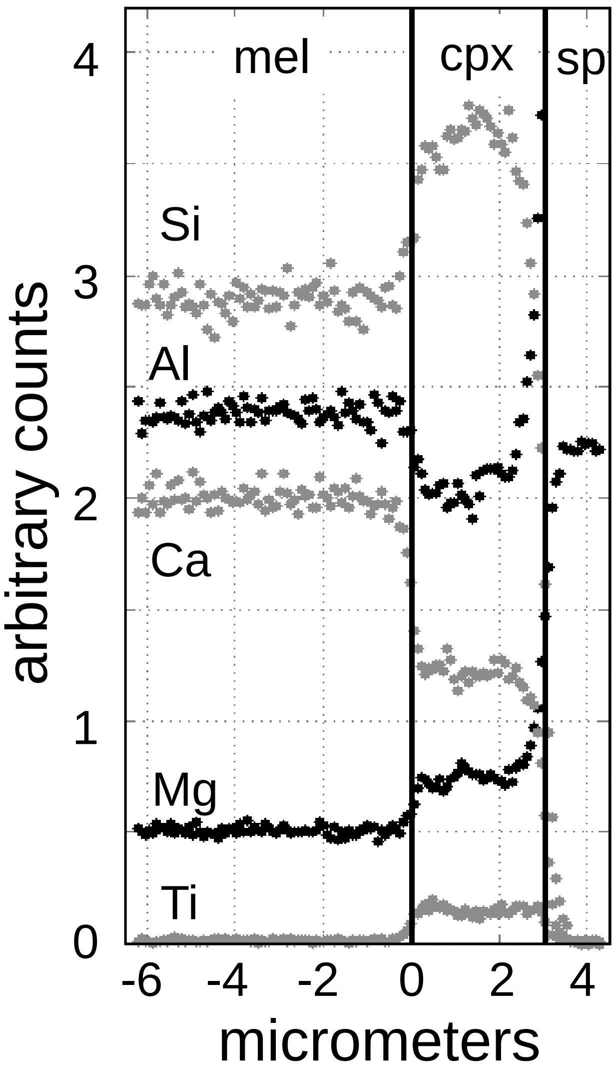
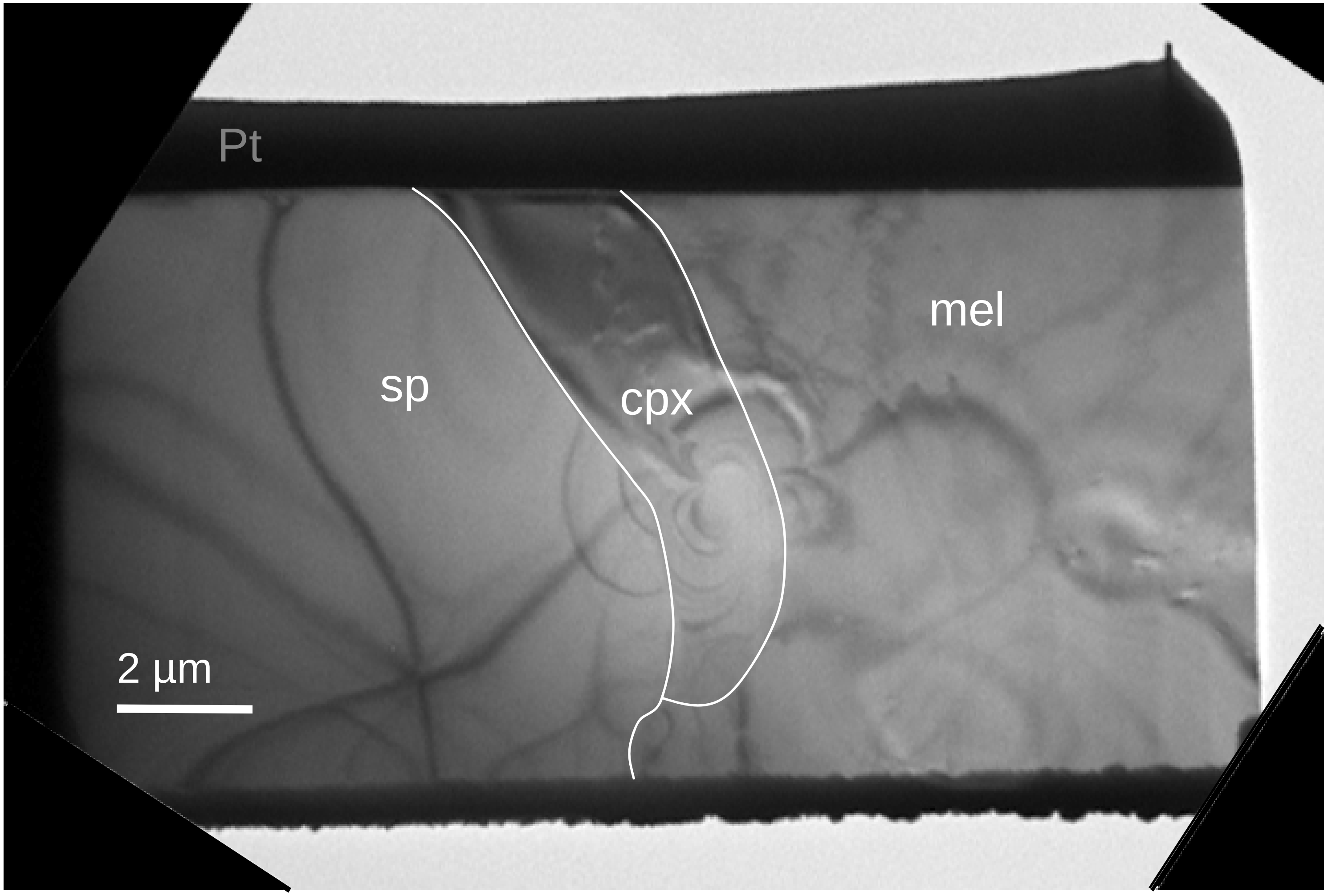


Figure 6a-2.



mel
cpx
sp
Si
Al
Ca
Mg
Ti
arbitrary counts
0
1
2
3
4
-6
-4
-2
0
2
4
micrometers

Figure 6b.



Note that the thinnest region at the center of the section is amorphized.

Figure 7a.

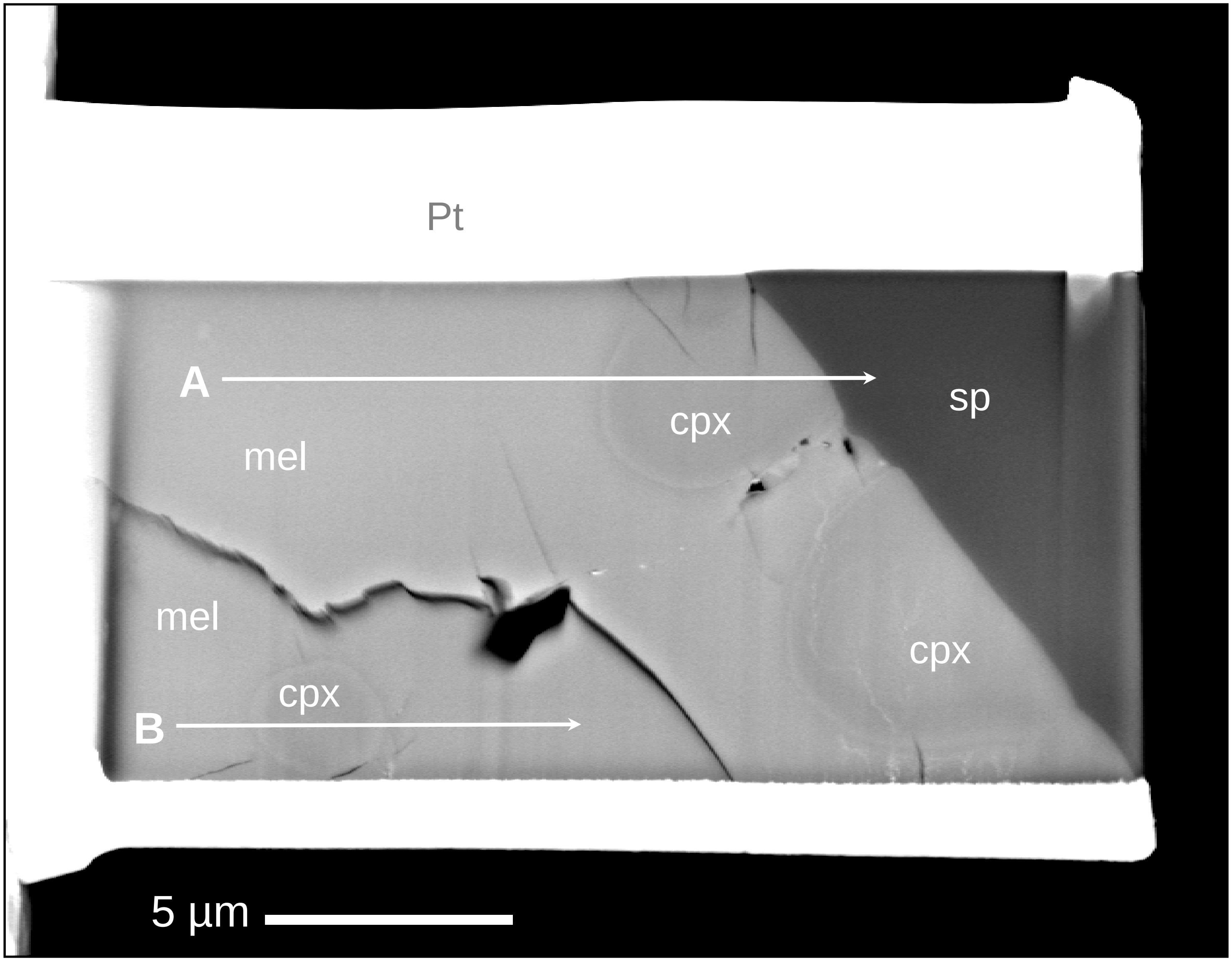
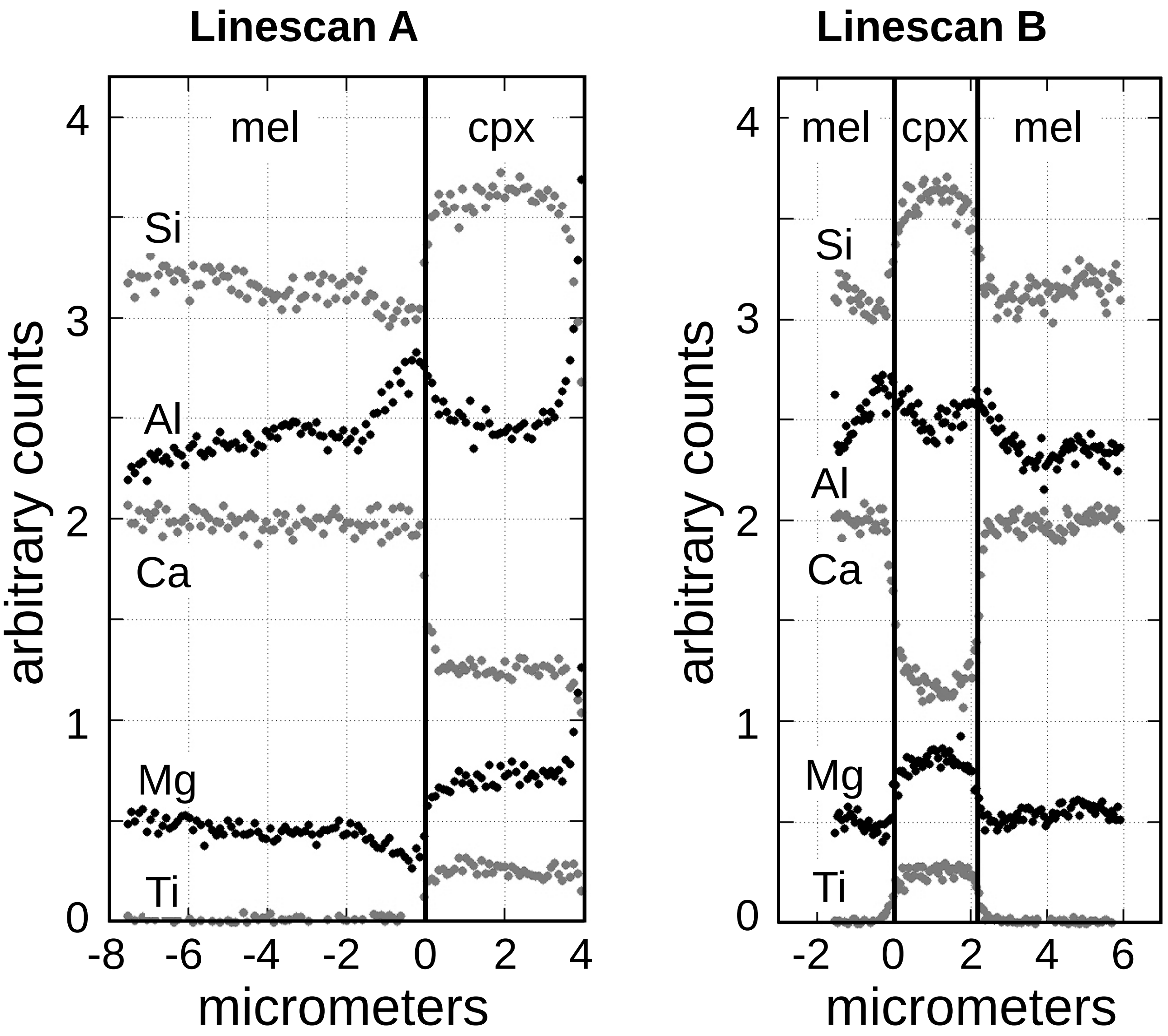
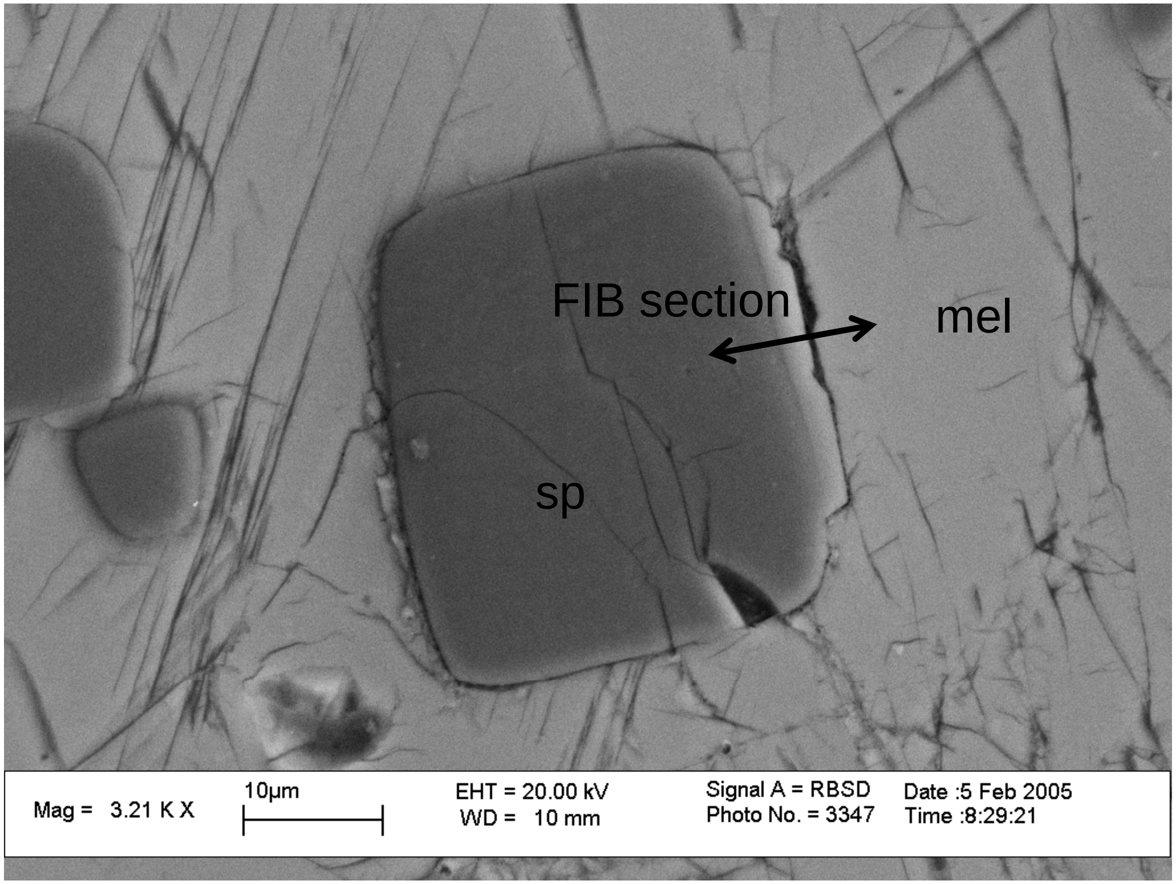


Figure 7b.



Linescan A
Linescan B
mel
cpx
mel
cpx
mel
Si
Al
Ca
Mg
Ti
Si
Al
Ca
Mg
Ti
arbitrary counts
arbitrary counts
0
1
2
3
4
-8
-6
-4
-2
0
2
4
-2
0
2
4
6
micrometers
micrometers

Figure 8.



FIB section
mel
sp
Mag = 3.21 K X
10µm
EHT = 20.00 kV
WD = 10 mm
Signal A = RBSD
Photo No. = 3347
Date :5 Feb 2005
Time :8:29:21

Figure 9.

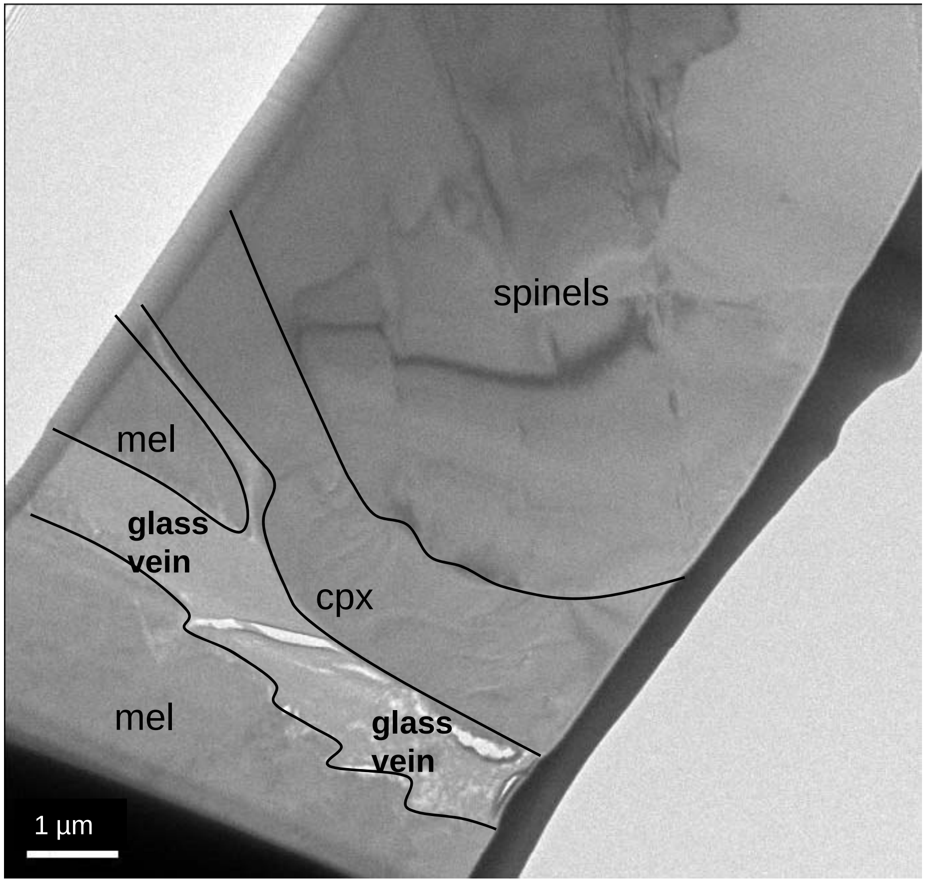


Figure 10.

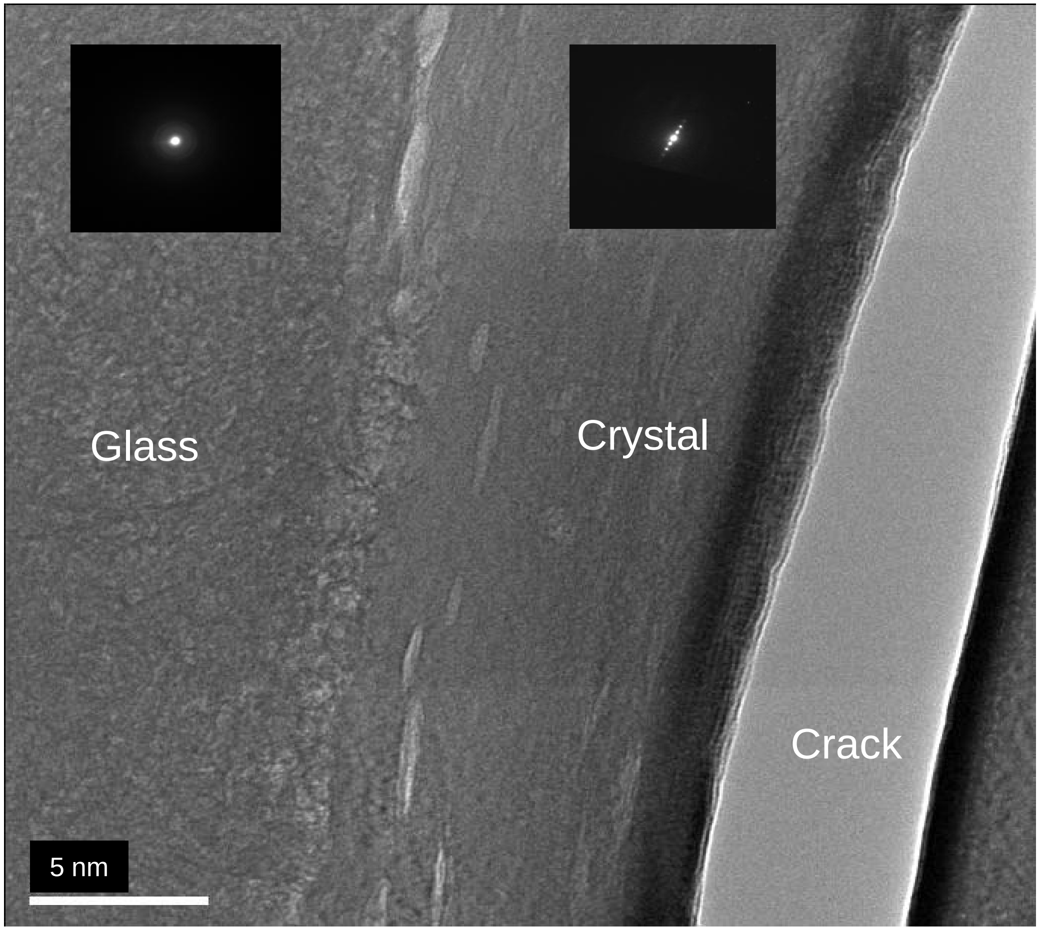


Figure 11.

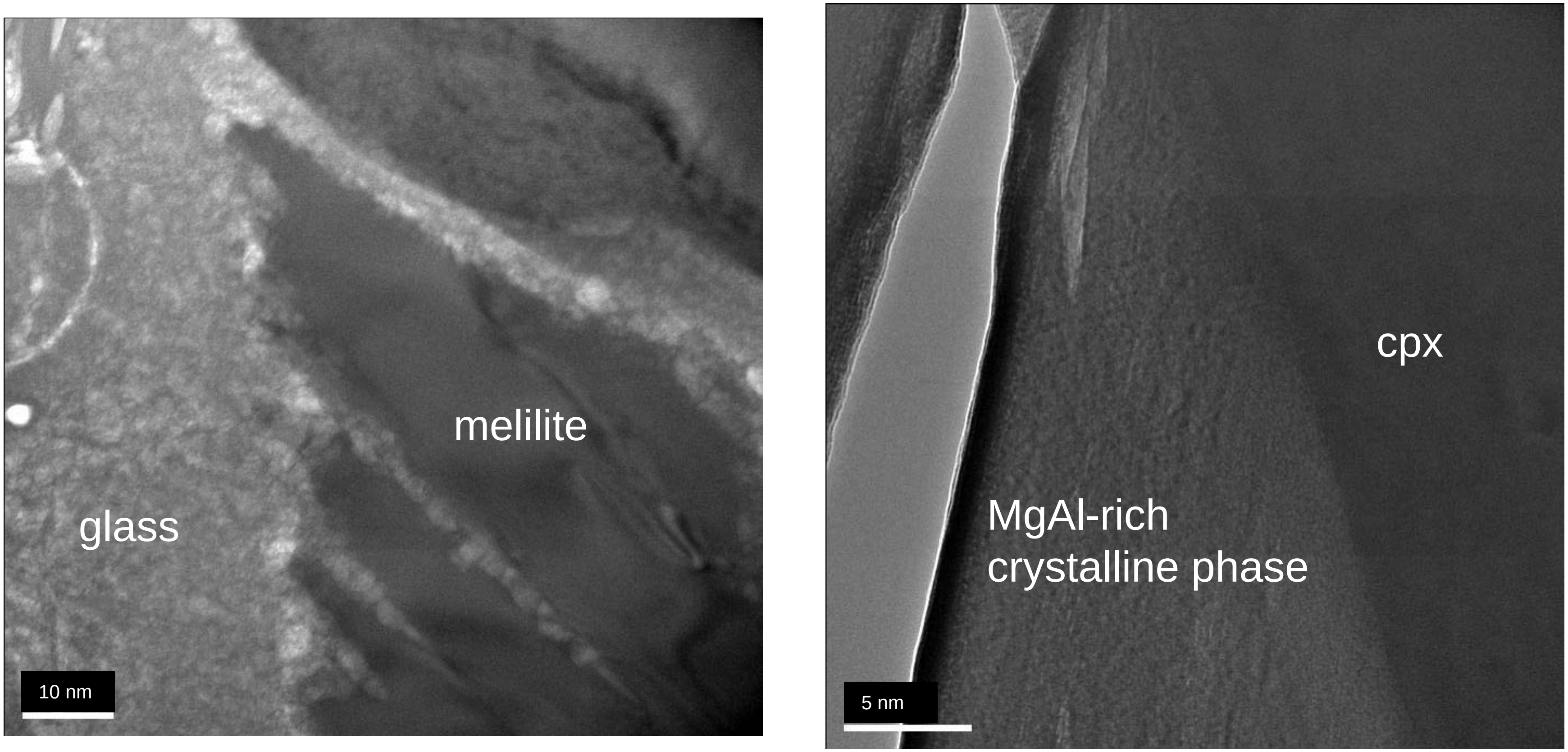
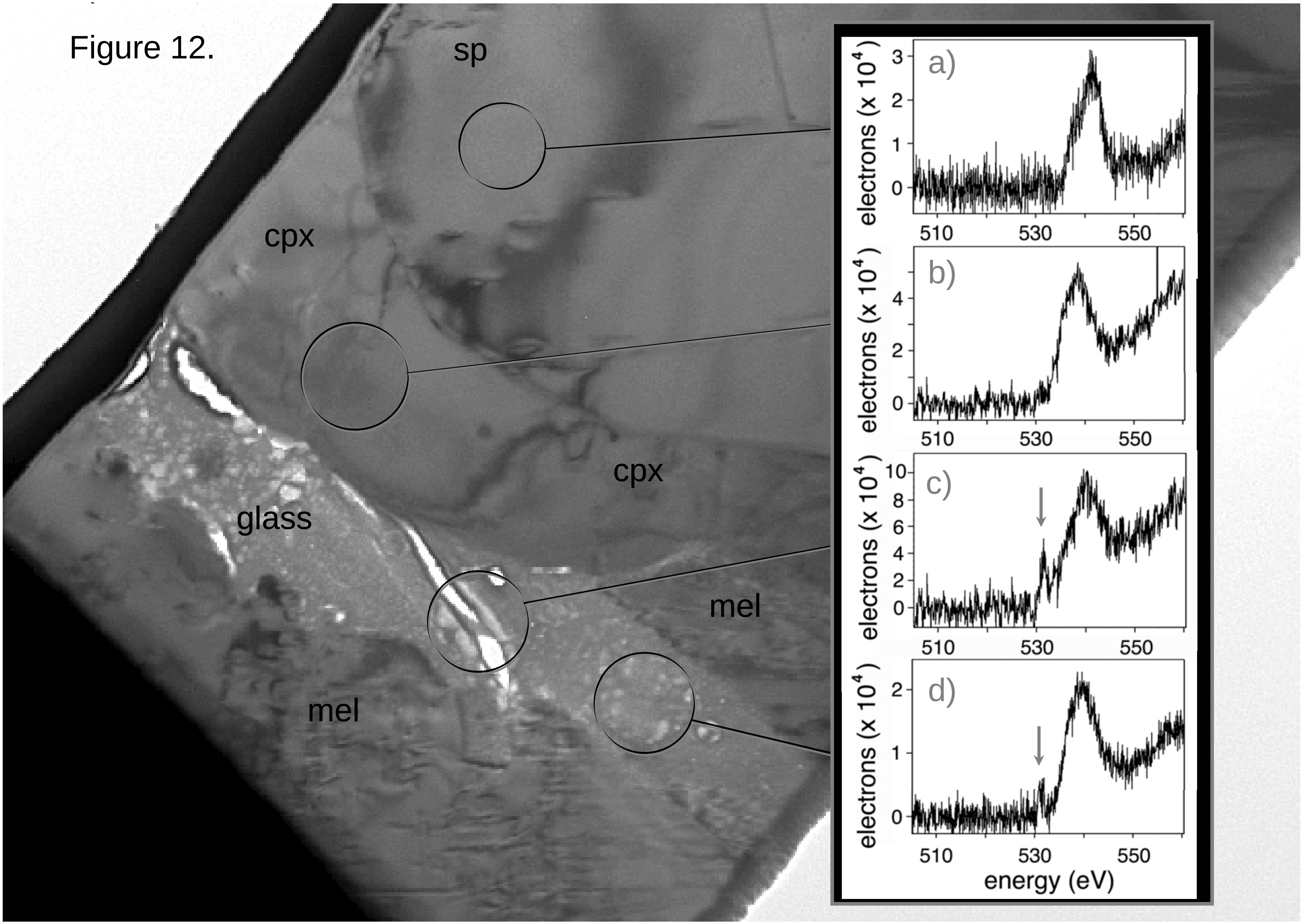


Figure 12.



sp
cpx
cpx
glass
mel
mel
a)
b)
c)
d)
electrons (x 10^4)
0
1
2
3
4
6
8
10
510
530
550
energy (eV)

Figure 13.

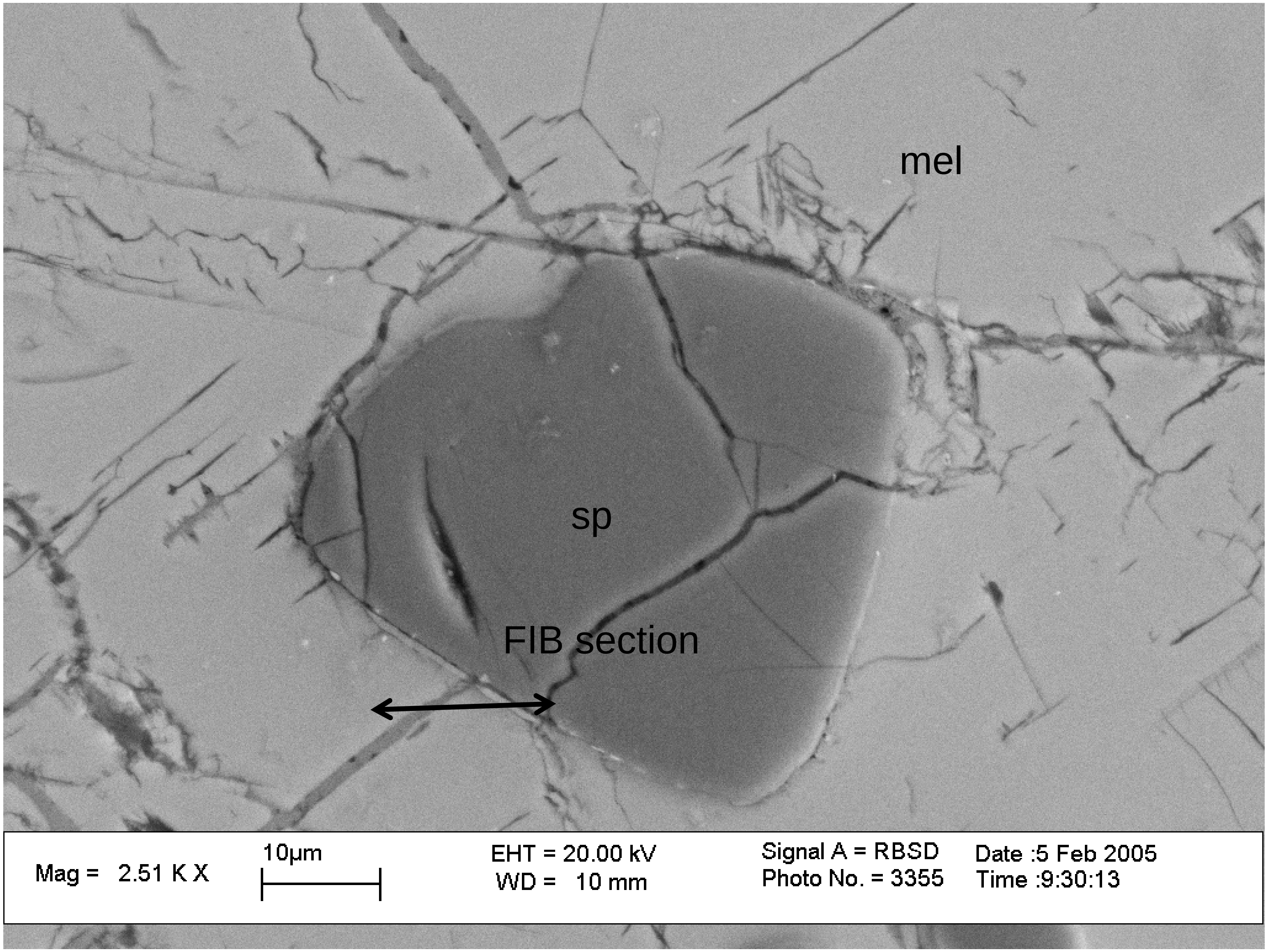

mel
sp
FIB section
Mag = 2.51 K X
10µm
EHT = 20.00 kV
WD = 10 mm
Signal A = RBSD
Photo No. = 3355
Date :5 Feb 2005
Time :9:30:13

Figure 14.

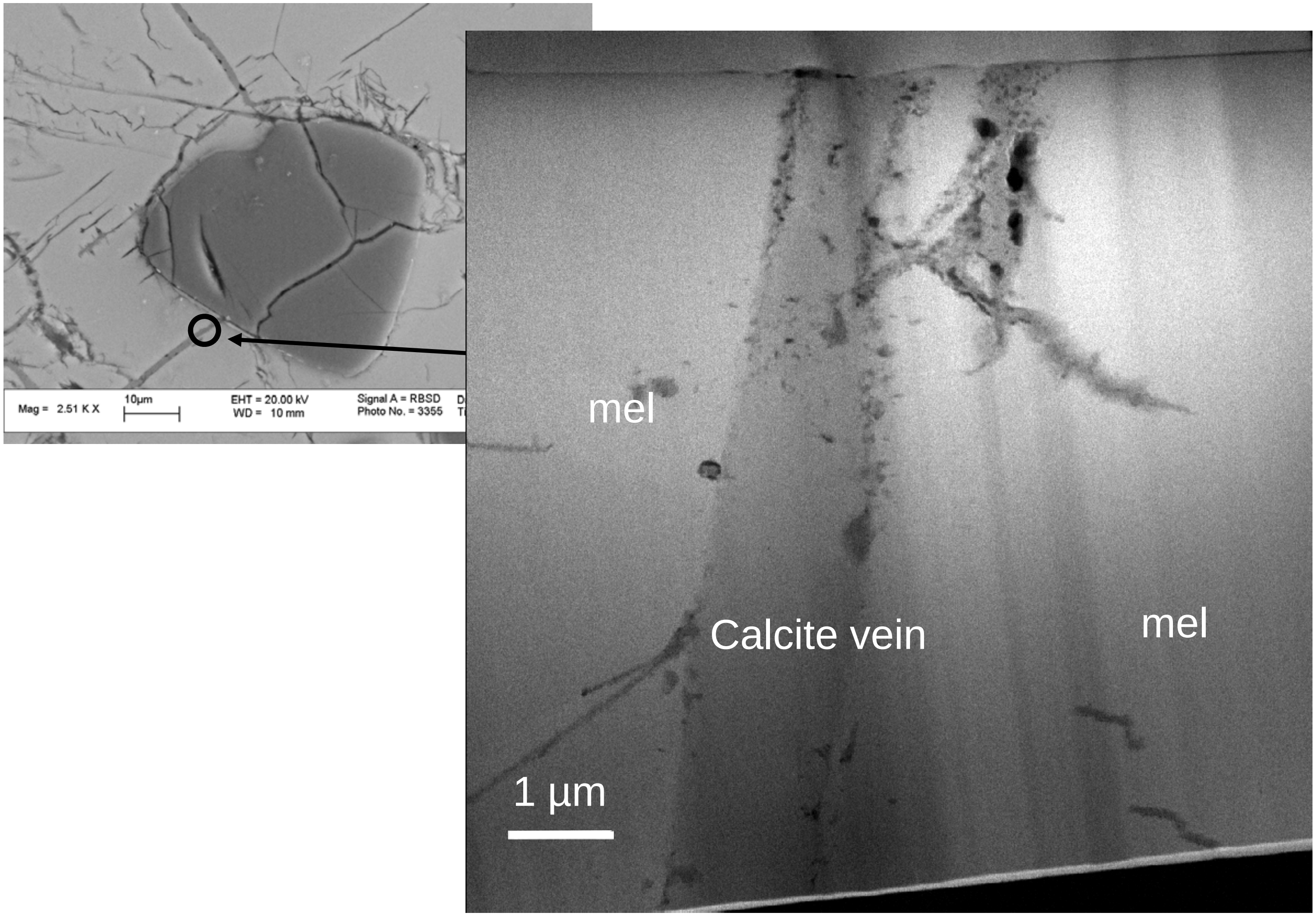

Mag = 2.51 K X
10μm
EHT = 20.00 kV
WD = 10 mm
Signal A = RBSD
Photo No. = 3355
mel
Calcite vein
mel
1 μm

Figure 15.

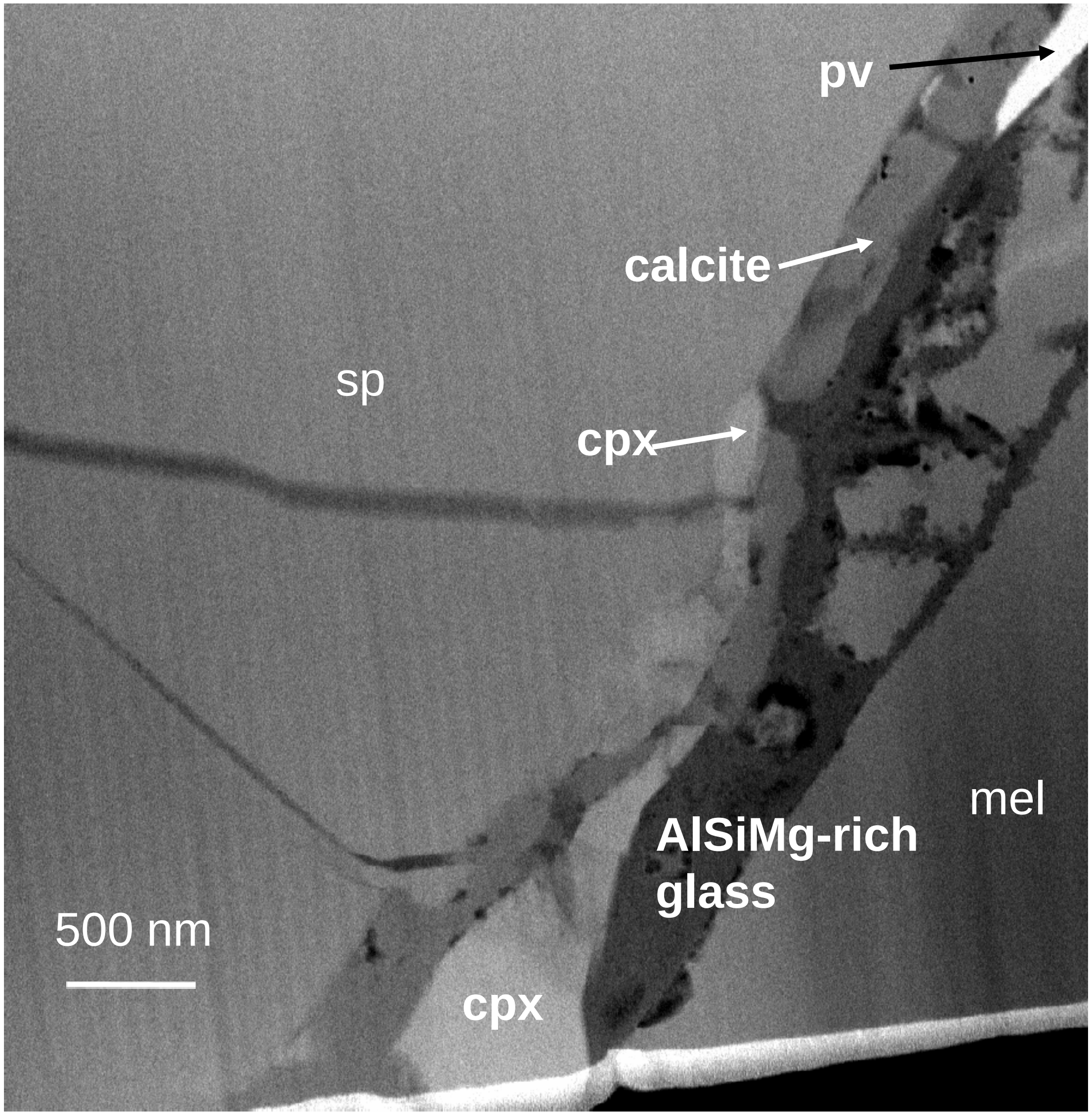
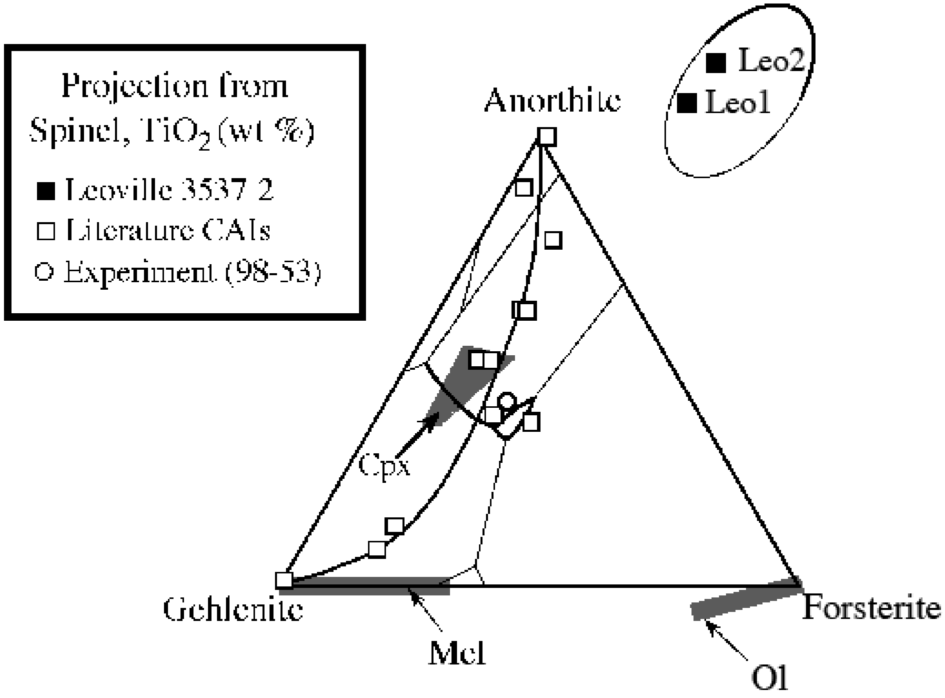
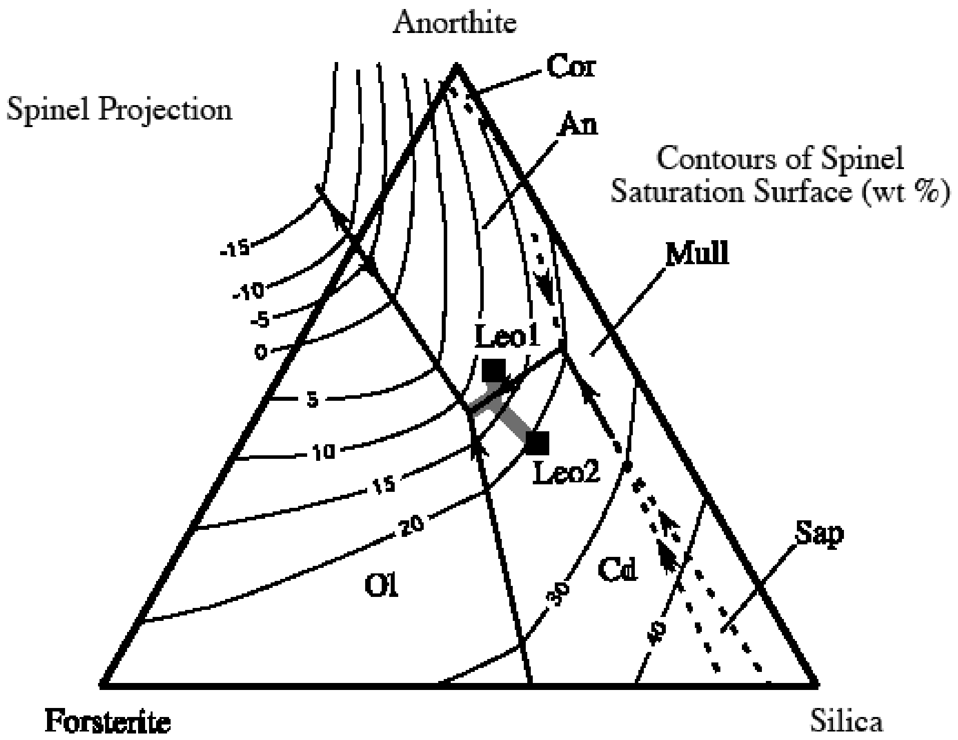


Figure 16a.



Projection from Spinel, TiO_2 (wt %)
■ Leoville 3537 2
□ Literature CAIs
○ Experiment (98-53)
Leo2
Leo1
Anorthite
Cpx
Gehlenite
Mel
Forsterite
Ol

Figure 16b.


Anorthite
Cor
Spinel Projection
An
Contours of Spinel Saturation Surface (wt %)
Mull
-15
-10
-5
0
5
10
15
20
30
40
Leo1
Leo2
Sap
Cd
Ol
Forsterite
Silica