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Further Observations Related To A Possible Occurrence Of Terrestrial Ahrensite

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Abstract: Clusters of aligned, highly elongate, prismatic quartz (Qtz) rods occur in a few fayalite (Fa) crystals in a eulysite from a recently identified ~1.8 Gy UHP site in central West Greenland (Glassley et al., 2014). Additional detailed analyses of the crystallography and phase compositions of these olivines were conducted to evaluate the postulate that the Qtz rods formed during inversion of super-silicic ahrensite to Fa+Qtz during decompression. These new observations show the Qtz rods consistently occur in crystallographically coherent clusters with the Qtz grains aligned parallel to [100] of Fa. The contrasting compositions of co-existing primary UHP Fa and Fa postulated to have formed by inversion of ahrensite are consistent with the inversion scenario. We thus conclude that all available data are consistent with the postulate that ahrensite was part of the equilibrium phase assemblage formed during UHP metamorphism and that it inverted

to Fa+Qtz upon decompression. If true, this would represent the first occurrence of terrestrial ahrensite formed through natural tectonic processes.

Introduction

In an earlier paper documenting evidence for a new UHP regime (ca. 6-8 GPa at ~1,000^{o}C; ~1.8 Gy) in central West Greenland (Glassley et al., 2014), we reported the occasional occurrence of quartz "lamellae" (for reasons noted below, we will henceforth refer to these as rods) in fayalitic olivines (Fa) in our sample 123220, an Fe-Mn-rich olivine-pyroxene-quartz-garnet metasediment (eulysite). Because the rods are prismatic, clustered in parallel arrays and have a uniform morphology reminiscent of exsolution features, we postulated they formed as a result of exsolution from the host Fa. Super-silicic Fa has not been reported in the literature, but excess silica has been reported for spinel-structured olivines (i.e., the wadsleyite-ringwoodite series) from experimental studies (Akaogi and Akimoto, 1979; Irifune and Ringwood, 1987; Hazen et al., 1993). Theoretically, therefore, spinel-structured, super-silicic olivine could exsolve silica upon decompression and inversion to olivine. On the basis of these experimental results we therefore postulated that the Qtz rods formed in response to inversion of high-pressure super-silicic ahrensite (Fe-rich ringwoodite) to Fa during decompression, the reaction being

$$(Fe_2SiO_4 + (Fe_2SiO_4 + \square SiFe_{-2})) \Leftrightarrow Fe_2SiO_4 + 2\ SiO_2.$$

(ahrensite) (Fa) (Qtz)

where excess Si in the ahrensite is accommodated via a vacancy substitution mechanism in which □$SiFe_{-2}$ (Day and Mulcahy 2007) occurs. If correct, sample 123220 contains the first known occurrence in which ahrensite resulted from tectonic processes on earth, rather than shock-induced transformations related to meteorite impacts (Xie et al., 2002; Feng et al., 2011; Ma et al., 2014, 2016) or anthropogenic activity (Diaz-Martinez and Ormō, 2003).

To further document the characteristics of this unusual phase relationship, we report here the results of additional optical and chemical analyses of this sample. This research involved a grain-by-grain examination of every olivine crystal in a thin section of sample 123220, and further comparison of the observed olivine compositions with published experimental data of olivine (α-phase) and Fe-ringwoodite (i.e., ahrensite; γ-phase).

Assumptions

If the Qtz rods formed as a result of exsolution, a systematic relationship would be observed in thin section in which: 1) the crystallographic orientation of the host Fa and the elongation direction of the rods is consistent; 2) the crystallographic orientation of the Fa host and the enclosed Qtz rods is consistent (which also requires that all of the rods in a given host have the same crystallographic orientation); and 3) all of the rods occur along a low-energy interface such as a primary crystallographic axis. Assuming that the rods are aligned parallel to one of the principal Fa crystallographic axes, the maximum elongation of the Qtz rods would be observed when the crystallographic axis of interest lay in the plane of the thin section. When that same crystallographic axis is oriented perpendicular to the plane of the thin section, the rods would be seen in cross section and exhibit minimum dimensions. In any other orientation, the maximum rod length would be some intermediate value, the absolute magnitude of which would depend upon the angle between the axis of interest and the plane of the thin section. Hence, if the rods result from exsolution, a sufficiently large number of measurements would exhibit a correlation between measured rod lengths and the Fa crystallographic orientations. In addition, all Qtz rods in a given host crystal, and the host crystal itself, would go to extinction at the same time.

The advantage of this optical petrography approach is that the abundance, grain geometry (size and shape) of the original ahrensite, and the rod morphology can all be established with a single observational technique. A limitation, however, is that the thin section slice is a random 30 μ slab through crystals that, in this instance, have much longer observed lengths. Hence, measurements of rod lengths are most likely to provide minimum values.

Optical Observations

Every olivine grain in a thin section of 123220 was surveyed for the presence of quartz rods using a polarizing microscope. For each Fa grain that contained such clusters, the optical orientation of the olivine was established, and the optical retardation (i.e., the wavelength difference between the fast and slow rays) were estimated. The maximum rod lengths were measured using a calibrated graticule.

Out of several hundred Fa grains examined, seventeen were identified that contained clusters of Qtz rods. In each cluster, every rod is exactly parallel with others within the host Fa, and each rod consists of a single Qtz crystal (Fig. 1). The clusters consistently have dimensions of ~ 0.1 mm perpendicular to the rod elongation direction, and ~0.3 – 0.4 mm parallel to the rod elongation direction. The maximum rod length that is measured is ~180 μ (Fig. 2), which is observed when either the (001) or (010) planes are parallel to the microscope stage. The minimum elongation of ~15 μ is observed at a retardation value very close to that for a crystal viewed along the x-axis (i.e., in the [100] direction). All Qtz rods in a given cluster go to extinction at the same stage rotation position, which is also the same extinction position as the host Fa (Fig. 1E, F). Where it is possible to determine cross sectional morphology of the rods (e.g., Fig. 1D), they are consistently 4-sided rhombohedra, suggesting crystallographic control imposed by the host Fa.

The maximum measured rod length for a given inclination angle relative to the plane of the thin section can be computed from $l_i = l \times \text{sine}(ø)$ where l_i is the observed length, l is the actual length and ø is the angle of inclination. Plotted in Figure 2 are the envelopes for what would be the observed rod lengths if the actual lengths were either 200μ or 500μ, assuming the rods were parallel to the x-axis. All of the data points fall within the 500μ envelope (within analytical uncertainty). These observations require that the Qtz rods are aligned parallel to the [100] direction in all occurrences, with maximum lengths of less than 500μ.

Exsolved magnetite (Mag) rods were observed in close proximity to Qtz rods in one Fa host (Fig. 1A). Given that Mag exsolution occurs in the [010] direction (Zhang et al., 1999; Franz and Wirth, 2000) and that the observed Mag rods are perpendicular to the coexisting Qtz rods in a host with modest birefringence, this observation is consistent with the inference above that the Qtz rods are aligned parallel to the [100] direction. This alignment is also consistent with the Qtz rods occurring along low energy planes in Fa, which exhibits parting along {010} and {100}.

A Leitz four-axis universal stage was also used to obtain orientation data for three clusters of rods in grains that were suitably located in the thin section to allow end-on observations of the rods. In this case, the stage was used to orient the thin section such that the maximum retardation could be estimated when the rods were vertically oriented. In each case, maximum retardation values of ~1230 nm (+/- 50 nm) were obtained, which is consistent with rod orientations parallel to [100].

These results show that the rods are highly elongate prismatic forms, with a maximum length of <500μ. The rods are consistently parallel to the Fa x-axis (i.e., the [100] direction). All of the Qtz rods in a given cluster have identical crystallographic orientations and are single crystals. Each cluster occurs in a domain that is ca. 0.1 mm across and ca. 0.3-0.4 mm long. These observations support the suggestion that the Qtz rods are exsolution features.

Olivine Compositions

Experimental data for the Fe- and Mn-rich portion of the MgO-FeO-MnO-SiO_2 system that would be relevant for the compositions of minerals in this rock are not available. However, Akaogi et. al. (1989) examined phase relationships in the entire compositional range in the MgO-FeO-SiO_2 system under conditions relevant for this sample. Their experiments indicate that α and γ phases would have coexisted during the peak UHP conditions this sample experienced. According to their results, the fayalitic α phase would have a slightly higher Mg content than the γ phase with which it coexisted. If it is postulated that during ahrensite inversion to Fa the Fe:Mg:Mn mole proportions were preserved, the Fa in proximity to the Qtz rods would be expected to possess a lower Mg content than olivines preserved from the UHP conditions.

Three distinct occurrences of olivine can be identified in this sample. Matrix Fa is common, making up ~35% of the rock volume. Olivine is also observed in pigeonite (Pgt) grains in bands and multiphase inclusions composed of Fa + Qtz with minor Cpx, always with the same relative volumetric proportions. We interpret the consistent phase volume proportions (Fa ≅ Qtz > Cpx) and the occasional idiomorphic form of the inclusions to indicate that these are the breakdown products of orthoferrosilite (Fs). Finally, a few olivine inclusions occur in the diamond-bearing mantles of garnets. Because these olivine inclusions occur in the garnet that is inferred to preserve evidence of the UHP conditions (Glassley et al., 2014), it is these olivines that would have coexisted with the γ phase. The compositions for the olivines included in garnets, as well as the compositions of olivines in the other environments were obtained through electron microprobe (EMP) analysis and are shown in Figure 3.

The binary phase loop derived by Akaogi et al (1989), for coexisting α and γ phases at the conditions inferred for this sample should differ by ~2 mole % Fo (the α phase being richer in Fo). The double- headed arrow in Fig. 3 indicates this compositional range. The Fa inclusions in garnet, which would correspond to the α phase, are consistently the most Fo-rich of all olivines observed in this rock (Fig. 3) and are nearly 2 mole % richer in Fo than the Fa adjacent to the Qtz rods (postulated to be derived from the γ phase). These compositional characteristics are therefore consistent with that predicted from the experimental data. However, the high Mn_2SiO_4 (tephroite [Tep]) content makes this comparison with the experimental data somewhat equivocal, given the fact that Mn often contributes notable non-ideality to mixing models. Even so, the striking correspondence between experimental data and observations lends support to our suggestion that the Qtz-rod – bearing olivines in this sample preserve evidence of a precursory ahrensite phase.

In summary, Qtz rods aligned parallel to [100] exhibit optical properties consistent with an exsolution origin, i.e., coherent crystallographic alignment within host Fa and with other rods in a given cluster, and occurrence along a low energy plane. The rods have width dimensions of 1-5μ and likely maximum lengths of <500μ, which gives them an aspect ratio of ~100 to 1. The rod clusters define domains of approximately 0.1 x 0.3-0.4 mm, which would have been the minimum grain size for the γ phase. The Fo : (Fa + Tep) ratios for Fa inclusions in garnets (remnants from the UHP phase of metamorphism) and the Fa in proximity to Qtz rods are consistent with that expected for coexisting Fa and ahrensite, based on experimental data.

These results provide tentative support for the hypothesis that UHP metamorphism of this sample resulted in the development of coexisting α and γ $(Fe,Mn)_2SiO_4$ phases (the latter being somewhat supersilicic). Following peak metamorphic conditions, ascent to shallower levels led to inversion of the γ phase to Fa, accompanied by exsolution of excess SiO_2. The precise conditions at which inversion and exsolution occurred are difficult to establish, however, because of the unusually high Mn content of these phases, for which appropriate experimental data and thermodynamic properties are lacking.

Implications

These results imply that other occurrences of inverted γ phase are likely to be present in UHP regimes in which iron- and manganese-rich lithologies occur. Finding such occurrences would allow more thorough characterization of subduction systems and processes, as well as providing concrete observational data useful for constraining mantle mineralogy. Additionally, the absence of adequate experimental data for the Fe-Mg-Mn-SiO_2 to characterize UHP mineral assemblages points to the need for an experimental program that would address this deficiency.

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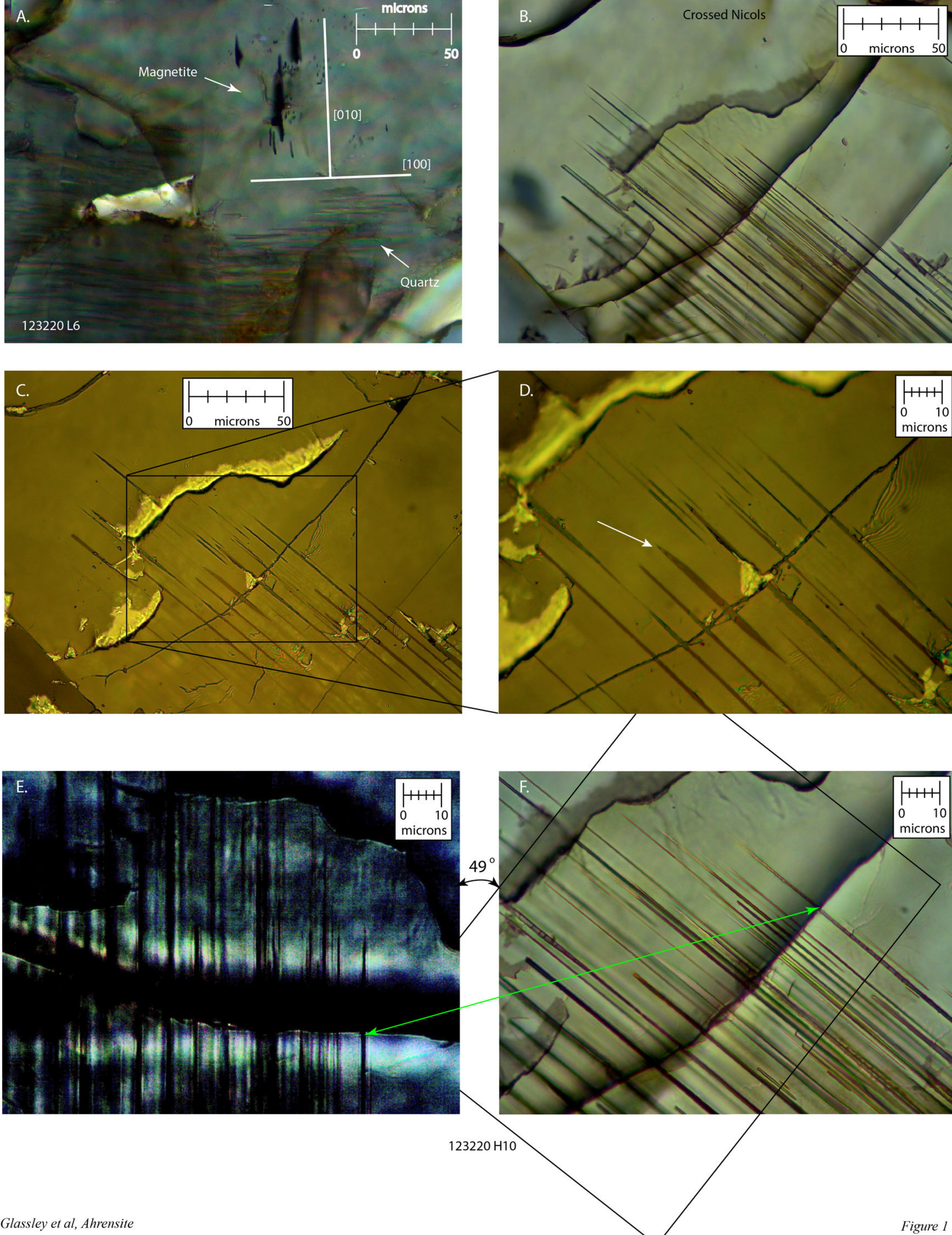
Figure Captions

Figure 1. Two examples of Qtz lamellae in Fa. A. Cross-nicols view of Mag exsolution and Qtz rods (both indicated by arrows) in Fa (area L6). The orientation of the (010) and (100) planes is shown. B-F. Transmitted (B., E. and F.) and reflected (C. and D.) light images of area H10 at different magnifications. Qtz rods are the parallel dark lineations. The arrow in D. indicates an obvious prismatic form of a Qtz rod very slightly inclined to the plane of the thin section. E. shows the Fa crystal at extinction (shadow enhanced) with the Qtz rods also uniformly at extinction. Note the slight strain in the Fa crystal, which accounts for the very slight, irregular birefringence. F. shows the area in E. (boxed region), rotated to show maximum birefringence. The green arrow points to the same location on one of the Qtz rods, for reference.

Figure 2. Graph of maximum measured rod length (in microns) vs estimated optical retardation (in nanometers). The vertical bars indicate the optical retardation that would be expected for Fa when viewed along the indicated directions. The dashed lines are calculated envelopes of rod lengths that would be observed for rods inclined to the plane of the thin section, assuming maximum rod lengths of 200μ (long dashed lines) and 500μ (short dashed, arrowed lines) and the rods are elongate parallel to the x axis.

Figure 3. Histogram of number of olivine analyses with Mg atoms per formula unit (assuming 4 oxygens; bin size of 0.001). Analyses from inclusions of olivine in garnet zones containing relict diamond are blue (Fa in garnet). Also shown are analyses for olivines in immediate vicinity of Qtz lamellae (Fa in proximity to quartz lamellae; black), matrix olivines (Fa in matrix; orange), olivines that formed during inversion of ferrosilite (Fa after Fs; green), and matrix olivines in contact with garnet (Matrix Fa adjacent to garnet; gray). The mean values for each Fa group are shown by the color-filled squares. The horizontal bar running through each square is the standard deviation, based on EMP analytical statistics. The heavy horizontal arrows show expected Fa compositions, as explained in the text.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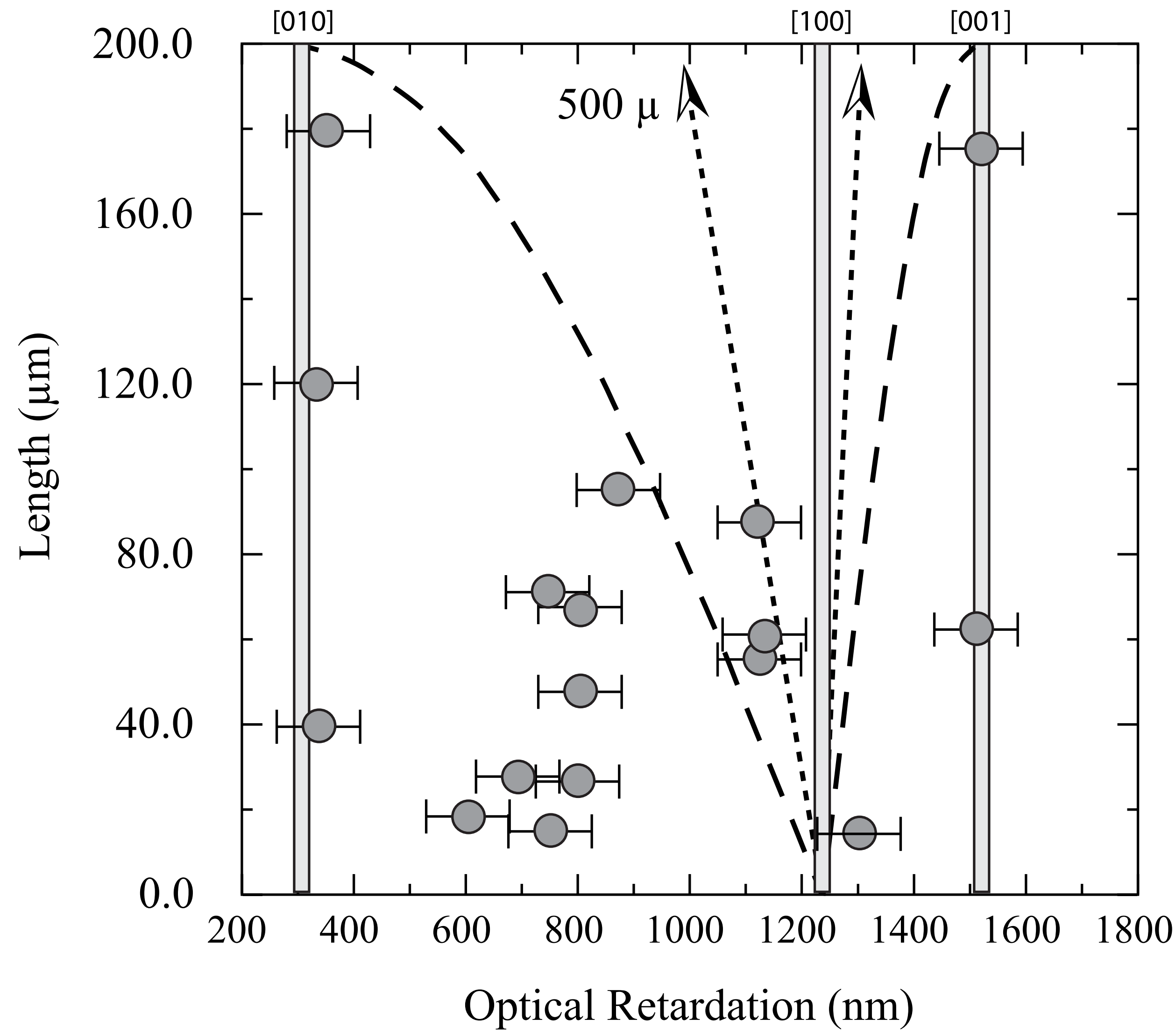
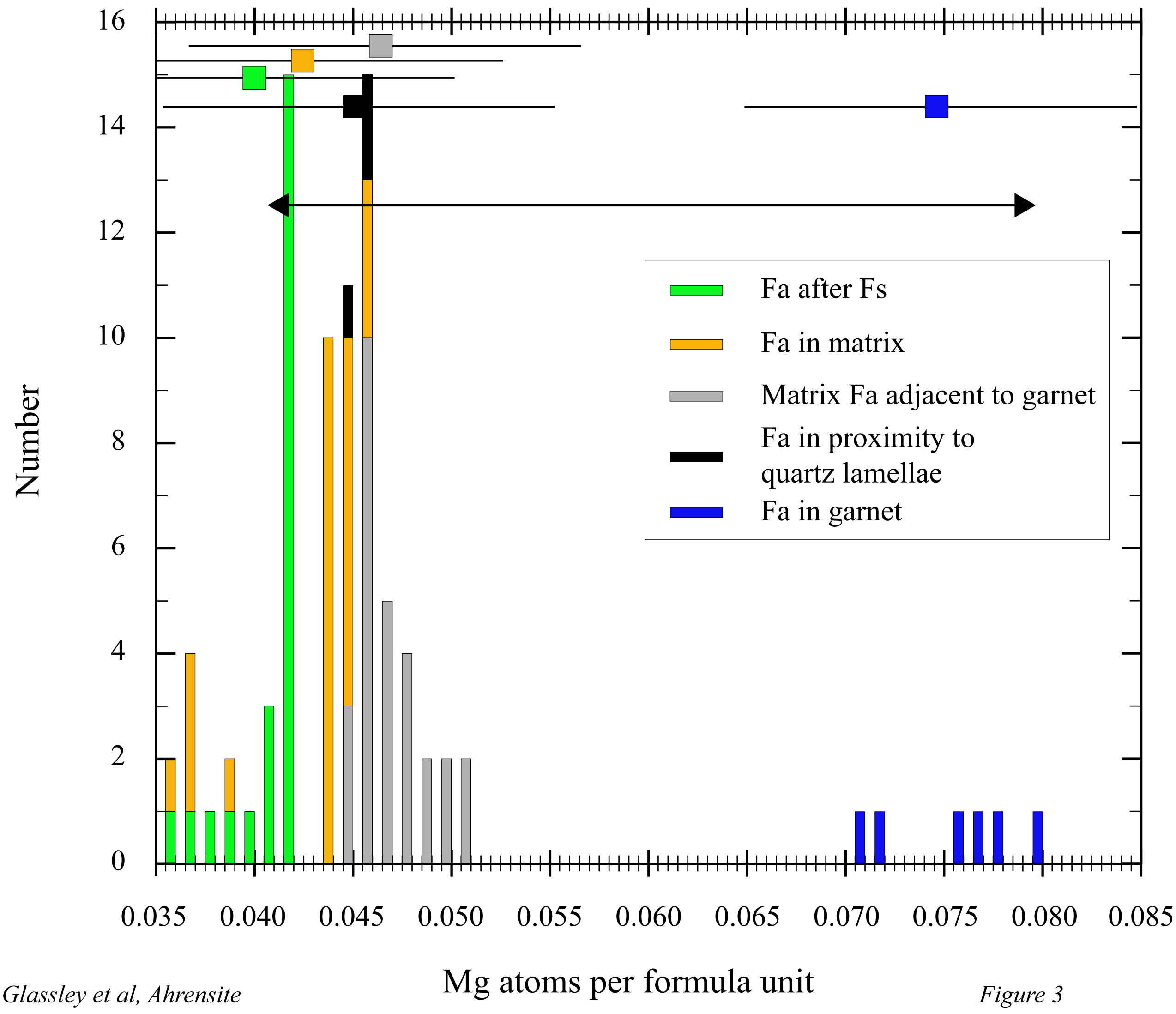


Glassley et al, Ahrensite

Figure 2



Glassley et al, Ahrensite *Figure 3*