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On the Formation of Arrays of micro-Tunnels in Pyrope and Almandine Garnets

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Abstract

A recent paper devoted to unusual fine-scale tubular tunnels found in pyrope and almandine garnets suggested that the 5 to 100 micron diameter tunnels were produced by an endolithic organism that is able to chemically dissolve and penetrate the mineral, perhaps in search of nutrients. The hypothesized microbial boring of the garnets was based on the finding of endolithic remains in the tunnels, but boring alone does not adequately explain the linear, highly aligned or occasionally branched tunnels that have been imaged. We have prepared this short Letter, in the spirit of *Occam's Razor*, to highlight the very probable role that dislocations play in the creation of such tunnels by preferential etching of a dislocation-rich deformation microstructure. The geometrical features of the tunnels possess all the characteristics of classical dislocation substructures that have been observed in natural and synthetic garnets.

Introduction

The intricate and beautiful X-ray computed tomographic images recently published by Ivarsson *et al.* (2018) contain clear evidence of highly aligned parallel tunnels that originate at the mineral surface and extend into the interior, see for example Figure 1. These tunnels form highly regular miniature palisades in some regions; in others, they exist as more chaotic branched networks with kinks and junctions with uniquely prescribed angles. The networks of curvilinear, branching and anastomosing (interconnected) tunnels were interpretated as evidence that these tunnels are independent of crystallography, thus providing an indirect foundation for the authors' hypothesis of biological tunneling (Ivarsson *et al.* 2018). Unfortunately, this interpretation completely misses the striking geometric similarities between the tunnels in these tomographic images and published observations and understanding of dislocation microstructures in both natural and synthetic garnets -- see for example, Rabier (1995); Rabier *et al.* (1976); Rabier (1979); Rabier *et al.* (1981); Garem *et al.* (1982); Rabier and Garem (1984); Allen *et al.* (1987); Karato *et al.* (1995); Blumenthal and Phillips (1996); Voegelé *et al.* (1998 a,b).

[Insert Figure 1]

As is well known, dislocations are prominent in virtually all crystalline materials. Dislocation generation, multiplication, and motion is widely recognized as a common deformation response of crystalline materials to externally applied shear stresses, and have been extensively observed and characterized in metals and alloys, minerals, ceramics, and semiconductors. The absence of dislocations in the pyrope and almandine garnets under discussion, if true, would be remarkable.

Here, we briefly review and discuss dislocations in garnets, tunnel formation due to abiogenic etching of dislocations in minerals, and the similarities between the geometry of dislocation substructures and the intricate tunnels and networks observed in these pyrope and almandine garnets (Ivarsson *et al.* 2018).

Dislocations in garnets

The relationship between dislocations and plasticity in garnets is well established. Synthetic garnets of technological interest such as $Y_3Al_5O_{12}$ (YAG, yttrium aluminum garnet), $Y_3Fe_5O_{12}$ (YIG, yttrium iron garnet) and $Gd_3Ga_5O_{12}$ (GGG, gadolinium gallium garnet) were first studied by Rabier and colleagues (Rabier J, Garem H, and Veyssiere P. 1976, Rabier J. 1979) and have exceptional plastic properties compared to other oxide crystals (Garem *et al.* 1982; Rabier and Garem, 1984; Blumenthal and Phillips 1996). Likewise, the resistance to plastic deformation in natural garnets is significantly greater than that of most

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other minerals of the Earth's mantle (Karato *et al.* 1995; Voegelé *et al.* 1998a). This is related to the very large Burgers vectors of dislocations in garnets, and to a "corrugated" oxygen sublattice, which promotes very high atomic-level friction stresses on moving dislocations.

The description of the garnet structure in terms of coordination polyhedra, so common in the mineralogical literature, has proven to be very useful in understanding dislocation properties in synthetic garnets (Rabier J, Veyssiere P, and Grilhé J. 1976b). The garnet structure can be regarded as a body centered cubic (bcc) lattice with a very large unit cell. The edge of the bcc unit cell is of order 1.2 nm, whereas most common minerals have considerably smaller unit cells. Thus, the magnitude of the smallest perfect unit Burgers vector, $\boldsymbol{b} = ½<111>$, is about 1.0 nm. This results in a very large strain energy, proportional to Gb^2 per unit length of dislocation (G is the elastic shear modulus). The strain energy of a dislocation can be lowered by spreading of its core and by dissociation of the parent dislocation into partial dislocations that bound a planar stacking fault. The dissociated configuration is glissile as long as it remains on the glide plane, but it becomes sessile when reconfigured off of the glide plane (Garem *et al.* 1982; Blumenthal and Phillips 1996).

In synthetic garnets, perfect dislocations have been shown to dissociate into co-linear partial dislocations according to the reaction

$$\frac{1}{2} < 111 > \rightarrow \frac{1}{4} < 111 > + \frac{1}{4} < 111 >,$$

(Rabier *et al.* 1976b; Rabier *et al.* 1981), in grossularite ($Ca_{2.9}Fe_{0.2}Al_{1.9}Si_3O_{12}$) (Allen *et al.* (1987) and in gem quality single crystal garnet (Voegelé *et al.* (1998a) and in a variety of natural samples (Voegelé *et al.* 1998b). Even with this dissociation, the partial dislocations have very large strain energies that have important consequences for the observed dislocation microstructures. The work of Rabier *et al.* already cited has shown that dislocations are clearly aligned along the screw direction in synthetic garnet single crystals that have undergone high temperature deformation up to moderate strain; this appears not to be the case for the natural garnet deformed under hydrostatic confining pressures at elevated temperatures (Voegelé *et al,* 1998a). Finally, the large unit cells in garnets make possible the formation of hollow dislocation cores, as suggested by Nabarro (1984).

A representative micrograph is shown in Figure 2a; it was taken from a $Gd_3Ga_5O_{12}$ (GGG) single crystal that had been deformed in compression along [100] at 1350˚C (0.81 of the absolute melting temperature, T_M) to a strain of 0.4% at a strain rate of $3.3x10^{-6}$ /s (Rabier 1979). The two most prominent dislocations in this figure are clearly aligned along <111> and thus are in a screw orientation. Moreover, the rapid transition to screw character from the source pinning point (upper white arrow) further attests to the anisotropy of dislocation glide in this material. The micrograph in Figure 2b shows dislocations in GGG that had been compressed along [110] to a plastic strain of 0.1% at 1450˚C (0.86 T_M) at a strain rate of $3.3x10^{-6}$/s. Here, dislocation glide loops are segmented along orientations corresponding to both screw and mixed character. In Fig. 2b, the vector **b** is the projection of the Burgers vector ½ [1-11] and the straight dislocation parallel to it is a screw dislocation.

[Insert Figure 2]

Studies have also shown that dislocation glide in garnets occurs on {110}, {112}, or {123} slip planes and that the plane with the highest resolved shear stress is not always activated. This violation of the Schmid law (Rabier and Garem 1984), which describes the geometric relationship between the applied stress and the shear stress resolved onto specific slip planes, is analogous to what is found in bcc metals at low temperatures and may be taken as another indication of the effect of dislocation character on dislocation mobility.

In bcc metals, screw dislocations have non-planar cores and are difficult to move, while edge and mixed character dislocations remain planar and are relatively easy to move.

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The consequence is that the more mobile dislocations run out and are underrepresented in the dislocation substructure, resulting in a preponderance of crystallographically oriented, long, straight screw segments. In bcc metals, thermal activation of the screw dislocations facilitates a transformation from "low" to "high" temperature deformation microstructures involving the disappearance of long screw dislocation segments. By contrast, the screw dislocations in synthetic garnets remain immobile even at high temperatures owing to the magnitude of their Burgers vector. At high temperatures, in addition to straight screw segments, rectilinear mixed and edge character dislocation segments, resulting from diffusive climb dissociation out of the glide plane, can also be found. Diffusive climb of edge and mixed dislocations out of their glide planes also leads to the presence of curved dislocations (Rabier 1995), and the final result is that both straight and curved dislocation segments can co-exist in garnets that have undergone high temperature plastic deformation. Lastly, we note that deformation by pure dislocation climb in garnets may also be important in mantle dynamics (Ritterbex *et al.* (2020).

The dislocation microstructures that form in natural garnets are the result of geological heating and stresses and the thermo-mechanical deformation that ensues at elevated temperatures. Once cooled, the dislocation structures are frozen into the crystals, and subsequent "decoration" of the dislocations by impurities or the formation of etch tunnels along the dislocation lines can occur, with the natural consequence that the tunnels and impurities will maintain the network topology of the underlying dislocation substructure.

Etched tunnels arising from dislocations in minerals

It is well known that the localized strain fields associated with dislocations affect the reactivity of the material by providing favorable areas for chemical reactions such as precipitation and dissolution. They also provide rapid diffusion paths for ingress of fresh reactants. The formation of etch tunnels along dislocations after specific treatments has been documented in a number of minerals, *e.g.* quartz (SiO_2), forsterite (Mg_2SiO_4), and olivine $(Mg,Fe)_2SiO_4$ - see for example Tingle and Green (1992). The decoration of dislocations in forsterite (Jaoul *et al.* 1979) and olivine (Karato 1987) has been used to study the dislocation microstructures of these materials, and a comprehensive description of these dislocation microstructures has improved our understanding of the thermo-mechanical properties of these minerals.

As far as garnets are concerned, similar observations of etched dislocations have also been reported. Dislocation microstructures in pyropes were revealed by HF etching by Carstens (Carstens 1969). Studying the elongated shapes of garnets in high-grade metamorphic rocks, Azor *et al.* (1997) concluded that "dislocation-enhanced dissolution, which occurs at low temperatures and low dislocation mobility, is arguably the mechanism responsible for partially dissolving the garnet grains". Recently Liu *et al.* (2018) presented a new method for decorating dislocations in garnets based on a pre-melting decoration process. This work indicated that the decorated lines were generated by a pre-melting reaction that occurred along the dislocation cores of individual dislocations and low-angle sub-grain boundaries, which are essentially an ordered array of dislocations. These experiments clearly show that a number of abiogenic processes can naturally lead to etched tunnels along dislocations in garnets.

Ivarsson *et al.* (2018) performed time-of-flight SIMS analyses of freshly fractured surfaces of their garnets and reported high organic content (fatty acids) localized to newly exposed tunnels. They interpreted this as the physical and chemical remains of endolithic microorganisms within the tunnels, and they further hypothesized that the tunnels were the result of microbially mediated boring of the garnets for nutritional reasons. The geometrical precision inherent to the palisades and interconnecting networks that were elucidated by Ivarsson *et al*. would be hard to maintain while tunneling through an opaque solid. Moreover, it is important to note that the finding of organic content in the tunnels is also fully consistent with the abiogenic etching of dislocation substructures and subsequent habitation of the tunnels by endoliths.

Intricate tunnels in Thai garnets from soils and river sediments

Most if not all of the tunnel-like geometrical features exhibited in the work of Ivarsson *et al.* (2018) can be explained by dislocation theory. Correlation with location-specific crystallographic orientation maps, which is now possible with state-of-the-art electron microscopes, would allow for direct confirmation or refutation of the role of dislocations, but the following observations and comparisons are very convincing on their own.

The findings of Ivarsson *et al.* that the tunnels all originate from the mineral surfaces and extend into the mineral interiors points to the role of an external etchant or agent, as suggested by the authors. However, it is also important to recognize that dislocations cannot end within a grain and must terminate at exterior surfaces, interior grain or phase boundaries, or by making junctions with other dislocations. For example, the short lines in Figure 2 are inclined dislocations that intersect the top and bottom surfaces of the thin electron-transparent TEM foils that were prepared from plastically deformed garnet samples. Moreover, the emergent point where a dislocation intersects a free surface is known to be more reactive, and when etched, has geometrical features that reflect the underlying crystal symmetry. The observation that most tunnels in the images of the garnets published in Ivarsson *et al.* (2018) have hexagonal cross-sectional symmetry is fully consistent with the presence of screw

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dislocations aligned along <111> crystallographic orientations. Similarly, the minority of tunnels that have rectangular cross-sections are easily explained by the presence of a smaller number of edge and mixed dislocations.

The straight and highly parallel and aligned nature of the miniature palisades and tunnels in Figs. 1B and 3A-E of Ivarsson *et al.* (2018) are very striking and also very suggestive of screw dislocation microstructures. Measuring the orientation of individual grains should be undertaken to confirm or disprove the relation of the tunnels to screw dislocations, and this would further support the evidence provided by the hexagonal cross-sections. Knowing the grain orientation would also allow development of a quantitative model of the very regular kink angles that have been observed, suggestive of either dislocations lying along two intersecting <111> directions or a single dislocation with adjacently locked screw, mixed or edge character segments, similar to what is shown in Fig 2B. We further note that qualitative measures such as observable tunnel densities (in the range of 10^7-10^{10} tunnels per square meter) are comparable to dislocation densities that are associated with modest amounts of plastic deformation.

The more complex curved and branching microstructures shown in Figs. 1C, 2A and 4A in Ivarsson *et al.* (2018) that form deeper in the grains led Ivarsson *et al.* to disregard any crystallographic influence on the formation of the tunnels, but these too are easily explained by the presence of dislocations. Curved tunnels most likely form from mixed dislocations, or dislocations that have undergone diffusive climb out of their glide plane. Branching of the tunnels is analogous to dislocation microstructures that arise from elastic interactions that create dislocation junctions and networks, and that involve several families of interacting dislocations. Ivarsson *et al.* have pointed out the similarity of the connecting branches they observed (*e.g.* their Fig. 4A) to anastomoses (interconnections) that are observed in biological systems such as blood vessels and leaf veins, but such segments and junctions are also

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commonly formed and observed in dislocation networks. For example, Rabier *et al.* (1976b) have shown that dislocation junctions with connecting segments of <100> and <110> Burgers vectors result from the interaction of two families of dislocations with ½ <111> and ½ <11-1> Burgers vectors in $Y_3Fe_5O_{12}$ (YIG) deformed at 1350 ˚C, see for example Fig. 3. The narrowing and eventual termination of the tunnels in the grain interior of the Thai garnets is an indication that the etching or attack that starts on the surface had not run to completion.

[Insert Figure 3]

Implications

The intricate tunnels imaged in pyrope and almandine garnets found in soils and river sediments (Ivarsson *et al.* 2018) can be fully explained, without straining credulity, by abiogenic etching of dislocation microstructures contained within the minerals. There are striking geometric similarities between these tunnels and dislocation networks that have been observed and published in numerous natural and synthetic garnets, and further studies involving local crystallographic orientation mapping via electron backscatter diffraction (EBSD) or similar techniques would be highly informative.

Acknowledgments

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Figure 1

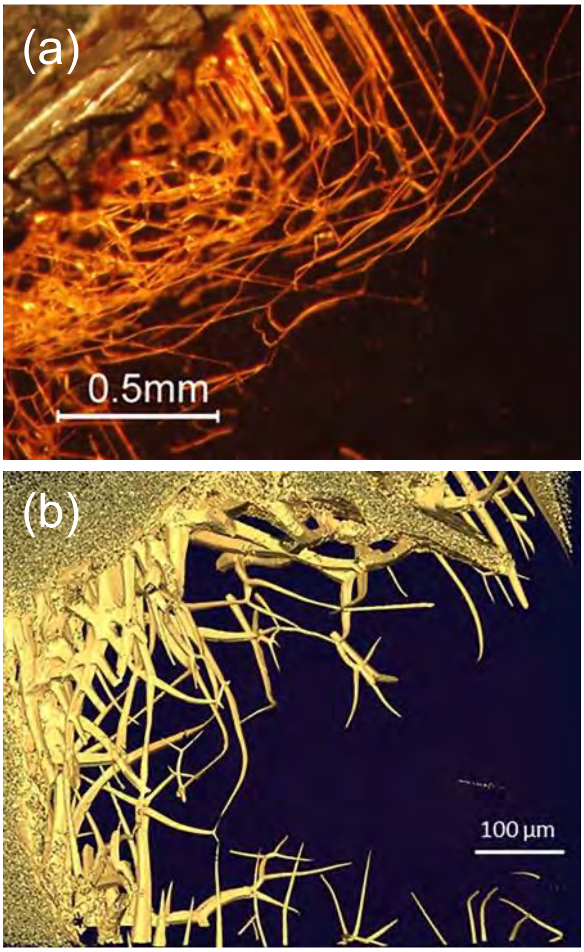

Figure 1*. Intricate tunnels in pyrope garnets, taken from Ivarsson et al. (2018). (a)** *A network of highly parallel and wandering tunnels that originate at the mineral surface and extend into the interior.* ***(b) *Tomographic isosurface reconstruction of another garnet with tunnels of defined cross-section. These tunnels originate at the surface, intersect and branch at repeatable angles, and taper to a point as they extend into the interior.*

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Figure 2

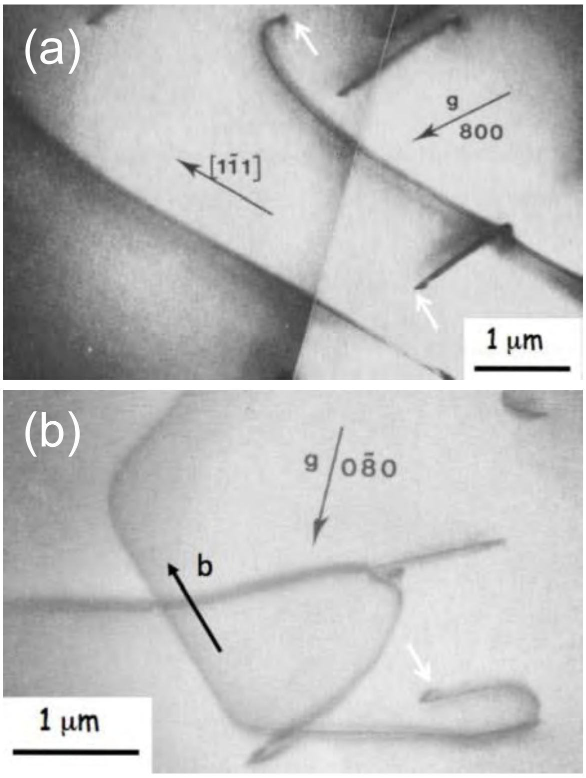

Figure 2**. TEM micrographs of dislocations in synthetic garnets illustrate a preponderence for straight dislocations that are aligned along specific crystallographic directions*. ***(a) *Long, straight screw dislocations in single-crystalline $Gd_3Ga_5O_{12}$ (GGG) that was deformed to 0.4% strain at 1350˚C. The short dislocations are also straight; their length is simply truncated by intersection with the top and bottom surfaces of the TEM thin foil. Examples of surface intersections are noted with white arrows. At lower magnification in a bulk crystal, long-straight screw dislocations would align to create an array similar to what is shown in Figure 1a.* ***(b)*** *Glide loops are commonly observed to be segmented into carefully-aligned screw and mixed dislocation segments imaged in GGG compressed to 0.1% strain at 1450˚C. The mixed dislocations curve and wind in a manner similar to the wandering tunnels in Figure 1a.*

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Figure 3

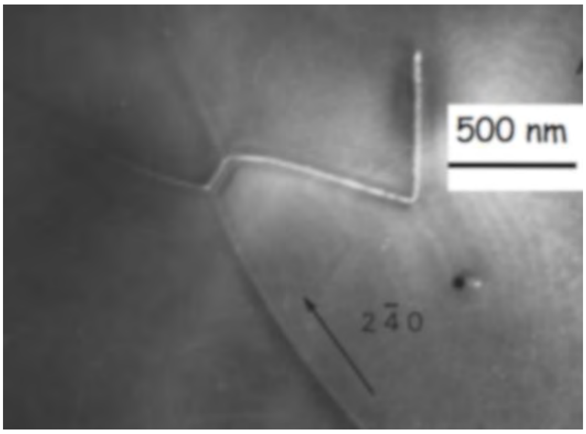

Figure 3. TEM observations of dislocation junctions, which lead to branching and aligned palisades in synthetic garnets. *<100> junctions resulting from the interaction of two <111> dislocation slip systems in* $Y_3Fe_5O_{12}$ *(YIG) that had been deformed at 1350˚C. These intersections are analogous to the geometrical branching shown in Figure 1b.*