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Interphase misorientation as a tool to study metamorphic reactions and crystallization in geological materials

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Abstract

Interphase boundaries are planar defects that separate two different minerals, which in general have different compositions and/or crystalline structures; they may play an important role as a pathway for fluids in rocks and affect their physical properties. To completely characterize interphase boundaries, one needs to define the misorientation between adjacent grains and the orientation of the grain boundary plane. The analysis performed here is limited to the misorientation characterization and the trace of the interphase boundary. Although the determination of possible orientation relationships between the two adjacent phases is routinely performed by selected-area electron diffraction in a transmission electron microscope, this method lacks statistical representativeness. With the advent of techniques like electron backscatter diffraction (EBSD), it is possible to calculate orientation relationships not only in single pairs of crystals of the same phase but in full thin sections and between different minerals. The interphase misorientation is calculated from two orientations of two adjacent crystals of different phases. A set of single misorientations is then used to calculate the misorientation distribution function (MDF), from where it is possible to identify a maximum and its crystallographic interpretation. If we then know the misorientation and the unit-cell parameters of the individual phases, the crystallographic relationships between the different phases can be described with the pairs of parallel crystallographic planes and the pairs of crystallographic directions. In this paper, I present examples of the use of interphase misorientation analysis on the transformation of calcite-aragonite, olivine-antigorite, magnetite-hematite, and on the study of orientation relationships between plagioclase-olivine-ilmenite in mid-ocean ridges gabbros (ODP Hole 735).

Keywords: Interphase misorientation, EBSD, orientation relationships, phase transformation

Introduction

Polycrystalline materials such as rocks, metals, and ceramics are made of different grains with different crystal orientations. Where those grains meet each other, there is normally an interatomic mismatch between the lattices of the two adjacent crystals, which is called grain or phase boundaries. Grain and phase boundaries are a very important part of the microstructure of rocks because they are high-diffusivity paths for both fluid and solid-state diffusion. They play an important role in the rheology of rocks and influence petrophysical properties, such as the strength of rocks, resistance to cracking, and permeability. As grain and phase boundaries are relatively disordered structures, they can accommodate large amounts of impurities, which may influence, for example, boundary migration.

Grain boundaries are interfaces that separate grains of the same phase (e.g., quartz grain boundaries), whereas phase boundaries separate grains of different compositions and/or structures (e.g., quartz-feldspar or calcite-aragonite phase boundaries). The structure and energy of grain boundaries are defined by the misorientation of the two neighboring grains and the orientation of the boundary plane itself. To fully define a grain boundary, one must define five variables related to the grain boundary misorientation angle, misorientation axes, and the orientation of the interface itself. Standard classification of grain boundaries distinguishes two end-members, named tilt and twist boundaries. In tilt boundaries, the rotation axis to bring the lattices of two neighboring crystals into overlap is parallel to the interface plane, whereas in twist boundaries, the rotation axis is normal to the interface, and pretty much all grain boundaries lie in between these two end-members. Grain boundaries are also classified according to the misorientation angle. Adjacent grain boundaries with less than (roughly) 10° misorientation between neighbor grains (the actual angle can be quite variable depending on the crystallographic system) are said to be low-angle grain boundaries while neighboring grain boundaries with higher degrees of misorientations are classified as high-angle grain boundaries. In deformed materials, low-angle grain boundaries are commonly associated with an array of aligned dislocations along a certain plane (forming in this case a "subgrain"). It is important to note that low-angle grain boundaries are very important in biomineralization and have nothing to do with intracrystalline defects.

Phase boundaries, on the other hand, are classified according to the degree of mismatch between the lattices of the two phases along the interface (e.g., Sutton and Baluffi 1995; Porter and Easterling 1992). In coherent (or commensurate) phase boundaries (Fig. 1), the two neighbor crystals match perfectly

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along the interface, and the interfacial plane has the same atomic configuration in both phases. An important aspect of the coherency definition is that the crystallographic plane comprising the phase boundary does not need to be the same in the different phases, but an orientation relationship between the two grains needs to be satisfied. This can be described by a Burgers orientation relationship that specifies a pair of parallel planes and directions, i.e., $(hkl)_{\text{phase A}} \parallel (hkl)_{\text{phase B}}$ and $[uvw]_{\text{phase A}} \parallel [uvw]_{\text{phase B}}$ for the general case of single planes and directions. To keep the interface coherent, small differences in the lattice parameters between the two phases can be accommodated by elastic strains on both sides separated by the interface. Such an effect reduces the interface energy at the expense of increasing the internal energy of both phases adjacent to the interface. As such, elastic straining to force a perfect coherency only occurs if the interface is strong, if the mismatch is small, and if the grain size is small. Although the structure at the interface is perfect, the interfacial energy at the boundary is quite variable but depends essentially on the composition of the phases separated by the interface. In semi-coherent (or discommensurate) phase boundaries, the elastic strain described previously becomes too large, and the lattice mismatch is accommodated by an array of misfit dislocations that do not create long-range strain fields. The total energy of semi-coherent phase boundaries results from both compositional and structural components. In incoherent (or incommensurate) phase boundaries, the different lattices of the two phases at the interface prevent the good matching at the phase boundary, leading to a more disorder structure, similar to those observed in high-angle grain boundaries. The surface energy of both grain and phase boundaries are a function of the misorientation angle, and it is known from the materials science literature that during deformation, grain boundaries in metals tend to rotate to minimize such energy, leading to the development of grain boundaries with specific misorientation angles.

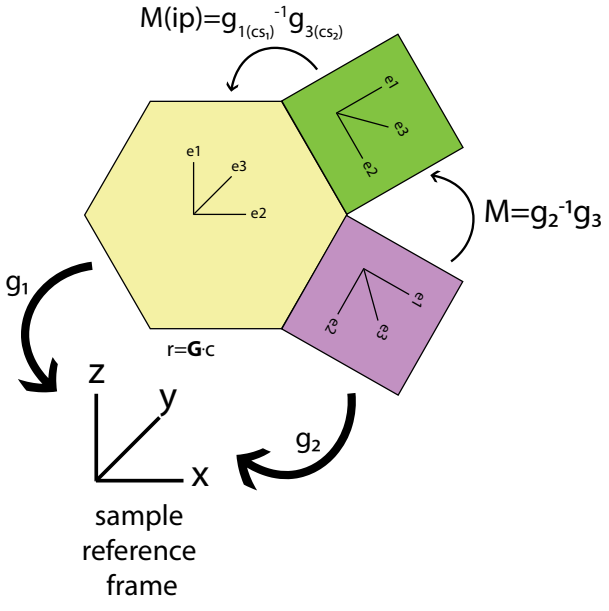


Figure 1. Schematic drawing showing the misorientation between two different phases, one "hexagonal" (yellow grain) and a second, "cubic" (purple and green grains). The orientation of the individual crystallites is described by an orientation $\mathbf{g}_1$, $\mathbf{g}_2$, or $\mathbf{g}_3$, which describes the transformation from crystal reference frame (c_i) and sample reference frame ($\boldsymbol{r}$), here denoted as x, y, and z. The misorientation ($\boldsymbol{M}$) between grains of the same phase can be described as $\boldsymbol{M} = \mathbf{g}_2^{-1}\mathbf{g}_3$, where g are their respective orientations. The misorientation along different phases nevertheless $\boldsymbol{M(ip)}$ needs to consider the crystallographic system of the individual phases (cs), and can be described like $\boldsymbol{M(ip)} = \mathbf{g}_{1(cs1)}^{-1}\,\mathbf{g}_{3(cs2)}$, where cs_1 is the crystal symmetry of phase 1 (e.g., hexagonal) and cs_2 the crystal symmetry of phase 2 (e.g., cubic). The combined symmetries of the different cs is what defines the dimensions of the fundamental zones for the plots presented here.

Grain boundaries on common minerals such as quartz, olivine, and calcite are relatively well understood in different length scales (e.g., McLaren 1986; Faul and Fitz-Gerald 1999; Fliervoet et al. 1999; Wheeler et al. 2001; Bestmann and Prior 2003; Lloyd 2004; Hiraga et al. 2004; Wenk et al. 2011a, 2011b; Menegon et al. 2011a, 2011b; Kilian et al. 2011; Kruhl et al. 2013; and others). In olivine, for example, special grain boundaries have even been characterized in terms of grain boundary character distribution (Marquardt et al. 2015) and in terms of grain boundary energies (Duyster and Stöckert 2001). However, although "real" rocks are mostly composed of two or more phases, our understanding of phase boundaries between different minerals is very scarce and predominantly studied at the nanometric scale, with most observations performed with transmission electron microscopes (TEM) (e.g., Boudier et al. 2010; Plümper et al. 2012; Obata and Ozawa 2011; Marti et al. 2018). Although this is a very powerful tool to investigate interphase boundaries, particularly due to its angular resolution (interphase orientations can be determined up to a precision of 0.1°), it has a very limited statistical representativeness, which is because an individual TEM lamella will show at most a few interfaces. However, the TEM is not the only technique available to study orientation relationships between different phases, and any technique involving local diffraction of an electron beam by the crystalline structure of the phases separated by the interface will allow us to calculate the orientation relationship. Here it is proposed to use orientation maps generated via electron backscatter diffraction (EBSD) in a scanning electron microscope (SEM) to calculate the interphase misorientation angle/axis pairs and determine from them potential orientation relationships. It is important to clarify here that the "orientation relationships" described here have a different meaning than that described in crystallography, where there is partial/total coincidence between the lattices of the two materials separated by an interface. Here I use the term in a more "loose" sense to describe that, in certain cases, two different minerals may show some degree of parallelism along certain interfaces without necessarily sharing the same lattice along the interface. Advantages of this method include: (1) the higher statistical representativeness of the data; (2) the potential to calculate the misorientation angle-axis pair of any pair of mineral phases; (3) the potential to plot phase boundaries with different misorientation angles in the map, and highlight those, which have special misorientation angles/axis pairs and even possible orientation relationships; and (4) to use EBSD results and subsequent calculations and then perform more detailed studies of specific interphase boundaries at the TEM scale, preparing TEM lamellae using target preparation with focused

ion beam methods. Here I present four examples of interphase misorientations and interphase orientation relationships between olivine-antigorite from a serpentinite, calcite-aragonite from high-*P*-*T* experiments, magnetite-hematite from an undeformed iron ore, and plagioclase-ilmenite relationships from a mid-ocean ridge gabbro. The results are presented in terms of interphase misorientation angles, axes, and plotted directly in the EBSD maps. To facilitate the use of this method, a MATLAB script to be used in the MTEX toolbox from Hielscher and Schaeben (2008) is provided as Online Materials[1].

Interphase boundary misorientations

Interphase boundary misorientations calculations are relatively new in Earth and Materials Sciences. For instance, McNamara et al. (2012) explored interphase misorientation relationships in the study of crystallographic preferred orientation (CPO) development of barroisite due to mimetic growth at the expense of glaucophane and omphacite. Later, Morales et al. (2018) used the interphase angle/axis pair on the study of olivine-antigorite transformation relationships, where they reported two new orientation relationships never described in the literature. I will briefly review the concept of intraphase misorientation. A complete overview of this topic is given by Wheeler et al. (2001).

Crystal orientations $\boldsymbol{g}$ as determined via EBSD and consistent with the definitions of MTEX can be described as passive rotations $\boldsymbol{r}$ to bring the coordinates from the crystal reference into coordinates in the sample reference frame. Both reference frames are right-handed, the three axes are orthogonal to each other, and both share a common origin for the sake of simplicity (note however that in some cases, the crystal reference frames might not be orthogonal). The rotation angle is always positive if the rotation is counterclockwise when viewed along the rotation axis toward the origin. Using the definitions of Krakow et al. (2017), if we define the specimen reference frame as $\boldsymbol{s}$ and the crystal reference frame as $\boldsymbol{e}$, the rotation has to satisfy:

$$r = \boldsymbol{G} \cdot c \tag{1}$$

where $r = (x,y,z)$ in specimen coordinates and $c = (e_1,e_2,e_3)$ in crystal coordinates. This equation states that a vector e can be transformed into a vector r by an operation $\boldsymbol{G}$, which is a matrix operation.

The misorientation angle in an EBSD map is the angle necessary to bring two adjacent objects of this map (e.g., two neighbor pixels or two neighbor grains) into coincidence, whereas the misorientation axis is the axis about which this rotation needs to occur to bring the lattices of the two objects into parallelism. These misorientations $\boldsymbol{M}$ are also passive rotations, but in this case between two crystals reference frames, where the two crystals normally have two different orientations (g_1 and g_2). The misorientation $\boldsymbol{M}$ between these two crystals transforms the crystal coordinates c_1 into crystal coordinates c_2, as follows (e.g., Krakow et al. 2017):

$$\boldsymbol{M} = g_2^{-1} \cdot g_1 \tag{2}$$

and

$$\boldsymbol{M}c_1 = g_2^{-1} \cdot g_1 c_1 = g_2^{-1}\boldsymbol{r} = c_2 \tag{3}$$

When dealing with one single phase, the lattice parameters for the adjacent objects are the same, and so the misorientation axis can be defined by several symmetrically equivalent axis/angle pair combinations that are directly dependent on the symmetry of the studied phase. In the case of two neighbor plagioclase (triclinic) grains, there is only one set of misorientation angle/axis capable of bringing the lattices of these two grains into coincidence, while in the case of magnetite or garnet (cubic minerals), there are 24 different possibilities (Mainprice et al. 1993; Lloyd et al. 1997; Wheeler et al. 2001). In the case of olivine (orthorhombic) there will be <24 possibilities due to this large number of possibilities in non-triclinic phases; the current convention is to adopt the rotation pair with the minimum misorientation angle(e.g., Morawiec 1995; Wheeler et al. 2001).

On the other hand, when dealing with the misorientation between two phases that belong to different crystallographic systems, the reference misorientation is not unique. Because of that, and due to the fact, that in most cases, we will deal with phases of different symmetries, the asymmetric domain for the misorientation axis plots is not "fundamental." That implies that the shape and form of misorientation angle/axis distribution depends on the choice of reference misorientation. If we consider the example of olivine (orthorhombic) and antigorite (monoclinic), the fundamental region requires the entire hemisphere due to the combination of these two different symmetries. In this case, we must define in relation to which crystal reference frame we will plot the misorientation axes. In the case of phase transformations, it makes sense to use the parent phase reference frame, but if one suspects that a different interphase orientation relationship can be deduced from the interphase misorientation data, one has to examine the misorientation axes plot also using the daughter phase reference frame.

In most of the studies dealing with misorientations, fundamental zones are based on Rodrigues-Frank parameters (e.g., Morawiec 1997), but in MTEX this construction is based on quaternion geometry (see Krakow et al. 2017 for details). The definition of a particular fundamental zone depends on the alignment of crystal axes and the order in which the symmetry operators are combined for the misorientation calculations. These fundamental zones are calculated by selecting, in a family of symmetrically related equivalent points, the ones with the smallest angle of rotation. If then multiple points have the same distance from the origin, the choice is made based on the direction of the rotation axis.

Crystallographic point groups control the symmetry operations related to misorientations. If we have misorientation $\boldsymbol{M}$ relating point groups S_1 and S_2 with crystal coordinate systems c_1 and c_2, and using Equation 3, we can write the following expression:

$$\boldsymbol{M} = s_2\boldsymbol{M}s_1,\ s_1 \in S_1,\ s_2 \in S_2. \tag{4}$$

Here we use the smallest unique rotation angle defined as the disorientation angle and the axis of rotation within the inverse pole figure sector that correspond to the point group common to both symmetries, fulfilling the relation $SC = S1 \cap S2$. The fundamental zones for all possible combinations of proper point group symmetry operations are presented in Krakow et al. (2017), but for the sake of simplicity, all the misorientation axes plots are presented in inverse pole figures resulting from those combinations.

Description of the samples

To test the potential of misorientation analysis on the study of metamorphic reactions and magmatic processes, we have studied four different samples (one synthetic and three natural). Three of these samples are known examples of phase transformations or crystallographically controlled metamorphic reactions: (1) calcite-aragonite; (2) olivine-antigorite; and (3) magnetite-hematite. In all these cases, the neighboring phases that share a common boundary do not belong to the same crystallographic system. The fourth example is an oxide-rich gabbro coming from the Atlantis Bank (Indian Ocean), where I have tested all the possible pairs of 6 different minerals that compose this rock (plagioclase, diopside, olivine, ilmenite, magnetite, and pargasite), and I found that plagioclase-olivine and plagioclase-ilmenite have specific misorientation angle/axis pairs that suggest that both olivine and ilmenite crystallized using specific plagioclase crystal planes as substrate.

Calcite-aragonite phase transformation produced experimentally

The calcite-aragonite aggregated studied here (sample 010-SC-3-X) belong to the collection of deformation experiments performed by Sebastian Cionoiu during his Ph.D. thesis at ETH Zürich, whose objective was to understand the effect of stress on mineral reactions (see thesis volume for sample preparation details, see also Cionoiu et al. 2019). The calcite-aragonite phase transformation observed in this sample occurred under hydrostatic conditions (i.e., no axial load applied) under 1.6 GPa pressure and temperatures of 600 °C for about 12 h. In the studied sample, aragonite comprises about 25% of the total aggregate and occurs predominantly wrapped around large calcite crystals, as if forming tails of recrystallized material. Calcite is heavily twinned and has some undulose extinction, but no clear subgrains or recrystallized grains, and no noticeable grain growth has been observed. Aragonite grain sizes vary from 3 to 12 μm, and there is no clear evidence of crystal plasticity in this phase, such as undulose extinction or subgrain walls.

Tremolite-chlorite-antigorite schist from Moses Rock (U.S.A.)

The sample of tremolite-chlorite-antigorite schist studied here (MR-1) was collected from the Moses Rock dike and was previously studied by Boudier et al. (2010) and Morales et al. (2013). The Moses rock dike belongs to the Navajo Volcanic Field (NVF) that is exposed in the central part of the Colorado Plateau, in the Four-Corners region, of southwest U.S.A. The Moses Rock dike belongs to kimberlitic and lamprophyric breccias that contain a large variety of mantle and lower crustal xenoliths of a variety of compositions (Smith 1995, 2010). The mantle fragments, associated with the subduction of the Farallon slab, include metaperidotites rich in hydrous phases, jadeite clinopyroxenites and eclogites, spinel websterite, and spinel lherzolites and were formed at depths between 50 and 150 km and temperatures ~900 °C according to clinopyroxene thermometry (Hunter and Smith 1981).

Magnetite-hematite phase transformation

The magnetite-hematite studied here was collected in the Corrego do Feijão mine in the western part of the Quadrilátero Ferrífero, southeastern Brazil. This "iron quadrangle" lies within the Cauê formation of the Itabira group, a metasedimentary sequence of Archean/Paleoproterozoic ages that lies on the southern boundary of the São Francisco craton (Alkmim and Marshak 1998). This sequence hosts large iron ore deposits in the form of itabirites and polycrystalline hematite with variable contents of magnetite. Deformation intensity and metamorphic conditions increase from east to west (Rosière et al. 2001), and the iron ores present a progressive enrichment of hematite with respect to magnetite toward the east. The studied sample is still relatively rich in magnetite and is composed approximately of 60% magnetite and 40% hematite, with goethite occurring as alteration material.

Plagioclase-olivine and plagioclase-ilmenite in an oxide gabbro from the Atlantis Bank

The Atlantis Bank is an oceanic core complex that was exhumed by a large-scale detachment fault on the Southwest Indian Ridge (Karson and Lawrence 1997; Kelemen et al. 2007). Deformation in these rocks is localized along hypersolidus and HT shear zones, later overprinted by brittle faults of different scales, as detailed described by Miranda and John (2010) and Allard et al. (2021). Here, we studied oxide-rich gabbros that occur with higher frequency toward the top of the borehole and are interpreted to have intruded the more primitive gabbros at a later stage. Composition of the studied samples varies considerably from sample to sample, between clinopyroxene and plagioclase-rich gabbros, but the content of oxides (mostly magnetite and ilmenite) is between 5–10% volume. The studied sample has well-developed foliation, but the lineation is not well marked. In general, plagioclase occurs as equigranular aggregates, whereas clinopyroxene occurs predominantly as porphyroclasts. Olivine occurs as equigranular, idiomorphic grains within the gabbros but also as "pods" rich in olivine in pressure shadows of clinopyroxenes. Ilmenite and magnetite occur along bands parallel or oblique to the foliation.

Methods

The crystallographic preferred orientations of the studied samples were determined by electron backscatter diffraction technique (EBSD) in a scanning electron microscope. All the samples were measured in a FEI Quanta 200 F with EDAX Hikari EBSD camera operating at the Scientific Centre for Optical and Electron Microscopy (ScopeM) of ETH Zürich. They were mechanically polished to a 0.25 μm diamond suspension and chemically mechanically polished with an alkaline solution of colloidal silica (0.025 μm) for 3–10 min on a neoprene polishing cloth. All the EBSD maps were acquired using an accelerating voltage of 20 kV, beam current of 8 nA, the working distance of 17 mm, and variable stepsizes from 0.5 to 1 μm, depending on the scale of the map. With the exception of the olivine-antigorite sample, all the EBSD maps used 4 × 4 binning of the patterns. The antigorite was indexed using the structure determination proposed by Capitani and Mellini (2006), using an a-axis of 35 Å, typical of high-temperature antigorite. As antigorite generates poor patterns in the above standard EBSD mapping conditions, a binning of 2 × 2 combined with a pixel Hough binning of 160 and about 120 reflectors were used for the correct indexation. Post-acquisition processing in the EDAX-OIM 8 software included the standardization of the confidence index (CI) using a minimum grain tolerance angle of 10°, and minimum 10 indexed pixels per grain, followed by a CI correlation between neighbor points, where pixels with low CI (<0.1) are reassigned to the orientation and the CI of the neighbor data point with highest CI in the individual grains. All the EBSD maps, calculations, and plots were carried out with the MTEX toolbox for MATLAB (Hielscher and Schaeben 2008). The orientation distribution functions (ODFs) were calculated using the complete data sets with the de La Vallee Poussin kernel with a half-width

of 10°, which is equivalent of a band width of 28 in the spherical harmonic coefficients. All the data are plotted in equal-area, upper hemisphere pole figures, with a resolution of 5°. Interphase misorientation pairs between phase A and phase B were calculated for the entire maps using a common misorientation threshold of 10°, and therefore low-angle interphase misorientations, if present, are not studied here. Detected grains with <10 pixels were also not considered in the calculations.

Results

Calcite-aragonite

In the studied sample, calcite is the dominant phase (~75% sample), while aragonite is secondary (making up the other ~25% volume; Fig. 2a). Calcite grain size varies between 25–120 µm, some of the large grains are heavily twinned, and most of the large calcite grains have large internal misorientations, up to angles of 10° (Fig. 2b). The aragonite occurs predominantly wrapped around the calcite large grains along discontinuous, anastomosing bands (Figs. 2a and 2c), except for the small aggregate of coarser grain aragonite that occurs in the bottom of the Figure 2a. It has grain sizes varying from 4 to 12 µm, and from the orientation maps, it seems that the crystallographic preferred orientation of both calcite and aragonite is very weak (Figs. 2a and 2d). This is confirmed on the pole figures (Fig. 3), where both minerals show a certain degree of CPO that is slightly stronger in calcite [4.3 multiples of uniform distribution (MUD)] than aragonite (2.6 MUD). The pole figures are also used here to look for possible similarities between different poles of the studied mineral pairs, which may indicate that the development of a CPO of phase 2 is crystallographically controlled by phase 1, but do not fully proof that both phases have any orientation relationship along the interfaces. A careful comparison between the pole figures of both phases shows similarities. For instance, the [100] axes of aragonite are distributed in a broad girdle that is parallel to a similar girdle of poles to $(2\bar{1}\,\bar{1}0)$ of calcite, whereas the distribution of [001] of aragonite is similar to the distribution of $(01\bar{1}8)$ of calcite. In addition, the strongest concentration of [010] and [110] in aragonite are subparallel to the maximum concentrations of (0001) and $(10\bar{1}4)$ of calcite, respectively.

The uniform misorientation angle distribution (i.e., the misorientation distribution expected in the case of a uniform, "random" ODF) shows a progressive increase in frequency to a maximum of 90° (Fig. 4a) and a sudden drop to a maximum misorientation angle ~92° (for the trigonal-orthorhombic relationship). The uniform misorientation axis distribution (Fig. 4b) has a weak maximum parallel to the poles of $(\bar{6}245)$ and symmetrically related, which are about 10° from the poles to $(1\bar{2}10)$, with a maximum of uniform distribution (MUD) around 2.5. The misorientation angle distribution for correlated (neighbor) interphase boundaries tends to follow the distribution expected in the case of a uniform distribution (Fig. 4c). In detail, however, the red bars that represent the misorientation angle between neighbor phase boundaries show that the peaks between 25 to 50° occur in higher frequencies than the ones expected in the case of non-neighbor pairs (red line) or uniform distribution (orange line). This suggests that phase boundaries within this angle range show some sort of physical relationship that the uncorrelated distribution does not present, which might indicate a special orientation relationship between calcite and aragonite.

For the orientation relationship $(11\bar{2}0)$ calcite || (100) aragonite and [0001] calcite || [110] aragonite, the misorientation axis

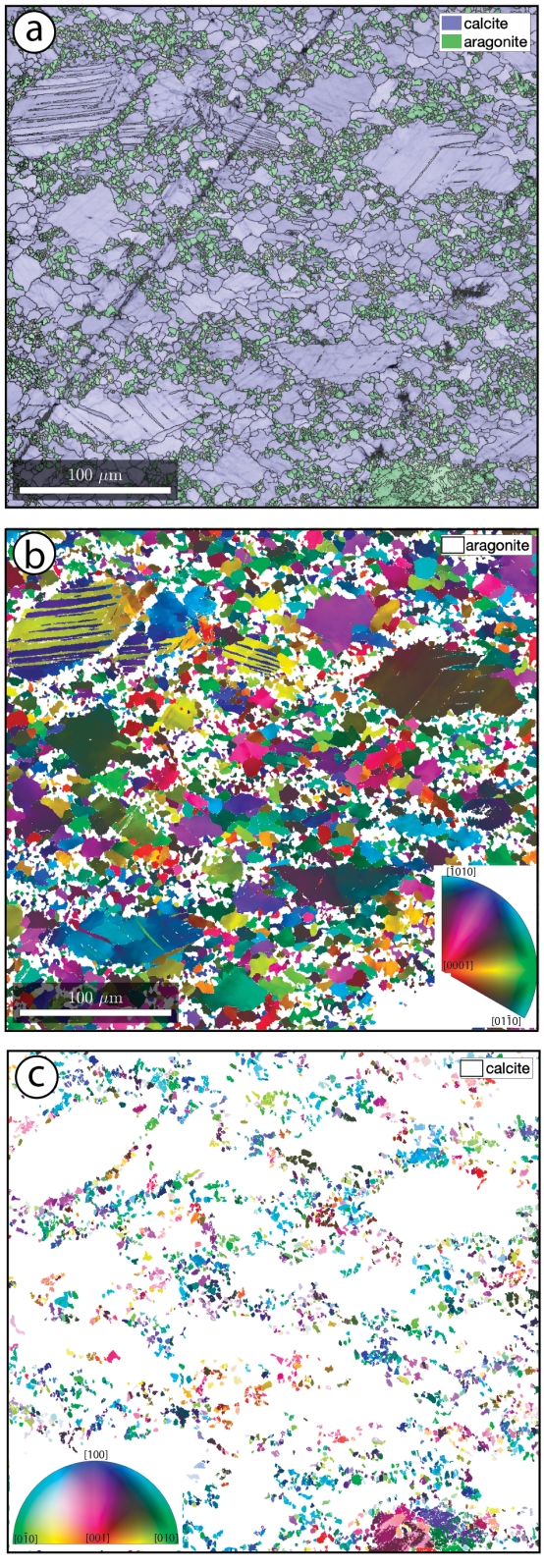


Figure 2. (**a**) Combined phase and image quality map, showing the distribution of calcite and aragonite. (**b** and **c**) Orientation maps (IPF color-coded, direction of view normal to the screen) for calcite (**b**) and aragonite (**c**). Inverse pole figure color-coded in the inset.

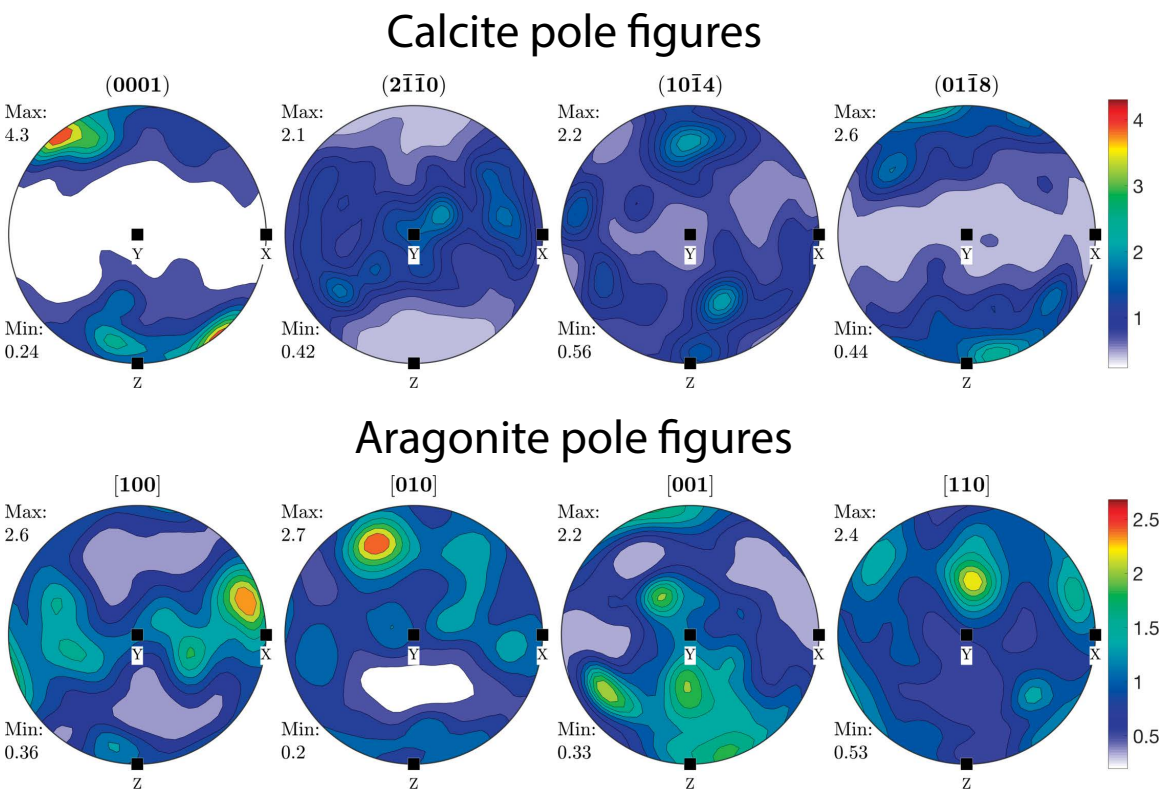


Figure 3. Pole figures for calcite and aragonite considering all points in the orientation maps from Figure 2. Scale is given in multiples of uniform distribution. ODFs calculated assuming a halfwidth of 10°. (Color online.)

is 54.2°, and the misorientation axis is parallel to (2$\bar{1}$ $\bar{1}$0) in the calcite reference frame and to (100) in the aragonite reference frame. If we now plot the misorientation axes for the whole range of misorientation angles for the calcite-aragonite phase boundaries, there is a vast distribution around the primitive circle of the stereonet and a weak maximum parallel to the pole of (2$\bar{1}$ $\bar{1}$0), in agreement with a dominant topotactic relationship transformation between calcite and aragonite (Fig. 4d). Note that due to the symmetry, only two out of four symmetrically equivalent pole to planes of aragonite are parallel to two out of three pole to planes in calcite, which are $(1\bar{1}08)_{cal} \parallel (\bar{1}1\bar{3})_{ar}$ and $(\bar{1}01\bar{8})_{cal} \parallel (\bar{1}\,\bar{1}\,3)_{ar}$. The interface trace map in the Figure 4e shows a broad range of distribution of misorientation angles for the interface traces, but about 41% of the phase boundaries between calcite and aragonite have a range of misorientations between 40–70°.

Olivine-antigorite

The sample MR-1 contains about 60% volume of hydrous phases (chlorite, tremolite, and antigorite), and about 40% of the lithospheric mantle olivine framework is still preserved (e.g., Fig. 5). The sample's microstructure is described in details by Morales et al. (2013). The thin section studied here was cut normal to the antigorite foliation and parallel to the dominant lineation. The phase boundaries between olivine and the hydrous phases in this sample are predominantly straight and sharp, while the contacts between hydrous phases might be blurred and difficult to identify visually.

Olivine and antigorite bulk crystallographic preferred orientation is given in the Figure 6. Due to the relatively coarse grains and the dismembering due to the antigorite, the olivine CPO is relatively complex but not very strong (maxima of 3.9 MUD), with [100] orientated around 20° from the antigorite lineation and [010] and [001] distributed along incomplete girdles, normal and parallel to the XZ plane, respectively. Antigorite, on the other hand, has a strong texture [8.5 MUD for (001)] and has a typical (001) fiber-texture, with the poles of (001) strongly orientated at a small angle to the pole of the foliation and the poles of (100) and (010) distributed along girdles parallel to the reference foliation. Although it is not possible to establish clear orientation relationships between olivine and antigorite primary maxima from these figures, in detail the secondary maxima show some similarities. For instance, the secondary maxima of olivine [010] and [001] close to Z is parallel to the maxima of poles to (010) of antigorite.

The uniform misorientation angle distribution for olivine-antigorite (Fig. 7a) shows a progressive increase up to a maximum peak at 90°, when it drops down substantially, reaching a maximum misorientation angle ~120° for the combination of orthorhombic-monoclinic. The uniform misorientation axis distribution (Fig. 7b) shows a maximum peak on <947> with a MUD 1.6. The correlated misorientation angle distribution shows some peaks that are much higher than the expected distribution of non-correlated phase boundaries or the misorientation expected in the case of uniform ODF. In particular, the misorientation angles between 70–100° are considerably higher. If the

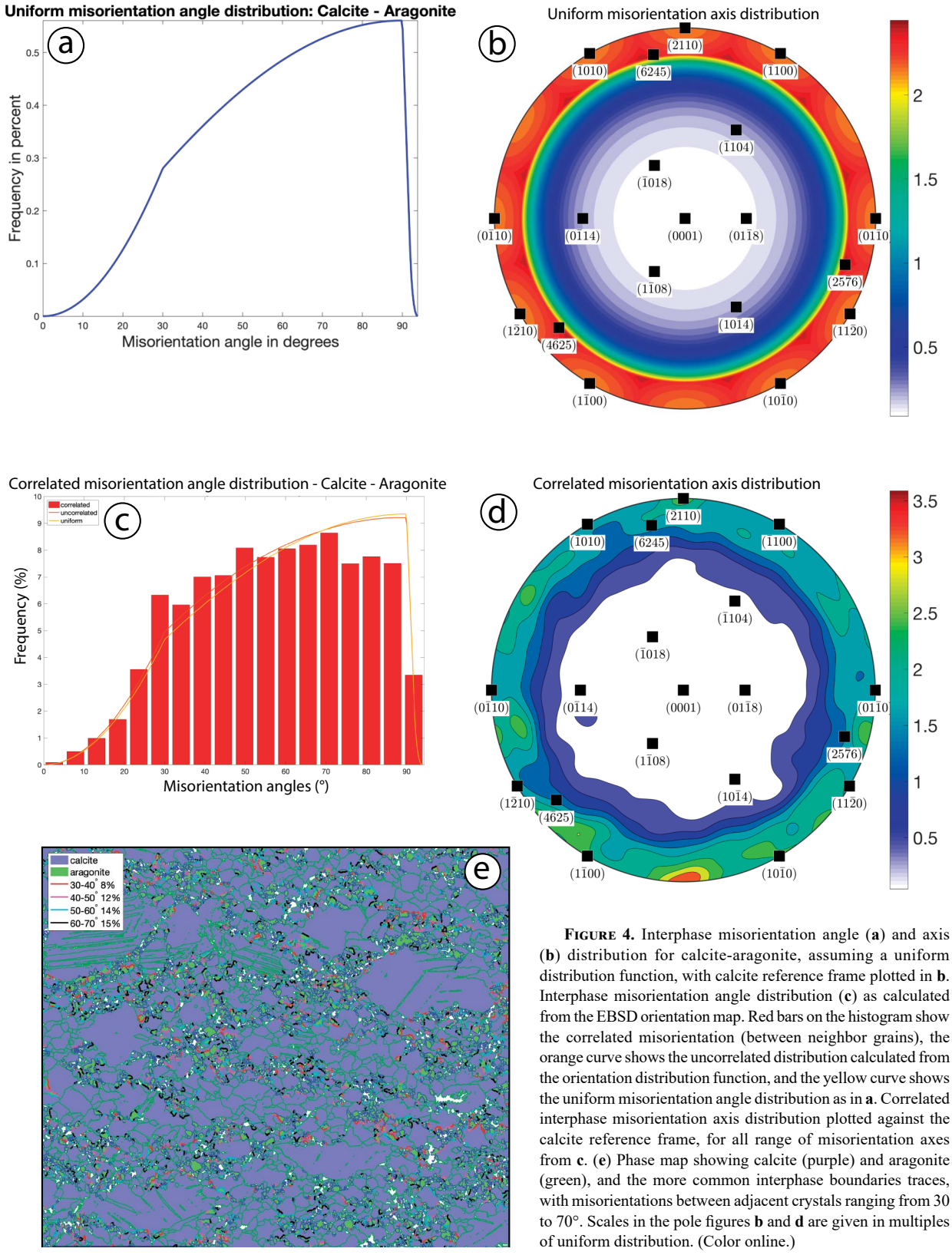
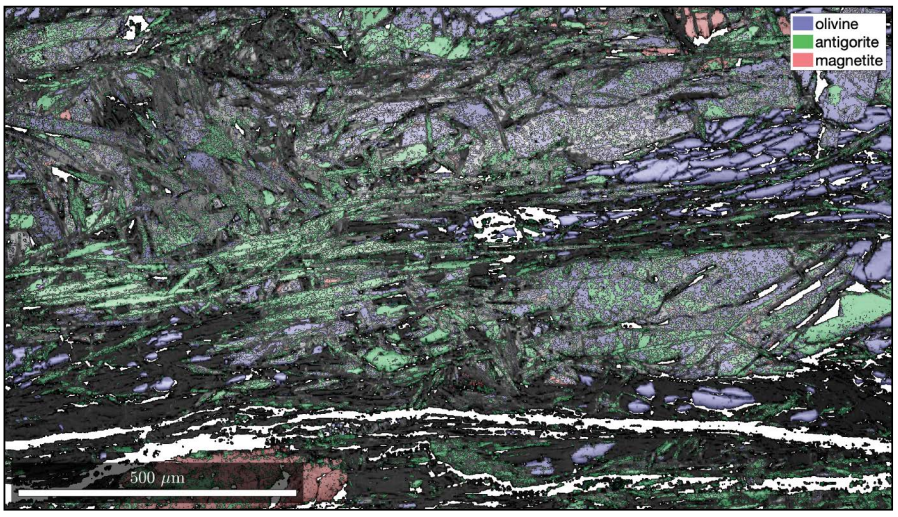
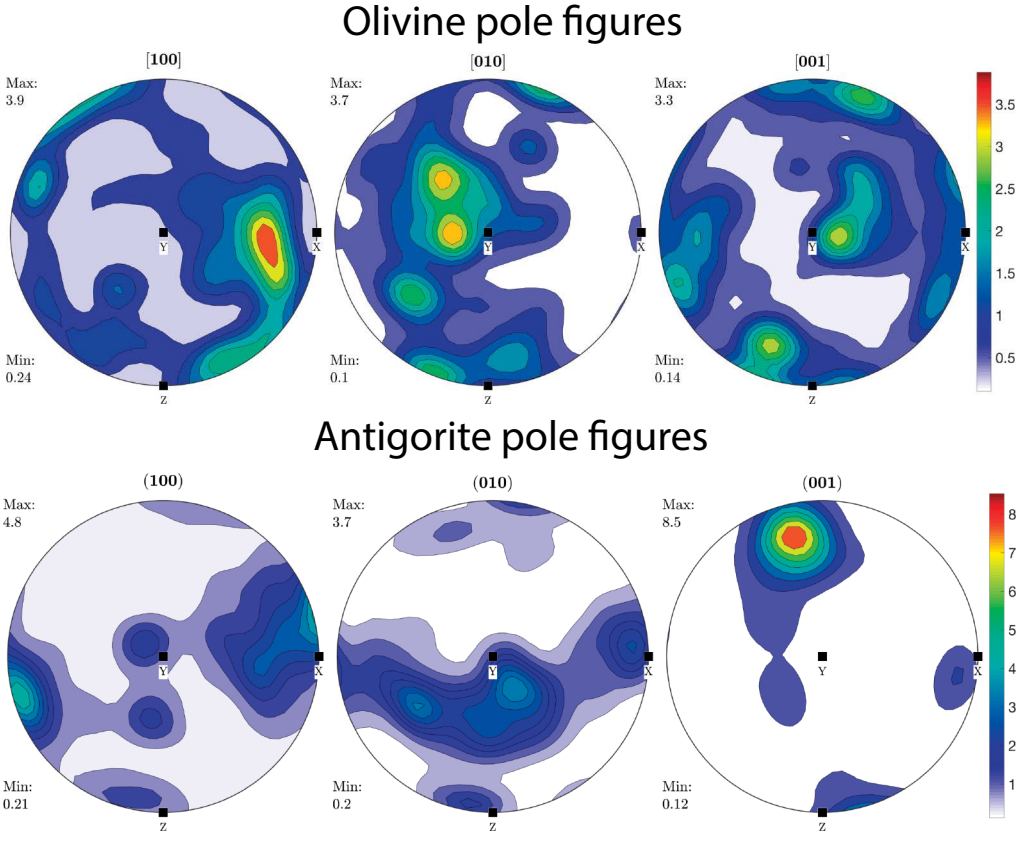


Figure 4. Interphase misorientation angle (**a**) and axis (**b**) distribution for calcite-aragonite, assuming a uniform distribution function, with calcite reference frame plotted in **b**. Interphase misorientation angle distribution (**c**) as calculated from the EBSD orientation map. Red bars on the histogram show the correlated misorientation (between neighbor grains), the orange curve shows the uncorrelated distribution calculated from the orientation distribution function, and the yellow curve shows the uniform misorientation angle distribution as in **a**. Correlated interphase misorientation axis distribution plotted against the calcite reference frame, for all range of misorientation axes from **c**. (**e**) Phase map showing calcite (purple) and aragonite (green), and the more common interphase boundaries traces, with misorientations between adjacent crystals ranging from 30 to 70°. Scales in the pole figures **b** and **d** are given in multiples of uniform distribution. (Color online.)



►**Figure 5.** Combined phase and image quality map, showing the distribution of olivine (purple) and antigorite (green), whereas the red phase at the top right and bottom left are isolated grains of magnetite.



►**Figure 6.** Pole figures for olivine and antigorite, considering all points in the orientation maps from Figure 5. Scale is given in multiples of uniform distribution. ODFs calculated assuming a halfwidth of 10°.

misorientation angle is now limited to this angular range, the resulting misorientation axis plot show a maximum parallel to the poles (094), which lies about 30° from [010]. This is almost equivalent to the [5$\bar{9}$4] axis described in Morales et al. (2018). The interphase boundary map presented in the Figure 7e shows that about 48% of the interfaces between olivine and antigorite have a range of misorientations between 80–100°, from which 27% have a 10° misorientation range of 90–100°.

Magnetite-hematite

In the studied sample, magnetite comprises ~60% volume and hematite ~40% volume, and the whole sample presents a massive structure. Hematite nevertheless seems to occur in "patches" on the EBSD map (Fig. 8). Magnetite shows almost uniform distribution of its main crystal directions [100], [110], and [111] with only [100] showing some degree of orientation subparallel to Z in the sample reference frame (Fig. 9). Hematite CPO, on the other

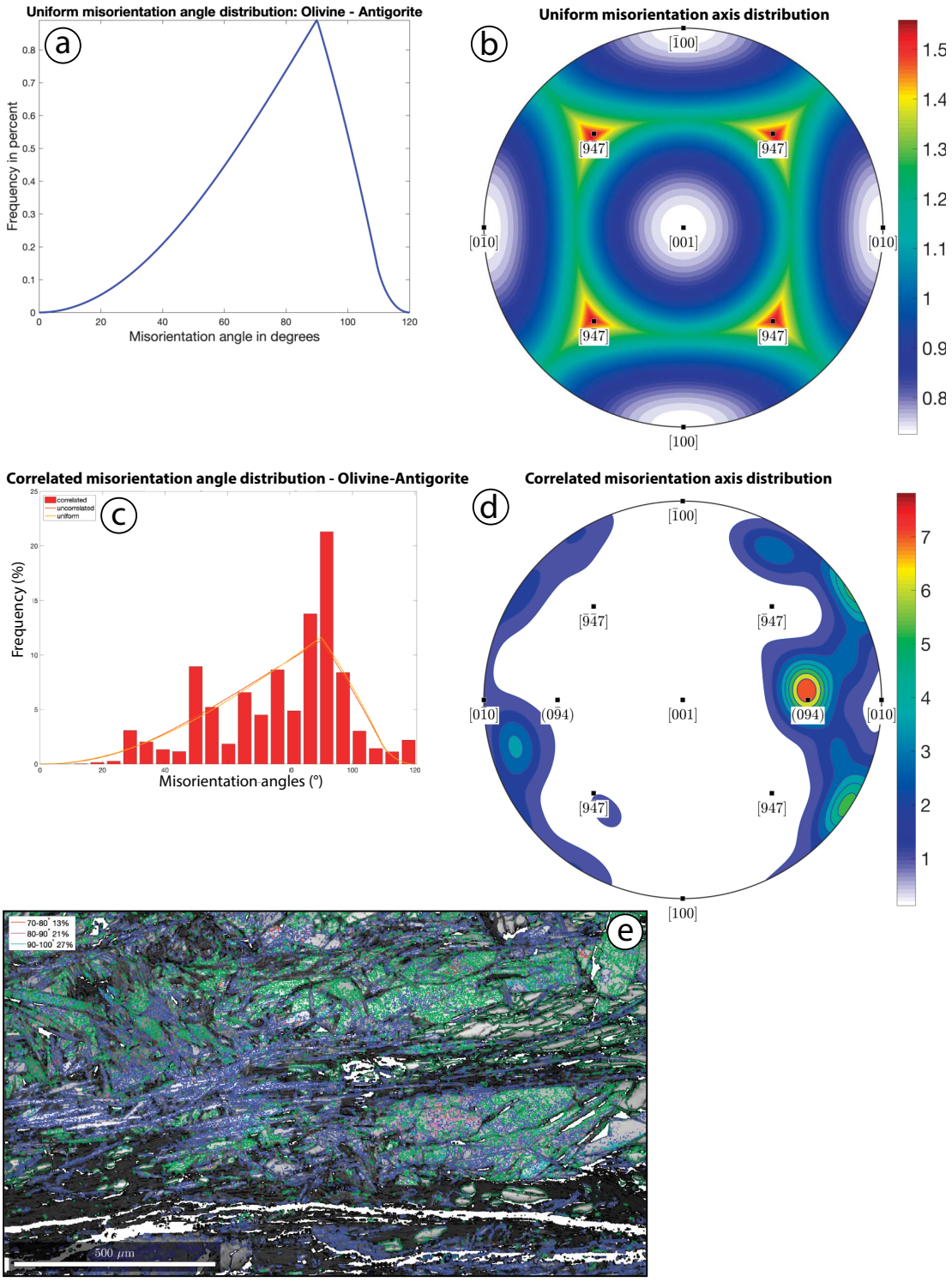


Figure 7. Interphase misorientation angle (**a**) and axis (**b**) distribution for olivine-antigorite, assuming a uniform distribution function, with olivine reference frame plotted in **b**. Interphase misorientation angle distribution (**c**) as calculated from the EBSD orientation map. Red bars on the histogram show the correlated misorientation (between neighbor grains), the orange curve shows the uncorrelated distribution calculated from the misorientation distribution function, and the yellow curve shows the uniform misorientation angle distribution as in **a**. Correlated interphase misorientation axis distribution (**d**) plotted against the olivine reference frame, for misorientations ranging from 70–100°. (**e**) Image quality map showing the more common interphase boundaries, with misorientations ranging from 70 to 100°. Scales in the pole figures (**b** and **d**) are given in multiples of uniform distribution. The phase map is not presented here for better visualization of the interfaces.

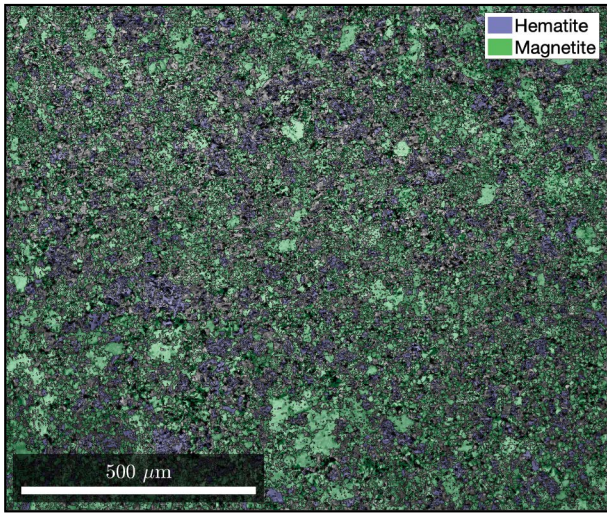


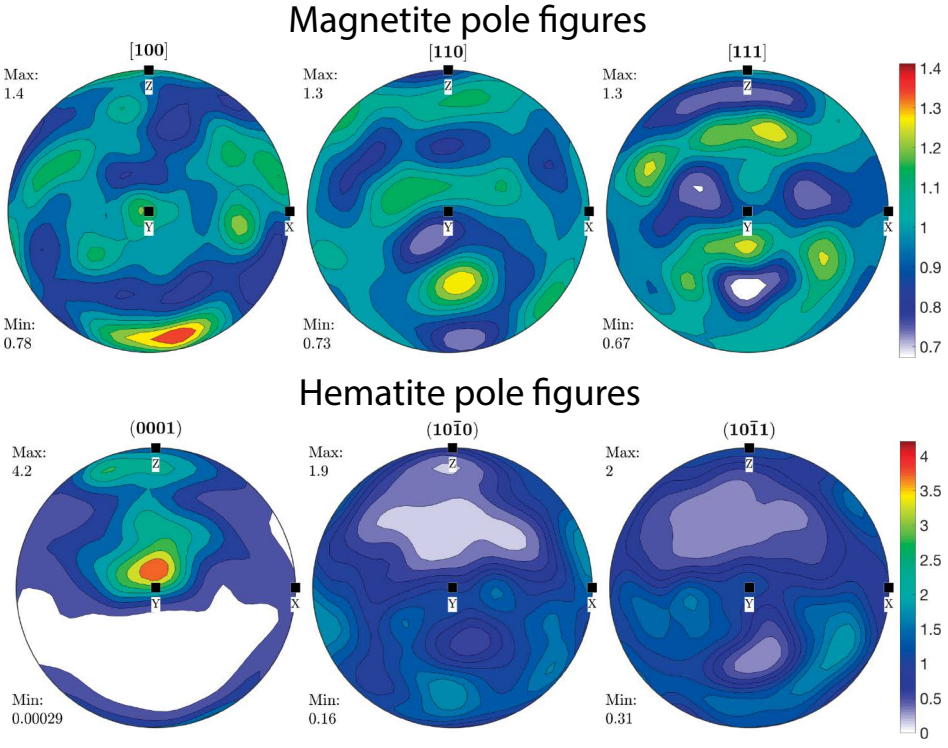
Figure 8. Combined phase and image quality map, showing the distribution of magnetite (purple) and hematite (green).

hand, is stronger (Fig. 9b) and shows a maximum concentration of poles to (0001) parallel to Y and a more complex distribution of poles of $(10\bar{1}0)$ and $(10\bar{1}1)$. At first, it seems that no clear relationships between the pole figures of magnetite and hematite exist. However, as magnetite is cubic, a rotation of 90° around x in the pole figure is allowed and would bring this maximum into parallelism with hematite (0001) pole figure.

The uniform misorientation angle distribution of magnetite-hematite shows a peak around 42° (Fig. 10a), followed by a fast drop to the maximum possible interphase misorientation angle between these two phases at 60°. The uniform misorientation axis distribution (Fig. 10b) shows a maximum peak on <231> with a MUD 3.5. The interphase misorientation angle distribution for neighbor crystals follows the same trend for the uncorrelated grains or the distribution expected in the case of uniform distribution (Fig. 10c). Nevertheless, it shows frequencies around 5% higher than the frequency expected in the case of uniform distribution. The correlated interphase misorientation axis (Fig. 10d) show a similar distribution as the uniform one, but only one stronger concentration parallel to [231] with MUD of ~8, with the other symmetrically equivalents ($[\bar{2}31]$, $[\bar{2}\bar{3}1]$, $[3\bar{2}1]$) showing weaker concentrations. The interphase boundary map (Fig. 10e) shows that 73% of the interphase boundaries have misorientations between 30–50°, and 41% lie in a range of 40–50°.

Plagioclase-olivine-ilmenite

In the studied sample of gabbro from the Atlantis bank, plagioclase is the dominant phase, and together with clinopyroxene, are the primary phases to crystallize in this sample. Plagioclase are predominantly subhedral, grain size varies from 100 to 600 μm (Fig. 11a), and a considerable number of grains still preserve magmatic twinning. The smaller plagioclase grains are interpreted as plagioclase subgrain rotation recrystallization (Allard et al. 2021). Plagioclase CPO is relatively weak, as seen in the orientation map with a large variety of colors (Fig. 11c). Olivine, on the other hand, occurs predominantly as anhedral grains that are much smaller in grain sizes (50–100 μm). In this sample, olivine seems to be (at least in part) a late phase, as it commonly occurs along interstitial spaces between plagioclase and diopside grain/phase boundaries and along pressure shadows adjacent to clinopyroxene porphyroclasts. Ilmenite grains are mostly anhedral in shape, grain sizes are between 20–70 μm, and occur predominantly in contact with plagioclase (Fig. 11a).



►**Figure 9.** Pole figures for magnetite and hematite, considering all points in the orientation maps from Figure 8. Scale is given in multiples of uniform distribution. ODFs calculated assuming a halfwidth of 10°.

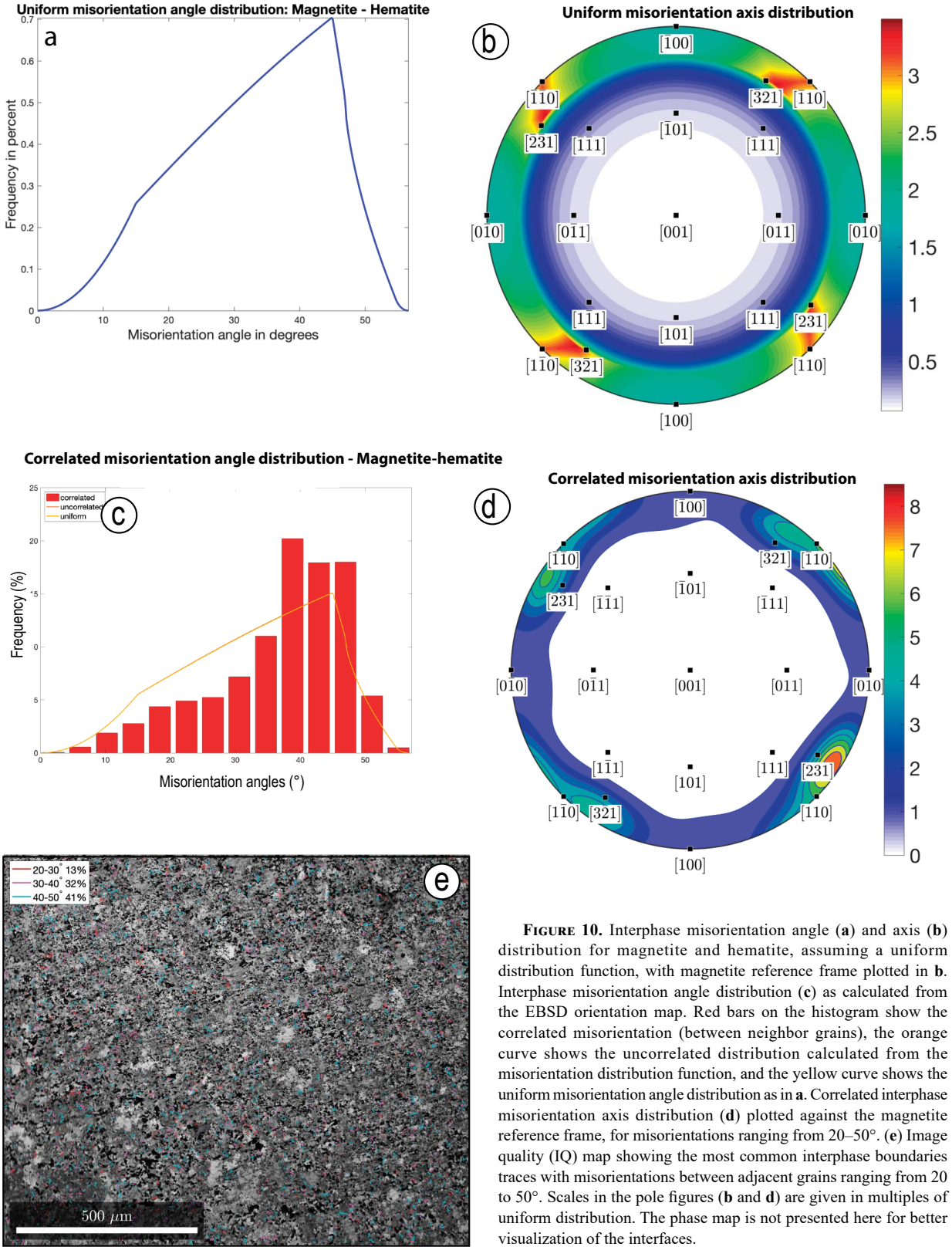


Figure 10. Interphase misorientation angle (**a**) and axis (**b**) distribution for magnetite and hematite, assuming a uniform distribution function, with magnetite reference frame plotted in **b**. Interphase misorientation angle distribution (**c**) as calculated from the EBSD orientation map. Red bars on the histogram show the correlated misorientation (between neighbor grains), the orange curve shows the uncorrelated distribution calculated from the misorientation distribution function, and the yellow curve shows the uniform misorientation angle distribution as in **a**. Correlated interphase misorientation axis distribution (**d**) plotted against the magnetite reference frame, for misorientations ranging from 20–50°. (**e**) Image quality (IQ) map showing the most common interphase boundaries traces with misorientations between adjacent grains ranging from 20 to 50°. Scales in the pole figures (**b** and **d**) are given in multiples of uniform distribution. The phase map is not presented here for better visualization of the interfaces.

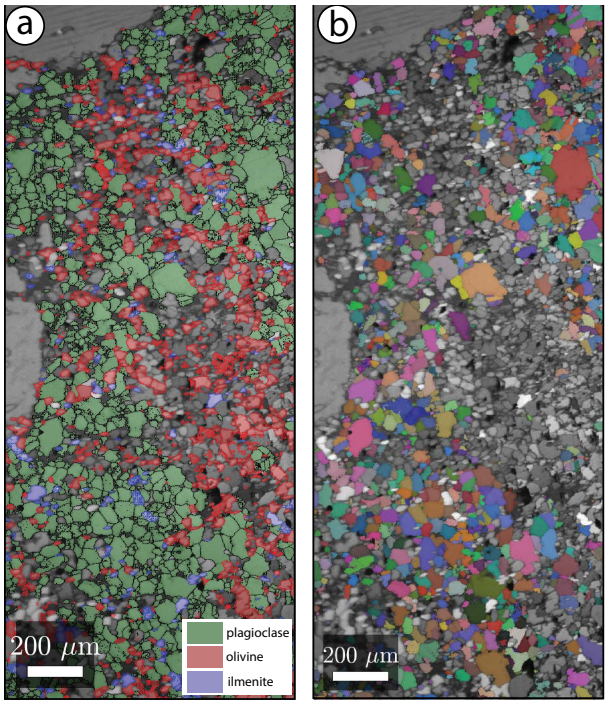


Figure 11. (**a**) Combined phase and image quality map, showing the distribution of plagioclase (green), olivine (red) and ilmenite (blue) in the studied gabbro sample. (**b**) Combined orientation map for plagioclase (IPF color-coded) and image quality for the rest of the phases.

The pole figures for plagioclase, olivine, and ilmenite are plotted in a sample reference frame where the foliation is vertical N-S (so the pole of the foliation is at E in the pole figure), and the lineation also N-S, but horizontal (Fig. 12). All the pole figures show a weak crystallographic preferred orientation. Plagioclase (100) poles are distributed along a broad, asymmetrical vertical girdle cross-cutting Y, while the poles to the (010) are mainly concentrated at an angle of ~15° with the pole of foliation. Olivine [100] axes are predominantly concentrated parallel to Y, [010] and [001] broadly distributed with weak maxima parallel to the pole of the foliation (the former) and parallel to the lineation (the latter). The (0001) pole of ilmenite are preferentially aligned with Y, while the poles of the $(10\bar{1}1)$ rhombs are at low angle with the pole of the foliation Z and the poles to the $(10\bar{1}0)$ prisms subparallel to the lineation, but showing secondary, symmetrically related maxima every ~60°. However, in this case, similarities between pole figures are more important than CPO strength. For instance, the distribution of [100] and [010] of olivine shows similarities with the (100) and (010) poles of plagioclase, while the poles of (0001) and $(10\bar{1}0)$ of ilmenite shows similarities with the (100) poles of plagioclase, and the distribution of $(10\bar{1}1)$ poles of ilmenite are comparable to the poles of the (010) planes of plagioclase (Fig. 12).

The misorientation angle distribution assuming a uniform distribution show, for the plagioclase-olivine, a peak at misorientation angles ~83° and a sudden drop to a maximum misorientation of ~120° (Fig. 13a). Due to the triclinic-orthorhombic combined symmetry (plagioclase-olivine), the misorientation axes have to be presented in both upper and lower hemispheres, where the maximum misorientation angle expected in the case of a uniform distribution is subparallel to the <253> of olivine, with a MUD of 1.7 (Fig. 13b). In the case of plagioclase-ilmenite, the maximum misorientation angle expected in the uniform case is ~90°, with frequencies dropping progressively to a maximum angle of 180° (Fig. 13c). The misorientation angle distribution for the plagioclase-ilmenite seems to be distributed all over along the primitive circle of the stereonet, but the calculation of the misorientation distribution function shows a weak maxima close to the poles of the $\{32\bar{1}0\}$ planes of ilmenite and subparallel to [100] of plagioclase, with a MUD of 3 (Fig. 13d).

The distribution of interphase misorientation angles for neighbor (correlated) plagioclase-olivine grains show abnormal frequencies for misorientation angles between 65 and 90° (>2% of the uncorrelated/uniform distribution; Fig. 14a). If we limit the range of misorientation angles to the one above and plot the misorientation axes, the orientation is not very strong (2.5 MUD), but it shows a maximum parallel to the pole to the (100) of plagioclase, two other maxima with similar MUD, and a secondary maximum parallel to [010] of plagioclase [parallel to the pole to the (010) plane; Fig. 14b]. The misorientation angle distribution for the pair plagioclase-ilmenite shows several higher frequency peaks intercalated with lower frequency peaks (Fig. 14c) when compared with the uncorrelated/uniform distributions. Also, the studied sample does not show misorientation peaks larger than 165°. For simplicity, we focus on the misorientation peaks between 85–130°. When limited to this range, most of the misorientation axes are parallel to the [100] of plagioclase, with a MUD of 9. The interphase boundary map (Fig. 15a) shows that about 70% of the boundaries between plagioclase and olivine have a narrow range of misorientations between 60 and 100°, while in the case of plagioclase-ilmenite the range is more variable (Fig. 15b), and about 50% of the interphase boundaries between these two phases have a range of misorientations between 60 and 120°.

Implications

Easier assessment of interphase boundary orientation relationships

Different from grain boundaries separating grains of the same composition and structure, interphase boundaries are interfaces that normally separate grains with different structures and/or compositions. Because of this complexity, only individual interfaces are normally studied at the time, in most cases via selected area diffraction (SAD) in a transmission electron microscope (TEM). SAD-TEM provides very detailed information in terms of angular and spatial resolution of orientation relationships between the two phases separated by the interface (atomic-scale resolution with angular resolutions <0.1°) at the expense of statistical representativeness. Electron-transparent sample preparation for TEM is not trivial and for certain geological materials can be challenging. As an example, to prepare standard in situ TEM lamellae via focused ion beam techniques, one needs around 2 h. However, one has to consider that the area of such a sample is around 150 μm^2 and ~100 nm thick, so in the case of a very fine-grained material, one may observe a few interphase boundaries, but in the case of a more coarse-grained rock, one might be able to see only one interface. In addition, TEM operation and correct indexing of diffraction patters from SAD (particularly for

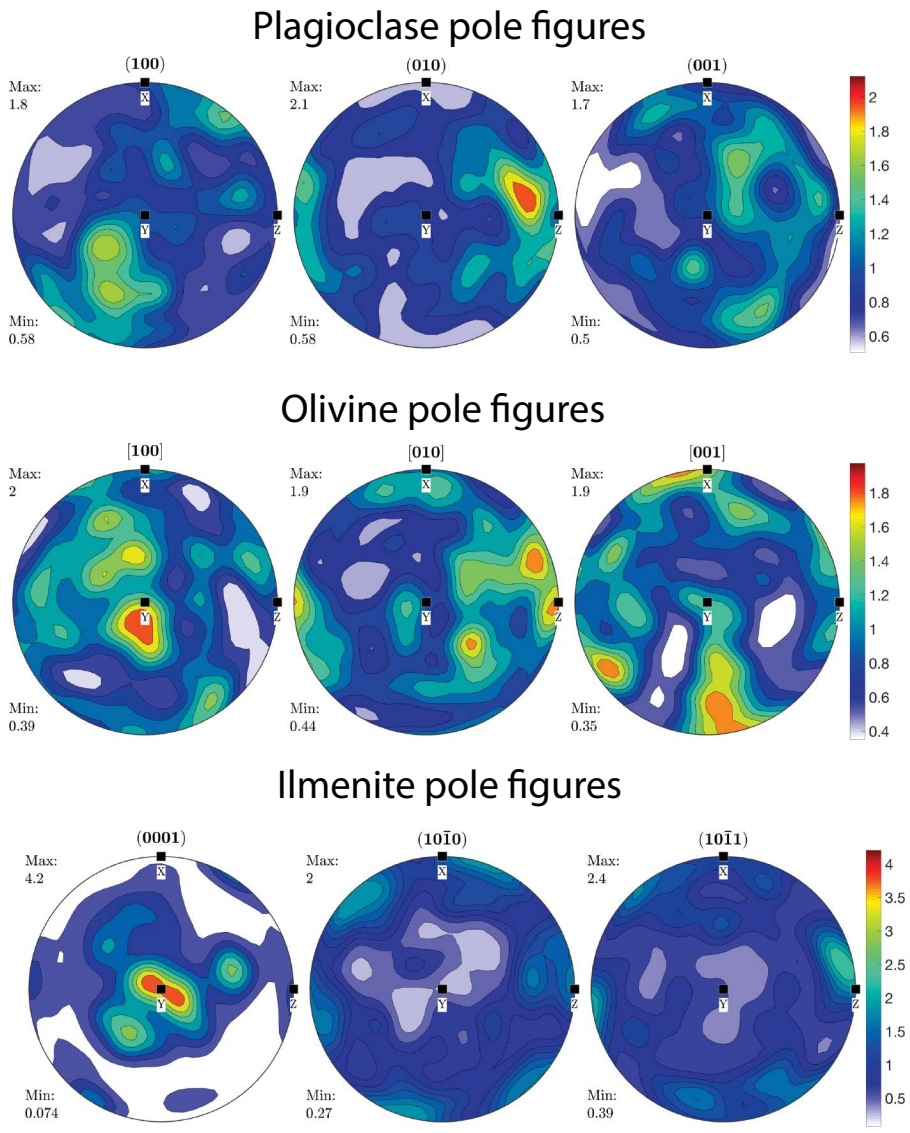


Figure 12. Pole figures for plagioclase, olivine and ilmenite, considering all points in the orientation maps from Figure 8. Scale is given in multiples of uniform distribution. ODFs calculated assuming a halfwidth of 10°.

low-symmetry phases) are more complex and time-consuming than SEM operation and EBSD mapping and require extensive training to be done effectively. As demonstrated here with EBSD maps, one can see a statistically representative number of interfaces on samples that have different phases and different grain sizes. As we know the orientation of the grains separated by the interface, we can then calculate the misorientation angle/axis between these grain pairs, which can be used to infer possible orientation relationships between the two phases. As an example, we know that $(11\bar{2}0)_{cal} \parallel (100)_{ara}$ and $[0001]_{cal} \parallel [011]_{ara}$. If we know now the orientation of the daughter phase (in this case, aragonite), we can compute the orientation of the parent phase following the MTEX script presented in the Online Materials[1].

The intention here is not to say that EBSD-derived interphase misorientation is a substitute for TEM analysis. In fact, the idea is to use EBSD mapping to precisely locate the orientation and misorientation of specific interphase boundaries and use this data to select the interfaces one wants to study in more detail in the TEM. The interphase misorientation analysis does not give us the degree of coherency between the phases separated by the interface, nor any atomic resolution along the interface separating two minerals. On the other hand, once you have an EBSD map, you can test possible misorientation relationships between any phase present in the map. That was the case of the gabbro sample whose results are presented in Figures 11 to 15; I have tested all the possible pairs of phases within the map and found that plagioclase-olivine and plagioclase-ilmenite have an orientation relationship that can further be analyzed in the TEM.

Interphase orientation relationships

Phase transformations in geological materials leading to interphase orientation relationships between parent→daughter

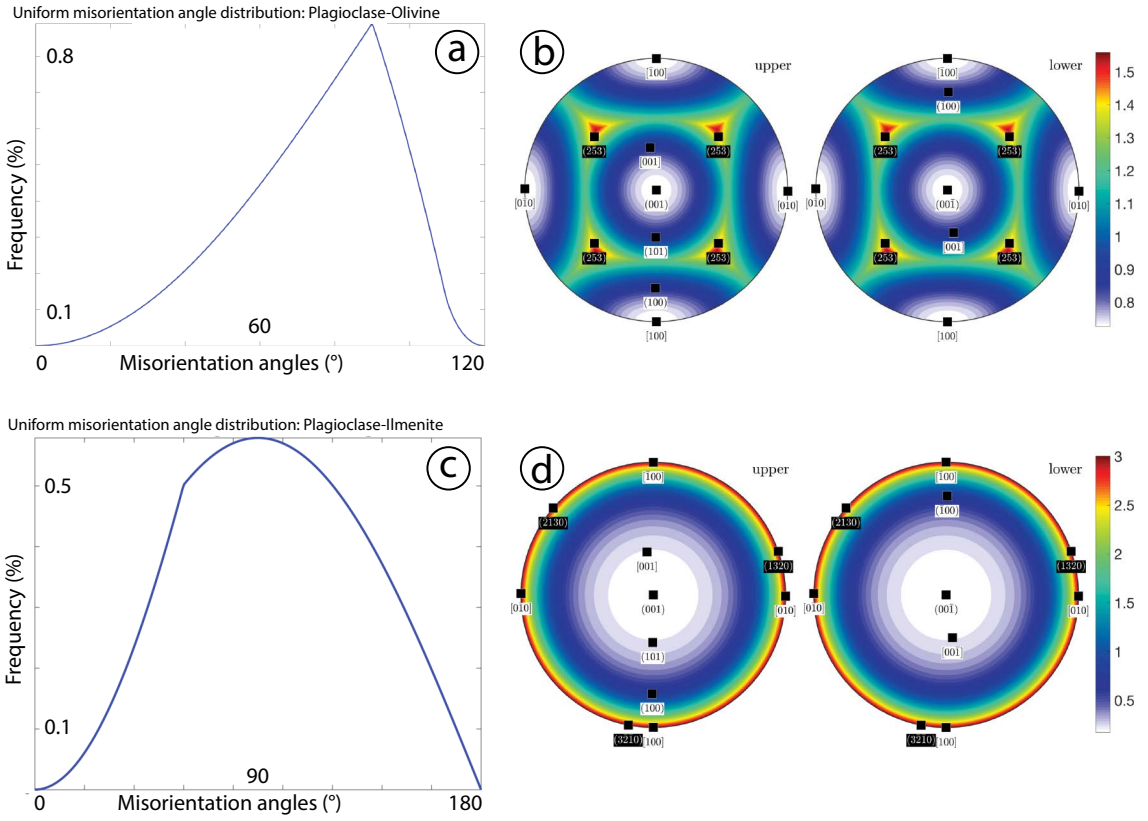


Figure 13. Interphase misorientation angle (**a** and **c**) and axis (**b** and **d**) distribution for the pair's plagioclase-olivine and plagioclase-ilmenite, respectively, assuming a uniform orientation distribution function. On stereogram (**b**) plagioclase reference frame is given as black letters in white background, whereas certain olivine directions are given in black background and white letters. The same is valid for the plot (**d**), but for ilmenite. Scale bars in **b** and **d** are given in multiples of uniform distribution.

phases occur predominantly by two major mechanisms: martensitic and nucleation/growth mechanisms. From the four different systems studied in this paper, two belong to the nucleation/growth mechanism (olivine→antigorite and magnetite→hematite), one can be either interpreted as a martensitic or nucleation/growth (calcite→aragonite) and are discussed in a bit more detailed below. In fact, martensitic transformations have been referred to in the material sciences literature as a type of nucleation/growth type of transformation that occurs in much shorter time scales (e.g., Olson and Cohen 1972; Guimarães and Rios 2008). Plagioclase→olivine and plagioclase→ilmenite, on the other hand, do not represent phase transformation of any sort, but because the misorientation angle/axis pair show what looks like special relationships, these results are discussed in terms of orientated growth below.

Nucleation and growth mechanisms are normally associated with diffusion and therefore tend to be thermally activated or enhanced. The growth of one phase into another also depends on the interfacial free energy, the Gibbs free energy of the reaction, and the strain-free energy (e.g., Mainprice et al. 1990; Porter and Easterling 1992). Phase transformation from parent phase to daughter phase may occur by only changing the structure from the parent phase (e.g., calcite-aragonite) or by changing both the composition structure between the two phases (e.g., magnetite-hematite or olivine-antigorite). This process starts with the homogenous (or heterogeneous) nucleation of the daughter phase. The homogeneous nucleation is controlled by the energy to form the nucleus of the daughter phase, and because of that, it requires activation energies much higher than those required for heterogeneous nucleation (e.g., Porter and Easterling 1992; Sunagawa 1994). Heterogeneous nucleation refers to the nucleation of the daughter phase along the parent phase substrate and requires much less activation energy because the interface between the old and new phases considerably reduces the surface energy value. Heterogeneous nucleation normally occurs along intracrystalline defects (dislocations, grain/interphase boundaries) or due to the presence of inclusions where the initial nuclei of the daughter phases grow normally by diffusion processes.

Classical examples of this mechanism include the hydration of olivine and formation of antigorite and the transformation of magnetite into hematite. Plümper et al. (2012) showed that the initial exchange of Fe-Mg along (100) dislocation walls in olivine lead to the first steps of topotactic formation of antigorite along this plane in olivine, something also observed in Boudier et al. (2010). As demonstrated in Figure 7c, the highest frequency interphase misorientation range is between 80–100°, with a dominant misorientation axis parallel to the (094) poles, which departs 15° from the interphase misorientation axes parallel to

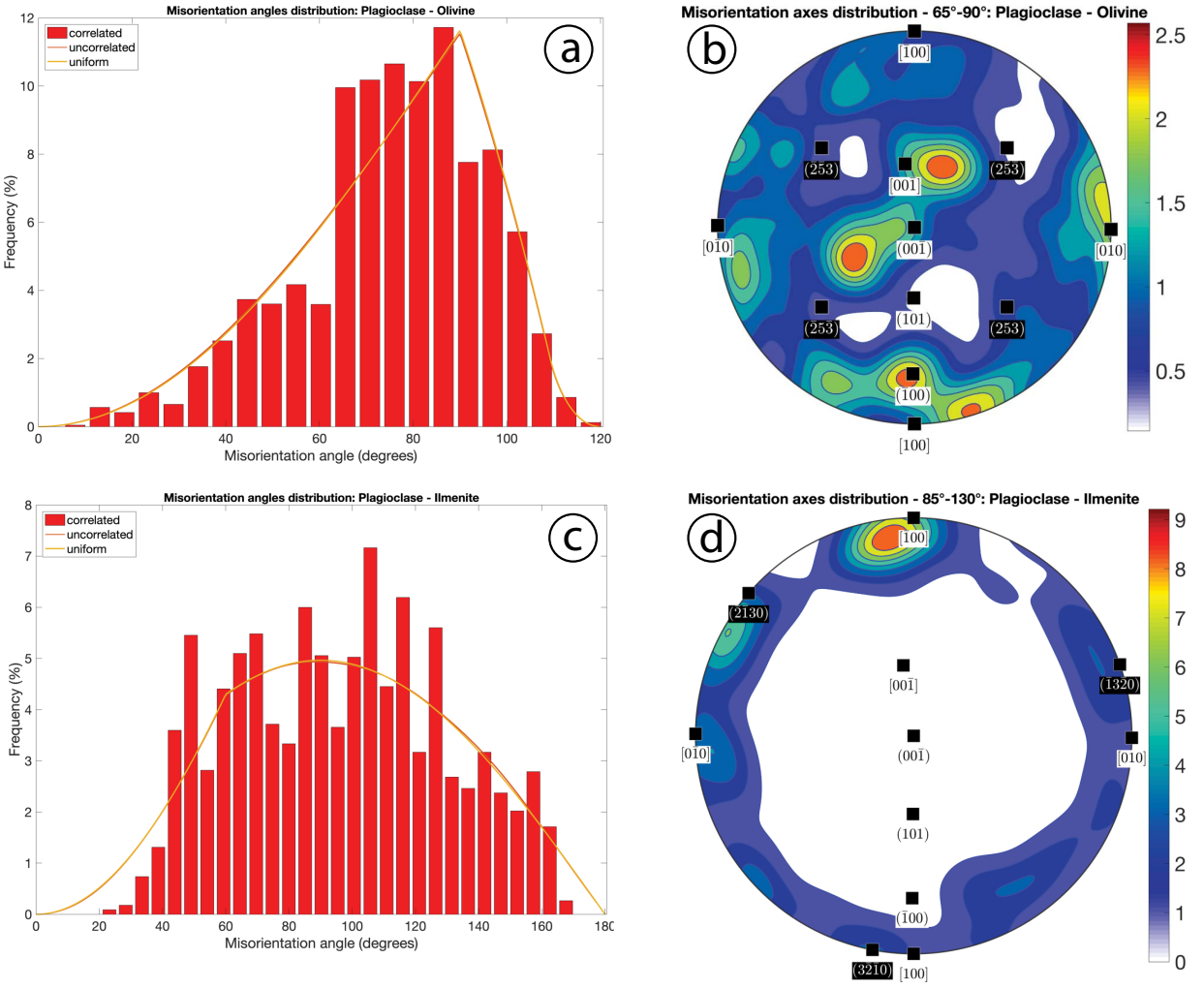


Figure 14. Interphase misorientation angle distribution (**a** and **c**) and axes (**b** and **d**) as calculated from the EBSD orientation map, for the pair's plagioclase-olivine and plagioclase-ilmenite, respectively. Red bars on the histogram show the correlated misorientation (between neighbor grains), the orange curve shows the uncorrelated distribution calculated from the misorientation distribution function, and the yellow curve shows the uniform misorientation angle distribution as in Figures 13a and 13c. On the plot of **b** misorientation angles are limited to a range between 65–90° for plagioclase-olivine, whereas in **d** the misorientation range is from 85–130°, for plagioclase-ilmenite pair. On stereogram (**b**) plagioclase reference frame is given as black letters in white background, whereas certain olivine directions are given in black background and white letters. The same is valid for the plot (**d**), but for ilmenite. Scale bars in **b** and **d** are given in multiples of uniform distribution.

the (5$\bar{9}$4) poles determined in Morales et al. (2018). Considering that the sample studied here is less deformed and has the olivine grain network much better preserved than the antigorite schist investigated in the aforementioned study, we conclude that the interphase misorientation relationships are compatible with the type 4 phase transformation of $(010)_{ol} \parallel (210)_{atg}$ and $[100]_{ol} \parallel [001]_{atg}$, determined by Morales et al. (2018) using the interphase misorientation angle/axes.

Calcite-aragonite transition and the orientation relationships between the two phases have been extensively studied in the past (e.g., Carlson and Rosenfeld 1981; McTigue and Wenk 1985; Gillet et al. 1987), and two main mechanisms for the phase transformation has been proposed. While the experimental results suggest that the heterogeneous nucleation and topotactic growth is the dominant mechanism under a variety of conditions in agreement with the model from Carlson and Rosenfeld (1981), Gillet and Madon (1982) proposed a martensitic mechanism for the calcite-aragonite transition. In this model, stacking faults dragging by partial dislocation movement is responsible for the phase transformation. In contrast to (normally) slow nucleation and growth mechanisms, martensitic phase transition can be a very fast mechanism, normally producing a metastable phase. Martensitic transformation occurs by the progressive and systematic shearing of the lattice of the parent phase in a way that the distance in which any atom moves is less than one atomic spacing, which implies that the lattice is distorted, but the atoms retain the same neighbors. Because of that, martensitic transformation only leads to change in the structure of the phases, and not in composition, to accommodate the shearing described above.

Gillet et al. (1987) described the dominant phase transition orientation relationship for calcite→aragonite as $(11\bar{2}0)_{cal} \parallel (100)_{ara}$ and $[0001]_{cal} \parallel [011]_{ara}$. McTigue and Wenk (1985) on

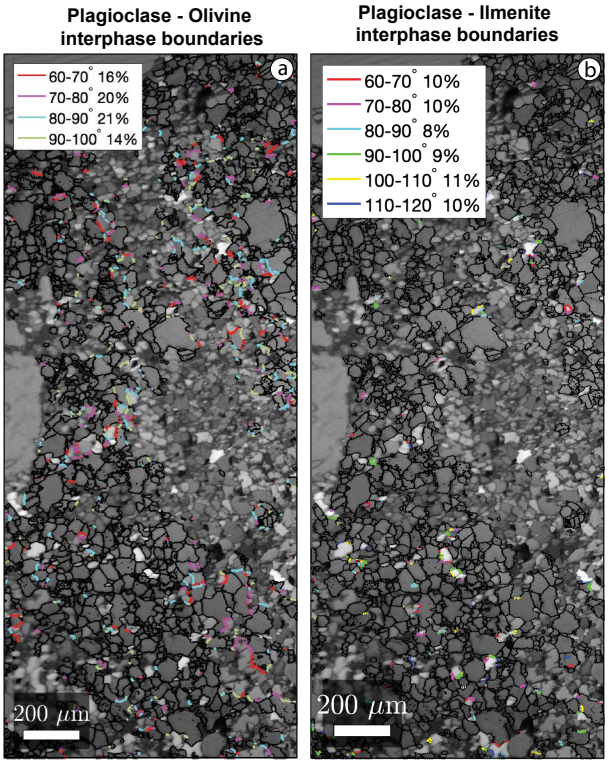


Figure 15. Image quality maps showing plagioclase-olivine interphase boundaries traces with adjacent interphase misorientations ranging from 60–100° misorientation (**a**) and plagioclase-ilmenite interface traces with misorientation ranging from 60–120°.

the other hand described $(11\bar{2}0)_{cal} \parallel (010)_{ara}$, $(10\bar{1}4)_{cal} \parallel (011)_{ara}$ and $[r2{:}f1]_{cal} \parallel [001]_{ara}$. The predominant misorientation angle of 54.2° with a dominant axis parallel $(2\bar{1}\,\bar{1}0)$ of calcite reference frame of the studied sample indicates that, in general, the transformation orientation relationship, in this case, is the one described by Gillet et al. (1987). However, when the misorientation angle is limited to a narrow range between 25° and 50°, the misorientation axis change to parallel to the pole to the $(01\bar{1}8)$, which is the twin plane of e-twins in calcite. Although we do not have access to the orientation of the interface along twin planes, it seems from the EBSD map that the red interphase boundary traces are visually subparallel to the twin planes, for example, of the grains on top-left of the map (Fig. 4e). This observation is in agreement with Figures 2a–2b, where several aragonite grains occur wrapped around a heavily twinned calcite grain, and those grains in contact with that specific calcite grain are the ones that produce the misorientation axis subparallel to $(01\bar{1}8)$.

Transformation from magnetite to hematite is another example of nucleation and growth mechanism, where hematite growths topotactically on magnetite, following the main orientation relationship $(111)_{mag} \parallel (001)_{hem}$ and $(\bar{1}01)_{mag} \parallel (100)_{hem}$ (Heizmann et al. 1981; Lagoeiro 1998; Barbosa and Lagoeiro 2010). These authors described other orientation relationships, and the transformation magnetite-hematite-magnetite is, in their case, reversible and always topotactically controlled. The misorientation angle for the topotactic orientation described above is ~56°, and the misorientation axis is parallel to <793> of magnetite, which is about 4° from the direction <231> expected in the case of a uniform distribution (Fig. 10b) As we see in the histogram from Figure 10c, all the misorientation angles above 40° occur more frequently than expected in the case of a uniform distribution, with the highest bin showing misorientations between 45–50°. However, the misorientation axis is very close to the one expected in the case of a random orientation of both magnetite and hematite. As demonstrated in the pole figures (Fig. 9), hematite CPO is stronger than magnetite, and no clear relationship between the pole figures can be made, unless we consider a rotation of 90° of magnetite around x, which would bring the maximum now at the S to parallelism with (0001) hematite. That would imply, however that, in this specific sample, we have a $(100)_{mag} \parallel (001)_{hem}$ sort of relationship. Although this may represent a new possible topotactic orientation relationship, one must consider that the studied EBSD map has a very large number of grains and already around 40% of hematite. At these conditions, it is difficult to imagine that every single crystal of hematite resulted from the transformation of magnetite on one of the symmetrically related $(111)_{mag}$ planes. I believe that the transformation magnetite-hematite indeed initiates along $(111)_{mag}$ as clearly shown by Barbosa and Lagoeiro (2010), but once the reaction is initiated, magnetite starts to be transformed to hematite along other low-index interfaces, and the initial orientation relationship was progressively lost. Deformation localization in iron ores like the studied sample normally leads to the oxidation of magnetite and consequent transformation to hematite, and deformation is predominantly accommodated by hematite. In this case, hematite can develop stronger CPOs than magnetite (e.g., Morales et al. 2018), and that may potentially affect the interphase misorientation distribution angles. It seems that in all studied cases here, the transformation from parent to daughter phase occurs preferentially (but certainly not exclusively) following certain orientation relationships.

Exploring unknown orientation relationships

So far, we have explored the interphase misorientation analysis in examples where we know that the orientation of a daughter phase is partially/completely controlled by the orientation of the parent phase. However, if one has EBSD orientation maps of "normal" rocks (polymineralic), one can explore potential interphase misorientation angle/axis relationships and find possible "orientation relationships" between the phases presented in these maps. We shall obviously not expect that all the phases will have any sort of relationship with the other phases in the aggregate, but let us consider the example of the oxide-rich gabbro studied here. The EBSD map of this sample has six different minerals (plagioclase, clinopyroxene, olivine, pargasite, ilmenite, and magnetite; Fig. 11 only shows the three where orientation relationships were found). Tests conducted in all possible pairs of minerals within this list resulted in 15 different interphase misorientation angle/axis pairs. From these 15 pairs, only two (plagioclase-olivine and plagioclase-ilmenite) have shown some sort of orientation relationships between the two phases. In both cases, the orientation relationships have nothing to do with nucleation/growth nor martensitic transformations, as the minerals have different compositions and structures. The orientation relationships between plagioclase-olivine and plagioclase-ilmenite in the studied sample seem to be related to epitaxial growth of olivine and ilmenite on

plagioclase, possibly controlled by the surface energy of plagioclase and wetting surfaces on this phase.

In the studied sample, plagioclase (together with diopside) is the primary phase and crystallizes first in its magmatic history, while both olivine and (later) ilmenite seem to crystallize from residual melts later in the cooling history of the gabbro. The surface energy along a solid-liquid interface is mainly controlled by the atomic structure on the interface, which in turn depends on its crystal orientation (e.g., Laporte and Watson 1995). In addition, the crystallization of second phases using a host crystal as "substrate" depends on the crystal structures of the two phases, and any possible relation orientation between the host and the precipitate depends on the fit of the lattices between these two phases (e.g., Sutton and Balluffi 1995). In the case of the studied gabbro, the interphase misorientation axis for the pair plagioclase-ilmenite is subparallel to plagioclase [100]. If we assume that the interphase misorientation axis is contained along the interface, in a similar fashion as tilt grain boundaries (e.g., Lloyd 2004), and if we assume that the interface has a high-tilt angle, this interface of plagioclase can have any orientation between (010) or (001). From the literature, we know that the distance between the oxygen atoms connecting the SiO_4–AlO_4 tetrahedra in labradorite is between 4.23 and 4.26 Å, based on the determinations of Wenk et al. (1980). This distance is very close to the distance between O-Fe-O along the long axis of FeO_6 octahedra of ilmenite, which is 4.224 Å, determined by Wechsler and Prewitt (1984) and visualized with Crystal Maker. Although plagioclase is either monoclinic or triclinic and ilmenite is trigonal, it is not uncommon to find higher symmetry in certain plagioclase crystal directions. For example, plagioclase is surprisingly symmetrical along [001] as noticed by Wenk et al. (2011a, 2011b) and Ageeva et al. (2020). Along this direction, there are six-component tetrahedra "rings" that can easily accommodate the FeO_6 octahedra from ilmenite. If ilmenite is then the late phase, it can crystallize using the pre-existent plagioclase as substrate, where the FeO_6 octahedra are accommodated along plagioclase [001] axis by sharing some of the oxygen atoms in the crystalline structure of plagioclase (substrate) with those with similar distances (precipitate). Although more detail is needed and it is out of the scope of this paper, it is possible that the ilmenite (0001) plane and [$10\bar{1}0$] direction of ilmenite are parallel to (120)/($\bar{1}$20) planes and [001] direction of plagioclase, respectively, previously reported in Wenk et al. (2011a, 2011b), or one of the parallelism relationships described in Ageeva et al. (2016) controls the interphase boundaries between plagioclase and ilmenite.

As a final remark, the calculation of interphase misorientations from EBSD maps is a potential tool to, for example: study topotactic relationships between minerals; explore potential "orientation relationships" of different phases in a rock; to plot interphase boundaries with variable misorientation in a map and highlight those which have special misorientation angles/axis and even possible orientation relationships; and to use those maps to precisely pinpoint specific interfaces that can be further analyzed with TEM, using target preparation with focused ion beam methods for example. Steps for the calculations include: (1) calculate the interphase misorientation angle distribution assuming uniform ODFs for both phases; (2) calculate the actual correlated and uncorrelated misorientation angle distribution for the two studied phases; (3) compare the correlated misorientation with the uncorrelated/uniform distributions in a histogram and find correlated misorientation peaks that are more frequent than those calculated for a uniform/uncorrelated distribution. After that, one can limit the misorientation angle to those higher frequent peaks of any range and then plot those in inverse pole figures of combined crystal symmetries and plot the different range of interphase misorientations directly on EBSD maps. If, for example, topotactic relationships exist between the two phases, one can calculate what is the pair misorientation angle/axis pair for such a relation, and look into an EBSD map for the presence of these relationships, based on a misorientation angle range that includes the specific misorientation angle for the specific topotactic relationship.

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