Heterogeneous nucleation and epitaxial crystal growth of magmatic minerals

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ABSTRACT
Electron backscatter diffraction analysis of dendritic clinopyroxene (cpx) forming in rapidly cooled basalt reveals two features that are unexpected for phases forming from a liquid: (1) helical growth about {010}cpx, the crystallographic b-axis, with incremental rotation (up to 0.4° µm–1) within branch segments and large rotational jumps (10°–46°) between closely spaced branch segments, and (2) strong crystallographic preferred orientation (CPO) between cpx and titanomagnetite (timt) decorating branch tips, such that {010}cpx aligns with one of the six symmetrically equivalent {110}timt face poles. More than 80% of timt crystals occur within 5° of the CPO with cpx substrate, as do 22% of timt crystals in contact with euhedral cpx in natural Etna basalt. The probability distribution of distances between an arbitrary unit vector and the nearest {110}timt normal unit vector was found by numerical simulation to be closely spaced branch segments, and (2) strong crystallographic preferred orientation (CPO) between cpx and titanomagnetite (timt) decorating branch tips, such that {010}cpx aligns with one of the six symmetrically equivalent {110}timt face poles. More than 80% of timt crystals occur within 5° of the CPO with cpx substrate, as do 22% of timt crystals in contact with euhedral cpx in natural Etna basalt. The probability distribution of distances between an arbitrary unit vector and the nearest {110}timt normal unit vector was found by numerical simulation and indicates that the observed alignment to within 5° occurs with frequency 0.024; thus the CPO occurs 9–33 times more commonly than expected from randomly distributed crystals. The CPO matches previous observations of epitaxial relationship between spinel and host pyroxene during subsolidus exsolution, but has not previously been reported among magmatic cpx and timt. Conspicuous contiguity among phenocryst phases is inferred to result from heterogeneous nucleation facilitated by epitaxy associated with CPO, an inference supported by high-resolution electron microscopy observations of 150 nm thin cpx crystals adhering preferentially to silicate substrates. Epitaxial relationships among phases nucleating from a melt may contribute to fabrics in magnetic rocks promoting development of crystal clusters, and even influence magma transport and eruption styles through a control over magma rheology.

INTRODUCTION
Crystal clustering, a topic of intensifying investigation in solidifying melts (Day and Taylor, 2007; Ikeda et al., 2002; Jerram and Chandrasekharam, 2000) and aqueous systems (e.g., Banfield et al., 2000), is attributed to processes occurring at a wide range of spatial scales. Monominerallic clusters are attributed to density-driven accumulation, followed by disruption and dispersal as sintered clots into an invading magma (Higgins and Chandrasekharam, 2007; Seaman, 2000), while adhesion of fortuitously impinging grains is a “pressure solution” mechanism (Park and Means, 1996) may explain cognate clusters in magmas of intermediate and mafic composition (e.g., Guilbaud et al., 2007). Clustering of clinopyroxene (cpx) and titanomagnetite (timt) is conspicuous in both phenocryst (Figs. 1A and 1B) and groundmass crystal populations (Fig. 1C; Fig. DR1 in the GSA Data Repository1) of oxidized arc magmas. Indeed, clusters composed of mixed mineral phases (e.g., plagioclase, pyroxene, and titanomagnetite) are ubiquitous (Bard, 1986; Williams et al., 1954) and have been attributed to heterogeneous nucleation (Walker et al., 1978) and synneusis, adhesion of crystals in specific orientations that minimize interfacial energy (Schwindinger, 1999; Vance, 1969). It is not yet clear whether crystals more typically cluster upon formation (possibly even prerequisite to formation), or much later as crystals begin to impinge. Recent experimental studies (Ikeda et al., 2002) and simulations (Haxhimili et al., 2006) suggest an important role for crystal-melt and crystal-crystal surface energetics in controlling igneous rock texture. Here we employ backscattered electron (BSE) imaging and the electron backscatter diffraction (EBSD) technique to investigate clinopyroxene-titanomagnetite (cpx-timt) clustering in experimental and natural igneous rocks.

PYROXENE-MAGNETITE CLUSTERING
Dynamic cooling experiments performed under controlled fO2 conditions on synthetic Fe-rich basalt (described in detail by Hammer, 2006) were conducted from 1210 °C to 300 °C at 3–230 °C h–1 with fO2 fixed at buffers ranging from iron-wüstite to hematite-magnetite. Samples that crystallized at or above the fayalite-magnetite-quartz buffer and ≥19 °C h–1 are considered here. The volumetrically dominant phases are cpx (Wo7En77Fs16–18), spinel-structured Fe-Ti-Al-Mg oxide (Fe0.99Mg0.008Fe2+0.06Al1.0O4, Fe2+0.06Al1.25Ti0.01Fe2+0.01O4) hereafter abbreviated timt, and olivine (Fo30–46). The experiments were designed to emulate likely crystallization environments in the shallow crust of Mars. However,

Figure 1. Thin section photomicrographs captured in plane light (A and B) and with backscattered electron imaging (C) illustrating prevalence of cpx-timt contiguity (circled) at a range of spatial scales and two rock types. pl—plagioclase; gm—groundmass; gl—glass; v—vesicle. A: Andesite dome lava from 1995 effusive eruption of Mount Merapi. B and C: Basaltic scoria from the 122 B.C. Plinian eruption of Mount Etna. A less vesicular clast from the Etna deposit (Fig. DR3) proved more amenable to electron backscatter diffraction work (less charging of the uncoated sample).

1GSA Data Repository item 2010093, three figures and a description of the EBSD methods, is available online at www.geosociety.org/pubs/f2010.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
with respect to kinetic controls on textural development, we regard these runs as being germane to any basalt in which cpx and timt are co-crystallizing phases.

Cpx dendrite branches are conspicuously decorated by timt crystals (Fig. 2A), suggesting timt nucleation on cpx substrate. The fraction of mineral surface area that is shared with another phase may be quantified using contiguity ratios:

\[
c_{\text{cpx}} = \frac{2N_{\text{cpx-timt}}}{N_{\text{cpx-matrix}} + 2N_{\text{cpx-timt}} + 2N_{\text{cpx-cpx}}}
\]

\[
c_{\text{int}} = \frac{2N_{\text{int-matrix}} + 2N_{\text{cpx-timt}}}{N_{\text{int-matrix}} + 2N_{\text{cpx-timt}} + 2N_{\text{tim-tim}}}
\]

(modified after Gurland, 1968), where “matrix” refers to all other phases, and \(N\) values are the quantities of intersections of a specified interface with a randomly oriented test line. For example, \(c_{\text{cpx}} = 0.14\) in the experimental sample, indicating that 14% of cpx surface area is shared with timt. We evaluate whether the observed contiguity values exceed expectation for randomly distributed crystals by creating separate cpx and timt maps from each base image and then recombining them in random pairings and rotations. The results are cast as the ratio of observed contiguity of phase \(i\) \(c_i\) normalized by the degree of contiguity expected for a random arrangement of the same grains \(c_i^*\), i.e., \(c_i/c_i^* = c_i^*\). This procedure preserves textural attributes (phase area fractions, crystal shape and size) that affect contiguity but would be problematic to simulate numerically. For the experimental sample, \(c_i^* = 1.5\), indicating 50% greater degree of shared cpx surface area than anticipated for randomly oriented cpx and timt crystals.

The \(c_i^*\) values thus obtained from the experimental sample and three natural reference samples exhibit a tendency for cpx and timt to share surface area (Table 1). The fraction of shared area is greatest for holocrystalline samples and weakest in glassy samples in which cpx is fine-grained and dispersed. Surface sharing may result from local constitutional undercooling during diffusion-limited crystal growth. Slow-diffusing components rejected by one phase may locally increase the supersaturation of a second phase that requires the rejected components, thus establishing a mutually beneficial relationship between stoichiometrically complementary phases. Alternatively, contiguity could reflect surface energy minimization due to crystallographic alignment of a growing phase on a substrate (i.e., epitaxy). Both mechanisms could develop during early stages of crystal growth, although only the latter is relevant during nucleation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(c_{\text{cpx}})</th>
<th>(c_{\text{cpx}}^*)</th>
<th>(c_{\text{int}})</th>
<th>(c_{\text{int}}^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA41*</td>
<td>0.14</td>
<td>1.5</td>
<td>0.49</td>
<td>1.2</td>
</tr>
<tr>
<td>E3-21†</td>
<td>0.13</td>
<td>1.7</td>
<td>0.22</td>
<td>1.1</td>
</tr>
<tr>
<td>E3-27‡</td>
<td>0.43</td>
<td>2.5</td>
<td>0.61</td>
<td>1.9</td>
</tr>
<tr>
<td>M95c§</td>
<td>0.45</td>
<td>7.3</td>
<td>0.45</td>
<td>4.1</td>
</tr>
</tbody>
</table>

*Experimental sample (Fig. 2A). †Groundmass crystals in glassy, vesicular Etna basalt (Fig. 1C). ‡Groundmass crystals in dense, holocrystalline Etna basalt (Fig. DR1). §Phenocrysts in Merapi andesite lava (Fig. 1A). Uncertainty (5%) assessed by intrasample heterogeneity.

<table>
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<th>CRISTALLOGRAPHIC PREFERRED ORIENTATION</th>
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| Regions of experimental samples that exhibit conspicuous pyroxene-magnetite contiguity were selected for orientation mapping projects. Region A (Fig. 2A), spanning 2443 \(\mu m^2\), is composed of glass (62%), cpx (33%), and titanomagnetite (5%). It contains \(\sim 100\) timt grain intersections and \(\sim 50\) cpx grain intersections. Region B (679 \(\mu m^2\); Fig. DR2) is similar, with 63%, 24%, and 9% of these phases, respectively. Indexible diffraction patterns were captured for 44 of the pyroxene intersections in region A and 17 in B. The principal face pole plots for region A (Figs. 2C and 2D) reveal that each grain intersection belongs to one of two distinct crystal lattices and that all pyroxene intersections in region B are part of the same crystal lattice (Figs. DR2C and DR2D). It is not surprising that segmented dendrite arms are connected outside the section plane (O’Driscoll et al., 2007); the EBSD technique vividly demonstrates the magnitude of error that would be introduced if segments were to be considered separate crystals, e.g., for the purpose of nucleation rate determination. A second observation afforded by the upper-hemisphere principal pole plots (Figs. 2C and 2D) is more intriguing. While the \([010]_{\text{cpx}}\) poles migrate little along the lengths of a given branch, the \([001]_{\text{cpx}}\) pole rotates about the \([010]_{\text{cpx}}\) pole up to 170° in a branch that is 80 \(\mu m\) long. That is, the lattices of both curving (region A) and straight cpx crystals (region B) rotate in helical fashion about the b-axis as the crystal grows. Close inspection of individual branches reveals incremental rotations within branch segments (e.g., 0°–0.4° \(\mu m^{-1}\)) and large jumps (e.g., 10°–46°) between adjacent

Figure 2. A: Backscattered electron (BSE) image of timt crystals decorating curving cpx dendrites in a glass matrix. The square box indicates region A, discussed in text. Cpx growth direction (yellow arrows) inferred from bifurcation orientation. B: Cpx phase orientation map of region A overlaid on electron backscatter diffraction band contrast image (similar to BSE). Color scheme matches the \([001]_{\text{cpx}}\) pole figure (C). All colored pixels are attributed to one of two distinct pyroxene lattices, shown in C as two arrays; dashed line in B separates the crystals in the section plane; note crystal 2 surrounds crystal 1. Curved and straight crystals exhibit rotation about \([010]_{\text{cpx}}\) (C and D), although branch rotation is dominantly accommodated by intersegment jumps. Blue lines i and ii (A), spanning one and six segments, respectively, exhibit \([010]_{\text{cpx}}\) rotations of 0° and 60°, respectively. The \([010]_{\text{cpx}}\) poles are coincident with \([110]_{\text{cpx}}\) poles, as shown in frequency-contoured face pole plot (E).
Because curvature is prevalent in highly crystalline samples, we speculate that it develops as compositional boundary layers from neighboring branches impinge on one another. Although we were unable to detect compositional gradients by X-ray mapping, they may have existed during dendrite propagation and then relaxed with subsequent cooling. The helical rotation of the crystal lattice is less satisfactorily envisioned. Even crystals that bend during growth in a convecting fluid do not necessarily exhibit rotating lattices (Henry et al., 1998). Crystal lattice rotation is observed in strongly stirred (cast) alloys (Doherty, 2003), and given enough time, surface energy minimization between crystals drives lattice rotation and grain boundary migration (Upmanyu et al., 2006). However, to our knowledge, lattice rotation during growth from a stationary melt has not been reported or modeled. The EBSD technique therefore presents an intriguing opportunity for further study of crystal growth phenomena in geologically relevant materials.

Insights on the CPO are provided by long-recognized subsolidus relationships between these phases. An epitaxial relationship is widely observed in spinel exsolution lamellae within pyroxene (e.g., Feinberg et al., 2004; Okamura et al., 1976), facilitated by similar spacing and plane group symmetries of oxygen atoms of (010) \( cpx \) and (110) \( \text{timt} \). However, the cpx-timt CPO has apparently never been documented in minerals forming from melt. Its prevalence in both experimental and natural magmas suggests that the surface energy of at least one of these phases is reduced in contact with the other. We conclude that clustering and physical contact of these phases are not likely to depend solely on constitutional supercooling in a boundary layer, but rather develop from heterogeneous nucleation followed by epitaxial crystal growth.

In an attempt to capture incipient co-crystallization, we sought a sample bearing cpx + timt suitable for high-spatial-resolution analysis. Unfortunately, none of the above samples is suitable for characterization at the submicrometer scale. Well-characterized, experimentally crystallized rhyodacite samples (described in Brugger and Hammer, 2010) were selected for their high groundmass crystal number density, fine grain size, and well-constrained thermal history. Pronounced clustering of timt and cpx crystals is evident in all samples examined (e.g., Fig. 3), even for samples containing <1 vol% crystals. Furthermore, although timt-cpx spatial contiguity persists as crystals coarsen, some phenocrysts exhibit a clear antivetiseth relationship (Fig. 3C). Cpx-timt avoidance appears to reflect a reversal in the ratio of crystal-crystal surface energy to crystal-melt surface energy, possibly brought about by (1) heterogeneous nucleation and initial epitaxial growth (as postulated above), followed by differential grain rotation and growth in an energetically unfavorable configuration, or (2) impingement of crystals long after nucleation, resulting in random lattice orientations and an energetically unfavorable grain boundary.

**CONCLUSIONS**

Clinopyroxene and titanomagnetite are clustered in a variety of natural and synthetic rocks, with variable degrees of interface sharing. Not coincidentally, crystallographic lattice preferred orientations between these phases occurs at frequencies far exceeding random chance. Although preliminary, our investigation hints that heterogeneous nucleation plays a role in crystal aggregation in a variety of magma types. The cpx-timt nucleation relationship may have important implications for the magnetic properties of some igneous rocks as well as aspects of magma evolution. For example, if crystal clusters become aligned during magma flow (e.g., Castro et al., 2002) or crystal accumulation (Gee et al., 2004), a preferred orientation relationship of timt crystals may lead to fabrics in magnetic susceptibility (Feinberg et al., 2006), direction, and intensity (Selkin et al., 2000). Clots containing magnetite have higher settling velocities than similarly sized isolated...
silicate grains. If clustering is enhanced by the epitaxial relationship as we suggest, heterogeneous fint-cpx crystallization could play a role in crystal layering, with possible consequences for minor and trace element distribution patterns (Boudreau and Philpotts, 2002). Clusters preserve extensive networks of touching crystals that control interstitial melt flow as well as igneous rock texture (Jerram et al., 2003). Most intriguingly, cluster-laden magma develops yield strength at lower crystal volume fraction than nonclustered magma of the same particle fraction (Hoover et al., 2001), and thus clusters may influence subsurface magma flow and eruption dynamics. Although the hypothesis demands deeper investigation, the prominence of crystal clusters in the Etna 122 B.C. basalt investigated here may be causally linked with the explosive Plinian eruption style that it ejected.

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