Interface coupled dissolution-reprecipitation in garnet from subducted granulites and ultrahigh-pressure rocks revealed by phosphorous, sodium, and titanium zonation

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Abstract

Garnet zonation provides an unparalleled record of the pressure-temperature-time-fluid evolution of metamorphic rocks. At extreme temperature conditions >900 °C, however, most elements preserve little zonation due to intracrystalline diffusional relaxation. Under these conditions, slowly-diffusing trace elements including P, Na, and Ti have the best chance of recording metamorphic histories. Here we map dramatic zoning patterns of these elements in subducted high-pressure felsic granulite (Saxon Granulite Massif) and ultrahigh-pressure diamondiferous “saidenbachite” (Saxonian Erzgebirge, Bohemian Massif). The results show that garnet replacement via interface coupled dissolution-reprecipitation can strongly affect garnet compositions in subduction zones and that P, Na, and Ti record burial and exhumation histories that are otherwise lost to diffusion. In these samples, P diffuses the slowest, and Ti the fastest.

Introduction

Chemical zonation in garnet is widely used to reconstruct the pressure, temperature, time, and fluid histories of mountain belts. Most documented chemical zonation in garnet is the result of changing pressure-temperature-fluid conditions during growth as well as post-growth intracrystalline diffusion. In addition to diffusion, interface coupled dissolution-reprecipitation (ICDR) is another important process that can modify mineral compositions (e.g., Putnis and Austrheim, 2010; Harlov et al. 2011; Putnis and John, 2010). During ICDR, a disequilibrium fluid reacts with mineral surfaces, replacing the pre-existing composition with a new one that is likely to be in equilibrium with the fluid, although kinetic effects are also possible (e.g., Geisler et al. 2010). The interface between the old and new portions of the mineral is extremely sharp and propagates inward, leaving a zone of fluid-filled micro- or nano-porosity in its wake. Fresh reactants are transported to the reacting interface through the fluid-filled porosity, normally by
diffusion, whereas products are transported out. In this way, the interface advances until the entire crystal is replaced, commonly with little or no overall change in volume. Because diffusional transport occurs through a fluid phase, ICDR is in general much faster than intracrystalline diffusion. Successive episodes of ICDR can cross cut or replace earlier-formed replacement zones.

ICDR has been well-documented in minerals such as feldspar (e.g., replacement of albite by K-feldspar; e.g., Niedermeier et al. 2009) and zircon (Geisler et al. 2007; Rubatto et al. 2008). A growing body of evidence demonstrates that it can also play a significant role in garnet, as revealed by chemical and/or oxygen isotope zonation (e.g., Hames and Menard, 1993; Whitney et al. 1996; Alvarez et al. 2005; Pollock et al. 2008; Faryad et al. 2010; Martin et al. 2011; Page et al. 2013; Xu et al. 2013; Centrella et al. 2015; Chen et al. 2015). Nonetheless, the potential for trace element zonation to reveal ICDR processes remains relatively little explored.

Regardless of how garnet acquires zonation, at ultrahigh-temperature conditions >900 °C, diffusion for most elements is rapid and, thus, growth and recrystallization histories are largely erased. To have some chance of reconstructing these histories, the most slowly-diffusing elements must be identified. We focus on phosphorous, sodium, and titanium. Their concentrations in garnet generally increase with $P$ and $T$, making their measurement via electron-probe microanalysis (EPMA) feasible (e.g., Hermann and Spandler, 2008; Auzanneau et al. 2010). Phosphorous, which substitutes mainly for Si$^{4+}$ on tetrahedral sites, has been shown to preserve zoning in magmatic olivine (e.g., Mallmann et al. 2009) and garnet from amphibolite facies, near-UHT, UHT, and >900 °C ultrahigh-pressure (UHP) rocks (e.g., Spear and Kohn, 1996; Vielzeuf et al. 2005; Kawakami and Hokada, 2010; Kobayashi et al., 2011; Ague and Eckert, 2012; Axler and Ague, 2015a; 2015b; Jedlicka et al. 2015). Sodium substitution is linked
to P substitution in garnet by mechanisms such as NaP M$^{2+}$Si$_{-1}$ (e.g., Hermann and Spandler, 2008), and complementary Na-P zonation patterns are documented for UHP rocks (e.g., Axler and Ague, 2015b). Titanium zonation tends to be somewhat smoother than that for P, but well-defined retrograde Ti-depletion halos surrounding rutile or ilmenite precipitates in garnet can be preserved in UHT and UHP garnets (e.g., Ague and Eckert, 2012; Axler and Ague, 2015b).

In this study, we use chemical maps to examine P, Na, and Ti zonation in subduction-related high-pressure (HP) eclogite facies granulite from the Saxon Granulite Massif (e.g., O’Brien, 2006; Rötzler et al. 2008) and UHP diamondiferous saidenbachite from the Saxonian Erzgebirge (e.g., Massonne, 2003). Our goals are to determine: (1) the nature and extent of zoning preservation and (2) what the implications of the zoning are for metamorphic processes.

EPMA analyses were done using the JEOL-JXA8530F at Yale University; analytical methods are described in Axler and Ague (2015b). Element mapping employed 300 nA beam current and 200 ms dwell times. To avoid confusion, the abbreviation “P” is used only for phosphorous; pressure is written out in full except for the abbreviations “HP” and “UHP”.

**Geologic Settings**

One example is from UHP microdiamond-bearing quartzofeldspathic lenses of “saidenbachite” in the gneiss-eclogite unit of the Saxonian Erzgebirge (Bohemian Massif) adjacent to the Saidaenbach reservoir (Germany; 56.220° N, 45.886° E; e.g., Massonne, 2003). The rock contains plagioclase + quartz + phengite + paragonite + garnet + kyanite + rutile + apatite + zircon + graphite + microdiamond. It underwent partial melting (e.g., Massonne, 2003; Stoeckhert et al. 2009) and has been interpreted to be magmatic in origin (Massonne, 2003; Massonne and Fockenberg, 2012). Estimates for peak conditions (Variscan orogeny) range from
4–5 to 7–8 GPa (e.g., Hwang et al. 2000; Massonne, 2003) at temperatures of at least ~1000 °C, possibly as high as 1400 °C (Massonne and Fockenberg, 2012).

The second example is classic felsic “Saxony granulite” from Röhrsdorf in the Variscan Saxon Granulite Massif, Germany (e.g., O’Brien, 2006; Rötzler et al. 2008). The rock is finely laminated due to a ribbon quartz foliation, whitish, and contains plagioclase + quartz + garnet + kyanite + biotite + rutile + apatite + zircon. The rocks record eclogite facies conditions of 1000-1050 °C and 2.2-2.3 GPa (e.g., Rötzler and Romer, 2001; Rötzler et al. 2008).

Following subduction, exhumation of both rocks occurred rapidly, largely under ultrahigh-temperature conditions >900 °C (Rötzler et al. 2008; Stöckert et al. 2009; Massonne and Fockenberg, 2012; Müller et al. 2015).

**Results**

The UHP Erzgebirge garnet preserves a striking increase in P content from core to rim, followed by a narrow zone of low P at the outermost rim (Figs. 1a and 1b). The P zoning between compositional domains ranges from somewhat diffuse in the core to sharp; the sharper transitions dominate. The zones are roughly concentric, but they clearly overlap and cross-cutting relationships are evident. In all cases of cross cutting, the zone closer to the rim transects, and is thus younger than, the more interior zone. Sodium preserves a similar, although somewhat more subdued zoning pattern (Fig. 1c). Ti zoning, in contrast, is much more diffuse, being highest in the core and then dropping toward the rim (Fig. 1d). Major elements preserve very broad compositional zoning that we infer has been heavily influenced by intracrystalline diffusion (e.g., Ca and Mg; Figs. 1d and 1e).

The second example is a garnet in the HP granulite that preserves spectacular zoning. The P$_2$O$_5$ concentrations are very high in the interior portions of the garnet (~0.5 wt.%; Table 1), and
drop toward the rim (Figs. 2a and 2b). The high-P core is transected by irregular, finger-like
domains of lower P content (Table 1). In detail, these low-P domains clearly cut, and are thus
younger than, pre-existing high-P garnet regions, including areas preserving relic oscillatory
growth zoning (Fig. 2b). Islands of partially replaced or unreplaced material persist in the low-P
domains. The boundaries between the high-P and low-P domains are extremely sharp. Faint
radial crack-like features are preserved around a multiphase inclusion composed mostly of
phengite and biotite. The zoning patterns of Na and Ti mimic those of P, but are slightly more
diffuse, particularly for Ti (Figs. 2e and 2f). High-P and high-Na domains coincide spatially, as
do the corresponding low-concentration domains. In contrast, low-P and low-Na correlate with
high-Ti, and *vice versa*. Interestingly, the Na-Ti relations are antithetical to well-known coupled
substitutions such as NaTi\(^{VI}_1\)M\(^{2+}_1\)\(\text{Al}^{-1}\) (e.g. Ringwood and Major, 1971; Hermann and Spandler,
2008; Auzanneau et al. 2010).

Major element zonation is considerably smoother than that for the trace elements. The
highest Ca concentrations coincide with the region of sharply-defined P zonation, but no
corresponding sharp Ca zonation is evident (Fig. 2b). Magnesium is largely flat, except for low-
Mg halos around mica inclusions reflecting retrograde Mg-Fe exchange (Fig. 2c). Similar to the
Erzgebirge example, we conclude that major element zonation has been strongly smoothed by
diffusion. Calcium preserves somewhat more compositional structure than Mg, consistent with
recent diffusion coefficient calibrations that show that Ca diffuses more slowly than Mg (Chu
and Ague, 2015).

**Discussion**

One explanation for the P (and Na) zonation in the Erzgebirge example is multiple
episodes of uncoupled dissolution followed by precipitation of rim overgrowths. While some
episodes of this type cannot be ruled out and may have occurred, we consider them unlikely to be responsible for the bulk of the zoning, as experiments and pseudosection modeling provide no evidence for such episodes along the probable pressure-temperature path (Massonne and Fockenberg, 2012).

The sharply-defined, overlapping, and cross-cutting chemical zonation patterns are also inconsistent with any simple growth or diffusion processes. They are consistent, however, with multiple ICDR events (Putnis and Austrheim, 2010; Putnis and John, 2010). In felsic, peraluminous systems, P and Na in garnet increase with pressure and temperature (e.g., Hermann and Spandler, 2008). Thus we interpret the core-rim increases in P and Na to trace progressively increasing metamorphic intensity during subduction to UHP conditions. Major elements do not record this, as their zonation has been heavily influenced by diffusion. Garnet may have been largely grown at relatively low metamorphic grades, and then progressively replaced by ICDR events with increasing subduction. The very low-P garnet rims developed during exhumation and cooling; they could reflect growth, ICDR, or some combination. Isolated fluid inclusions are present in garnet, but the interconnected porosity needed for ICDR is either at the nano scale and too small to observe optically, or was obliterated subsequent to ICDR.

Chemical profiles for P (Axler and Ague, 2015b) and the map (Fig. 2a) show some limited smoothing of zoning that almost certainly reflects diffusion, but the original abrupt transitions between compositional domains remain distinct. Sodium zoning is somewhat smoother than P, but still retains clear evidence for the compositional domains. As P and Na substitutions are likely coupled to some degree, it could be that the preservation of Na zoning is linked to extremely sluggish diffusion of P such that the two elements cannot move entirely independently. Titanium, however, exhibits much smoother zoning patterns, so it diffused more
readily than either P or Na in this setting (Fig. 1d). Nonetheless, small diffusional Ti depletion halos surround exsolved plates and needles of rutile. This relationship demonstrates that Ti for the rutile was locally sourced from garnet (e.g., Ague and Eckert, 2012; Axler and Ague, 2015b), and that the halos formed after most of the overall smoothing of Ti in garnet occurred.

The maximum P and Na contents measured by Axler and Ague (2015b; ~0.02–0.025 atoms per 12 O) correspond to pressure-temperature conditions of 700–800 °C and ~3–3.5 GPa according to the metapelitite experiments of Hermann and Spandler (2008, their Fig. 4b). This is clearly UHP, but is not in the diamond stability field and the temperature is lower than current estimates (Massone and Fockenberg, 2012). These discrepancies likely reflect the need for more experimental data over a wide range of bulk compositions. In addition, as Na zoning is somewhat smoother than P, Na may have been lost preferentially, leading to anomalously low estimates. It is also possible that the highest-pressure parts of the garnet rim were modified by ICDR during the early stages of retrogression.

For the HP granulite, the extremely sharp, cross-cutting P zoning is once again consistent with ICDR, as is the near-isovolumetric replacement of the garnet crystal. The low-P and low-Na “fingers” are interpreted to have developed during retrogression while the garnet attempted to equilibrate to lower-P and lower-Na compositions at lower pressures and/or temperatures. Temperatures were likely still quite high, however, as major element zoning is largely smoothed and preserves no record of garnet replacement via ICDR. The radial, crack-like P zoning features around a micaeous multiphase inclusion probably reflect fluid-driven decrepitation during exhumation (e.g., Stöckhert et al. 2009). The interconnected nano-porosity for ICDR has either been destroyed or is not optically resolvable, although isolated fluid inclusions are present.
The maximum P$_2$O$_5$ content of the garnet is very high, approaching 0.5 wt.% (Table 1). This suggests UHP metamorphism given available experimental data; however, corresponding Na contents are not as high as observed by, e.g., Hermann and Spandler (2008), so we have not attempted a pressure estimate.

**Implications**

Complex zoning in garnet P, Na, and Ti may be preserved even in rocks that experienced extreme metamorphic conditions, and can record growth, diffusion, and both prograde and retrograde ICDR processes. Chemical mapping, as opposed to profiles, is essential to reveal the nature of this zoning. As ICDR is strongly associated with the presence of fluid (including melt), the core-to-rim increases in P and Na in garnet from UHP saidenbachite probably record successively deeper episodes of fluid-rock interaction on the prograde path during subduction, including the generation of partial melt at $T$ possibly as high as 1400 °C (see Massonne and Fockenberg, 2012). In contrast, ICDR in the HP granulite, clearly illustrated by sharply-defined interpenetrating compositional domains, likely occurred during retrograde fluid-rock interaction. Major element zonation is strongly influenced by diffusion and is unable to record these histories. Diffusion of major elements almost certainly occurred simultaneously with ICDR across the advancing interface, and continued after cessation of ICDR.

Qualitatively, of the three elements, P diffused the slowest and Ti the fastest; given sufficient temperature and time, the Ti record of ICDR can be completely smoothed (Fig. 1d). It is likely that diffusion rates for the elements are not fully independent and are controlled to some extent by coupled substitutions such as NaP M$^{3+}$Si$^{-}$.$^{-}$. The Ti contents of natural UHT and UHP garnets are commonly less than predicted by experiments (e.g., Hermann and Spandler, 2008; Ackerson et al. 2013). Thus, garnets probably lose Ti during retrogression; some of the escaping
Ti can be trapped as oriented rutile or ilmenite precipitates. Phosphorous and Na concentrations are also commonly lower than predicted. Local exsolution-related diffusion that forms apatite rods or plates can occur (e.g., Ye et al. 2000), and deformation may enhance their precipitation (e.g., Axler and Ague, 2015b). But for very slowly-diffusing elements like P, ICDR likely provides a much faster way of modifying crystal chemistry on a large scale (Figs. 1 and 2). Considerable work remains to determine trace element transport mechanisms in garnet, but tracer concentration systematics provide unique perspectives on processes operating at extreme conditions in the lithosphere.

**Acknowledgements**

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**References Cited**


Figure Captions

Figure 1. Chemical maps of Erzgebirge garnet (sample SB2). Color scale ranges from blue to light yellow with increasing concentration. 500 µm scale bar. (a) Phosphorous. (b) Phosphorous, with successive cross-cutting compositional zones highlighted. There are at least six major compositional domains (c) Sodium. (d) Titanium. (e) Calcium. (f) Magnesium.

Figure 2. Chemical maps of HP granulite garnet (sample W12 4452). (a) Phosphorous. Note multiphase inclusion with radiating cracks (arrow). (b) Detail of boxed area shown in part (a). Note relic oscillatory growth zonation in northwestern part of garnet. (c) Calcium. (d) Magnesium. Note retrograde Mg depletion halos surrounding biotite inclusions. (e) Sodium. (f) Titanium.
Ague and Axler, Figure 1
Ague and Axler, Figure 2
Table 1. Representative garnet analyses.

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<tr>
<th></th>
<th>Erzgebirge1 Low-Phosphorus Domain</th>
<th>Erzgebirge2 Low-Phosphorus Domain</th>
<th>Saxony1 Low-Ca Domain</th>
<th>Saxony2 High-Ca &amp; Low-Phosphorus Domain</th>
<th>Saxony3 High-Ca &amp; Low-Phosphorus Domain</th>
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<td>38.73(1)</td>
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<td>TiO$_2$</td>
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<td>0.020(3)</td>
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Structural Formulas (12 O)

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Notes: b.d. = below detection. $n$ is the number of analyses averaged for each table entry. Fe$^{2+}$ and Fe$^{3+}$ in garnet estimated based on 8 cations per 12 O. The values in parentheses represent the 1σ uncertainties in the last digits.