XAFS Spectroscopic Study of Ti Coordination in Garnet
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Abstract

Ti can be incorporated either tetrahedrally ($^{IV}$Ti) or octahedrally ($^{VI}$Ti) in most silicate minerals. Ti K-edge X-ray Absorption Fine Structure (XAFS) spectroscopy enables observation of Ti coordination in minerals and melts. In this study, XAFS is used to determine the coordination of Ti in synthetic and natural garnets. Garnets grown synthetically at eclogite- and granulite-facies conditions can contain several wt. % TiO₂, most of which is incorporated as $^{VI}$Ti. This observation aligns with major element trends in these garnets. In natural garnets grown at lower temperatures and pressures, on the other hand, Ti is observed to occupy both the octahedral and tetrahedral sites in garnet— in some cases Ti is almost entirely IV-fold coordinated. Combined with previous research (see Ackerson et al., this issue) on substitution mechanisms for $^{VI}$Ti, the results of this study demonstrate that Ti is incorporated on two crystallographic sites in garnet by at least three primary substitution mechanisms. In both natural and synthetic garnets, there is a discernible increase in $^{VI}$Ti content in garnet with increasing temperature and pressure, suggesting a significant role for these two parameters in determining Ti solubility. However, a continuous increase in $^{VI}$Ti with increasing grossular content also suggests that the Ca content of the garnet plays a critical role.

Keywords: garnet, Ti substitution, XANES, XAFS
Introduction

Titanium is one of the only crustal major elements capable of being incorporated to major-element concentrations in garnet whose substitution mechanisms and coordination remain poorly constrained. Exsolved rutile and ilmenite needles from ultra-high temperature and pressure (UHT and UHP, respectively) garnets suggest Ti solubility in garnet increases with increasing metamorphic grade. The presence of exsolved rutile and ilmenite in garnet has therefore been suggested as a possible indicator of high-grade metamorphism (Bishop et al. 1978; Snoeyenbos et al. 1995; Zhang et al. 2003; Tropper et al. 2005; Hwang et al. 2007; Ague and Eckert 2012; Proyer et al. 2013). In addition to the relevance for understanding high-grade metamorphism, Ti in garnet could be utilized to develop novel exchange or trace-element geothermobarometers. To assess the potential of Ti in garnet for understanding metamorphic processes, it is critical to understand the substitution (mechanisms and coordination) of Ti in garnets over a wide range of geologic environments.

If the Ti content of garnet is high enough, major-element chemical trends can be used to infer the substitution mechanisms for Ti in garnet. In synthetically-grown garnets, major element trends reveal that Ti incorporation at simulated eclogite- and granulite- facies conditions occurs primarily on the octahedral site via multiple substitution mechanisms (Ackerson et al., this issue). While this is a useful insight, there are significant limitations to the information obtainable from major-element correlations, primary among them being that Ti coordination is inferred rather than
directly measured. In addition, the conditions at which garnets can be grown synthetically in natural bulk compositions (>800 °C, >1.2 GPa) are generally more extreme than the crystallization environments of many crustal garnet-bearing metamorphic rocks. Most naturally-occurring garnets have Ti contents at or below the analytical uncertainty of the major elements measured using electron probe microanalysis (EPMA), making studies of substitution mechanisms and coordination via EPMA infeasible.

X-ray absorption fine structure (XAFS) spectroscopy can be utilized to directly determine the coordination and valence state of Ti in both synthetic and natural garnets at concentrations lower than the resolution of EPMA-based major-element chemical trends. Specifically, the energy and peak intensity of the Ti K-edge pre-edge feature is dependent on Ti coordination, while the absorption edge energy is sensitive to valence (Waychunas 1987; Farges et al. 1996a, 1996b, 1997). In this study we describe the use of XAFS to observe the coordination and valence state of synthetically-grown and natural garnets from a wide range of geologic conditions. Combining XAFS spectroscopy and electron microprobe measurements of Ti content enables assignment of Ti concentrations to specific crystallographic sites and provides a platform to discuss the factors influencing Ti solubility and coordination in garnet.

**X-ray absorption fine structure**

The Ti K-edge X-ray absorption near-edge structure (XANES) pre-edge feature of the XAFS spectrum is a 1s-3d orbital transition whose normalized peak height and energy is sensitive to the coordination state of Ti and can be used
to differentiate between IV-, V-, and VI-fold Ti (Waychunas 1987; Farges et al. 1996a, 1996b). In materials where Ti exists in multiple coordination states, residual-minimizing linear combination fitting can accurately predict the relative contributions of multiple coordination sites to the overall observed signal (Fig. 1). Additionally, the absorption edge of Ti$^{3+}$ occurs at a lower energy than that of Ti$^{4+}$, making it possible to determine if a sample contains multiple valence states of Ti (Waychunas 1987).

**Sample locations**

In order to investigate a broad range of garnet-forming environments, this study examines both synthetically-grown garnets (eclogite- and granulite-facies conditions) and natural garnet-bearing rocks from low-grade contact metamorphic rocks to high-grade eclogites and mantle lherzolite xenoliths. Synthetic garnets were grown in solid-media piston cylinder devices at Rensselaer Polytechnic Institute at eclogite and granulite facies conditions. The starting materials includes pelite, mid-ocean ridge basalt and amphibolite bulk compositions with 10 wt. % H$_2$O from 800-900 °C and 1.5-2.5 GPa. Experiments were buffered at the fayalite-magnetite-quartz (FMQ) buffer using a Pd-foil membrane between the experimental charge and the buffer (Trail et al. 2012).

Natural samples from a wide range of metamorphic facies were analyzed to observe Ti coordination under conditions where synthetic garnet growth is not feasible (supplementary material). These natural garnets cover a crystallization temperature range from 427 to 1000 °C and pressures from 3 to 38 kbar. Garnets from natural systems also record a wide range of growth histories from primarily
peak-metamorphic growth with retrograde metamorphic rims (e.g. garnet from the Valhalla Metamorphic Complex) to continuous prograde growth (e.g. garnet from the Fall Mountain nappe).

**Analytical techniques**

**Microprobe analyses**

Wavelength-dispersive X-ray maps for Ti, Fe, Mg, Ca and Mn in garnet were collected on the Cameca SX100 electron microprobe at RPI prior to analysis at Brookhaven National Laboratory (BNL), and quantitative analyses were performed using the analytical routine described in Ackerson et al. (this issue). Due to the low Ti content of natural garnets, Ti was measured for 300 s on two spectrometers at 15 eV accelerating voltage and 200 nA current, yielding a detection limit near 40 ppm. Backgrounds of the Ti K-edge peaks at ± 700 eV were verified using wavelength dispersive scans above and below the Ti K-edge peak to reduce the possibility of peak overlap interferences from other elements.

**XAFS spectral fitting**

Synthetic samples were mounted in 2.54 cm epoxy rounds and polished using 1 µm alumina powder and colloidal silica. Natural samples were prepared as either thin sections or epoxy rounds for analysis at BNL. XAFS fluorescence and transmission spectra were collected on beamline X26A at the National Synchrotron Light Source (NSLS) at BNL. Beamline X26A uses a focused, monochromatic X-ray source with a ~0.5 eV energy resolution (ΔE/E=1E-4). The monochromatic beam is generated via energy filtering using a channel-cut silicon crystal monochromator cut along (111). The incident X-ray beam is focused to a 10x8 µm spot which hits the
sample at a 45° angle. This produces an effective spot size on the sample of 12x9 µm
with a maximum penetration depth of ~20 µm at the Ti K-edge. All garnet samples
were analyzed in fluorescence mode. In samples where Ti content was low, multiple
spectra were collected and merged with equal weighting to increase the signal to
noise ratio.

Possible energy drift was monitored throughout the analytical sessions using
Mg\textsuperscript{II}Ti\textsubscript{2}O\textsubscript{5} powder in transmission mode. Energy drift of the monochromators
occurs as a function of thermal load on the Si crystal due to variations in X-ray flux
over time can affect the relative position of the absorption edge. Drift is a
demonstrated analytical issue for Fe XAFS analysis (Cottrell et al. 2009) who saw
absorption edge drifting up to 0.2 eV over the course of experimentation. Observed
energy drift of the Ti pre-edge feature in this study was very low (standard
device of 0.04 eV) and was subsequently disregarded during spectral
comparisons between samples (Supplementary Fig. S1).

**XAFS normalization**

Normalization of Ti K-edge XAFS spectra to the pre- and post-edge regions
enables concentration-independent comparison of the pre-edge features between
multiple spectra and ultimately determination of Ti coordination in the crystal
lattice. All XAFS data processing was performed using the software program Athena
(Ravel and Newville 2005). The absorption edge for each spectrum was selected by
converting the I₀-normalized absorption spectrum to first derivative space and
selecting the maximum first derivative of the spectrum within the anticipated edge
region (4982 ± 10 eV). Pre- and post-edge normalization regions were held constant
between samples to maintain a reproducible normalization. Pre-edge normalization was selected from -58 ± 10 to -20 ± 5 eV, and the post-edge region from 114 ± 15 to 212 ± 5 eV. The post-edge fitting was performed using a second-order polynomial fit (Fig. 2). In some samples, low Ti concentrations in garnets resulted in spectra with erratic, high-noise post-edges that required adjustments to the post-edge fitting regions. However, changing the pre- and post-edge normalization regions does not shift the energy of the pre-edge absorption feature. High-noise spectra fitted with multiple normalization regimes (to assess the impact of normalization on the pre-edge peak height) resulted in shifts of the normalized pre-edge peak height of less than 0.1 normalized absorption units.

**Selection of analytical spots**

In many natural and synthetically-grown garnets, sub-surface Ti-bearing mineral and/or melt inclusions can contaminate the XAFS spectra. This is a specific concern in experimental charges, where most garnets contain high densities of ilmenite and/or rutile inclusions. Beamline X26A is equipped with three energy dispersive spectrometers (EDS) — one four-element and two single-element vortex Silicon Drift Detectors from SII NanoTechnology. These detectors can be used simultaneously to collect 2D composition maps of the analytical regions of interest. Inclusion-free regions can then be selected for analysis (Fig. 3). See supplementary information for more details on data reduction and data validation techniques.

**Linear combination fitting**

Linear combination fitting (LCF) of normalized XAFS spectra was used to determine the ratio of IV- to VI-fold coordinated Ti in garnets. A synthetic quartz
crystal (QTiP-39 from Thomas et al., 2010) and schorlomite from Magnet Cove, Arkansas (Waychunas 1987; Flohr and Ross 1990) were used as the endmember IV- and VI-fold spectra, respectively (Fig. 8). Ti in quartz has been observed to occur entirely in IV-fold coordination (Thomas et al. 2010). Fitting was performed between 4962-4977 eV using a residual-minimizing technique in Athena. LCF results were then combined with Ti concentration data from microprobe analyses to extract $^{IV}$Ti and $^{VI}$Ti concentrations.

While the variations in pre-edge peak energy and intensity due to differences in Ti coordination for end-member (e.g. pure VI-fold Ti) have been established through multiple investigations (Waychunas 1987; Farges et al. 1996a; Farges 1997), no systematic attempt has been made to quantify coordination ratios in crystalline samples containing Ti in multiple coordination states. Using simulations and mechanical mixtures of oxide powders with varying proportions of $^{IV}$Ti, $^{V}$Ti, $^{VI}$Ti, Farges et al. (1996) demonstrated that mixtures exhibit pre-edge features that are linear combinations of the end-member spectra. In other words, a 50:50 mixture of $^{IV}$Ti- and $^{VI}$Ti-bearing glasses produces a pre-edge spectrum that is a convolution of 50% of a pure IV-fold spectrum and 50% of a pure VI-fold spectrum.

**Selection of $^{IV}$Ti and $^{VI}$Ti standards**

Variations in pre-edge spectra due to local bonding environment and multiple scattering phenomena (Fig. 4) require careful selection of end-member spectra for accurate linear combination fitting. One of the main uncertainties in selecting a $^{IV}$Ti end member arises from the fact that no well-characterized garnet samples (either natural or synthetic) contain only $^{IV}$Ti. This requires a “proxy.”
spectrum with a well-characterized $^{IV}$Ti pre-edge feature. As shown in Figure 4, the pre-edge peaks for the $^{IV}$Ti-bearing quartz and zircon samples analyzed in this experiment exhibit a similar range of intensities and energies. However, Ti in zircon exhibits an additional pre-edge peak at higher energy than the primary peak. This peak does not manifest in quartz spectra or the spectra from garnets with apparent high $^{IV}$Ti content. Additionally, the energy of the pre-edge feature in zircon varies with orientation, whereas spectral anisotropy does not occur in quartz or garnet. For these reasons we chose the synthetic quartz crystal QTIP-39 (Thomas et al. 2010) as an end-member $^{IV}$Ti standard.

In contrast to quartz, garnet has a significantly distorted tetrahedral site (Novak and Gibbs 1971). Whereas tetrahedral site distortion has no significant impact on pre-edge energy, it can influence the height of the pre-edge peak, particularly for $^{VI}$Ti (Waychunas 1987). The degree to which site distortion on the tetrahedral site in garnet will influence the $^{IV}$Ti peak height is not clear in the literature. However, the height of the $^{IV}$Ti pre-edge feature has been shown to vary from 0.7 to 1 (Farges et al. 1996a, 1996b, 1997). The quartz spectrum chosen has a normalized peak height of $\sim$0.8 (Fig. 1b) making it possible that fitting garnet $^{IV}$Ti to $^{IV}$Ti in quartz could result in a minor over- or underestimation of $^{IV}$Ti in garnet. Fitting garnet spectra using the selected quartz standard and several $^{IV}$Ti samples from the literature (Farges et al., 1997) resulted in deviations of calculated $^{IV}$Ti on the order of $\pm$5%.

A natural schorlomite from Magnet Cove, Arkansas was selected as a representative $^{VI}$Ti standard (Waychunas 1987; Flohr and Ross 1990). This sample
was selected because of the small full width half maximum (FWHM) of its pre-edge peak (a small amount of $^{IV}\text{Ti}$ could result in broadening of this peak; Fig. 1). Also, Magnet Cove schorlomite has been previously shown to contain entirely $^{VI}\text{Ti}$ (Waychunas 1987; Chakhmouradian and McCammon 2005; Antao 2014).

**Results**

In all samples, the absorption edge between analyses was consistent at 4982 ± 0.3 eV, indicating no detectible $^{III}\text{Ti}$ (Waychunas 1987). Linear combination fitting to the pre-edge regions of synthetic and natural garnets demonstrates that Ti can be incorporated into both the octahedral and tetrahedral sites. All synthetically-grown garnets have $^{VI}\text{Ti} > 95\%$ (Table 1). Coordination in natural garnets varies between $>90\%$ $^{IV}\text{Ti}$ and 100% $^{VI}\text{Ti}$ (supplementary material). LCF fits return low errors typically less than 2% of the resultant fit. Athena calculates uncertainties ($1\sigma$) in LCFs by multiplying the diagonal of the covariance matrix of the standards by the square root of the reduced $\chi^2$ of the fit (defined here as: $\chi^2 = \frac{\sum(data-fit)^2}{N}$, where $N$ is the degrees of freedom). In samples with low Ti and higher noise (e.g. pyrope from the Dora Maira Massif, sample H11A, Fig. 8) errors can be as high as 5% (supplementary material).

Microprobe analyses of natural garnets yield Ti concentrations ranging from ~31 ppm in garnets from Mica Creek to over 1100 ppm in garnet from Harpswell Neck, while synthetic garnets can contain Ti in excess of 2 wt. % $\text{TiO}_2$. Concentrations of $^{IV}\text{Ti}$ and $^{VI}\text{Ti}$ were calculated by multiplying the weights of IV- and VI-fold LCF results by Ti content measured by EPMA. Four-coordinated Ti ranges from below the detection limit (40 ppm) to 192 ppm, while $^{VI}\text{Ti}$ ranges from near
the detection limit to over 1000 ppm. Although the errors on Ca measurements are typically greater than $^{VI}\text{Ti}$ concentrations, Ti generally increases with increasing Ca content of the garnets. No clear relationship exists between Ti and other major elements. There is no discernible relationship between $^{IV}\text{Ti}$ with either $^T$ or $^P$ in natural garnets, but $^{VI}\text{Ti}$ increases with increasing Ca and decreasing $^T$ and $^P$.

**Discussion**

Ackerson et al. (this issue) describe Ti substitution and solubility in synthetic garnets grown at simulated high-grade metamorphic conditions, but the observations in that study do not necessarily apply to the incorporation of Ti into garnet in low-mid grade metamorphic systems. In the following discussion we will show that: (1) Ti in high-grade synthetic garnets is primarily $^{VI}\text{Ti}$; (2) minor $^{IV}\text{Ti}$ solubility in garnet reflects a $^T$ solubility dependence similar to calibrated $^{IV}\text{Ti}$ thermobarometers in other minerals; and (3) $^{VI}\text{Ti}$ in individual garnets across the entire observed geologic range is linked to $^{VIII}\text{Ca}$ content.

**Limitations of $^{IV,VII}\text{Ti}$ for thermobarometry**

$^{IV}$-Ti K-edge XAFS pre-edge spectra from a suite of natural and synthetic garnets demonstrate that Ti incorporation occurs on both the octahedral and tetrahedral sites in garnet. These observations—combined with the major-element trends in synthetically-grown garnets (Ackerson et al., this issue)—show that Ti incorporation into garnet involves at least three significant substitution mechanisms. Octahedral incorporation of Ti likely occurs primarily through three coupled substitution mechanisms:

$^{VI}\text{Ti}^{4+} + ^{VI}\text{M}^{2+} \leftrightarrow 2^{VI}\text{Al}^{3+}$
(2) \( \text{VI}^4\text{Ti}^4+ + \text{IV}^3\text{Al}^3+ \leftrightarrow \text{VI}^4\text{Al}^3+ + \text{IV}^3\text{Si}^4+ \)

(3) \( \text{VI}^4\text{Ti}^4+ + \text{IV}^3\text{Fe}^3+ \leftrightarrow \text{VI}^4(\text{Al},\text{Fe})^3+ + \text{IV}^3\text{Si}^4+ \),

whereas tetrahedral substitution most likely occurs via:

(4) \( \text{IV}^3\text{Ti}^4+ \leftrightarrow \text{IV}^3\text{Si}^4+ \).

In practical terms, \( \text{IV}^3\text{Ti}:\text{VI}^4\text{Ti} \) represents the convolution of multiple substitution mechanisms operating on several crystallographic sites, making application of thermodynamically-constrained Ti coordination ratios an ineffective technique for directly estimating the temperatures and pressures of garnet formation. Changes in \( \text{IV}^3\text{Ti} \) concentrations are relatively minor compared to those of \( \text{VI}^4\text{Ti} \), and ultimately the range of Ti coordination-mixing behavior demonstrated in the XAFS spectra is primarily a reflection of changes in the solubility of \( \text{VI}^4\text{Ti} \).

The concentrations of tetrahedrally-coordinated Ti in garnet are on the same order of magnitude as other \( \text{IV}^3\text{Ti} \)-bearing silicate minerals [e.g., Ti in quartz (Thomas et al. 2010), Ti in zircon (Watson and Harrison 2005)]. This is the expected result given the similarity of the Si tetrahedral sites for which Ti substitutes in these minerals. As an example, the calculated \( \text{IV}^3\text{Ti} \) content for the interior of garnet V6-B from the Valhalla Metamorphic Complex is \( \sim 85 \text{ ppm} \) (820 °C, 8 kbar). Ti-in-quartz calculations (Thomas et al. 2010) at unity \( a_{\text{TiO}_2} \) for this sample predict a Ti-in-quartz content of 253 ppm, and Ti-in-zircon estimate 23 ppm in co-crystallizing zircon (Ferry and Watson 2007). Ultimately, the low concentrations of \( \text{IV}^3\text{Ti} \) and associated high errors in both EPMA analyses and XAFS spectral fits hinder any practical thermobarometric calibrations of \( \text{IV}^3\text{Ti} \).
**Ti coordination in synthetic garnet**

Garnets crystallized in multiple bulk compositions over a range of eclogite- and granulite-facies temperatures and pressures (buffered at the FMQ oxygen fugacity buffer) contain up to several wt. % TiO$_2$. Major-element trends in these garnets suggest Ti is incorporated primarily on the octahedral site (Ackerson et al., this issue). Linear combination fitting of the pre-edge peaks of all synthetic garnets supports the major-element trends, returning fits over 98% $^{VI}$Ti (Fig. 6) for almost all garnets. $^{VI}$Ti is between 95 and 98% in several garnets, suggesting either multiple-scattering events are broadening the pre-edge peak relative to the $^{VI}$Ti standard, or a minor contribution of $^{IV}$Ti. Given the errors in the linear combination fits are around 1-1.5%, it is difficult to assign $^{IV}$Ti concentrations to the experiments. The fact that there is no discernible $^{IV}$Ti suggests $^{IV}$Ti concentrations in the synthetic garnets are at most several hundred ppm.

**Examples from nature**

The coordination behavior observed in synthetic garnets aligns with the Ti coordination and substitution mechanisms observed through major-element chemical trends (Ackerson et al., this issue). However, growth of synthetic garnets is limited to temperatures and pressures greater than experienced by most natural garnets. Furthermore, the synthetic garnets were grown at static T and P and do not record the range of prograde and retrograde histories recorded in many natural garnets. We analyzed Ti coordination in natural garnets from a range of conditions (low-grade contact metamorphism to mantle conditions) to assess whether the observations made in the synthetic garnets can be applied to garnets from a range of
natural conditions. Furthermore, by observing core-rim XAFS transects of garnets with well-characterized metamorphic histories, we can observe the interplay between T, P and composition on Ti solubility and coordination in garnet.

**Harpswell Neck** Sample 96-1 is a garnet-grade schist from the Jewel Formation in Harpswell, Maine. Garnets from this formation have been the topic of considerable discussion as to whether garnet porphyroblasts form from the coalescence of multiple garnet nuclei (Daniel and Spear 1998; Spear and Daniel 2001) or nucleation of a single garnet around a Mn-rich precursor mineral phase (Hirsch et al. 2003).

Core-rim variations in Fe, Mg and Mn in garnets from sample 96-1 indicate equilibrium, prograde garnet growth. Ca zoning does not match the zoning patterns of the other major elements and suggests disequilibrium Ca incorporation along an isobaric heating path due to garnet growth outpacing diffusive Ca replenishment to the mineral-matrix interface (Spear and Daniel 2001). Ti in these garnets is almost entirely VI-fold ($^{IV}$Ti content is near the detection limit of the technique as applied at beamline X26A), and variations in Ti concentration trend with Ca (Fig. 7). The correlation between Ti and Ca suggests that either Ti replenishment to the garnet-matrix interface is kinetically similar to Ca replenishment or Ti solubility in garnet is influenced primarily by the grossular content.

The effect of $T$ and $P$ on Ti incorporation in sample 96-1 is difficult to ascertain. Given that the prevailing petrogenetic theory for garnet growth in this sample assumes isobaric heating, pressure likely did not directly influence Ti solubility. Temperature is modeled to increase throughout garnet growth, yet Ti
does not display a systematically constant increase or decrease from core to rim.

These observations support the notion that garnet composition (in particular the grossular content) have a large influence on $\text{VI}_\text{Ti}$ solubility, and compositional variations exert greater control over the $\text{VI}_\text{Ti}$ than $T$ and $P$ over the garnet crystallization interval.

**Nelson Aureole** The Nelson contact aureole provides another example of the influence of Ca content on Ti concentration in garnet. The Nelson aureole is a pelitic contact metamorphic aureole surrounding the Jurassic-aged Nelson Batholith. The contact aureole is characterized by an isobaric (3.5 kbar), pluton-ward increasing metamorphic grade defined by mineral-in reactions — from garnet-in reactions at $527 \, ^\circ\text{C}$ to K-feldspar-in reactions at $653 \, ^\circ\text{C}$ (Pattison and Vogl 2005; Pattison and Tinkham 2009). In the present study we analyzed garnets from the garnet-in, staurolite-in, (557 °C), andalusite-in (560 °C) and K-feldspar-in zones.

As an example of the effect of Ca on Ti uptake, we note that garnets from sample 93CW22 of Pattison and Tinkham, 2009 from the andalusite-in zone exhibit Ca zoning patterns similar to those expressed in garnet from Harpswell Neck. The garnets have increasing rimward Ca content to an abrupt low Ca rim (Fig. 8). Like Harpswell Neck, these garnets are believed to form through isobaric, increasing temperature prograde growth. The interior of these garnets likely formed through the reaction muscovite + chlorite + quartz = garnet + biotite + $H_2O$, while the low-Ca rim formed through muscovite + staurolite + quartz = andalusite + garnet + biotite + $H_2O$. The low-Ca rim is thought to form via the shift to an andalusite-forming reaction creating a new equilibrium assemblage with a lower
grossular activity (Pattison and Vogl 2005; Pattison and Tinkham 2009). All of these
reactions occur at rutile saturation, indicating constant unity $a_{TiO_2}$ throughout
garnet crystallization. Composition maps again reveal the influence of grossular
content on Ti incorporation in garnet and bolster the notion that Ti content is
influenced by grossular content over the garnet crystallization interval (Fig. 8).

Valhalla Metamorphic Complex and retrograde equilibration Garnets
from the Valhalla Metamorphic Complex crystallized at peak metamorphic
conditions around 820 °C and 8 kbar after which they experienced a complex
retrograde re-equilibration path during exhumation to the surface (Hallett and
Spear 2011; Spear 2004; Spear and Parrish 1996). Garnets in the paragneisses were
subject to retrograde net-transfer reactions that resulted in garnet consumption.
Core-rim variations in Fe/(Fe+Mg) help constrain the cooling rates and exhumation
history of the region. Retrograde equilibration near garnet rims is demonstrated in
the rimward decrease in Mg and increase in Fe. The XAFS pre-edge spectra of Ti in
sample V6B reflect this retrograde re-equilibration. Octahedral Ti is relatively
constant across most of the grain, but increases near the rim of the garnet (Fig. 9).
As with the examples above, this increase coincides with a marked increase in Ca
content.

While the rimward increase in $^{VI}Ti$ reflects a retrograde increase in Ca, $^{IV}Ti$
decreases toward the rim. The decrease in $^{IV}Ti$ within the re-equilibrated zone can
occur either as a function of the changing garnet composition or a decrease in
solubility as a function of changes in T or P. Given that $^{IV}Ti$ substitutes directly for Si
(as opposed to requiring a coupled substitution), changes in dodecahedral or
octahedral element substitutions are unlikely to influence $^{IV}$Ti solubility. The notable exception to this is $^{IV}$Al$^{3+}$, where appreciable $^{IV}$Al$^{3+}$ solubility could influence the solubility of Ti on the tetrahedral site, although cation-normalization of the garnet formula for sample V6B show no evidence of appreciable $^{IV}$Al solubility.

The retrograde rim on garnet V6B may provide insight into the influence of $T$ and $P$ on $^{IV}$Ti solubility. If $^{IV}$Ti solubility in garnet behaves like experimentally-calibrated trace element thermobarometers, $^{IV}$Ti solubility will increase with temperature and decrease with increasing pressure (Thomas et al. 2010).

Retrogression occurs via a decrease in both temperature and pressure. If decreasing pressure had a greater effect on $^{IV}$Ti solubility than decreasing temperature, $^{IV}$Ti would increase in the retrograde rim. The fact that $^{IV}$Ti increases in the rim suggests that either temperature has a greater control on $^{IV}$Ti solubility in garnet than pressure, or $^{IV}$Ti decreases with decreases in both $T$ and $P$.

**Fall Mountain Nappe** The Fall Mountain nappe is a thrust system along the New Hampshire-Vermont border where thrusting emplaced a regionally-metamorphosed (upper) pelitic rock atop another (lower) pelitic rock. Whereas the garnets from Harpswell Neck and Nelson Aureole experienced isobaric prograde metamorphism, the lower unit of the Fall Mountain nappe experienced near-isothermal prograde metamorphism through loading via emplacement of the upper unit of the nappe (Spear, Hickmott, and Selverstone 1990). Sample BF-18C is a staurolite-kyanite grade garnet, biotite, chlorite, muscovite, plagioclase and quartz-bearing schist from the lower plate of the nappe complex. Modeling of zoning in garnet from BF-18C suggests prograde growth from ~3.2 kbar and ~450 °C to ~ 5.3
kbar and 500 °C. Tetrahedral Ti does not change significantly across the garnet, while $\text{VI}_{\text{Ti}}$ decreases with prograde growth (Fig. 10). The decrease in $\text{VI}_{\text{Ti}}$ could represent a decrease in solubility with increasing temperature and pressure, but the effect is difficult to deconvolve from the effect of decreasing Ca content.

**Comparison between natural and synthetic garnets**

Combining $\text{VI}_{\text{Ti}}$ concentration data from natural garnets with that of synthetically grown garnets affords the opportunity to observe Ti in garnets over almost the entire range of crustal geologic conditions—from shallow crustal contact metamorphism to UHT and UHP conditions present in the lower crust and upper mantle. Comparing the natural and synthetic garnet databases gives some insight into the factors influencing Ti solubility in garnet, and support the notion that $\text{VI}_{\text{Ti}}$ solubility is strongly influenced by grossular content.

There is a general increase in pyrope and decrease in almandine content with temperature over the range of both synthetic and natural samples (Fig. 11a,b). These relatively constant trends are not reflected in the Ti content, which has a distinct gap between the natural and synthetic garnets in temperature, pressure, pyrope and almandine space. Titanium content generally decreases with increasing $T$ and $P$ in natural garnets (Fig. 12a,b). However, Ti demonstrates a near-constant increase with increasing grossular content (Fig. 11c, Fig. 12c). Ultimately, there is a stronger correlation with Ti and $X_{\text{grs}}$ than with $T$, $P$, $X_{\text{alm}}$ or $X_{\text{pyr}}$.

**High-grade natural garnets and rutile exsolution**

Garnets from high-grade continental metamorphic and mantle sources serve as representations of the interplay between $T$, $P$, and composition at elevated...
temperatures and pressures and again demonstrate the effect of garnet chemistry on Ti incorporation. Coesite-bearing pyrope garnets from ultra-high pressure (UHP) Mg-rich metapelites of Dora Maira Central Massif experienced peak metamorphic growth at 800 °C and 37 kbar pressure (Schertl et al. 1991). Dora Maira garnets analyzed in this study are almost entirely pyrope, and despite crystallizing in the presence of rutile ($a_{TiO_2} = 1$) contain less than 40 ppm Ti. In contrast, synthetically-grown garnets from metapelitic bulk compositions at 800 °C and 35 kbar contain ~10 wt. % CaO and 1.2 wt. % TiO_2 (sample C-3155 from Tailby, 2009). The presence of intact coesite and a lack of crystallographically-aligned exsolved rutile needles in Dora Maira pyrope crystals suggest it is unlikely the garnets would have undergone complete retrograde diffusive re-equilibration of Ti, and that Ti in these garnets is near the primary crystallization composition.

The low Ti content of Dora Maira garnets yield noisy pre-edge spectra (Fig. 13), but these spectra indicate that Ti is almost entirely in VI-fold coordination. Compared with garnets from Valhalla that grew at similar temperatures, the lack of IV Ti in Dora Maira garnet suggests an inverse relationship between pressure and IV Ti incorporation.

The low solubility of VI Ti is in marked contrast to other UHP/UHT terranes where oriented rutile needles in garnets have been suggested as possible UHP/UHT indicators in garnet peridotites and eclogites (Van Roermund et al. 2000; Mposkos and Kostopoulos 2001; Zhang et al. 2003; Ague et al. 2013). In terms of Ti content of garnet, the main difference between rutile-bearing and rutile-absent UHP/UHT rocks is garnet composition. For example, garnets from eclogites of the Sulu UHP
terrane experienced peak metamorphism at 825-880 °C and 42-45 kbar and contain well-characterized exsolved rutile needles (Hwang et al. 2007). These garnets contain a much lower pyrope content and appreciable almandine and grossular components (Zhang et al. 2005). It should be noted that Hwang et al. (2007) dismiss exsolution from garnet as a primary mechanism for rutile formation in these rocks. However, recent studies (Proyer et al. 2013, Ackerson et al., this issue) shed light on novel exsolution mechanisms and bolster the notion that these rutile needles can be formed through exsolution in lieu of alternative explanations (rutile entrapment during growth, dissolution-reprecipitation or crystallization through fracture-healing).

The influence of garnet composition on $^{VI}_{Ti}$ solubility and the presence of retrogressively-exsolved rutile needles from high-grade rocks is evident in other systems as well. Samples were also analyzed from garnet lherzolite xenoliths from the Wessleton kimberlite pipe (Ene and Schulze 2013) and eclogites from the Western Gneiss Region. Both samples were pyrope-rich and contain very little Ti (Fig. 13), all of which is in VI-fold coordination.

Implications

Natural garnets contain Ti in both IV-fold and VI-fold coordination, and XAFS analysis show variations in Ti coordination within individual garnet crystals. As has been shown by other investigations, $^{VI}_{Ti}$ can be incorporated by a number of substitution mechanisms, several of which can account for the exsolution of rutile from high-grade garnets. In individual natural garnets, major-element composition (particularly Ca content) has a larger apparent influence on $^{VI}_{Ti}$ solubility than do
temperature or pressure. Solubility and variations therein of $^{IV}$Ti in the suite of natural garnets indicate that $^{IV}$Ti obeys similar trends to $^{IV}$Ti in other minerals (e.g. Ti in quartz, Ti in zircon). Changes in Ti coordination and $^{IV}$Ti and $^{VI}$Ti solubility within garnets can be used to interpret geochemical events during garnet growth. This study is limited by intrinsic errors in P and T estimates for natural systems, and correlation between Ti and Ca in garnets (e.g. Harpswell Neck) suggest coupled disequilibrium incorporation in some samples. Better constraints on garnet growth conditions in the studied samples using modern thermobarometric techniques could serve to increase the efficacy and utility of Ti in garnet calibrations. Also, better constraints on the chemical and mechanical properties of Ti end member garnets could aid in thermodynamic modeling of the activities of system components over the assumed T and P intervals of garnet growth and could inform the underlying chemical processes involved in $^{VI}$Ti incorporation. Ultimately this could lead to the development of a thermodynamically-constrained $^{VI}$Ti thermobarometer.

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References


Ene, V.V., and Schulze, D.J. (2013) Major and trace element geochemistry of ilmenite suites from the Kimberley diamond mines, South Africa. AGU Fall Meeting Abstracts, 23, 2765.


List of Figure Captions

Figure 1: Typical Ti K-edge XAFS spectra for $^{IV}_{Ti}$ and $^{VI}_{Ti}$. (a) XAFS spectra for $^{IV}_{Ti}$ from quartz QTiP-39 (blue) and $^{VI}_{Ti}$ from a schorlomite garnet from Magnet Cove, Arkansas (red) have pre-edge features (b) at different normalized absorptions and energies. (c) Combinations of the two coordination states result in spectra that are linear combinations of the two end-members.

Figure 2: Normalizing a $^{VI}_{Ti}$ XAFS spectrum of schorlomite from Magnet Cove, with absorption expressed as $[\mu(E)]$. (a) The height of the edge step absorption is proportional to the X-ray flux and Ti concentration in the sample. (b) Normalization of spectra by selecting the pre- and post-edge normalization regions and selecting the absorption edge allows for (c) concentration-independent comparison of spectra to an edge step of 1.

Figure 3: Compositional mapping of a synthetic garnet from sample 8-GLOSS. Fly scan imaging enables selection of inclusion-free zones within garnets. In this example, (a) Fe and (b) Ca maps help distinguish between seed garnets and new
garnet growth, while (c) Ti maps indicate the locations of Ti-rich inclusions. Field of view is 250X250 μm at 5 μm/pixel with a dwell time of 2 ms.

**Figure 4:** Pre-edge features of multiple minerals analyzed in this study. Spectra are offset for ease of comparison. (a) $^{VI}$Ti in a suite of silicate and oxide minerals show various contributions of the three pre-edge peaks described by Waychunas, 1987. (b) $^{IV}$Ti of zircon and quartz. The energy of the pre-edge peak in zircon is dependent on the crystal orientation relative to the polarization vector of the incident beam.

**Figure 5:** Linear combination fitting of the pre-edge spectrum of sample H11A with end-member $^{VI}$Ti and $^{IV}$Ti.

**Figure 6:** Pre-edge spectra of synthetically-grown garnets suggest Ti is almost entirely VI-fold coordinated.

**Figure 7:** Garnets in sample 96-1 from Harpswell Neck. (a,b,c) Garnets exhibit core-rim variations in all major elements. (d) Core-rim combined XAFS and EPMA analyses of garnet show little variation in the coordination of garnet from core to rim, but $^{VI}$Ti concentrations change concomitantly with changes in Ca content.

**Figure 8:** Garnet from sample 93CW22 of the Nelson aureole. (a-e) Composition maps showing correlation between Ca and Ti. (f) Results of XAFS pre-edge fitting demonstrate near-constant Ti coordination throughout the garnet.

**Figure 9:** Garnet from sample V6B from the Valhalla Metamorphic Complex. (a,b,c) Major-element composition maps displaying chemically uniform cores and retrogressed rims. (d) XAFS and EPMA core-rim transects show a rim-ward decrease in $^{IV}$Ti and increase in $^{VI}$Ti.
Figure 10: Garnet from sample BF18C from the lower unit of the Fall Mountain nappe exhibiting prograde growth. $^{v_T}$Ti is relatively constant from core-rim, while $^{v_T}$Ti content decreases with prograde growth and decreasing Ca.

Figure 11: $^{v_T}$Ti versus $T$ and (a) $X_{\text{alm}}$, (b) $X_{\text{pyr}}$, and (c) $X_{\text{grs}}$.

Figure 12: $^{v_T}$Ti versus $T$ and $X_{\text{grs}}$.

Figure 13: Pre-edge spectra for pyrope-rich high $T$ and high $P$ garnets, demonstrating Ti incorporation is almost entirely octahedral.
Table 1: Results of linear combination fitting of Ti XAFS pre-edge features in synthetic garnets from Ackerson et al., this issue.

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</table>
Figures

Figure 1

(a) XANES and EXAFS spectra showing pre-edge, tetrahedral (IV-FOLD) and octahedral (VI-FOLD) features. 

(b) Normalized absorption spectra for different IV-FOLD states.

(c) Normalized absorption spectra for different VI-FOLD states.
Figure 2

a

\[ \mu(E) \]

- post-edge
- edge step
- edge
- pre-edge

b

\[ \frac{d[\mu(E)]}{dE} \]

- maximum first derivative

c

\[ \text{normalized } \mu(E) \]

Energy (eV)

4950 5000 5050 5100 5150 5200
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7

(a) Ca

(b) Fe

(c) Mn

(d) Ti (ppm)

- ▲ Vt-fold
- □ IV-fold
- ■ Vβ-fold

Distance (μm)

0 50 100 150 200 250

Core Rim

% Vt-fold

0 0.5 1.0

500 μm
Figure 8

697

698

699
Figure 9

(a) Mg (b) Ca (c) Mg/Fe

(d) Ti (ppm) vs. distance (mm)

(e) Ca (apfu) vs. distance (mm)
Figure 10
Figure 11

![Graph showing normalized absorption over energy (eV)]

- **Dora Maira**
- **Wessleton**
- **Western Gneiss Region**
Figure 12
Figure 13

(a) Experimental vs natural $V_{\text{Ti}}$ (ppm) vs P (kbar)

(b) $V_{\text{Ti}}$ (ppm) vs T ($^\circ$C)

(c) $V_{\text{Ti}}$ (ppm) vs $X_{\text{GRS}}$