High precision microsampling and preparation of zoned garnet porphyroblasts for Sm–Nd geochronology

Anthony D. Pollington⁎,1, Ethan F. Baxter
Department of Earth Sciences, Boston University, 675 Commonwealth Ave., Boston, MA 02215, USA

Abstract
Zoned garnet porphyroblasts contain one of the longest continuous records of tectonic processes, with growth histories spanning many millions of years. Well known challenges exist in the physical preparation, purification, and geochronologic analysis of zoned garnets, which have limited the progress and application of this potentially powerful geochronologic tool. Here, we present details of an integrated methodology specifically for the acquisition of high-resolution Sm–Nd geochronologic records from zoned garnets that overcome these challenges. We develop and demonstrate our methods on large test garnets from a shear zone in the Tauern Window in western Austria. Chemically contoured microdrilling permits physical sampling of many discrete age annuli (each as narrow as ~100 μm) within a single garnet. Refined HNO3/HF/HClO4 partial dissolution methods cleanse coarse crushed (75–150 μm size) garnet annuli of detrimental inclusions yielding high 147Sm/144Nd ratios (0.9 to 4.6) and consequently accurate and precise ages. Experiments on powdered garnet (~75 μm size) gave low 147Sm/144Nd (<0.18) indicating failure to cleanse powders of inclusions. An example of the potentially significant effect of inclusions on age accuracy is presented. Because total garnet sample loss due to crushing and purification can be 40–75% (depending on inclusion density), and because Nd concentrations in garnet are very low (<1 ppm), resulting Nd mass per annulus can be <10 ng. Recently developed techniques for the analysis of 1–10 ng Nd samples yield 143Nd/144Nd with 10–20 ppm (2 RSD) precision, good enough for ±1 Ma age precision in most cases when garnet 147Sm/144Nd ~ 1.0. In total, this integrated sampling and analytical protocol permits the acquisition of 3–11 discrete high precision (~±1 Ma) age annuli in a single 2 cm diameter garnet.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction
The value of garnets for investigating the evolution of tectonic and metamorphic systems is well known. Garnet is involved in a number of prograde reactions and is therefore used frequently for thermobarometry and reconstructing P–T paths (e.g. Spear, 1993). Because of its heavy rare earth element (HREE) enrichment garnet commonly has relatively high ratios of Sm/Nd (e.g., Thöni, 2002) and Lu/Hf (e.g., Duchene et al., 1997), which provides the potential for precise geochronology. Several studies have taken garnet geochronology a step further by sampling cores and rims of growth zoned garnets to constrain the duration and rate of garnet growth (Christensen et al., 1989; Vance and O’Nions, 1990; Burton and O’Nions, 1991; Vance and O’Nions, 1992; Christensen et al., 1994; Vance and Harris, 1999; Stowell et al., 2001; Baxter et al., 2002; Ducea et al., 2003; Sölva et al., 2003; Pollington and Baxter, 2010). Such growth duration information is valuable in constraining reaction rates (e.g., Baxter, 2003), deformation rates (e.g., Christensen et al., 1989), and the overall pacing (i.e., gradual vs. pulsed) of metamorphic processes in general (e.g., Pollington and Baxter, 2010). However certain issues that make differential (i.e., core to rim) garnet geochronology challenging both in practice and in interpretation, have limited its progress and application.

In this study, we have employed—and will report on—the use of the Sm–Nd system integrated with new sample preparation methods for zoned garnet geochronology. Other isotopic systems (e.g., Lu–Hf, Rb–Sr, and U–Pb) may alternatively be used in concert with the approaches described herein, though considerations and adjustments would be necessary to accommodate the differences inherent in each system including sample size requirements, analytical precision, zoning in parent to daughter ratios, isotopic mobility in the garnet and rock system, and the effect and removal of inclusions. Neodymium concentrations in garnet are typically very low (<1 ppm). Fortunately, recent advances in techniques for measuring small samples of Nd (Harvey and Baxter, 2009) with thermal ionization mass spectrometry (TIMS) have reduced the sample size required for precise measurements. In addition to being able to measure small amounts of Nd, advances in partial dissolution cleansing techniques of samples dominated by REE-rich inclusions leads to accurate, high Sm/
Nd ratios in pure garnet in many cases. In this contribution we present details of an integrated method for sampling, recovering, and preparing discrete micromilled samples from zoned garnets while greatly increasing spatial and temporal resolution with Sm–Nd geochronology. We demonstrate our microsampling and inclusion cleansing techniques on garnets from the Tauern Window of western Austria, including the sample studied by Pollington and Baxter (2010) wherein these methods were successfully employed.

2. Differential garnet geochronology

2.1. Introduction

Only a handful of studies report ages from more than two zones in a single garnet (Christensen et al., 1989, 1994; Stowell et al., 2001). The vast majority of studies that have investigated durations of garnet growth have been limited to measuring only two zones within a garnet because of the technological ability to accurately sample and precisely date small enough growth zones. These studies have provided valuable information on durations of tectonic processes, but as advances in instrumentation provide the ability to measure small sample sizes the opportunity arises to investigate variable rates and paces of these same processes.

2.2. Garnet growth models

If only the core and rim are measured, then the pace (i.e., constancy or fluctuation of rate) of garnet growth cannot be evaluated. Most differential garnet geochronology studies assume a constant growth rate over the total duration of garnet growth, in large part because the lack of intermediate growth zone ages precludes any other interpretation. In order to understand the limitations associated with measuring only two broad zones within a garnet and to explore some of the questions that could be explored if multiple zones could be sampled we calculate models of garnet growth with varying growth rates (Fig. 1). In each of these models, we assume a fractional radius and a fractional duration of garnet growth, which represents total durations that could range from as little as 1.4 Myr (Vance and O’Nions, 1992) to as much as 14.7 Myr (Christensen et al., 1989). As can be seen in the models from Fig. 1 it is possible that this assumption greatly deviates from the true growth rate, whether that rate was constant in volume, constant in surface area, or whether growth was not at a constant rate at all. In addition to theoretical models, recent studies have shown evidence of distinct thermal pulses in metamorphic terranes (Camacho et al., 2005; Ague and Baxter, 2007; Lancaster et al., 2008). Such pulses could manifest themselves as pulses of mineral (i.e., garnet) growth and would impart distinct age zonation in garnet.

In addition to the advantage obtained by measuring a large number of samples in a single porphyroblast, by microsampling the grain one is able to more accurately measure distinct growth zones without smearing across multiple zones. Core, rim and intermediate samples are classically sampled by cutting a garnet into rectangular sections using a microsaw (Fig. 2). Due to the radial growth symmetry of nominally spherical grains (like garnet), shells of constant volume will get progressively thinner towards the edges of the mineral. This leads to most of the age information being concentrated near the rims. While a relatively wide sample in the core will not greatly affect the accuracy of total garnet growth duration measurements, the same sample width could greatly smear age information at the rim (Fig. 3).

Fig. 1. Models of garnet age. a) Constant volumetric growth rate resulting in total growth (1 fractional radius) in total time (fractional age). b) Decelerating growth rate; starting growth rate of panel a decelerating by 5% of the previous value every 0.1 mm. c) Accelerating growth rate; starting growth rate of panel a accelerating by 5% of the previous value every 0.1 mm. d) Pulsed growth rate; three evenly spaced pulses with growth rate of panel a and duration 0.01 total duration (i.e., 100 kyr pulse in 10 Myr growth).

Fig. 2. a) MnO weight percent contours in a garnet from Vermont (Baxter, 2000). Hatched area represents a single growth zone that could be sampled with the micromill. The mass of sample collected from the hatched area is greater than the mass of sample collected from rectangle 4 in the photo. Scale bar is 1 mm. b) Photograph of garnet from Vermont showing saw marks from the classic sampling method.
Fig. 3. Model of constant volumetric growth rate from Fig. 1a with sample sizes from Fig. 2 superimposed. Due to the spherical growth symmetry of garnet, even a relatively wide sample can be obtained at the core with little effect on the accuracy of the measured age. However, a sample collected at the rim is much more sensitive to the radial width of the zone measured. Using the sampling size from the core, middle and rim rectangles in Fig. 2, apparent “ages” of 0.990, 0.896 and 0.396 would be measured. The age of each sample represents a weighted average that is skewed towards the younger portion of the zone. In order to give an accurate duration, the rim age ought to be 0. The only way to measure this age would be to sample an infinitesimally small zone right at the edge of the garnet. By sampling a larger zone the apparent “rim” age is older than the end of garnet growth. This leads to an underestimation of total growth duration by, in this case, 40%. Such crude sampling would also mask information on the changing pace of growth (as in Fig. 1).

By taking a wide sample at the rim, spanning a long fractional growth duration, and inaccurately interpreting it as the end of garnet growth, it is possible to underestimate the total duration of growth by as much as 40% (Fig. 3).

There is of course a limit to how narrow a sample can be and still yield precise data. The precision on a calculated age is dependent on many factors, including the difference in parent–daughter ratios of the different minerals on the isochron as well as the measured precision of a given sample. By utilizing recent methods to measure small samples of Nd (Harvey and Baxter, 2009) it is possible to measure 143Nd/144Nd in ~4 ng Nd samples at 10–20 ppm precision. Setting 4 ng as the desired quantity of Nd, the width of the growth zone that can be precisely recovered and measured is therefore largely a function of the cleanliness of the sample recovered (inclusion free) and the concentration of Nd in the pure garnet. In order to recover narrow zones but still recover enough sample, we sample concentric growth zones using a micromill rather than being limited to wider angular shaped samples cut using a microsaw (Fig. 2). By following distinct chemical zones we can be more confident that we are sampling over fewer growth zones than a similar rectangular cut. The hatched region in Fig. 2a would yield a mass greater than the corresponding rectangular saw-cut section #4, but does not smear across multiple growth zones. This method is analogous to sampling tree rings for age information. Sampling of multiple distinct zones within a single garnet porphyroblast will provide researchers the opportunity to investigate rates in greater detail.

A final consideration when planning zoned garnet geochronology is zonation in the parent and daughter elements, Sm and Nd; Sm and Nd concentrations are a factor in determining the amount of sample needed in each zone. The 147Sm/144Nd ratio in the pure garnet in each zone is a factor in predicting ultimately attainable age precision. The magnitude of Sm–Nd zonation by Rayleigh distillation in most garnets is relatively small (perhaps up to a factor of two variation; Lapen et al., 2003; Kohn, 2009; Skora et al., 2009; Peterman et al., 2009). Consideration and investigation of parent and daughter element zonation in garnet via laser ICP or bulk methods are worthwhile in planning zoned garnet geochronology.

3. Samples

The test samples used here to develop and demonstrate the utility of our methods were collected from a small (1–3 m) shear zone located in the Stillup Tal (Stillup Valley) of western Austria (Lat 47°03’00.2’’ Long 011°56.271’’, WGS 84 datum). The shear zone is described in Selverstone et al. (1991) and Barnes et al. (2004). The core of the shear zone contains very large garnets surrounded by a chlorite–biotite matrix. The garnet used for this study (ST-7) is from Zone IV as described in Selverstone et al. (1991); it is ~5 cm in diameter and hosts apatite, zircon, biotite, chlorite, rutile and ilmenite inclusions. While there are several very large (>1 mm) patches of micaeous inclusions, much of the garnet appears to be relatively free of inclusions in the petrographic microscope. We also include data from sample 07PST-4Y (a 6 cm garnet from Zone IV in the same shear zone) reported in Pollington and Baxter (2010) where sample details may be found.

Three methods of sampling were explored on ST-7: 1) a wafer from the center was cut to utilize the methods described in Section 4.1 (ST-7 AN-5); 2) a “bulk” section was cut from near the rim (approximately three-fourths of the distance from the core to the rim) of the garnet with a saw blade to test partial dissolution techniques and the effect of inclusions (ST-7 BG); 3) two microdrilled bulk garnet sections were collected to test the possibility of using microdrilled powders. The two microdrilled samples include 1) a small portion of the garnet which was of gem quality and was visually free of inclusions at least as deep as the sampling depth (ST-7 DGT-Gem) and 2) a bulk sample across the entire area of the garnet (ST-7 DBG).

4. Methods

4.1. Sampling

4.1.1. Chemical mapping and contouring

Accurate estimates of garnet growth duration require accurate measurements of core and rim isotope ratios, and if any information about pacing is desired accurate sampling of particular zones is required. Locating the rim of a euhedral garnet for accurate sampling is relatively trivial. However, accurately locating the core of the same garnet, or locating the rim in a non-euhedral garnet can be much more difficult. If the garnet was cut off-center, then the geometric center of the thick-section will not necessarily be the growth core. This still assumes though that growth of the grain was uniform in all directions, which for most cases is probably a good assumption but is not always the case (Wilbur and Ague, 2006). We use a more direct method for guiding sampling and ensuring that not only is the growth core sampled, but that any distinct zones of interest can be targeted and sampled discretely.

The test garnet was cut across its equator. A 2 mm thick wafer was cut in the garnet with the equator at the top of the section (Fig. 4). This wafer was directly analyzed on the JEOL JXA-733 electron microprobe at MIT. For chemical contouring a grid of points with a 500 μm spacing was measured at 150 nA for 5 s at each point. For these analyses only isotopic analysis and finely resolved spatial sampling. In the case of diffusion limited garnet growth, it is possible for Sm to be strongly partitioned into the rim and for low Sm/Nd ratios to dominate the garnet interior (Skora et al., 2009). Lutetium, in contrast, is strongly fractionated by garnets with relative enrichments in the core (due to Rayleigh distillation) often by a factor of ten or greater causing a related core to rim decrease in Lu/Hf ratio (e.g., Lapen et al., 2003; Kohn, 2009; Skora et al., 2009; Peterman et al., 2009). Consideration and investigation of parent and daughter element zonation in garnet via laser ICP or bulk methods are worthwhile in planning zoned garnet geochronology.
the major cations in garnet (Fe, Mg, Ca, and Mn) were analyzed. The data was filtered to remove points that yielded anomalously high or low oxide wt.% totals (poor focus) or that had values of any cation that were abnormally high or low compared to surrounding points (inclusions analyzed due to setting up a grid over the entire sample). This data is imported to a contouring program written in Matlab. It is also necessary to have reference points in the same frame of reference as the contour map, which can be achieved by taking reference points on the wafer before microprobe analysis.

When the contour map is prepared it can be overlain on a photo of the garnet in an image program such as Adobe Illustrator. It is important that reference points are taken that exist both on the contour map and on the photo used, so that contours can be correctly placed. Because we are using the polished wafer for the microprobe analysis (rather than the mirror image on a thin section) the map plots directly onto the wafer surface and thus represents an accurate guide for microsampling. The contour map will be used to guide sampling of distinct chemical, and presumably, growth zones. Previous studies (e.g., Hollister, 1966; Tracy et al., 1976; Thompson et al., 1977) have shown that manganese is partitioned early into the growing garnet, such that Rayleigh fractionation produces a bell-shaped pattern of MnO concentrations concentric about the crystal core, thus making it a useful element to see concentric patterns in growth. MnO has been used as a proxy for garnet age in previous studies (e.g., Chernoff and Carlson, 1997); here, we will measure the actual ages at high spatial precision.

4.1.2. Microdrill

The MicroMill manufactured by New Wave provides an excellent tool for obtaining small and spatially complex samples from a number of solid materials. For a description of the instrument and its subsystems see Charlier et al. (2006). One of the uses of the instrument in our method is the ability to import a drilling pattern based on the chemical map described above from an image program such as Adobe Illustrator into the MicroMill software. This allows sampling of distinct zones which are not visible to the naked eye.

Sampling with the MicroMill offers two methods for sample recovery. The method of sample recovery that is developed in this contribution is to use the MicroMill to cut out a discrete zone and collect that solid, unpowdered region. The major drawback to sampling solid annuli and discarding the powder is the significant amount of sample loss from the 800 μm wide drill bit. The method which results in the highest spatial resolution and the least sample loss is similar to the method described in Ducea et al. (2003) where the powdered material from microdrilling is collected and analyzed. To achieve the highest spatial resolution, the best choice for sampling would be to collect all the powder so that no area of the garnet is lost during sample recovery; unfortunately this can lead to poor age precision if the powder is not pure garnet. In Section 4.2.1.1 we describe the challenges encountered in analyzing powdered samples and show that partial dissolution of MicroMill powdered samples fails to purify garnet. Both methods (solid annuli vs. powders), as well as potential limitations of each, are described below.

To collect solid annuli, the 2 mm thick wafer cut from the middle of the garnet is attached to a block of graphite using crystal bond. This block and a surrounding Teflon ring are attached to the sample stage using crystal bond (Fig. 7). Crystal bond is used because it is easy to melt on a countertop hotplate but is strong when cured, it dissolves in acetone and can be cleaned off fairly easily and it has a low concentration of Nd. Care must be taken when attaching the Teflon ring to the stage that the seal is watertight. The Teflon ring is filled with clean milli-Q (MQ) water so that the sample is covered in water. The water serves the dual purpose of cooling the drill bit and removing powder from around the drill bit while it is moving. If a sample is drilled with no water it leaves a ragged trench and also wears down the drill bit before a run is complete (Fig. 8).

Fig. 4. a) Cartoon of zoned mineral (cross section). Dashed lines represent composition contours. W is the 2 mm thick wafer that will be analyzed on the microprobe and used for sampling. T can be used to make a thin section. B is extra garnet that can be used for testing the particular partial dissolution method appropriate for a given sample. It is important to note that there is a finite but important thickness that is lost between the top of the wafer and the location of the thin section. For this reason it is preferable to analyze the wafer before microprobe analysis. b) Contour map of the type that would be created by analyzing the top of the wafer (plane view). From a garnet from Vermont (Baxter, 2000).

Fig. 5. Photo of garnet from Stillup Tal (ST-7) with MnO weight percent contours from electron microprobe. Black lines represent locations of microdrill lines; thickness of lines is the width of the conical drill bit at a depth of 2.5 mm. Black fields represent large areas of chlorite and biotite inclusions. Fine lines on scale bar are 1 mm each.
Two types of drill bits are commonly used in microsampling (Ducea et al., 2003; Charlier et al., 2006) and are shown in Fig. 9. The tungsten carbide drill bits are much finer (as fine as 100 μm) but do not cut through garnet efficiently based on our tests. The diamond particle drill bits are much wider, but are able to cut through garnet and therefore are the drill bits we use. Both styles, as well as many different shapes, are available from Brasseler Instrumentation. For all zones sampled the variable speed drill is set to 100% speed. The patterns are drilled 50 μm deep/pass with 50 passes over each line. A scan speed of 50 μm/s and a plunge speed of 100 μm/s are used.

Using the superimposed electron microprobe map as a guide to illuminate growth contours, discrete annuli of garnet growth can be sampled one at a time with the drill. A simple, but important practical benefit of this method is that very tight (i.e., narrow) spatial and age resolution can be achieved while sufficient total sample size can still be gained by following a single contour around the entire garnet. Coarser sampling, for example with a microsaw, would smear several growth rings together yet result in similar or smaller total sample size (Fig. 2). To collect a sample, trenches are drilled through the garnet into the graphite block, on either side of the zone of interest, leaving...
the desired sample as a plateau (Fig. 10). The only loss of resolution is in the z-direction where chemical contours mapped on the surface may be skewed from vertical over the 2 mm wafer thickness (e.g., Fig. 11). When wafer thickness approaches the radial location of the garnet annulus being sampled (i.e., nearer the core of the garnet), this effect becomes very large; otherwise it is a minor effect. In addition, the drill troughs (and annuli preserved) do not themselves have perfectly vertical walls, so there is minor smearing of chemical contours and loss of sampling resolution due to this effect. The minor age smearing that is caused by non-vertical trenches and chemical contouring is considerably less than that which is caused by sampling with a microsaw. Large, obvious inclusions may be avoided during drilling. Due to the conical shape of the drill bits being used, more material is drilled to a powder for thicker samples (Fig. 12). After drilling, the crystal bond attaching the garnet to the graphite block is melted and the sample is plucked out using tweezers. The sample is cleaned in acetone in an ultrasonic bath to remove any crystal bond that was not melted away. A narrow sample was collected to test the limits on the width of annulus that can be sampled. In this study the narrowest annulus collected was 180 μm at the top of the ridge (Fig. 10), but minimum annulus width (at the wafer surface) is theoretically unlimited, determined only by how close together two trenches may be drilled. Perhaps a ~100 μm annulus represents a practical minimum width for easy recovery. In this study, we have used drill bits which result in sample loss of 800 μm on each side of a collected annulus thus limiting the total number of annuli that can be extracted from a single sample; other opportunities to drill finer canyons could be explored in the future (i.e., laser, focused ion beam, etc.).

The sample annulus is hand crushed in a tungsten carbide mortar and pestle to a grain size of 75–150 μm (100–200 mesh) with the fines (<200 mesh) being discarded (see below). Because the drilled garnet sample still has many unavoidable microinclusions, an optically pure garnet sample is separated next using a Frantz magnetic separator and hand picking with a microscope to separate garnet from inclusions. Depending on inclusion density, as well as care in crushing, this entire process from solid annulus to crushed optically clean garnet can result in a 30–60% mass loss.
For samples where we do collect the microdrilled powder, we follow the same method described above for attaching the sample to the stage and using a Teflon ring filled with water. The sample is drilled to a depth of 500 μm, which results in a drilled width of 500 μm. The powder is suspended in the water during drilling. After the run is finished, the stage is removed from the drill without spilling the water, which is then poured into a cleaned Teflon beaker where it is dried and taken to dissolution. A concern associated with collecting microdrilled powder is how much Nd is introduced to the system from the water/drill bit/open air. Samarium and Nd concentrations from multiple blanks were analyzed including dissolving a drill bit, leaving a beaker open in the room for the duration of a run and comparing microdrilled with hand crushed garnet. The highest measured blank, which was a result of comparing the two quartz samples, was 0.91 ng Nd and 0.47 ng Sm. These values yield a sample to blank ratio much higher than desired. The dissolved drill bit and room blanks each gave total amounts of ~1 pg Nd and ~0.5 pg Sm so it is unclear where the dirtiness of the drilled quartz derives from. One possibility is heterogeneities of rare earth concentration in the quartz sample used. All these issues are avoided when using solid annuli because the plucked sample is washed in acetone after sampling and all drilling related contaminants are cleaned off.

4.2. Chemistry

4.2.1. Partial dissolution

One of the most common issues that must be considered in geochronology is the incorporation of inclusions into samples to be analyzed. Varying treatments of garnets containing inclusions have been shown by many authors to have a large effect on both the accuracy and precision. By removing microscopic inclusions that may be older than the garnet we also improve the accuracy (see Section 5.4 for discussion). We tested our partial dissolution methods on both powdered and crushed garnet samples. As described in the following two sections, we were able to successfully remove inclusions from crushed garnet with our partial dissolution method, but we were unable to do so for powdered samples.

4.2.1.1. Powdered samples. To test our partial dissolution methods on powdered samples such as those that would come from microdrilled areas, a large, bulk garnet sample was collected as fine powder using the MicroMill. After the sample had been drilled and collected it was homogenized and split into 37 separate samples. These samples were partially dissolved with a combination of different acids, times and temperatures. Acids used in the experiments were concentrated HF paired with concentrated HClO4 (Amato et al., 1999; Baxter et al., 2002), 7 N HNO3, 98% H2SO4 (Anckiewicz and Thirlwall, 2003) and 6 N HCl; reaction times in each acid ranged from 15 min to 24 h; temperatures ranged from 20 °C (room temperature) to 180 °C. After partial dissolution, the leachate was discarded and the residue was fully dissolved and measured for Nd and Sm concentrations and 147Sm/144Nd ratio. Table 1 shows results from a representative sampling of these experiments. Regardless of the combination of acid, temperature or time used during 37 partial dissolution experiments on powders, no sample showed significant increases in 147Sm/144Nd (powder residues from partial dissolutions ranged from 0.116 to 0.164 as compared to untreated garnet with 147Sm/144Nd = 0.115) or decreases in REE concentration, which would be indicative of approaching pure garnet chemistry (Thöni, 2002).

It is unclear why all of our partial dissolution experiments failed to purify the microdrilled powdered garnet. The expectation had been that the finer grain size would expose a greater proportion of inclusions and lead to better, not worse, cleansing as compared to crushed samples. Instead, perhaps the fine grain size effectively enhanced the dissolution kinetics of the garnet itself more so than the included phases such that more garnet was dissolved than inclusion. Because of the failure to cleanse microdrilled powders, we abandoned the collection and use of drilled zones and focused instead on solid annuli. It is unfortunate that the drilled powders cannot be used at this time as this results in loss of analyzable sample (the width of one drilled trough, or about 800 μm) and some reduction in spatial and age sampling density in a given garnet. We identify this as an important area for future improvements and investigation.

In addition to the sample collected for partial dissolution experiments, an area of garnet that was optically pure was microdrilled in order to investigate the effect of microinclusions. Large areas of inclusions can easily be avoided with the MicroMill (Duceta et al., 2003), however microinclusions are impossible to avoid. This sample was fully dissolved with no partial dissolution and gave a 147Sm/144Nd ratio and Nd concentration indicative of a sample dominated by inclusions rather than garnet (Table 1). This underscores the point that even seemingly inclusion free garnet can still require cleansing of tiny mineral inclusions.

4.2.1.2. Crushed solid garnet annuli. Plucked solid annuli are prepared using the method described in Section 4.1.2. Once the garnet is visually clean of inclusions, it is partially dissolved using a method modified from Baxter et al. (2002). Samples are dissolved at ~120 °C for 3 h in 3 mL concentrated HNO3 with 5 min ultrasonic at the beginning, end and each hour. The HNO3 is decanted and the sample is rinsed and ultrasonicated in MQ water twice. The sample is dried and 2 mL 1.5 N HCl and 1 mL concentrated HF are added. This solution is placed on a hotplate at ~120 °C for 30 to 40 min, depending on sample size. Longer or shorter durations in HF might be considered for samples with different inclusion density or inclusion mineralogy; every new garnet sample is different and the partial dissolution method should be tested and refined for a given sample set before use. The sample is placed in the ultrasonic bath for 5 min half way through and at the end of hotplate dissolution. The leachate is decanted and the sample rinsed and ultrasonicated twice in 1.5 N HCl and twice in MQ water. The sample is dried and 1 mL 1.5 N HCl and 2 mL HClO4 are

Fig. 12. Photos showing dimensions of drilled areas. a,b) Holes drilled at different depths in graphite block using conical diamond particle drill bit. c) Trough drilled 500 μm deep in garnet using conical diamond particle drill bit. Each scale bar is 1 mm.
added. The HClO₄ will re-dissolve secondary fluorides that have formed during HF dissolution. The solution is placed on a hotplate at ~143 °C for 1.5 h capped and then left uncapped overnight to dry down. Once the HClO₄ is dry, ~12 mL 1.5 N HCl are added and ~140 °C for 1.5 h capped and then left uncapped overnight to dry

Table 1
Partial dissolution experiment data for powdered samples.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Acid&lt;sup&gt;a&lt;/sup&gt;</th>
<th>T (°C)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Time on hotplate (min)</th>
<th>Total time in acid (min)</th>
<th>Mass before partial (mg)</th>
<th>Mass after partial (mg)</th>
<th>Total mass loss (mg)</th>
<th>Percent mass loss (%)</th>
<th>Nd (ppm)</th>
<th>Sm (ppm)</th>
<th>147Sm/144Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-7 H₂SO₄</td>
<td>120</td>
<td>540</td>
<td>555</td>
<td>9.25</td>
<td>21.85</td>
<td>13.75</td>
<td>8.10</td>
<td>37.1</td>
<td>7.88</td>
<td>2.01</td>
<td>0.1542</td>
</tr>
<tr>
<td>ST-7 HCl</td>
<td>25 (180)</td>
<td>30 (840)</td>
<td>15 (840)</td>
<td>0.25 (14)</td>
<td>32.75</td>
<td>16.93</td>
<td>15.82</td>
<td>48.3</td>
<td>11.44</td>
<td>3.05</td>
<td>0.1611</td>
</tr>
<tr>
<td>ST-7 HNO₃</td>
<td>128</td>
<td>30</td>
<td>45</td>
<td>0.75</td>
<td>19.87</td>
<td>16.89</td>
<td>2.98</td>
<td>15.0</td>
<td>13.11</td>
<td>3.55</td>
<td>0.1639</td>
</tr>
<tr>
<td>ST-7 Full dissolution-control</td>
<td>15</td>
<td>0.25</td>
<td>2</td>
<td>0.02</td>
<td>2.27</td>
<td>1.27</td>
<td>0.99</td>
<td>22.67</td>
<td>4.33</td>
<td>0.1154</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Acid strengths are concentrated HF, concentrated HClO₄, 98% H₂SO₄, 7 N HNO₃, and 6 N HCl.

<sup>b</sup> Only the experiment for each acid that resulted in the highest 147Sm/144Nd ratio (by mixed spike analysis) is shown.

<sup>c</sup> Values in parentheses are the temperature and time for the HClO₄ step.

Fig. 13 shows a Sm–Nd isochron for one bulk garnet sample, treated with three different partial dissolution techniques (HF + HClO₄, HCl, no partial dissolution). As progressively aggressive partial dissolution is applied, the 147Sm/144Nd ratio and the precision on garnet age calculations both increase as a more pure garnet is approached. The three differently treated samples represent different mixtures of garnet and varying components of the inclusion population some which may be in age equilibrium with garnet, some which may not. Any two-point isochron between dirtier (i.e., lower Sm/Nd) garnet samples and the matrix yields older ages, likely representing age inheritance from older included minerals that formed earlier in the rock’s history. Alternatively, it is possible that the matrix itself has shifted off the isochron due to open system exchange of Sm or Nd subsequent to garnet growth. The latter possibility is discussed in Section 5.2.

4.2.2. Chemical separation and TIMS analysis

Isotopic analyses were performed in the Boston University TIMS facility using a TheromoFinnigan-Triton TIMS using faraday cups in static collection mode. All matrix samples and garnets that have been partially dissolved and screened for inclusions are subsequently fully dissolved and chemically separated using standard methods as described in Harvey and Baxter (2009). Dissolutions are carried out using HF and HNO₃. For most samples two stage Nd column chemistry is performed with TRU-spec resin followed by 2-methyl-lactic acid (MLA) columns. It was found that large amounts of Fe tend to overwhelm the TRU-spec column resulting in low yields, so for Fe rich samples (such as garnet) a third Fe clean up column is run prior to passing the sample through TRU-spec. Neodymium was measured on single rhenium filaments as an oxide (NdO⁺) using the new Ta₂O₅ loading method described in Harvey and Baxter (2009). Our in-house 4 ng Ames Metal Nd standard gave a value of 143Nd/144Nd = 0.5121302 ± 0.0000093 (2 SD, n = 153) over the duration of analyses. Samarium was measured as a metal using a double rhenium filament assembly. The long-term mean on our in-house Sm standard is 147Sm/150Nd = 0.560834 ± 0.000052 (2 SD, n = 57). The Sm and Nd isotope data of all samples analyzed from Stillup Tal garnets is shown in Table 2.

Even with advances in TIMS technology and chemistry, there still remains a finite garnet sample size limitation. This limitation ultimately comes down to extracting enough Nd from the purified garnet to load on the TIMS and run with sufficient precision. Pollington and Baxter (2010) demonstrate 10 ppm external precision on 4 ng Nd load sizes with the Ta₂O₅ loading technique. Thus, the final usable mass of an individual garnet sample will be a function of several factors including: 1) Nd concentration in the garnet, 2) inclusion density, 3) sample loss during drilling, and 4) sample loss during partial dissolution. Neodymium concentrations in garnet range from ~0.03 ppm (e.g., in mafic blueschists; Dragovic et al., 2010) to ~20 ppm (Thöni, 2002), but most garnets with apparent Nd concentrations above ~1 ppm are probably still contaminated by inclusions. For representative garnet, Fig. 14 shows the width of an
annulus required to yield a 4 ng Nd sample size necessary for modern high precision TIMS analysis.

4.3. Summary of results

In total, we have conducted 53 experiments on Stillup Tal garnets samples: 37 powdered samples, 4 crushed samples from sample ST-7, and 12 crushed samples from 07PST-4Y (from Pollington and Baxter, 2010). From this total dataset, several broad observations are evident. First, none of the powdered samples yielded high enough $^{147}$Sm/$^{144}$Nd for geochronology. All partial dissolution methods attempted failed to cleave powders. Second, all of our partially dissolved crushed samples yielded high $^{147}$Sm/$^{144}$Nd, most notably the 12 annuli from 07PST-4Y all of which yielded $^{147}$Sm/$^{144}$Nd between 2.9 and 4.6. Third, the combined HNO$_3$/HF/HClO$_4$ acid method yielded the cleanest garnets and the best results. Crushed ST-7 samples yielded lower $^{147}$Sm/$^{144}$Nd (up to 0.95), probably reflecting differences in inclusion population. It is possible that better results might have been achieved for ST-7 with longer duration and/or different temperature of HF leaching. Ages determined for all Stillup Tal garnets fall within 27.5 to 20.0 Ma—the total growth duration determined for the concentrically zoned 07PST-4Y sample. The demonstrated ability to obtain $^{147}$Sm/$^{144}$Nd $>1.0$ is a prerequisite to ±1 Ma age precision (Harvey and Baxter, 2009) if we assume a 10 ppm analytical precision on the garnet $^{143}$Nd/$^{144}$Nd.

5. Interpretation of differential garnet age data

Two-point garnet-matrix isochrons are used to calculate ages. One of the fundamental assumptions of isochron geochronology is that all points used to calculate an isochron age have remained closed systems since the time of garnet growth. While there are statistical benefits in constructing an isochron with multiple points, this approach may be invalid when considering “isochrons” that contain minerals with varying closure temperatures in long lived metamorphic systems where different minerals may grow or close over many millions of years (Scherer et al., 2000). Additionally, given that garnet growth may span millions of years, even the addition of repeat preparations and analyses of multiple well-cleansed garnets on an isochron can lead to poor MSWD and poorer precision (Kohn, 2009).

Rather, the significance of each garnet zone two-point isochron age is bolstered by the geometric relationship to its concentrically adjacent ages. There can be more value in considering the ages of each garnet zone separately and appreciating their geometric relationship (Pollington and Baxter, 2010). We therefore consider only two-

---

**Table 2**

Summary of garnet ages from Stillup Tal.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Partial dissolution method</th>
<th>Samplea</th>
<th>Sm (ppm)</th>
<th>Nd (ppm)</th>
<th>$^{147}$Sm/$^{144}$Nd $^{b}$</th>
<th>$^{143}$Nd/$^{144}$Nd $^{c}$</th>
<th>± 2 SDd</th>
<th>2-point garnet-matrix age (Ma)</th>
<th>2 SD age uncertainty$^{e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>HClO$_4$—overnight, &gt;140 °C</td>
<td>WR-1</td>
<td>7.67</td>
<td>45.28</td>
<td>0.1025</td>
<td>0.5123119</td>
<td>0.0000034</td>
<td>20.5</td>
<td>2.6</td>
</tr>
<tr>
<td>Garnet: hand-crushed bulk garnet</td>
<td>HClO$_4$—overnight, &gt;140 °C</td>
<td>BG-1 F4</td>
<td>2.58</td>
<td>1.76</td>
<td>0.8908</td>
<td>0.5124175</td>
<td>0.0000064</td>
<td>9.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Garnet: hand-crushed annulus</td>
<td>HClO$_4$—overnight, &gt;140 °C</td>
<td>AN-5</td>
<td>4.60</td>
<td>2.90</td>
<td>0.9572</td>
<td>0.5124332</td>
<td>0.0000090</td>
<td>23.4</td>
<td>2.3</td>
</tr>
</tbody>
</table>

From Pollington and Baxter (2010)

---

**Fig. 14.** Minimum annulus width for a given radius and Nd concentration to recover the 4 ng Nd needed for a high-precision TIMS analysis. This takes into account a 60% sample loss during crushing and physical separation, 20 ng lost during partial dissolution and a further 20% of the final sample lost during column chemistry. Radius is the radius to the center of a circular annulus with vertical sides. For a garnet with typical concentrations of Nd (1–10 ppm) and a diameter of 2 cm, ~5–10 concentric growth zones could be collected that yield 4 ng Nd each separated by an 800 μm drilled trench. The gray area is the area where the width of the annulus is greater than the radius, and is therefore impossible to sample.
point isochrons with each garnet zone and the bulk matrix reservoir. As with all isochron studies a series of assumptions must be made when calculating and interpreting these ages. Assumptions that must be considered include: 1) the garnet and the matrix were initially in isotopic equilibrium, 2) since the time of garnet growth the matrix has remained a closed system to Sm and Nd exchange, 3) since the time of garnet growth the garnet has remained a closed system to Sm and Nd exchange and 4) that garnet has been sufficiently cleansed of mineral inclusions that might compromise age precision, and accuracy. Below, we discuss each of these in turn and describe methods to mitigate some of the issues at hand.

5.1. Initial garnet-matrix equilibrium

Thöni (2002) and Romer and Xiao (2005) have described this possible effect, which, in certain documented cases, can be severe enough to yield even negative ages (futurechrons). The problem arises when individual reactant mineral grains each have evolved a different \(^{143}\text{Nd}/^{144}\text{Nd}\) (due to differences in \(^{147}\text{Sm}/^{144}\text{Nd}\) and radiogenic in-growth over time) such that an individual garnet grain may inherit the initial \(^{143}\text{Nd}/^{144}\text{Nd}\) of a random array of local reactant grains, rather than a representative bulk matrix value. Fortunately, this effect will be insignificant in almost all cases for the Sm–Nd system for several reasons. First, as Romer and Xiao (2005) discuss, this issue is much more problematic when dating minerals with low parent to daughter ratios (for example, Rb/Sr in garnet). Fortunately, clean garnets typically have high Sm/Nd ratios and are therefore much less susceptible to initial disequilibrium with the bulk matrix. As long as garnets are properly cleansed and yield high enough \(^{147}\text{Sm}/^{144}\text{Nd}\) (Thöni, 2002 suggests \(^{147}\text{Sm}/^{144}\text{Nd} \sim 0.5\), the effects of minor heterogeneities in the matrix become insignificant compared to the relatively much higher Sm/Nd ratio in the garnet. Second, in the Sm–Nd system, almost all common rock forming minerals have very similar Sm/Nd ratios ranging from 0.10 to 0.25 (DePaolo, 1988) with the greatest variations found in more mafic assemblages with amphibole or pyroxene. Felsic or pelitic mineral inclusions that might compromise age precision, and accuracy. Below, we discuss each of these in turn and describe methods to mitigate some of the issues at hand.

5.2. Matrix closed system

If redistribution of Nd (i.e., the equilibration length scale \(L_e\), cf. Baxter and DePaolo, 2002a) in the matrix since the garnet grew was on a length scale shorter than the size of the hand sample, then the matrix can be said to have acted as a closed system. This assumption is probably less valid in areas where either 1) the bulk effective diffusivities of Sm and Nd were high, 2) advective transport (such as in a fluid medium) dominated the system for any period of time since garnet growth began, or 3) solubility of Sm and Nd in available fluids was high. Samarium and Nd are both generally immobile via intergranular diffusion or advection in most aqueous crustal fluids (e.g., Baxter and DePaolo, 2002b) such that open system disturbance can be negligible even in the presence of strong bulk chemical gradients near lithologic contacts (e.g., Baxter and DePaolo, 2002b), or in the presence of large fluid fluxes (e.g., Pollington and Baxter, 2010). Still, documented cases of Sm or Nd mobility exist (e.g., Ague, 2003; Bucholz and Ague, 2010) especially if the fluid chemistry creates enhanced Nd or Sm solubility. Thus, the possibility of open system matrix behavior should be evaluated on a case by case basis.

Measuring Sm and Nd isotopic values of multiple whole rock samples of the same initial protolith is one way to test the assumption that the matrix has remained a closed system to Rb transport over the length scale of interest. Many protoliths, in particular igneous rocks crystallizing out of an isotopically homogeneous magma, may have small initial variations in Sm/Nd ratios from which variations in (initially homogeneous) \(^{143}\text{Nd}/^{144}\text{Nd}\) can evolve. If several whole rocks (sampled over a length scale greater than the size of the hand sample) of a common protolith define an isochron age equaling the age of protolith deposition (or last equilibration), then Sm and Nd must both have been immobile at that scale since the age defined by that isochron. In cases where this age is older than the timing of garnet growth, then the matrix has remained a closed system for the purposes of garnet geochronology (Pollington and Baxter, 2010). If the whole rocks define an isochron that is younger than garnet growth, or no clear isochron is defined, then the matrix may not have remained a closed system to Sm and/or Nd movement and ages calculated from garnet–matrix isochrons may be compromised. The magnitude of scatter or deviations from a whole rock isochron may be used to evaluate the impact to age accuracy of syn- to post-garnet growth open system Sm or Nd exchange. In lithologically (and isotopically) homogeneous or layered protoliths, the preservation of sharp isotopic gradients may also be evaluated (e.g., Baxter and DePaolo, 2002b); this would also indicate immobility of Sm and Nd. If syn-metamorphic isotopic exchange over some length scale between neighboring lithologies is documented, sampling should avoid the near contact region within the length scale where open system matrix changes are evidenced. Because this cannot generally be ascertained in the field, sampling in general should avoid close proximity to lithologic heterogeneities if possible. Otherwise, careful evaluation of open system effects including the suggested approaches above should be undertaken.

Finally, there exists the possibility that the growth of the garnet itself may cause the matrix Sm/Nd ratio to shift to lower values as the garnet preferentially fractionates Sm over Nd. These potential effects may be evaluated by comparing both a garnet free matrix and a true
whole rock (including garnet) analysis (e.g., Stowell et al., 2001). If they differ significantly, then this effect should be considered. Sometimes, especially with very large garnets, analysis of a true whole rock is not possible given practical sample sizes. In general, this effect will be negligible if 1) garnet Sm and Nd concentrations are significantly lower than the matrix (which in general they are), 2) garnet mode is small, or 3) if the growing garnet also sequesters low Sm/Nd mineral inclusions.

5.3. Garnet closed system

In addition to the assumption that the matrix has remained a closed system, it must be assumed that the mineral of interest has also remained a closed system since its growth. Two broad categories of mineral openness can lead to inaccurate growth ages. The movement of elements can affect the Nd and Sm isotopic values of a mineral either diffusively (within the mineral structure), or advectively (fluids infiltrating along cracks). In differential garnet geochronology we are interested in how a particular radial zone can maintain its growth age. Thus, the effective “closure” of a single garnet annulus is adequately quantified by the diffusive length scale which describes the upper bound on Nd diffusion in garnet. Here we define the diffusive length scale, L, as:

\[ L = \sqrt{D t} \]

where \( t \) is the length of time the system remained at a temperature \( T \) and \( D \) is calculated from:

\[ D = D_0 e^{Q/R T} \]

with the constant values \( D_0 = 6.3 \times 10^{-5} \, \text{cm}^2/\text{s}, \, Q = 254,353 \, \text{J/mol}, \, R = 8.314472 \, \text{J/mol K} \) (Tirone et al., 2005). \( L \) is the characteristic length scale for Nd diffusion in garnet at temperature \( T \) over a duration \( t \). Fig. 15 shows the diffusive length scales for Nd in garnet using these parameters. Diffusion is modeled in one-dimension on a planar boundary with an initial step function. Except near the core of the garnet, the approximation of planar geometry makes little difference from spherical geometry. This step function could represent the boundary between the garnet and the matrix, or could represent a boundary between two growth zones of markedly different age separated by a hiatus in garnet growth. Care must be taken when sampling a zone next to such a step (e.g., rim-matrix boundary). Age compromise will potentially occur within a distance of \(-3L\) of the boundary (e.g., Fig. 15). This effect is considerably smaller for intragrain zones with no sharp step in age because the small and smooth differences in \(^{143}\text{Nd}/^{144}\text{Nd} \) values (and age) will lead to only minor diffusive smearing of age, except when the garnet grain radius is \(-3L\). In general, garnet will retain its growth age zonation over length scales \( >200 \, \mu\text{m} \) as long as heating at \( >700 \, ^\circ\text{C} \) does not proceed for greater than \(-1 \, \text{Myr} \). When higher temperatures or longer durations of post-garnet growth heating occur, the effect of diffusion on intragrain age preservation may need to be taken into account and modeled.

To investigate if a mineral has remained an advectively closed system one should observe cracks and inclusions to determine if there has been any retrograde mineral growth within the grain (Whitney, 1996). Also, one should investigate the chemical map of the grain (Figs. 5 and 6) and if easily interpretable inclusion fields or non-uniform chemistry exist, these zones should simply be avoided during sampling (Pollington and Baxter, 2010).

5.4. Inclusion cleansing

The observations shown in Fig. 13 shed light on the possible danger of including inclusions, leachates of inclusions, or poorly cleansed inclusion-rich garnets on a garnet-matrix isochron (assuming evidence for a closed system matrix has already been established, as discussed above). Because of the possibility that some inclusions are not in age equilibrium with the garnet (i.e., that they grew significantly before the garnet, which by virtue of the fact that they are inclusions, is quite possible), such data should not necessarily be placed on the isochron. The resulting age may be skewed by the incorporation of data which are not in equilibrium with the garnet and matrix. If such data do plot on the isochron within analytical uncertainty, then it could be argued that, in fact, they are in equilibrium and then could go into an age calculation and error assessment. As shown in Fig. 13, the “cleaner” the garnet, the higher the \(^{147}\text{Sm}/^{144}\text{Nd} \), the more accurate is the garnet age. This mirrors the case for any radiogenic isotope geochronometer; higher parent to daughter ratios reduce the effect of any uncertainty in the initial daughter isotope composition. In general, ages calculated on the basis of inadequately cleansed “garnets” with measured \(^{147}\text{Sm}/^{144}\text{Nd} \) significantly lower than expected (for example, by comparison to in
situ laser ICP-MS Sm and Nd analysis of pure garnet) should be regarded as potentially reflecting inclusion inheritance effects and thus interpreted with particular care.

6. Conclusion

The ability to measure distinct growth zones within a single garnet porphyroblast leads to new possibilities for studying rates and pacing of growth and evolution of the crust. We have developed a new method for microsampling garnet, guided by chemical zoning in a single porphyroblast.

Based on this work, one can estimate the maximum number of discrete microsampled zones that could be extracted and dated (at <1 Ma precision) with these methods for a garnet of a given size. Ultimately, this is determined by the mass of garnet needed in each annulus from which to extract at least 4 ng of Nd required for precise Sm–Nd geochronology (see Section 4.3). This is shown in Figs. 16 and 17. Key variables that go into this determination include: 1) Nd concentration in the cleansed garnet, 2) density of inclusions, 3) sample loss during crushing and sieving, and 4) sample loss during partial dissolution. As described in this paper, Nd concentrations in clean garnet can range from ~0.03 to >1.0 ppm, sample loss during crushing and sieving ranges from 30 to 60%, and further sample loss during partial dissolution ranges from 15 to 40%. Overall, depending on sample specifics, a single 2 cm diameter garnet could produce anywhere from 3 to 11 concentric high precision (i.e., ±1 Ma) ages. A 1 cm diameter garnet could produce as many as 6 concentric high precision ages. Smaller zones yielding less than 4 ng of Nd may still be collected and analyzed, though with consequently poorer age precision. It is important to stress that every garnet is different, and will require adjustment of partial dissolution (i.e., temperatures, acids, and durations) and crushing (i.e., grain size) parameters to optimize the balance between cleansing and sample loss for maximum concentric age resolution. The 75–150 μm grain size and HNO2/HF/HClO4 “recipe” reported here for the Stillup Tal garnets represent a good starting point, but will not necessarily produce the best results in every case.

Acknowledgements

We would like to thank J. Harvey, L. Samanta, and J. Barkman for assistance and discussions during development of these methods and A. Kurtz and P. Hall for informal reviews of an earlier manuscript. The manuscript was improved by editorial handling from R. Rudnick as well as constructive reviews from K. Mezger and an anonymous reviewer. This work was supported by NSF Grant EAR-0547996 (EBF). All geochronology was conducted in the Boston University TIMS Facility, funded by NSF MRI Grant EAR-0521266.

References


Amato, J.M., Johnson, C.M., Baumgartner, L.P., Beard, B.L., 1999. Rapid exhumation of the Zermatt–Saas zoisite SHA zirconium beryl zoned deduced zoned garnet wafer showing locations of drill trenches (black) and annuli (white) for case B in Fig. 16. This is a scale rendering of a 2 cm diameter garnet approximated with spherical growth geometry. Gray scale bar has 1 mm hashes.

Fig. 17. Map view of simplified garnet wafer showing locations of drill trenches (black) and annuli (white) for case B in Fig. 16. This is a scale rendering of a 2 cm diameter garnet approximated with spherical growth geometry. Gray scale bar has 1 mm hashes.