IMPROVED DISSOLUTION AND CHEMICAL SEPARATION METHODS FOR LU-HF GARNET CHRONOMETRY

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ABSTRACT

The prospects of garnet-based Lu-Hf geochronology returning accurate ages using conventional dissolution methods are limited by the likely incorporation of Hf-rich zircon inclusions. This study integrates two complimentary methods to substantially reduce or eliminate zircon digestion while simultaneously assuring complete dissolution of garnet. First, hand-picked garnet fractions are heat treated at +1000ºC to anneal radiation-damaged zircon inclusions, thereby making them more resilient to acid digestion. Secondly, garnet is dissolved mainly with HCl rather than HF-HNO_3 to limit dissolution of crystalline zircon. Analyses of garnet from Gore Mountain, New York demonstrate that the method is capable of routinely achieving sample-spike equilibration. Analyses of zircon-rich garnets from peletic paragneisses of Labrador by the heat treating - HCl method returns Lu-Hf ratios that are double those determined by analyses using total digestion. Lastly, a simple and robust chemical separation method for Lu-Hf is presented that supports analyses of garnet by MC-ICP-MS.

Keywords: Lu-Hf, Hf isotopes, garnet, geochronology, boric acid, HCl dissolution, MC-ICP-MS.

INTRODUCTION

There remains a long-standing desire to better link geochronologic (t) and geothermobarometric (PT) estimates to define PTt excursions for metamorphic rocks. The main hindrances in obtaining this goal reflect the typical dependence on different elements, analytical methods, minerals and mineral properties to constrain P, T and t. However, metamorphic garnet provides qualitative and quantitative information about the PT path of its host rock and may possess appropriate concentrations of radiogenic and daughter elements to constrain time. The main obstacles have included uncertain diffusion parameters, the relatively-large amount of sample required for chronometric measurements and the general inability to avoid digestion of near ubiquitous inclusions with elemental concentrations that may overwhelm the relevant elemental budgets of garnet. Whereas the U-Pb system showed early promise for dating garnet (Mezger et al., 1989; Frei and Kamber, 1995; Vance et al., 1998 and references therein), Sm-Nd and Lu-Hf geochronology have become more routinely applied (Mezger et al., 1992; Scherer et al., 2000; Blichert-Toft and Frei, 2001; Lapen et al., 2004).

Due in part to the long-standing ability of most isotope laboratories to routinely produce high-quality Sm-Nd data by conventional thermal ionization mass spectrometry, this system was explored earlier than the Lu-Hf system despite three main draw backs: 1) both Sm and Nd are light rare earth elements (REE), such that Sm/Nd ratios are of limited range, 2) garnets preferentially incorporate heavy REE’s (HREE’s) such that low absolute concentrations of light REE’s (LREE’s) require relatively-large sample sizes, and 3) where present, monazite inclusions in garnet are difficult to exclude from analyses and may overwhelm the Sm-Nd budget of garnet (Prince et al., 2000, and references therein).

The advent of MC-ICP-MS and its suitability to Lu-Hf analyses has re-invigorated interest in the Lu-Hf system. This system offers great promise for dating garnet given its propensity to preferentially include heavy REE’s, which encourages high absolute amounts of Lu and parent/daughter ratios. However, the common occurrence of zircon inclusions in garnet has been especially problematic given that zircon typically represents the main Hf-bearing phase (2-3% Hf) where present and is unlikely to be in isotopic equilibrium with metamorphic garnet.

This paper reports an alternative method that anneals zircon before dissolution by HCl, thereby minimizing the inclusion of zircon in the Lu-Hf analyses of garnet. Secondly, a simple and robust chemical separation method is presented for the concentration of Lu and Hf from garnet matrixes suitable for analyses by MC-ICP-MS. Given Scherer et al.'s (2000) comprehensive review of the potential for and effects of zircon contamination in Lu-Hf analyses of garnet, this paper offers only a brief review of this material. Furthermore, given the availability of papers evaluating different approaches to analyzing Lu and Hf by MC-ICP-MS, this study has not focused on this important step in deriving precise and accurate ages (see Blichert-Toft et al., 1997; Lapen et al., 2004).

Lu-Hf GEOCHRONOLOGY USING GARNET

Lu^{176} breaks down to Hf^{176} with half life of ca. 37 Ga (Scherer et al., 2001), making it an ideal chronometric system for earth and planetary processes. Some garnets have Lu^{176}/Hf^{177} ratios as high as 10 (Duchêne et al., 1997), but most ratios reported are lower than 0.5, many lower than 0.25. While these reported variations in Lu/Hf ratios must reflect bulk rock chemistry and the availability of REE's and Hf during garnet formation, they also likely reflect varying degrees of contamination by Hf-rich phases, most notably zircon. For example, the inclusion of 1µg of zircon with a Hf concentration of 2% will contribute 35% of the Hf to the analyses of 75 mg of garnet with a Hf concentration of 0.5 ppm.

Any reduction of the Lu/Hf ratios of garnet analyses by contamination of zircon inclusions has two consequences on the calculated isochron age: 1) unless the zircon formed as a metamorphic phase in isotopic equilibrium with garnet, it will pull garnet off its rightful isochron line, typically to less radiogenic values that translate into an erroneous younger age (see discussion by Scherer et al., 2000), 2) even if the zircon formed co-genetically with the garnet and was in isotopic equilibrium, it will lower the

Lu/Hf ratio substantially, thereby resulting in a less precise calculated age. Therefore, a means to avoid the inclusion of zircon inclusions during the dissolution of garnet is considered essential in the routine determination of accurate and precise Lu-Hf ages that are strongly controlled by garnet.

While it is desirable to physically exclude zircon inclusion in the garnet fraction being dissolved, the common presence of zircon as micro-inclusions in the garnet typically precludes this prospect, especially in metapelites. This paper advocates the reduction of zircon dissolution by annealing or partially annealing metamict zircon inclusions by a heat treatment at ca. 1050°C to, thus, reducing their potential to be dissolved. Secondly, samples are dissolved in concentrated HCl, a less aggressive acid on silicates than traditionally-employed HF-HNO_3 mixtures.

METHODS

Dissolution of Garnet by HCl

In an attempt to avoid the use of HF/HNO_3, tests were made to dissolve garnet with concentrated HCl at different temperatures, both on a hotplate and in pressurized Teflon bombs. Whereas it is well known that 6 M HCl will leach garnets in Teflon beakers on a hotplate at temperatures well below 150°C, attempts to completely dissolve garnet in 12 M HCl at the temperatures up to 150°C on a hotplate proved ineffective, regardless of time (up to 5 days) and replenishment of acid. In contrast, initial attempts to dissolve garnet in 12M HCl in a pressurized bomb in a 210°C oven for 24 hours were encouraging but the dissolution reaction failed to proceed to completion even if acids were replenished and/or more time was permitted. At the point when dissolution stalled, the undissolved grains of garnet were rimmed by a clear, raspberry-textured material inferred to be insoluble (in HCl) SiO_2 that was forming a physical barrier inhibiting further reaction. For dissolution to proceed, the 12 M HCl was removed from the dissolution capsule and replaced by either a small volume (50 μm) of cold 28 M HF or larger volume (1 ml) of warm 1 M HF to dissolve the SiO_2. Garnets can be fully dissolved in 2-3 cycles of 12 M HCl at 210° in 3 ml Savellix capsules inside a 125ml Teflon™ Parr™ bomb for 24 hours interspersed with short intervals (10 minutes) of cold, 28 M HF to dissolve residual SiO_2. While it is recognized that small amounts of HF for short periods of time are necessary, dissolution is mainly effected by HCl and is, therefore, referred to below as “HCl dissolution”.

Reducing the Dissolution of Zircon by HCl

It is well known that zircon is one of the most resilient common silicates with respect to traditional acid digestion techniques. Zircons for conventional U-Pb analyses are typically dissolved with $HF-HNO_3$ mixtures in pressurized Teflon™ bombs in an oven at 220°C where the length of time required for full dissolution is predicated by their size and degree of crystallinity. Despite the known greater resiliency of zircons to acid digestion, tests were made here to quantify the effect of the HCl-based dissolution methods defined above for garnet..

Tests were conducted on fractions of large (+150 μm) zircons grains (U - 100 ppm) from a ca. 1.4 Ga granite in the Wet Mountains of Colorado. Two fractions were first subjected to 12 M HCl in a 3 ml Savillex™ capsule in a Parr™ bomb at 210°C for 48 hours. This 12 M HCl step yielded 0.905 and 0.619 ng of Hf per microgram of zircon for the two fractions analysed (Table 1) or ca. 3.0-4.5% of the total available Hf (assuming 2% Hf). Having initially determined that the SiO_2 dissolution step could be accomplished by either a small volume of cold 28 M HF or a larger volume of warm 1 M HF, the zircon fractions from the 12 M HCl step were subjected to each method to test which released more Hf. Neither the cold concentrated or warm 1 M HF step released significant amounts of Hf from the zircon (0.0057 and 0.0090 ng Hf per microgram of zircon), likely reflecting the fact that the most readily soluble or leachable zircon was already affected in the preceding 12 M HCl step.

Considering the amount of Hf released from these untreated zircon fractions during the 12 M HCl dissolution step to be unacceptable for routine Lu-Hf analyses of zircon-rich garnet, means were sought to reduce the amount of zircon consumed by this step. Assuming that neither the temperature nor duration of the 12 M HCl or HF steps could not be significantly reduced, the effect of decreasing the solubility of zircon by increasing its crystallinity was investigated. This follows the work of Mattinson (in press) who has convincingly demonstrated that metamict portions of zircons can be made more crystalline by annealing radiation-damaged zircon at high temperatures. Two fractions of zircon from the same 1.4 Ga granite sample were heated to 1000°C for 24 hours in alumina crucibles. Subjected to the same dissolution steps as outlined above, the annealed grains released only 0.0173-0.0148 ng of Hf per microgram of zircon in the 12 M HCl solution (Table 1), or about 2% of the Hf released by the unannealed grains. The cold and hot HF steps released 0.0034 and 0.0036 ng of Hf per microgram of zircon, respectively, or about 50% of that from the unannealed grains during this step.

Whereas it is preferable to physically avoid inclusion of zircon from the outset where possible, this data confirms the benefit of annealing zircon inclusions in garnet prior to HCl dissolution methods. The final method adopted here heats pre-picked garnets to 1050°C for 48 hours. Garnet fractions treated to date turn dark red to black, presumably related to the oxidation of Fe, but there appears to be no detrimental effects on the Lu-Hf analyses of garnet by the methods described here. For the sake of convenience in the discussions here, "treated" vs "untreated" garnet fractions refers to whether samples were heated to 1050°C for 48 hours or not. The term "annealed" and "unannealed" are avoided when referring to this step since the treatment anneals only the metamict zircon inclusions rather than the garnet itself.

Heat Treating and HCl Digestion Methods

Combining the results of the garnet dissolution and zircon heat treating experiments described above, the following section outlines the recommended procedures for minimizing the dissolution of zircon inclusions during the dissolution of garnet by HCl:

1. Picked, high-quality garnets 0.3-0.5 mm in diameter are annealed for 48 hours in covered alumina crucibles at 1050°C,
2. Garnets are repeatedly rinsed and briefly sonicated in clean ethanol until no further red coloration of the ethanol is noted,

3. Garnets are transferred in ethanol into 3 ml Savillex™ hex-cap Teflon capsules, rinsed several times with clean water, most of which is removed in the last rinse cycle,
4. 2 ml of 2 M HCl is added and left at room temperature for 30 minutes as a cleaning cycle,
5. Sample is rinsed once with 2 M HCl and discarded,
6. 2.5 ml of distilled 12 M HCl are added, leaving the caps only finger tight to avoid excessive pressure buildup in the beakers during heating in the bombs,
7. The beakers are stacked in a 125 ml Parr™ bomb containing 1 ml of 12 M HCl and placed in a 210°C oven for 24 hours,
8. Upon cooling, the 3 ml capsules are removed, acid drops knocked to the bottom and the contents carefully transferred with a pipette to a 15 ml Savillex beaker (loss of solution at this stage may preclude correct Lu/Hf ratios),
9. 50-100 ul of room temperature 28 M HF is placed on the undissolved residue in the 3 ml beakers for 10-15 minutes to remove the clear silica rims. Samples should be checked with a microscope to determine that the silica rims are fully dissolved,
10. Upon dissolution of the silica rims, HF is transferred to the 15 ml Savillex beaker already containing the 12 M HCl from step 8 above,
11. Samples are rinsed twice with 0.5 ml 12 M HCl, which is pipetted into the 15 ml beaker,
12. Repeat steps 6-11 until the garnets and all silica rims or residues are fully in solution and all contents are transferred to the 15 ml beaker from step 8,
13. Upon complete dissolution of the garnet, add appropriate amount of Lu and Hf (+/- Sm and Nd) isotopic tracer to the 15 ml beaker,
14. Dry contents of 15 ml beaker on a hotplate,
15. Re-dissolve the precipitate in 0.5 M HCl that is saturated in clean boric acid.

The sample should be checked with a microscope to ensure that the sample is fully in solution before proceeding to the first step of the chemical separation. Boric acid is added to the solution to breakdown any REE-fluorides that formed in the evaporation step.

Chemical Separation Methods

As with all MC-ICP-MS measurements, the quality of the final data requires that the species of interested are effectively separated from the bulk matrix. In addition, accurate measurement of Lu and Hf by MC-ICP-MS requires that the chemical separation process ensures that:

1) the Ti/Hf ratio in the Hf fraction is reduced from natural abundances to less than 0.1 to minimize detrimental and unpredictable effects of Ti on the mass fractionation of Hf (Blichert-Toft et al., 1997; Ulfbeck et al., 2003; Müncker et al., 2001),
2) HREE's are minimized in the Hf fraction to reduce the correction for the direct interference of Lu^{176} and Yb^{176} on Hf^{176},
3) W and Ta are minimized from the Hf fraction to reduce the correction required for small but direct mass interferences on Hf^{180},
4) Hf is minimized in the Lu fraction to reduce the correction for the direct interference of Hf^{176} on Lu^{176},
5) Middle REE's (MREE's) should be minimized in the Lu and Hf fractions to reduce uncorrectable oxide interferences through the mass ranges of Hf, Lu and Yb,
6) Yb/Lu ratios in the Lu fraction are approximately 3-10, thus providing sufficient Yb to determine mass fractionation using Yb^{171}, Yb^{172} and/or Yb^{173} but without an onerous correction for interfering Yb^{176} on Lu^{176}.

A simplified and robust chemical separation method that meshes well with dissolution of garnet by HCl was developed to meet these requirements (Fig. 1). Lu and Hf are isolated from the matrix elements with two ion exchange steps, including a rapid first-stage cation resin column and a second stage TODGA resin from Eichrom Industries (Horwitz et al., in press; Connelly et al., in review). The first stage separates the high field strength elements (HFSE) and REEs from the matrix in preparation for the second stage chemistry, which purifies Hf (with Zr) and Lu (with Yb) for analyses by MC-ICP-MS.

First Stage Chemistry – 50W x8 Cation Resin (100-200 mesh)

The first stage chemistry utilizes a 2 ml cation column that provides sufficient capacity for at least 100 mg of garnet, the size of the largest fractions processed in this study. Once in solution in 0.5 M HCl with boric acid, samples are loaded onto the cation column, the HFSE's are eluted immediately in 0.5 M HCl + 0.1 M HF, followed by the removal of matrix elements in 1.5 M HCl and, finally, the elution of the REE's in 6 M HCl (Table 2). The separate HFSE and REE separates are evaporated to dryness and re-dissolved in 3.5 M HNO_3 + boric acid and 1 M HNO_3, respectively.

Second Stage Chemistry - TODGA

The second stage chemistry (Table 3) concentrates Hf (and Zr) from the HFSE separate and heavy REE's (HREE) using Eichrom Industries TODGA resin loaded into a disposable 0.2 ml resin bed volume column made from an eppendorf-type pipette tip (Fig. 2). A top frit is not strictly necessary but the low density of the TODGA resin causes significant amounts of suspended resin when solutions are loaded if left unconfined. The addition of boric acid to the loading solution for the HFSE separate is critical to avoid the formation of $(Zr,Hf)F_x$ species, which are not retained on TODGA resin in HNO_3.

With the HFSE's loaded first onto a pre-conditioned TODGA column, Ti is washed with 3.5 M HNO_3, after which Zr-Hf are eluted together with 1 M HNO_3 + 0.28 M HNO_3 (Table 3). The inclusion of Zr in the Hf separate has no detrimental effects on the isotopic analyses of Hf by MC-ICP-MS (Blicher-Toft et al., 1997). Provided care is taken to ensure that complete dissolution is achieved in all steps and that boric acid is used, this method returns yields of >95% for Hf. After re-conditioning the column, the REE separate is loaded and washed with 1 M HNO_3 to remove any Ca and Fe that tailed into the REE separate during the first stage chemistry. Switching to a weak HCl media, the light to middle REE's (L-MREE) up to Dy are removed with 0.5 M HCl, after which the HREE's are eluted with 0.05 M HCl. This method returns approximately natural relative abundances of Yb/Lu, which will be within acceptable limits for most garnets (<10;

Blichert-Toft et al., 1997; Ulfbeck et al., 2003). To reduce the amount of MREE's in the Lu separate, only approximately 30% of the Lu is intentionally collected.

Boric Acid

Boric acid plays two critical roles in this method. First, it facilitates the break down of REE-fluorides formed during the evaporation step after dissolution. Secondly, boron in the second stage chemistry loading solution complexes preferentially to form BF_3 over $(Zr,Hf)F_x$, the latter of which is not retained on the TODGA resin. This requires an excess of boric acid relative to F^- in the loading solution, the amount of which can be approximated by assuming all HFSE's in the preceding precipitate formed charge-balanced fluorides. Saturation of boric acid in 3.5 M HNO_3 was empirically determined to be approximately 0.028 g/ml boric acid. We have used J.T. Baker Ultrapur boric acid with a Hf blank of 2 pg per ml of saturated 3.5 M HNO_3.

MC-ICP-MS Methods

Lu and Hf analyses performed at The University of Texas at Austin were carried out on a Micromass (now GV) Isoprobe operating in hard extract mode. The samples were introduced to the plasma via a Cetac Aridus™ desolvating sample introduction system using an Ar carrier gas and a blended Ar and N_2 sweep gas. The Lu and Hf samples were introduced in 0.2% HNO_3 and 0.2% HNO_3 + 0.035 M HF solutions, respectively. Each analysis consumed approximately 0.5 ml and 0.25 ml of solution. Washout between Hf analyses was 3-5 minutes and included 0.2% HNO_3 - 0.25 M HF followed by the matrix solution of 0.2% HNO_3 - 0.07 M HF. Washout between Lu analyses was also 3-5 minutes but used 2% HNO_3 followed by the matrix solution of 0.2% HNO_3. All Hf masses were measured in faraday detectors (Table 4) operating in static acquisition mode (100 scans of 2 seconds). The determined ^{176}Hf intensity reflects a correction for ^{176}Yb and ^{176}Lu as determined by measuring ^{173}Yb and ^{175}Lu, respectively, using the natural ratio of 0.7911 for $^{176}Yb/^{173}Yb$ (De Bièvre et al., 1984) and the measured spiked $^{176}Lu/^{175}Lu$ ratio (see below). A fractionation correction determined by the measured $^{179}Hf/^{177}Hf$ analyses is applied to Yb and Lu. The second stage TODGA chemistry returns Hf concentrates with low $^{175}Lu/^{177}Hf$ and $^{173}Yb/^{177}Hf$ ratios (both $<10^{-5}$), ensuring that the corrections for Yb and Lu interferences on ^{176}Hf are negligible. Hf isotopic results for samples and standards were corrected assuming ideal fractionation according to the exponential mass fractionation law, normalizing to a ^{179}Hf/^{177}Hf ratio of 0.73250 (Blichert-Toft et. al., 1997). Interspersed analyses of Hf standard JMC 475 were monitored for the ^{176}Hf/^{177}Hf ratio, where two analyses of standards were run before and after every two to three unknowns.

Lu and Yb were measured in static mode using the same collector positions as for Hf analyses (Table 4). Fractionation was determined by comparing the measured ^{173}Yb/^{171}Yb ratio to the natural ratio of 1.12955 (De Bièvre et al., 1984). Lu and Yb were assumed to fractionate at the same rate and according to the exponential mass fractionation law. The measured ^{176}Lu reflects a correction for ^{176}Yb, as determined by simultaneous measurement of ^{173}Yb. The appropriate ^{176}Yb/^{173}Yb ratio was determined by measuring a mixed solution of natural Yb and a Lu spike with a known ^{176}Lu/^{175}Lu ratio of 2.5192 at the beginning and end of the analytical session. The measured intensity of ^{176}Lu also reflects a correction for ^{176}Hf, as determined by simultaneous measurement of ^{177}Hf and assuming that Hf fractionated exponentially at the same rate as Yb. This correction used the measured ^{176}Hf/^{177}Hf ratio for each sample. Low ^{177}Hf/^{175}Lu ratios (0.0002-0.0006) for Lu concentrates returned by the second stage TODGA chemistry ensured that the correction for ^{176}Hf was negligible.

RESULTS OF GARNET ANALYSES

The dissolution and chemical separation methods were developed and tested using garnet from Gore Mountain amphibolite, New York. This sample was selected for the ease in acquiring high-quality garnet fractions of sufficient size (60-80 mg) and the availability of published Lu-Hf data to estimate the initial ratio for this work and compare ages. However, lacking information regarding zircon content, it was not well suited to test the potential to exclude zircon during dissolution, Instead, this was evaluated directly using zircon-bearing garnets from the pelitic Tasiuyak Paragneiss in the Torngat Orogen of Labrador, Canada.

Gore Mountain Amphibolite

Garnet from the Gore Mountain amphibolite formed during the Grenville Orogeny and have yielded Lu-Hf and Sm-Nd ages ranging from 1060-1030 Ma (Mezger et al., 1993; Scherer et al., 2000; Lapen et al., 2004). A single, large (1.5 cm diameter), dark red garnet porphyroblast was crushed in a mortar and pestle and sieved to 30-50 mesh size (0.3-0.5 mm). Six fractions of this material, three of which were heat treated, were dissolved by the HCl method. These six fractions were processed in two separate dissolution and chemistry batches. A seventh fraction of garnet, constituting a single large fragment of a different garnet grain, was dissolved by $HF\text{-}HNO_3$ in a Savillex beaker on a hot plate at 140°C. This fraction was processed by the same chemical separation method than those dissolved by HCl, except an additional boric acid step was used after the HF/HNO_3 dissolution to ensure full dissolution of fluorides

All seven fractions yield overlapping model ages ranging from 1041-1055 Ma (Table 5) where the initial $^{176}Hf/^{177}Hf$ is constrained by the lower intercept of the Lu-Hf isochron defined by Lapen et al. (2004) for amphibole-garnet mixtures from the Gore Mountain ampbolite (Hf^{176}/Hf^{177} = 0.282273). Assigning the initial ratio of Lapen et. al. (2004; Hf^{176}/Hf^{177} = 0.282227+/-0.007%; where the error on published lower intercepts are assigned to be the same as errors on analyses in this study), the seven points yield a statistically acceptable line for all seven points corresponding to an age of 1049.5+/-9.3 (MSWD=1.7; Fig. 3). Using a lower intercept defined by Scherer et al. (2000; Hf^{176}/Hf^{177} = 0.282310+/-0.007%), the seven points define a statistically acceptable line corresponding to an age of 1040.5+/-8.8 Ma (MSWD=1.6).

Since this study has attempted only to test dissolution methods rather than rigorously date the garnets, a lower intercept has not been independently determined such that neither age is preferred. That all seven points are collinear with published initial Hf^{176}/Hf^{177} ratios and return isochron ages that overlap published metamorphic ages for this area (1041.6+/-6.6 Ma for Lu/Hf age by Lapen et al., 2004 and 1055+/-2 Ma for metamorphic zircon age by Mezger et al., 1992), indicate that the method facilitates complete garnet digestion and sample-spike equilibration.

Tasiuyak Paragneiss

The ca. 1.8 Ga Torngat Orogen of northern Labrador contains a 300 km long belt of pelitic metasediments known as the Tasiuyak Paragneiss (Wardle et al., 2002). Where sampled, this unit contains centimeter-size, typically zircon-bearing garnets that formed during the Torngat Orogen and that were variably resorbed in the aureole of 1.33 Ga high-temperature plutons of the Nain Plutonic Suite (McFarlane et. al., 2004a and 2004b). Consistent Tdm Sm-Nd ages of ca. 2.2-2.1 Ga (Thériault et al., 2001) and detrital zircon ages between 2.2-1.9 Ga (Scott and Gauthier, 1996) infers a relatively homogeneous source and composition for this unit. The initial Hf ratio used to calculate model ages below assumes a 2.15 Ga mantle separation age and fractionation factor for Lu/Hf of 0.2. An uncertainty of 0.055% (corresponding to +/- 5 ε_{Hf} units) was assigned to the lower intercept. These analyses were intended to evaluate the benefit of the heat-treating process and HCl dissolution method to garnets with known zircon inclusions rather than determine a rigorous age of metamorphism.

Garnets from two samples were dissolved by both flux melting and the methods described here, the latter including heating at 1050ºC for 48 hours followed by two cycles of HCl dissolution in teflon bombs at 210ºC for 48 hours with intervening cold HF cycles. The samples were processed by standard crushing, milling and mineral separation methods and garnet was hand picked from the 50-60 mesh (i.e. 0.3-0.5 mm) fraction. The presence of zircon inclusions in the garnet from these samples was confirmed by relatively wide-beam (50 um spot size) laser (266 nm) ablation traverses across garnet grains mounted in an epoxy mount while monitoring mass Zr^{90} with an Elan quadrupole mass spectrometer at the Geological Survey of Denmark and Greenland in Copenhagen, Denmark.

The flux melting method yielded Lu^{176}/Hf^{177} ratios between 0.217 and 0.332 and Hf isotopic ratios that corresponded to model ages of 1638+/-38 Ma and 1853+/-26 Ma, respectively (Table 6, Fig. 4). By contrast, the HCl dissolution method returned Lu^{176}/Hf^{177} ratios of 0.492 and 0.663 and Hf isotopic ratios that correspond to model ages of 1705+/-18 and 1826+/-15 Ma, respectively (Table 6, Fig. 4). Therefore, the HCl dissolution method returned Lu/Hf ratios that were approximately double that from the flux melting method (corresponding to reduced Hf concentrations) for each sample, and commensurate reductions in the uncertainty on the model age. The differences in the ages between samples and methods are inferred to reflect an interplay between Lu-Hf diffusion related to reheating by the 1333 Ma Makhaviniekh Lake Pluton (McFarlane et al., 2004a) and the varying degree of digestion of zircon (of three ages – detrital, 1850 Ma and 1322 Ma) that was not in isotopic equilibrium with garnet. Regardless of these complications, it is clear that the increased Lu/Hf ratios in the HCl dissolved garnet reflect a substantive reduction in the amount of zircon inclusions dissolved by this method.

DISCUSSION

That all fractions of garnet from the Gore Mountain amphibolite by three different methods (treated and untreated HCl dissolution and HF dissolution) fall along a statistically acceptable line corresponding to an age that overlaps previously-reported ages (Lapen et al., 2004) indicates that the HCl dissolution method is capable of complete garnet digestion and achieving sample-spike equilibration. Moreover, it demonstrates that heat-treating the samples to anneal zircon inclusions has no detrimental effect on the capacity of HCl to dissolve garnet by the method prescribed.

The lack of strong correlation between Lu/Hf ratio and method employed to dissolve garnet from the Gore Mountain amphibolite, combined with the linearity of the consequent data is interpreted to infer that the measured variations reflect real Lu/Hf heterogeneity in the garnet fractions rather than the preferential inclusion or exclusion of zircon in these analyses. The anomalously high Lu/Hf ratio of the HF-HNO_3 dissolved fragment is also attributed natural Lu and Hf variations in this piece.

The effectiveness of the heat treating and HCl dissolution method to preclude dissolution of zircon inclusions is tested directly by subjecting zircon separates to the full HCl dissolution routine and by treating and analyzing garnets with confirmed zircon inclusions. Dissolution of treated and untreated zircon by HCl demonstrate that annealing zircon inclusions by a heat treating step substantially reduces the amount of zircon dissolved by the HCl method. In tests here, annealing resulted in approximately 0.1% of the total amount of available Hf. These tests are in accord with the work of Mattinson (in press) who has more systematically demonstrated that annealed zircons are more difficult to leach and dissolve than unannealed grains. It is likely that longer annealing times and/or higher temperatures will further reduce the amount of Hf liberated from zircon during HCl dissolution, but this has not been systematically evaluated here.

In two samples of Tasiuyak Paragneiss in Labrador, Lu/Hf ratios of garnets that were heat treated and HCl dissolved were approximately double those fractions completely dissolved by flux melting. These results demonstrate the potential of this method to reduce the degree of digestion of zircon inclusions in garnets. The younger ages returned for sample M-22 reflects partial resetting of the Lu-Hf system related to heating due to its proximity to the 1322 Ma Makhaviniekh Lake Pluton (ca. 850ºC). The different ages returned for the two methods for garnets from each sample is inferred to reflect the digestion of detrital (2.1-1.9 Ga) and metamorphic (ca. 1850 Ma and 1322 Ma) zircon that was not in isotopic equilibrium with the garnet. A full discussion of the complex interplay between thermal resetting, formation of new zircon and the inclusion/exclusion of zircon requires detailed petrography, thermal modelling and the analyses of low Lu/Hf phases, zircon and whole rocks of these samples and is, therefore, beyond the scope and intent of this study. Regardless of these complexities, it is clear that the high temperature – HCl dissolution method is capable of substantially reducing the inclusion of zircon in garnet analyses.

Future Work

Whereas the heat treatment did not measurably affect the ultimate ability of HCl (alternated with cold HF) to dissolve garnet as prescribed, the 12 M HCl dissolution solutions became murky as the times and temperatures of the heat treatment were increased. To prevent un-dissolved material from being removed from the dissolution capsule, samples exposed to the longest heat treatment (48 hours) required a centrifuge step to ensure only the dissoloved component was transferred to the 15 ml savillex capsule. Assuming that the murkiness is related to the degree of oxidation of Fe+2 in almandine garnet during the heat treatment, means to limit the amount of oxygen in contact with garnet during heat treatment have been preliminarily explored. Of the methods tested, the most successful involves sealing pre-picked garnet separates wrapped in nickel foil in evacuated quartz tubes before the heat treatment step. Heating the garnets in the near absence of oxygen in the quartz glass tubes causes red garnets from the Gore Mountain amphibolite to change a beige-gray color, which is assumed to reflect reduction of Fe+3. Of the few tests made to date, garnets processed by this method have proven easier to dissolve in 12M HCl than garnets from the same sample heat treated at atmospheric conditions. Future work will determine whether this method will facilitate full sample digestion and consequent spike-sample equilibration.

CONCLUSIONS

The experiments and data presented here were intended to evaluate the feasibility of bringing garnets into solution using HCl rather than by conventional methods and the benefit of heat treating garnets to anneal zircon inclusions prior to dissolution. The data demonstrate that garnet can be fully dissolved by alternating cycles of 12 M HCl in an oven in pressurized Parr™ bombs at 210°C for 24 hours alternated with small amounts of cold, concentrated HF to dissolve residual SiO_2 rims. Whereas efforts were made to completely exclude HF in the dissolution processes, the brief exposure to cold HF was determined necessary to remove insoluble (in HCl) residual silica rims before dissolution can proceed in replenished 12M HCl. Experiments with finer grain sizes were not successful in avoiding use of HF.

Subjecting annealed and unannealed zircons to the HCl-based dissolutions steps determined necessary to dissolve garnet reveals that there is significant benefit to both the heat treatment and the use of mainly HCl during dissolution. The data indicates that approximately 0.1% of the total available Hf is released from zircon heated for 24 hours at 1000ºC. Increased annealing times will likely reduce this amount further, but this has not been quantitatively evaluated in this study. Heat treating garnets has no detrimental effect on the ability of HCl to dissolve garnet and for sample-spike equilibration to be achieved.

A simplified chemical separation method has been developed that exploits cation resin and a recently-available TODGA resin from Eichrom Industries. With a first stage cation chemistry returning separate HFSE and REE concentrates, Hf (with Zr) and Lu (with Yb) are isolated from their respective separates using TODGA column. Boric acid is extremely useful in the procedure to dissolve fluorides and to neutralize F^- in solutions during the chemical separation.

Lastly, the increased resiliency of zircon by heat treating may prove useful in Pb-Pb step leaching methods as applied to garnets by off-setting to higher acid strengths the point where significant amounts of Pb are leached from zircon inclusions. This may effectively increase the number of leach steps in which Pb is leached from garnet rather than both garnet and inclusions.

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TABLE 1: Amount of Hf (ng) released from per ug of zircon.

	Unannealed#1	Unannealed#2	Annealed#1	Annealed#2
12M HCl - bomb, 210°C, 48 hrs	0.905	0.619	0.017	0.015
% Total Hf dissolved*	4.52	3.09	0.09	0.07
28M HF - cold, 10 min	0.0057	-	0.0034	-
1M HF - 90°C, 2 hrs	-	0.0090	-	0.0036

* Assuming the zircon contains 2% Hf by weight

TABLE 2: Cation chemical separation procedure.

2 ml BioRad polypropyene column (0.8 x 4 cm) filled with 100-200 mesh cation resin (50W x8)
Precondition with 0.5 M HCl
Load sample in 2 ml 0.5 M HCl
Collect 10 ml 0.5 M HCl + 0.1 M HF (HFSE)
    Drydown
    Add 1.5 ml 3.5 M HNO_3 *+ saturated boric acid (0.028 g/ml) – to TODGA*
Wash 36 ml 1.5 M HCl (matrix)
Collect 15 ml 6 M HCl (REE)
    Drydown
    Add 2.5 ml 1 M HNO_3 *– to TODGA*

TABLE 3: TODGA chemical separation procedure for Lu and Hf.

Fill columns with 0.2 ml (see Fig. 2) of TODGA
Clean with 6 ml 0.05 M HCl
Pre-condition with 2 ml 3.5 M HNO_3
Load HFSE fraction in 2.5 ml 3.5 M HNO_3 + saturated boric acid (0.028 g/ml)
Wash 3.5 ml 3.5 M HNO_3 (Ti)
Collect 6 ml 1 M HNO_3 + 0.28 M HF (Zr-Hf)
- *Drydown*
- *Convert to nitrate form by adding 50 µl concentrated* HNO_3
- *Drydown*
- *Add 0.2%* HNO_3 *+ 0.035 M HF – ready for isotopic analyses*

Re-condition the column with 1 ml 1 M HNO_3
Load REE fraction in 1.5 ml 1 M HNO_3
Wash 3 ml 1 M HNO_3 + 0.28 M HF (Ca, Fe, ± Zr,Hf)
Collect 5 ml 0.5 M HCl (L-MREE)
Collect 2 ml 0.05 M HCl (HREE)
- *Drydown*
- *Convert to nitrate form by adding 50 µl concentrated* HNO_3
- *Drydown*
- *Add 0.2%* HNO_3 *– ready for isotopic analyses*

Table 4: Faraday detector arrangement for Hf and Lu analyses by the Isoprobe. Bolded text indicates masses used to determine fractionation.

	H6	H5	H4	H3	H2	H1	Axial	L1
Hf analyses	180Hf	**179Hf**	178Hf	**177Hf**	176Hf			
					176Lu	175Lu		
					176Yb		173Yb	
Lu analyses				177Hf	176Hf			
					176Lu	175Lu		
					176Yb		**173Yb**	**171Yb**

Table 5: Lu and Hf isotopic data for garnet from Gore Mountain amphibolite and estimates of initial ratios from two literature sources.

Sample		Lu	Hf	Lu176/Hf177	2SE	Hf176/Hf177	2SE	Model Age* (Ma)
Initial Ratios as determined from literature								
Lapen et al.	**(2004)**	-	-	0.0000	0.0010	0.282273	0.000023	
Scherer et al.	**(2000)**	-	-	0.0000	0.0010	0.282310	0.000023	
Garnet fractions not heat treated and dissolved with HCl								
1		0.4564	0.3293	0.1963	0.0010	0.286163	0.000023	1052.0
2		0.4509	0.3203	0.2004	0.0010	0.286251	0.000023	1053.3
3		0.4551	0.3217	0.2008	0.0010	0.286211	0.000023	1040.9
Garnet fractions heat treated and dissolved with HCl								
4		0.4583	0.3146	0.2068	0.0010	0.286352	0.000023	1046.8
5		0.4558	0.3236	0.2000	0.0010	0.286235	0.000023	1051.6
6		0.4536	0.3205	0.2009	0.0010	0.286265	0.000023	1054.6
Garnet fractions not heat treated and dissolved with HF/HNO3								
7		0.6795	0.4003	0.2410	0.0012	0.287029	0.000023	1047.8

* Model ages use initial ratio from Lapen et al. (2004)

Table 6: Isotopic data for garnet from samples M-12 and M-22 and estimated initial ratio.

	Fraction	**Lu**	**Hf**	**Lu176/Hf177**	**2SE**	**Hf176/Hf177**	**2SE**	**Model Age**
Initial Hf176/Hf177 ratio modelled for the Tasiyak Gneiss (see text)								
	-	-	-	0.0000	0.5	0.281759	0.055	
Sample M-12								
Flux	**1**	3.410	1.462	0.3315	0.5	0.293417	0.007	1853±26
HCl	**2**	3.841	0.822	0.6629	0.5	0.304729	0.007	1826±15
Sample M-12								
Flux	**1**	3.153	2.063	0.2169	0.5	0.288491	0.007	1638±38
HCl	**2**	3.122	0.901	0.4922	0.5	0.297668	0.007	1705±18

FIGURE CAPTIONS

Figure 1: Flow chart of the chemical separation methods recommended for Lu-Hf analyses of garnet by MC-ICP-MS.

Figure 2: Sketch of TODGA column constructed from eppendorf-type pipette and transfer pipette.

Figure 3: Lu-Hf isochron diagram for garnets from the Gore Mountain amphibolite, New York, USA.

Figure 4: Lu-Hf isochron diagram for garnets from the Tasiuyak Paragneiss, Torngat Orogen, Labrador, Canada.

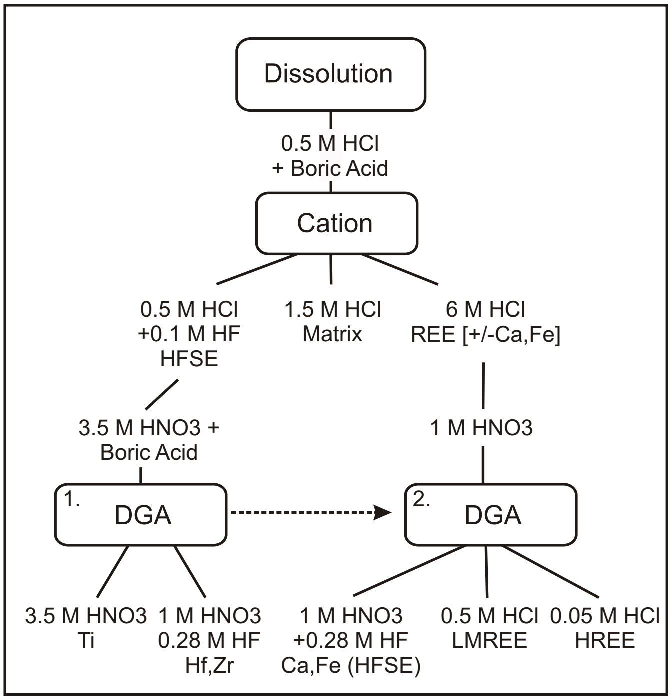
Dissolution
0.5 M HCl
+ Boric Acid
Cation
0.5 M HCl
+0.1 M HF
HFSE
1.5 M HCl
Matrix
6 M HCl
REE [+/-Ca,Fe]
3.5 M HNO3 +
Boric Acid
1 M HNO3
1.
DGA
2.
DGA
3.5 M HNO3
Ti
1 M HNO3
0.28 M HF
Hf,Zr
1 M HNO3
+0.28 M HF
Ca,Fe (HFSE)
0.5 M HCl
LMREE
0.05 M HCl
HREE

Figure 1

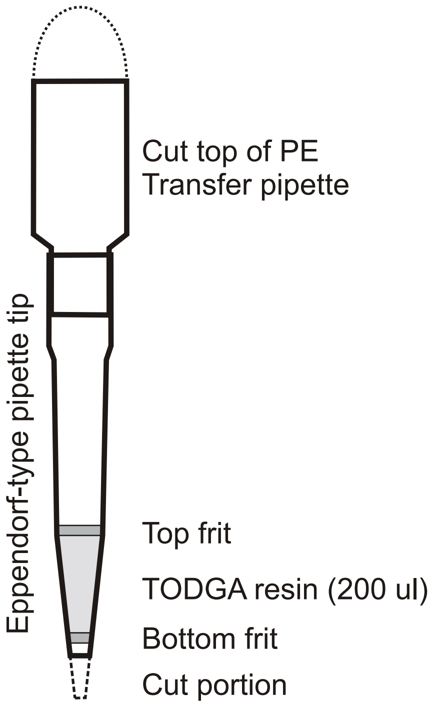
Cut top of PE
Transfer pipette
Eppendorf-type pipette tip
Top frit
TODGA resin (200 ul)
Bottom frit
Cut portion

Figure 2

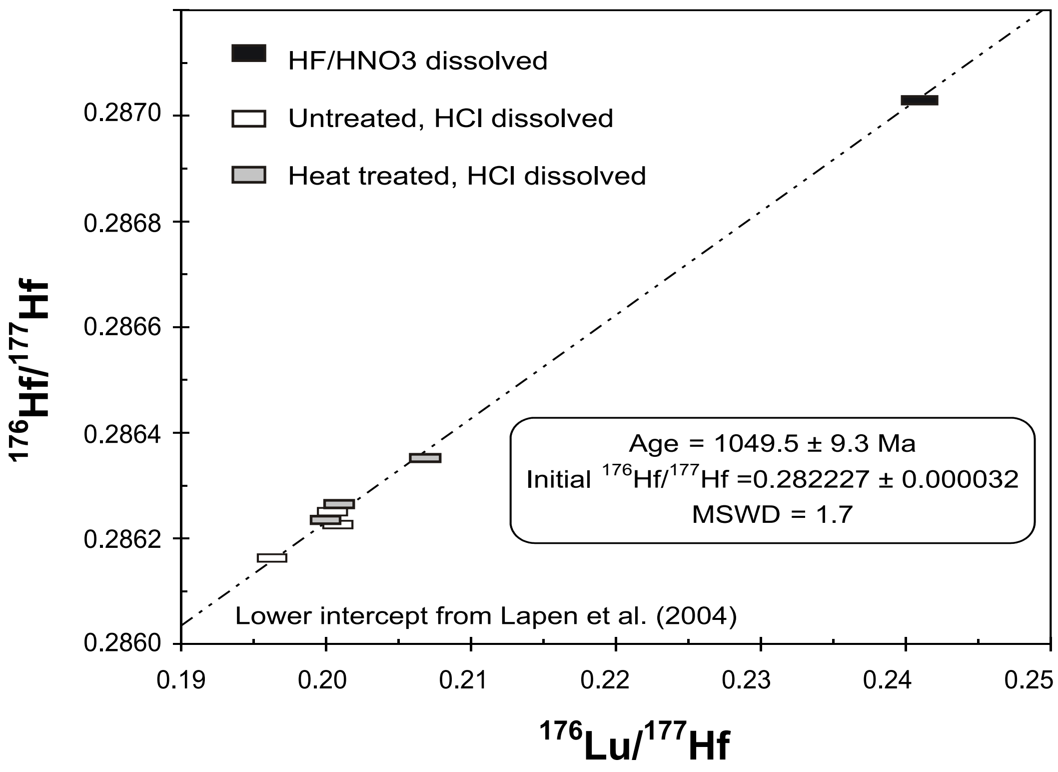
HF/HNO3 dissolved
Untreated, HCl dissolved
Heat treated, HCl dissolved
Age = 1049.5 ± 9.3 Ma
Initial ^{176}Hf/^{177}Hf =0.282227 ± 0.000032
MSWD = 1.7
Lower intercept from Lapen et al. (2004)
^{176}Hf/^{177}Hf
0.2860
0.2862
0.2864
0.2866
0.2868
0.2870
^{176}Lu/^{177}Hf
0.19
0.20
0.21
0.22
0.23
0.24
0.25

Figure 3

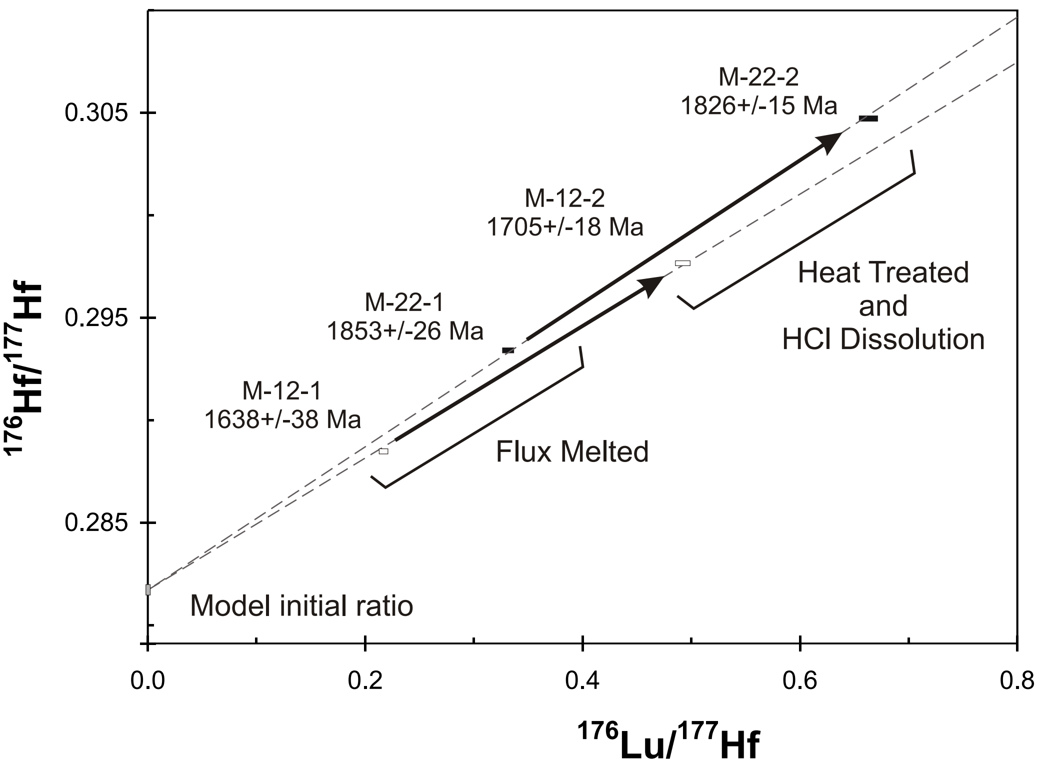
M-22-2
1826+/-15 Ma
M-12-2
1705+/-18 Ma
M-22-1
1853+/-26 Ma
M-12-1
1638+/-38 Ma
Heat Treated
and
HCl Dissolution
Flux Melted
Model initial ratio
0.305
0.295
0.285
0.0
0.2
0.4
0.6
0.8
^{176}Hf/^{177}Hf
^{176}Lu/^{177}Hf

Figure 4