

## Data Repository Item 2009250

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## Detailed Description of Chemical Separation Procedures and Lu-Hf Mass Spectrometry

Mineral separates were first prepared by crushing the sample using a stainless steel mortar and pestle. Crushed rock was then sieved and the grain fractions between 100-400 $\mu$ m were separated using a Frantz isodynamic magnetic separator. Lawsonite, quartz, and plagioclase were magnetically separated from other minerals (glaucophane, chlorite, epidote, garnet). Individual lawsonite and glaucophane separates were then picked by hand using a binocular picking microscope. Lawsonite was readily distinguished from quartz and plagioclase due to crystal habit and large grain size. In the case of fine-grained lawsonite blueschists, lawsonite may be separated from quartz, albite, epidote, and titanite with the use appropriate heavy liquids as the minerals have distinctly different densities (lawsonite = 3.05-3.12, quartz = 2.26-2.65, albite = 2.55-2.63, epidote = 3.15-3.37, and titanite = 3.48-3.60, Deer et al., 1992).

Mineral fractions for geochronology were digested using tabletop dissolution in Savillex beakers to avoid incorporation of Hf from refractory mineral inclusions such as zircon or rutile (see Scherer et al., 2000). Approximately 200 to 250mg of lawsonite, glaucophane, or whole rock was weighed within Savillex teflon beakers. Mineral fractions were then lightly leached in 1.0M HCl within an ultrasonic bath for 10-15 minutes to remove surficial contamination produced during physical mineral purification. This HCl leachate was discarded and mineral separates were rinsed twice in deionized water.

Digestion of the leached mineral separates occurred in two steps. First, a 10:1 acid mixture of 29M HF:15M HNO<sub>3</sub> was added and allowed to dry on a hotplate. This initial acid attack aims to break down some of the silicates prior to sealing the beakers. When dry, 10ml of the concentrated HF:HNO<sub>3</sub> mixture were added and the beakers were capped and heated at ~150°C for 24 hours. These digestions were then dried and the fluoride residues were converted to soluble chlorides via reaction with a saturated solution of H<sub>3</sub>BO<sub>3</sub> in ~6M HCl. This effectively removes solid fluorides by the favored production of BF<sub>3</sub> gas. Clear, final solutions were then spiked with a mixed <sup>176</sup>Lu-<sup>180</sup>Hf tracer, capped, and were equilibrated on a hotplate for 24 hours. Sample-spike mixtures are fully equilibrated by this method and have been confirmed by isotope dilution measurements for natural rock standards.

In order to investigate the effect of common Hf bound in zircon or other refractory phases, a glaucophane and whole rock split were additionally digested using Teflon bombs. This technique ensures the digestion of these refractory, Hf-bearing minerals that are common inclusions in major silicate phases. Methods for bomb digestions were identical to that above,

except that HF-HNO<sub>3</sub> digestions occurred in sealed bombs in an oven at 150°C for one week. Conversion and spiking of these bomb digestions followed the methods used for Savillex-type digestions, described above.

The first column consists of a 10mL bed of BioRad AG50w-X12 cation exchange resin. Samples were dissolved in 3mL 1.0M HCl. 20μL of 8M HF was added to each sample and then immediately centrifuged at 3500rpm for 15 minutes. This 1.0M HCl/0.1M HF solution was immediately loaded onto the columns. After loading, a rinse of 1mL of 1.0M HCl/0.1M HF was added. Hafnium (and other HFSE) was then eluted from the column using 6mL of 1.0M HCl/0.1M HF. An additional 5mL of 1.0M HCl/0.1M HF were then washed through the column. Major elements were then eluted from the column using 100mL of 2.5M HCl. This solution was discarded. Lutetium and other HREE were then eluted from the column using 60mL of 2.5M HCl.

Hafnium cuts from the first column were dried and re-dissolved in 5mL of 2.5M HCl and allowed to flux overnight in sealed beakers. The second Hf column consists of a 1.0mL bed of Eichrom Ln-Spec resin. Samples were introduced to the columns as 5mL of 2.5M HCl. Following loading, the columns were washed sequentially with 10mL of 2.5M HCl and 10mL of 6.0M HCl to remove potential REE contaminants. HCl was then rinsed from the column using 4mL of H<sub>2</sub>O. Titanium was then rinsed off the column using a 0.45M HNO<sub>3</sub>/0.09M Citric Acid/1% H<sub>2</sub>O<sub>2</sub> mixed acid. This mixed acid is an effective chelating agent for Ti and imparts an obvious orange color to the resin bed. The mixed acid was added in 10mL volumes until all Ti was removed (i.e., until the column was no longer orange), typically requiring a total of 40-60mL. Peroxide was then washed from the column using 5mL of 0.45M HNO<sub>3</sub>/0.09M Citric acid. Zirconium was then washed from the column using 20mL of 6.0M HCl/0.06M HF. Hafnium was eluted from the column using 5mL of 6.0M HCl/0.40M HF.

A third Hf column was used to clean up the Hf cut of potential REE contamination that would lead to isobaric interferences during mass spectrometry. We used a small, 180μL resin bed of BioRad AG50w-X12. The sample Hf was dissolved in 80μL of 1.0M HCl/0.1M HF and loaded onto the columns. Hafnium was then eluted using 200μL of 1.0M HCl/0.1M HF. Ideally, potential REE interferences are retained on this column. Final Hf fractions were attacked repeatedly with concentrated HNO<sub>3</sub> to remove organic contamination, subsequently attacked with 8M HF to complex Hf as fluorides, and then dissolved in 2% HNO<sub>3</sub> for mass spectrometry.

Lutetium must be further purified from the other REEs, but some Yb must remain in the Lu cut to allow for correction of mass fractionation and machine bias during mass spectrometry (Vervoort et al., 2004). The second Lu column consists of a 0.9mL bed of Eichrom Ln-Spec resin. Prior to column chemistry, Lu-HREE cuts from the first column were attacked with concentrated HNO<sub>3</sub> to remove organic residues, reconverted to chloride form with ~6M HCl, and then dissolved in 0.5mL of 2.5M HCl. The sample is loaded onto the columns in this 0.5mL of 2.5M HCl and then the column is washed with another 0.5mL of 2.5M HCl to ensure proper loading. Most of the Yb is removed from the column using 30mL of 2.5M HCl. Lutetium is then eluted using 5mL of 6.0M HCl. These final Lu cuts are attacked with concentrated HNO<sub>3</sub> to remove organics and then dissolved in 2% HNO<sub>3</sub> for mass spectrometry.

All isotopic data were determined using the ThermoFinnigan NEPTUNE at Washington State University. Hafnium data were measured relative to the external Hf standard JMC 475. A Cetac Aridus desolvating nebulizer was used for Hf mass spectrometry to improve signal quality. Hafnium isotope ratios were normalized to <sup>179</sup>Hf/<sup>177</sup>Hf of 0.7325 using an exponential law. Mass

bias corrected  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios were further adjusted slightly relative to the accepted  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of JMC 475 (0.282160; Vervoort and Blichert-Toft, 1999). The long-term average  $^{176}\text{Hf}/^{177}\text{Hf}$  for JMC 475 obtained over the course of this study was  $0.282150 \pm 0.000012$  ( $2\sigma$ ;  $n=18$ ). Lutetium was introduced to the NEPTUNE using a self-aspirating, 50 $\mu\text{l}/\text{min}$  Teflon nebulizer in a 2%  $\text{HNO}_3$  carrier solution. Procedures for analysis and data reduction of Lu are described in detail elsewhere (Vervoort et al., 2004). The overall external uncertainties applied to measured data are 0.5% for  $^{176}\text{Lu}/^{177}\text{Hf}$  and 0.01% for  $^{176}\text{Hf}/^{177}\text{Hf}$ , as encountered during the long-term reproducibility of external rock standards.

## **Laser Ablation Results for Individual Phases**

Prior to digestion of samples for geochronology, trace element compositions of lawsonite, titanite, and glaucophane were characterized using laser ablation ICPMS (LA-ICPMS). The close association of lawsonite and titanite within the sample is potentially problematic in that titanite, as an important host for Hf and other high field strength elements in the sample, could hinder accurate and precise determination of a lawsonite Lu-Hf isochron if digested concurrently (i.e., Scherer et al., 2000). Abundances of rare-earth elements (REEs) and Hf for lawsonite, glaucophane, and titanite are presented in **Figure 2**. Lawsonite is enriched in heavy REEs such as Lu, depleted in Hf, with elemental Lu/Hf ratios on the order of 20-60. Lawsonite Lu and Hf concentrations measured by LA-ICPMS agree extremely well with isotope dilution determinations for bulk digestions. Both titanite and glaucophane trace element signatures are enriched in Hf over Lu. The erratic patterns for glaucophane are most likely due to the very low abundances of REEs in these minerals.

TABLE DR1: MINERAL COMPOSITIONS FOR THE RING MOUNTAIN LAWSONITE BLUESCHIST

	Amphibole	Lawsonite	Chlorite	Garnet	Epidote	Albite
SiO <sub>2</sub>	56.15	37.79	27.80	36.72	37.88	67.97
TiO <sub>2</sub>	0.03	n.d.	0.01	0.00	0.14	0.00
Al <sub>2</sub> O <sub>3</sub>	8.92	31.03	18.34	21.27	26.57	19.97
Fe <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.00	0.00	8.60	0.00
FeO	13.97	1.47	23.08	25.80	0.00	0.09
MnO	0.16	n.d.	0.60	4.22	0.06	0.00
MgO	10.21	n.d.	18.92	1.27	0.18	0.00
CaO	1.61	17.52	0.00	9.67	23.47	n.d.
Na <sub>2</sub> O	6.17	n.d.	0.00	0.00	0.00	11.76
K <sub>2</sub> O	n.d.	n.d.	n.d.	0.00	0.00	0.01
H <sub>2</sub> O	2.12	11.32	11.66		3.79	
TOTAL	99.35	99.13	100.42	98.95	100.69	99.80
Si	7.93	2.00	5.72	2.97	2.99	2.98
Ti	0.00	0.00	0.00	0.00	0.01	0.00
Al	1.48	1.94	4.45	2.03	2.48	1.03
Fe <sup>3</sup>	0.00	0.00	0.00	0.00	0.51	0.00
Fe <sup>2</sup>	1.65	0.07	3.97	1.74	0.00	0.00
Mn	0.02	0.00	0.11	0.29	0.00	0.00
Mg	2.15	0.00	5.81	0.15	0.02	0.00
Ca	0.24	0.99	0.00	0.84	1.99	0.00
Na	1.69	0.00	0.00	0.00	0.00	1.00
K	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	15.17	5.00	20.06	8.02	8.00	5.01

TABLE DR2. LA-ICPMS DATA FOR THE RING MOUNTAIN LAWSONITE BLUESCHIST

	Lw1	Lw2	Lw3	Lw4	Lw5	Lw6	Lw7	Lw8	Lw9	Lw10	Gl1	Gl2	Gl3	Gl4	Ttn
La	1.04	4.40	1.15	0.58	1.03	6.47	1.76	0.64	0.57	1.13	0.43	0.32	0.37	0.10	8.60
Ce	4.01	16.91	4.72	1.95	4.44	28.19	7.20	2.36	2.32	4.54	1.30	0.97	0.84	0.10	21.11
Pr	0.70	3.62	1.02	0.35	0.84	5.74	1.37	0.43	0.47	0.75	0.16	0.17	0.11	0.02	1.35
Nd	4.46	25.67	7.10	2.13	5.45	40.81	10.25	2.92	3.14	4.74	0.85	0.84	0.57	0.12	6.20
Sm	2.18	13.05	2.77	1.00	2.70	20.76	4.78	1.28	1.67	1.95	0.24	0.46	0.21	0.07	1.44
Eu	1.43	5.65	1.19	0.38	1.00	8.63	1.60	0.50	0.58	1.00	0.12	0.18	0.07	0.01	0.27
Gd	3.00	18.70	3.63	1.18	4.10	27.35	5.62	1.98	2.65	2.22	0.31	0.47	0.22	0.08	1.14
Tb	0.81	4.06	0.75	0.33	1.02	5.81	1.05	0.46	0.60	0.62	0.08	0.14	0.05	0.02	0.19
Dy	5.87	26.27	4.78	2.77	7.34	37.09	5.87	3.83	4.45	4.78	0.63	1.21	0.43	0.17	0.93
Ho	1.38	5.88	1.43	0.87	2.13	8.27	1.40	1.14	1.37	1.48	0.15	0.26	0.10	0.04	0.17
Er	3.98	15.25	5.49	3.65	6.12	19.42	5.30	4.25	4.70	5.97	0.44	0.80	0.27	0.15	0.44
Tm	0.56	1.81	0.94	0.68	0.88	2.04	0.84	0.73	0.77	1.21	0.07	0.16	0.05	0.02	0.07
Yb	4.09	12.55	8.44	6.17	6.05	10.77	7.52	6.60	6.44	11.39	0.57	1.37	0.45	0.22	0.54
Lu	0.62	1.84	1.63	1.10	0.85	1.40	1.43	1.25	1.18	2.15	0.09	0.20	0.07	0.06	0.13
Hf	0.01	0.03	0.02	0.04	0.06	b.d.	b.d.	b.d.	0.02	0.03	2.36	4.01	0.92	1.13	6.53

Note: All concentrations are in parts per million (ppm). Mineral abbreviations are as follows: Lw, lawsonite, Gl, glaucophane; Ttn, titanite. "b.d." indicates that element was below detection limit. Analyses were performed at the Washington State University GeoAnalytical Lab using a 213-nm UV laser coupled to a ThermoFinnigan ELEMENT2 magnetic sector ICPMS. Operating conditions were a 20µm beam operating at 70% power (11J/cm) and an 11µm/second traverse rate.

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