Lawsonite Lu-Hf geochronology: A new geochronometer for subduction zone processes

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Notes
Lawsonite Lu-Hf geochronology: A new geochronometer for subduction zone processes

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ABSTRACT
We present a new method for Lu-Hf geochronology using lawsonite, an index mineral of high-pressure, low-temperature metamorphism. The method uses common cation exchange chromatography to purify Lu and Hf from the sample and analysis by multicollector inductively coupled plasma–mass spectrometry. Lawsonite 176Lu/177Hf ratios are elevated and are similar to other minerals commonly used in Lu-Hf geochronology such as garnet or apatite. We obtain an age of 145.5 ± 2.4 Ma for lawsonite-blueschist facies metamorphism at Ring Mountain within the Franciscan Complex, California, the lawsonite type locality. The age agrees well with published geochronology and thermochronology for the Franciscan Complex. The new method provides a powerful tool to investigate processes and time scales of blueschist to eclogite facies metamorphism, crust-mantle recycling via subduction, and the geodynamics of convergent margins.

INTRODUCTION
Lawsonite [CaAl₂Si₂O₇(OH)₂·H₂O] is a critical index mineral for high-to ultrahigh-pressure-temperature window where few alteration processes. Lawsonite is an important carrier of metamorphic events. Lawsonite is an important carrier of critical index mineral for high- to ultrahigh-temperature stability range (e.g., Okamoto and Maruyama, 1999), lawsonite can serve as a Lu-Hf geochronometer.

SAMPLE DESCRIPTION
The lawsonite blueschist sample was collected from Ring Mountain on the Tiburon Peninsula, California, the type lawsonite locality (Ransome, 1895; Rice, 1964). There, exotic blocks of lawsonite blueschist, epidote blueschist, garnet amphibolite, and eclogite occur within a serpentinite matrix mélangé. Previous workers have extensively studied the pressure-temperature conditions (Wakabayashi, 1990; Tsujimori et al., 2006) and age of metamorphism (Catlos and Sorensen, 2003; Anciaziewicz et al., 2004; Tsujimori et al., 2006), making Ring Mountain well suited to test lawsonite as a Lu-Hf geochronometer.

The sample comes from a large (~20 m × 14 m) exotic lawsonite blueschist block (37°54′39.96″N, 122°29′29.65″W, World Geodetic System 1984 datum). The matrix assemblage consists of glaucophane, lawsonite, chlorite, albite, titanite, and zircon. Mineral compositions are given in the online data set (see the GSA Data Repository†). Lawsonite grains are relatively large (~0.1–1.2 mm) and contain abundant inclusions of epidote, titanite, and glaucophane (Fig. 1A). Fine grains of garnet (100–150 µm) occur within <10% of lawsonite grains larger than 500 µm (Fig. 1B), but are absent in smaller (<125–400 µm) lawsonite grains; the latter were used for the geochronology. In the matrix aligned glaucophane, titanite, and chlorite define a foliation across which lawsonite grows (Fig. 1A). In rare cases garnet can be found within the matrix where it is completely rimmed by chlorite and titanite (Fig. 1C), and epidote is absent. The textures suggest growth of lawsonite, glaucophane, chlorite, and titanite by the breakdown of garnet and epidote via a retrograde path from garnet-epidote blueschist to lawsonite blueschist facies conditions and are consistent with previous observations (Wakabayashi, 1990). The chlorite geothermometer of Cathelineau and Nieva (1985) provides a minimum estimate of 305 ± 50 °C for metamorphic temperatures. The maximum temperature is constrained to be ~500 °C, within the stability field for lawsonite (Evans, 1990) at pressures below the albite = jadeite + quartz reaction.

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†GSA Data Repository item 2009250, description of chemical separation procedures and Lu-Hf mass spectrometry, Table DR1 (mineral compositions for the Ring Mountain lawsonite blueschist), and Table DR2 (LA-ICPMS data for the Ring Mountain lawsonite blueschist), is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

Figure 1. Photomicrographs from Ring Mountain sample. A: Typical lawsonite phryroblast. B: Rare garnet inclusions in large lawsonite phryroblasts. C: Rare matrix garnet rimmed by chlorite and titanite. Mineral abbreviations: chl—chlorite, ep—epidote, gln—glaucophane, grt—garnet, lws—lawsonite, ttn—titanite.
CHEMISTRY AND MASS SPECTROMETRY

All chemical procedures were performed in the radiogenic isotope clean laboratory at Washington State University. Procedures for lawsonite digestion are similar to those commonly used for whole-rock or garnet digestion. The full methods are detailed in the online data set (see the Data Repository). Whole-rock and glaucophane splits were analyzed by both hot plate and bomb digestion methods to investigate the role of Hf-bearing inclusions such as zircon in the sample; all lawsonite splits were digested by hot plate methods only. Details for Lu and Hf mass spectrometry are given in the online data set (see the Data Repository).

RESULTS

Lu-Hf isotope data for lawsonite, glaucophane, and whole rocks are presented in Table 1. The elevated $^{176}$Lu/$^{177}$Hf ratios of lawsonite (>4.0) are similar to other high Lu/Hf minerals commonly utilized in Lu-Hf geochronology such as apatite or garnet (e.g., Barfod et al., 2001; Söderlund et al., 2004) and $^{176}$Hf/$^{177}$Hf = 0.282785 and $^{176}$Lu/$^{177}$Hf = 0.0336 for CHUR (chondrite uniform reservoir) (Bouvier et al., 2008).

Two distinct regressions of the Lu-Hf isotopic data are possible (Fig. 3). Regression of data obtained by Savillex digestions (4 lawsonite, 3 glaucophane, and 1 lawsonite free whole-rock powder separate) yields an isochron with an age of 145.5 ± 2.4 Ma (Fig. 3) with an initial $^{176}$Hf/$^{177}$Hf of 0.28381 ($\varepsilon_{Hf} = +40$). Alternatively, regression of Lu-Hf data obtained from the lawsonite analyses and data obtained by bomb digestion methods (1 glauco- phane and 1 lawsonite free whole-rock powder separate) results in a significantly older age of 154.1 ± 4.7 Ma and a lower initial $^{176}$Hf/$^{177}$Hf of 0.28309 ($\varepsilon_{Hf} = +14$). Both isochrons are insensitive to exclusion of any individual data points. Isochrons based upon a reduced number of data points yield ages indistinguishable within error of the complete isochron. The mean square of weighted deviates (MSWD) values calculated for each regression are somewhat high (Fig. 3). Similar values are commonly seen in garnet Lu-Hf isochrons with large ranges in Lu/Hf ratios and low analytical uncertainties, indicating that the geological uncertainties exceed analytical uncertainties in such samples.

AGE INTERPRETATION

The younger age of ~145 Ma determined by regression of data obtained by lawsonite, glaucophane, and whole-rock Savillex digestions dates the growth of lawsonite during retrograde blueschist facies metamorphism. Lawsonite is in textural equilibrium with matrix glaucophane, chlorite, and titanite (Fig. 1), which compose the whole-rock fraction. Lawsonite and chlorite show textural evidence for having grown at the expense of garnet and epidote (Fig. 1). The above assemblage therefore reflects the Hf pool dominated by silicate reactions that accommodated the transition from amphibolite facies to garnet and lawsonite-blueschist facies during retrograde metamorphism. The high initial $^{176}$Hf/$^{177}$Hf ($\varepsilon_{Hf} = +40$), which is >25–30 $\varepsilon_{Hf}$ units higher than the probable initial Hf isotopic composition of the protolith) can be explained by radiogenic $^{176}$Hf in-growth from an elevated $^{176}$Lu/$^{177}$Hf phase (i.e., garnet) for ~9 Ma (the age difference between the two isochrons). For example, the $^{176}$Hf/$^{177}$Hf of a phase with a $^{176}$Lu/$^{177}$Hf of 4.2 will increase by 0.0007, or 25 $\varepsilon_{Hf}$ units in 9 Ma. This radiogenic in-growth results in a radiogenic Hf isotopic pool (initial $\varepsilon_{Hf} = +40$) that lawsonite + glaucophane + chlorite incorporate during their formation.

### TABLE 1. Lu-Hf isotopic data for the Ring Mountain lawsonite blueschist

<table>
<thead>
<tr>
<th>Sample</th>
<th>Digestion method</th>
<th>Lu (ppm)*</th>
<th>Hf (ppm)*</th>
<th>$^{176}$Lu/$^{177}$Hf</th>
<th>$^{176}$Hf/$^{177}$Hf</th>
<th>$\varepsilon^{*}$**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lawsonite 1</td>
<td>Savillex</td>
<td>1.31</td>
<td>0.045</td>
<td>4.081</td>
<td>0.295095</td>
<td>0.000013</td>
</tr>
<tr>
<td>Lawsonite 2</td>
<td>Savillex</td>
<td>1.44</td>
<td>0.047</td>
<td>4.307</td>
<td>0.295452</td>
<td>0.000011</td>
</tr>
<tr>
<td>Lawsonite 3</td>
<td>Savillex</td>
<td>1.39</td>
<td>0.041</td>
<td>4.679</td>
<td>0.299638</td>
<td>0.000013</td>
</tr>
<tr>
<td>Lawsonite 4</td>
<td>Savillex</td>
<td>1.39</td>
<td>0.044</td>
<td>4.470</td>
<td>0.296002</td>
<td>0.000015</td>
</tr>
<tr>
<td>Glaucophane 5</td>
<td>Savillex</td>
<td>0.233</td>
<td>0.101</td>
<td>0.3268</td>
<td>0.284639</td>
<td>0.000007</td>
</tr>
<tr>
<td>Glaucophane 6</td>
<td>Savillex</td>
<td>0.238</td>
<td>0.098</td>
<td>0.3454</td>
<td>0.284713</td>
<td>0.000009</td>
</tr>
<tr>
<td>Glaucophane 7</td>
<td>Savillex</td>
<td>0.242</td>
<td>0.091</td>
<td>0.3792</td>
<td>0.284906</td>
<td>0.000007</td>
</tr>
<tr>
<td>Glaucophane 8</td>
<td>Bomb</td>
<td>0.319</td>
<td>3.63</td>
<td>0.01244</td>
<td>0.283102</td>
<td>0.000004</td>
</tr>
<tr>
<td>Whole-rock A</td>
<td>Savillex</td>
<td>0.427</td>
<td>0.110</td>
<td>0.5493</td>
<td>0.285298</td>
<td>0.000014</td>
</tr>
<tr>
<td>Whole-rock B</td>
<td>Bomb</td>
<td>0.461</td>
<td>3.65</td>
<td>0.01792</td>
<td>0.283125</td>
<td>0.000004</td>
</tr>
</tbody>
</table>

*Lu and Hf values were calculated using a value for the $^{176}$Lu decay constant of $1.867 \times 10^{-11}$ $\text{y}^{-1}$ (Scherer et al., 2001; Söderlund et al., 2004) and $^{176}$Hf/$^{177}$Hf = 0.282785 and $^{176}$Lu/$^{177}$Hf = 0.0336 for CHUR (chondrite uniform reservoir) (Bouvier et al., 2008).

$^{176}$Hf and Hf values were calculated using $\varepsilon_{Hf} = 0.0336$ for CHUR (chondrite uniform reservoir).

Errors on $^{176}$Hf/$^{177}$Hf represent within-run uncertainty expressed as 2σ.

Errors on $^{176}$Lu/$^{177}$Hf are 0.2% based on external reproducibility of natural samples (see the Data Repository).

Errors on $^{176}$Hf/$^{177}$Hf ratios were corrected for instrumental mass bias using $^{176}$Hf/$^{177}$Hf = 0.7935 and normalized relative to $^{176}$Hf/$^{177}$Hf = 0.282160 for JMC-475.

Errors on $^{176}$Hf/$^{177}$Hf represent within-run uncertainty expressed as 2σ. SE. Estimated total uncertainty on individual $^{176}$Hf/$^{177}$Hf and $^{176}$Lu/$^{177}$Hf measurements for the purpose of regressions and age calculations is based on external reproducibility of low concentration Hf samples (i.e., garnets). This is estimated to be 0.01% and 0.5%, respectively, for $^{176}$Hf/$^{177}$Hf and $^{176}$Lu/$^{177}$Hf.

Errors on $^{176}$Hf/$^{177}$Hf and $^{176}$Lu/$^{177}$Hf ratios are <0.01% and <0.5%, respectively, for 176Hf/177Hf and 176Lu/177Hf.

**Compilation of data**

**Lu and Hf concentrations determined by isotope dilution with uncertainties estimated to be better than 0.5%.

**Uncertainties for $^{176}$Lu/$^{177}$Hf are 0.2% based on external reproducibility of natural samples (see the Data Repository).**

**Errors on $^{176}$Hf/$^{177}$Hf represent within-run uncertainty expressed as 2σ. SE. Estimated total uncertainty on individual $^{176}$Hf/$^{177}$Hf and $^{176}$Lu/$^{177}$Hf measurements for the purpose of regressions and age calculations is based on external reproducibility of low concentration Hf samples (i.e., garnets). This is estimated to be 0.01% and 0.5%, respectively, for $^{176}$Hf/$^{177}$Hf and $^{176}$Lu/$^{177}$Hf.**

**Note:**

Lu and Hf concentrations determined by isotope dilution with uncertainties estimated to be better than 0.5%.

Errors on $^{176}$Hf/$^{177}$Hf represent within-run uncertainty expressed as 2σ. SE. Estimated total uncertainty on individual $^{176}$Hf/$^{177}$Hf and $^{176}$Lu/$^{177}$Hf measurements for the purpose of regressions and age calculations is based on external reproducibility of low concentration Hf samples (i.e., garnets). This is estimated to be 0.01% and 0.5%, respectively, for $^{176}$Hf/$^{177}$Hf and $^{176}$Lu/$^{177}$Hf.

### Figure 2. Rare earth element and hafnium variations in lawsonite, glaucophane, and titanite from laser-ablation inductively coupled plasma–mass spectrometry analyses of grain mounts prepared from mineral separates used for geochronology. Note elevated Lu/Hf ratios in lawsonite. Concentrations are normalized to normal mid-oceanic ridge basalt (NMORB) values of Sun and McDonough (1989).
The older age of ~154 Ma is based upon bomb digestions that result in complete sample dissolution. The greater Hf concentrations and lower Hf isotopic compositions of the bomb solutions suggest incorporation of a high Hf phase, such as rutile or zircon, that was not dissolved by Savillex dissolution. Within the sample, rutile occurs as inclusions within titanite and the age may reflect the inherited Hf component from earlier amphibolite facies metamorphism. This interpretation is supported by observations within the Franciscan complex, where titanite commonly replaces rutile along the retrograde path (e.g., Wakabayashi, 1990; Tsujimori et al., 2006; Page et al., 2007). The age and initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are the same within error as the Ring Mountain rutile-bearing garnet amphibolite analyzed by Anczkiewicz et al. (2004), and indicate that the two distinct mineral assemblages resulted from metamorphism of similar basaltic protoliths.

The two Lu-Hf ages for the Ring Mountain lawsonite blueschist are consistent with existing thermochronology and geochronology for the Franciscan Complex. The temperature-time conditions of 300–500 °C at 145.5 ± 2.4 Ma ago for the sample agree with the proposed cooling history for the Franciscan Complex (Anczkiewicz et al., 2004; Wakabayashi and Dumitru, 2007). More important, the ages are consistent with geochronology from the amphibolite, blueschist, and eclogite blocks from the Tiburon Peninsula with high- to low-temperature assemblages spanning the ages of ~157–141 Ma (Catlos and Sorenson, 2003; Anczkiewicz et al., 2004).

LIMITATIONS AND APPLICATIONS OF LAWSONITE GEOCHRONOLOGY

The ability to date lawsonite offers a number of exciting prospects for constraining the ages and rates of processes occurring in subduction and/or collision zones. Here we first consider some limitations to the method and then discuss possibilities for future research.

The susceptibility of blueschist facies mineral assemblages to open-system Lu-Hf isotopic behavior is an important unresolved question. Eclogite and blueschist terranes are preserved from the latest Proterozoic to Eocene, yet lawsonite-bearing assemblages are relatively rare and lawsonite often exists as pseudomorphs, indicating its metastable state (e.g., Liou et al., 1990; Tsujimori et al., 2006). The limited occurrence of lawsonite is due in large part to the high water contents required for its formation and rapid cooling required for preservation (Clarke et al., 2006). The ability of other minerals in lawsonite-bearing assemblages such as glaucophane and chlorite to remain as closed systems is also of obvious importance for yielding meaningful Lu-Hf ages. Nevertheless, the Lu-Hf system represents a useful and unique geochronometer. Garnet strongly partitions heavy rare earth elements (e.g., Ota-mendi et al., 2002) and may deplete a system’s budget for Lu. Therefore, some potential garnet-lawsonite parageneses may be unsuitable for applications of lawsonite geochronology if lawsonite was stabilized after significant garnet growth, lawsonite growth did not occur at the expense of existing garnet, or if little Lu was available for incorporation into lawsonite due to garnet’s domination of the Lu budget.

Along a prograde path lawsonite will stabilize before garnet. In this scenario both garnet and lawsonite may contain significant amounts of Lu, such that it may be possible to investigate relative timing of mineral growth during subduction. Future studies may make significant contributions to subduction zone research by directly investigating age relationships between lawsonite and garnet in conjunction with petrologic constraints on reaction histories and fluid flow (e.g., John et al., 2004; King et al., 2004; Zack et al., 2004; Whitney and Davis, 2006; Tsujimori and Liou, 2007) to quantify the dynamics of mass transfer associated with prograde metamorphism during subduction.

The closure temperature (Dodson, 1973) for Lu or Hf diffusion in lawsonite is unknown. For garnet, the primary mineral of Lu-Hf geochronology, Lu-Hf closure is considered to be at a high temperature (>700 °C) due to slow diffusion in the garnet structure (e.g., Scherer et al., 2000; van Orman et al., 2002; Tironne et al., 2005). The stability of lawsonite in the mid-oceanic ridge basalt (MORB) + H2O system extends to a maximum of ~800 °C at 8 GPa (Okamoto and Maruyama, 1999), and if diffusion in lawsonite is similar to garnet, lawsonite would commonly decompose at temperatures below Lu-Hf closure. Diffusion rates in lawsonite, however, should be much faster than in garnet due to the likely buffering of diffusion within a hydrous mineral (e.g., Kohn, 1999). The Lu-Hf closure in lawsonite is therefore probably at a lower temperature than garnet, somewhere within the lawsonite stability field. Closure of the Lu-Hf system may not be a concern for comparatively low temperature blueschist geochronology, but may be significant for higher temperature lawsonite-bearing eclogites.

Despite its limited occurrence, Lu-Hf lawsonite dating may act as a powerful geochronometer in metamorphic assemblages that are difficult to otherwise date. Lawsonite forms only under restricted pressure-temperature conditions and lawsonite-forming reactions are also well understood (e.g., Okamoto and Maruyama, 1999). In the absence of garnet, methods appropriate for dating blueschist facies metamorphism are limited to $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology (e.g., Baldwin, 1996). Dating blueschist facies metamorphism by $^{39}\text{Ar}/^{39}\text{Ar}$, however, can be difficult due to the fine grain sizes of low-temperature assemblages.

Figure 3. Lu-Hf isochron diagrams for Ring Mountain lawsonite blueschist. Note that symbol sizes are exaggerated to improve clarity. See text for details. Isochrons were produced with the program Isoplot/Ex (Ludwig, 2003). MSWD—mean square of weighted deviates.
Wakabayashi and Dumitr, 2007), potassium-rich inclusions in blueschist minerals such as glaucophane (Sisson and Onstott, 1986), and the complex thermal history of subduction-accretion complexes (Mattinson, 1988). Lawsonite geochemistry should be especially applicable to high-Ca, low-K metabasites, where lawsonite is an abundant phase and more readily prepared for geochemistry than sparse K-bearing phases.

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