Speculations Linking Monazite Compositions to Origin: Llallagua Tin Ore Deposit (Bolivia)

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Abstract: Monazite [(Ce,Th)PO₄] from the Llallagua tin ore deposit in Bolivia is characterized by low radiogenic element contents. Previously reported field evidence and mineral associations suggest the mineral formed via direct precipitation from hydrothermal fluids. Monazite compositions thus may provide insight into characteristics of the fluids from which it formed. Chemical compositions of three Llallagua monazite grains were obtained using Electron Probe Microanalysis (EPMA, n = 64) and laser ablation mass spectrometry (LA-ICP-MS, n = 56). The mineral has higher amounts of U (123 ± 17 ppm) than Th (39 ± 20 ppm) (LA-ICP-MS, ±1σ). Grains have the highest amounts of fluorine ever reported for monazite (0.88 ± 0.10 wt %, EPMA, ±1σ), and F-rich fluids are effective mobilizers of rare earth elements (REEs), Y, and Th. The monazite has high Eu contents and positive Eu anomalies, consistent with formation in a highly-reducing back-arc environment. We speculate that F, Ca, Si and REE may have been supplied via dissolution of pre-existing fluorapatite. Llallagua monazite oscillatory zoning is controlled by an interplay of low (P + Ca + Si + Y) and high atomic number (REE) elements. We suggest monazite compositions provide insight into fluid geochemistry, mineral reactions, and tectonic settings of ore deposits that contain the mineral.

Keywords: monazite; rare earth elements; geochemistry; Bolivia; apatite; Llallagua

1. Introduction

The Llallagua ore deposit is part of the tin belt that extends from southern Peru to northern Argentina (Figure 1) (e.g., [1,2]). The region was once considered one of the largest hard-rock tin deposits in the world, and produced more than 0.5 million tons of metallic tin [3–7]. The richest ore deposits are located within a zone where the belt makes a sharp curve (Figure 1) and are commonly found in association with intrusive igneous rocks [1,2,4–10].

Monazite [(Ce,Th)PO₄] is found in almost every vein system in the Llallagua deposit in association with quartz, cassiterite, tourmaline in veins and vugs, and embedded in pyrite and marcasite [5]. The mineral occurs as prismatic or pyramidal crystals with contact or penetration twinning [6]. The Llallagua monazite is also known for oscillatory zoning in backscattered electrons (BSE) (Figure 2) [7,11]. This type of zoning is considered rare for the mineral, which is more commonly seen as sector zoned in BSE [12–14].

Numerous studies describing the mineralogy of the Llallagua mine have noted the importance of fluids in the formation of the Llallagua monazite (e.g., [5,6,15]) and its composition has the potential to provide important insight into the geochemistry of the fluids that formed the deposit.
The region was part of a back-arc basin for most of its history, but two major metallogenic episodes are
recorded during the late Triassic-early Jurassic and late Oligocene-early Miocene [18,19]. Based on its
ages, the Llallagua monazite analyzed in this study belongs to the second event.

The environment is characterized by low oxygen fugacity and high dissolved concentrations of tin (see review in [2]).

The origin of the Bolivian tin belt is suggested to be a series of compressional events between the
Farallon/Nazca oceanic plate and the South American continent, which generated peraluminous magma
that equilibrated with graphite-rich, metapelitic sources [4,17]. The environment is characterized by low oxygen fugacity and high dissolved concentrations of tin (see review in [2]).

The region was part of a back-arc basin for most of its history, but two major metallogenic episodes are
recorded during the late Triassic-early Jurassic and late Oligocene-early Miocene [18,19]. Based on its
ages, the Llallagua monazite analyzed in this study belongs to the second event.

Figure 1. Geological map and cross-section of the La Joya mining district after [16]. Inset shows the
location of the mining district within the tin belt of Bolivia, Peru, and Argentina after [7].

Figure 2. Backscattered electron (BSE) images of Llallagua monazite: (A) grain 1; (B) grains 2 and 3;
and (C) grain 4. Electron probe microanalysis (EPMA) and laser ablation pits are indicated with some
spot numbers labeled for reference. Secondary electron (SE) images showing laser ablation pits of
Llallagua monazite: (D) grain 1; (E) grain 3; and (F) grain 4. Pits are labeled. See the Supplementary
Materials, File S1 for compositions.
Monazite from the Llallagua deposit contains minor Th, U [5,7,11,15,20] and up to 99.9% common $^{206}$Pb [7]. Monazite is thought to exclude common Pb during crystallization (e.g., [20–23]). Despite this issue, monazite from the Llallagua mine has been dated using U-Pb methods and yields Miocene results at 23.4 ± 2.2 Ma [7] and 19.0 ± 1.6 Ma [11]. These results are in-line with Miocene K-Ar ages of “partially altered” [24] Llallagua quartz latite porphyry minerals (20.6 ± 0.4 Ma, K-feldspar; and 21.6 ± 0.4 Ma, biotite) [17]. However, they are much younger than Eocene crystallization ages reported from the same locality [15,24,25]. The reason for the wide range of ages is problematic because a genetic link between tin ore mineralization and proximal igneous intrusions has yet to be established. The composition and timing of fluids transporting and depositing the ore is important information for evaluation and exploitation of this deposit and others like it (e.g., [26,27]).

Here we present detailed compositional analyses from three Llallagua monazite grains to understand how it reflects on its tectonic setting and controls on zoning. Because monazite can incorporate a wide variety of elements into its structure, and thus may have variable stoichiometry, generating high quality compositional data from monazite can be challenging [28–30]. We apply both electron probe microanalysis (EPMA) and laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) to constrain what elements are present in its structure. The grains were obtained from a vein in the Llallagua tin-ore porphyry deposit, provided by Alfredo Petrov (mindat.org [6]) from a sample dated by [11]. Our only geological context is that the grains were collected from a vein in a tin mine in the Potosi Department (Figure 1). Although the sample set is small ($n = 3$), we obtained a large amount of high-quality chemical analyses ($n = 120$) and the monazite themselves have previous age constraints [11]. The monazite compositions have the potential to allow insight into mineral reactions that may have occurred as the tin deposit formed. The Llallagua region is a historically important mining district, and the data is used to compare to those from other important monazite ore-producing localities to explore its potential as a resource for rare earth element (REEs).

### 2. Analytical Approaches

#### 2.1. Sample Preparation and Imaging

The analyses were taken using the same standards and approach described in [28]. We followed a sample preparation protocol that would be typical for instruments that require polished monazite grains in a mounted environment (i.e., EPMA, ion microprobe, LA-ICP-MS). Individual grains were placed on dual-sided tape. A 1-inch diameter Teflon ring was placed around the grains and epoxy (Beuhler, EpoxiCure 2 Epoxy System) was poured around the grains to a depth of ~10 mm. After the epoxy cured, rings were broken away from the tape and grains polished using sand paper and Mother’s Billet Metal Polish. The back of the plug was cut using a high-precision saw to a thickness of ~5 mm. During this process, grains were exposed to Allied Low Speed Cutting Fluid. Mounts were cleaned in a sonicator bath with distilled water and an ultrasonic cleanser for 5 min and followed by three sessions of 5 min each in pure distilled water to remove traces of the cleanser or other impurities.

#### 2.2. Llallagua Monazite Electron Probe MicroAnalyses (EPMA)

Mounts were coated in carbon and imaged using the University of Oklahoma Cameca SX50 electron probe micro-analyzer equipped with five wavelength-dispersive X-ray spectrometers, integrated energy-dispersive X-ray analyzer, standard Secondary Electron Microscope (SEM) imaging capabilities. The instrument operated at a 20 µkV accelerating voltage, 20 nA current and a 2 µm spot size. These conditions were also maintained for the compositional analyses. Grains were imaged in backscattered electrons (BSE) to understand their zoning, potential compositional variations, and to select regions for quantitative analysis using EPMA and laser techniques (Figure 2). Analytical protocols followed methods developed by [30] and G. Morgan (personal communication) for xenotime with the exception that Pb was analyzed using the Mα emission rather than Mβ, as the Mα line was...
slightly better at resolving interferences. The element, X-ray emissions and diffracting crystals for analyses are listed in Table 1.

Table 1. Conditions used for quantitative monazite compositional analysis.

<table>
<thead>
<tr>
<th>Element(s)</th>
<th>Crystal</th>
<th>X-ray Line</th>
</tr>
</thead>
<tbody>
<tr>
<td>P, S, Ca, Cl</td>
<td>PET</td>
<td>Kα</td>
</tr>
<tr>
<td>As, Ti, Fe, Mn</td>
<td>LIF</td>
<td>Kα</td>
</tr>
<tr>
<td>Al, Si, Mg, Na, F</td>
<td>TAP</td>
<td>Kα</td>
</tr>
<tr>
<td>Y</td>
<td>TAP</td>
<td>Lα</td>
</tr>
<tr>
<td>La, Ce, Nd, Eu, Tb</td>
<td>LIF</td>
<td>Lα</td>
</tr>
<tr>
<td>Pr, Sm, Gd</td>
<td>LIF</td>
<td>Lβ</td>
</tr>
<tr>
<td>Th</td>
<td>PET</td>
<td>Mα</td>
</tr>
<tr>
<td>U</td>
<td>PET</td>
<td>Mβ</td>
</tr>
</tbody>
</table>

Standards for REEs were ternary rare earth orthophosphates (REP) described by [30]. Durango fluorapatite [31] was used for Ca, galena for Pb, and synthetic ThO$_2$ and depleted pure uranium metal (C.M. Taylor Corp.) was used for Th and U. Natural and synthetic crystalline solids were used for remaining elements. Note that phosphate standards are not available for all desired elements, thus we relied on a variety of standards. Counting times were 30 s on peak for all elements, except Mg and Si, which were 60 s each. Each background was counted for half the time of the peak, therefore total time on background equaled that of the peak. An overlap correction was applied for the Pr Lα emission on the Eu Lα line using the Pr-bearing Rare Earth Phosphate standard-2 (REP2) and analytical methods exactly the same as for Eu Lα. Each analysis required ~15 min. Standards analyzed as unknowns were only measured at the beginning of the analytical session because the beam current did not drift more than 0.2 nA, the laboratory temperature is stable (±1 °F), and compositional data fit the monazite formula (Table 2, Figure 3).

Table 2. Average Llallagua monazite EPMA compositions $^1$.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Grain 1 ($n = 23$) $^2$</th>
<th>Grain 3 ($n = 25$)</th>
<th>Grain 4 ($n = 16$)</th>
<th>All Grains ($n = 64$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_2$O$_5$ (wt %) $^3$</td>
<td>30.1 (0.7) $^4$</td>
<td>29.9 (0.4)</td>
<td>29.9 (0.4)</td>
<td>29.97 (0.51)</td>
</tr>
<tr>
<td>As$_2$O$_5$</td>
<td>0.02 (0.04)</td>
<td>0.02 (0.03)</td>
<td>0.04 (0.07)</td>
<td>0.03 (0.05)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.15 (0.027)</td>
<td>0.185 (0.024)</td>
<td>0.182 (0.024)</td>
<td>0.17 (0.03)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.010 (0.016)</td>
<td>0.012 (0.018)</td>
<td>0.006 (0.015)</td>
<td>0.01 (0.02)</td>
</tr>
<tr>
<td>UO$_2$</td>
<td>0.031 (0.043)</td>
<td>0.033 (0.053)</td>
<td>0.041 (0.035)</td>
<td>0.03 (0.05)</td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>2.1 (0.9)</td>
<td>2.0 (0.3)</td>
<td>2.1 (0.4)</td>
<td>2.07 (0.59)</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>16.1 (1.7)</td>
<td>14.3 (0.7)</td>
<td>14.5 (1.4)</td>
<td>14.97 (1.54)</td>
</tr>
<tr>
<td>Ce$_2$O$_3$</td>
<td>32.2 (1.0)</td>
<td>32.7 (0.8)</td>
<td>32.7 (0.7)</td>
<td>32.54 (0.87)</td>
</tr>
<tr>
<td>Pr$_2$O$_3$</td>
<td>2.97 (0.19)</td>
<td>3.21 (0.20)</td>
<td>3.23 (0.13)</td>
<td>3.13 (0.22)</td>
</tr>
<tr>
<td>Nd$_2$O$_3$</td>
<td>11.2 (0.8)</td>
<td>12.4 (0.7)</td>
<td>12.3 (0.7)</td>
<td>11.92 (0.91)</td>
</tr>
<tr>
<td>Sm$_2$O$_3$</td>
<td>1.15 (0.17)</td>
<td>1.19 (0.22)</td>
<td>1.22 (0.15)</td>
<td>1.18 (0.19)</td>
</tr>
<tr>
<td>Eu$_2$O$_3$</td>
<td>1.01 (0.22)</td>
<td>0.99 (0.16)</td>
<td>0.97 (0.07)</td>
<td>0.99 (0.17)</td>
</tr>
<tr>
<td>Gd$_2$O$_3$</td>
<td>0.67 (0.12)</td>
<td>0.72 (0.15)</td>
<td>0.64 (0.15)</td>
<td>0.68 (0.14)</td>
</tr>
<tr>
<td>Tb$_2$O$_3$</td>
<td>0.06 (0.05)</td>
<td>0.08 (0.05)</td>
<td>0.05 (0.04)</td>
<td>0.06 (0.05)</td>
</tr>
<tr>
<td>CaO</td>
<td>0.53 (0.32)</td>
<td>0.59 (0.45)</td>
<td>0.63 (0.32)</td>
<td>0.58 (0.37)</td>
</tr>
<tr>
<td>F</td>
<td>0.87 (0.09)</td>
<td>0.88 (0.11)</td>
<td>0.92 (0.09)</td>
<td>0.88 (0.10)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.06 (0.01)</td>
<td>0.06 (0.01)</td>
<td>0.06 (0.01)</td>
<td>0.06 (0.01)</td>
</tr>
<tr>
<td>Total</td>
<td>98.8 (0.9)</td>
<td>98.9 (0.6)</td>
<td>99.1 (0.5)</td>
<td>98.90 (0.7)</td>
</tr>
<tr>
<td>P (apfu) $^5$</td>
<td>0.999 (0.009)</td>
<td>0.995 (0.004)</td>
<td>0.994 (0.005)</td>
<td>0.996 (0.007)</td>
</tr>
<tr>
<td>Si</td>
<td>0.006 (0.001)</td>
<td>0.007 (0.001)</td>
<td>0.007 (0.001)</td>
<td>0.007 (0.001)</td>
</tr>
<tr>
<td>Y</td>
<td>0.044 (0.018)</td>
<td>0.042 (0.006)</td>
<td>0.043 (0.007)</td>
<td>0.043 (0.012)</td>
</tr>
<tr>
<td>La</td>
<td>0.233 (0.026)</td>
<td>0.207 (0.011)</td>
<td>0.209 (0.021)</td>
<td>0.217 (0.023)</td>
</tr>
<tr>
<td>Ce</td>
<td>0.462 (0.019)</td>
<td>0.471 (0.012)</td>
<td>0.471 (0.009)</td>
<td>0.468 (0.014)</td>
</tr>
<tr>
<td>Pr</td>
<td>0.042 (0.003)</td>
<td>0.046 (0.003)</td>
<td>0.046 (0.002)</td>
<td>0.045 (0.003)</td>
</tr>
</tbody>
</table>
Monazite P concentrations were assigned based on EPMA P using MAPS-4 as the primary calibration standard and NIST-612 and NIST-610 glasses. Elemental concentrations were derived with the Iolite software [36] NIST-612 and NIST-610 [33] and USGS MAPS-4. See [34,35] for evaluations of the quality of the measurements enabling 118 measurements to be made within the dwell interval (60 s), conditions suitable for robust analysis. Laser ablation parameters optimized for monazite grain transects (Figure 2). Laser ablation parameters optimized for monazite grain transects (Figure 2). Laser ablation parameters optimized for monazite grain transects (Figure 2). Laser ablation parameters optimized for monazite grain transects (Figure 2). Laser ablation parameters optimized for monazite grain transects (Figure 2). Laser ablation parameters optimized for monazite grain transects (Figure 2).

Figure 3. Plot of monazite EPMA compositions (see Supplementary Materials, File S1): (A) Rare Earth Element (REE) (atoms per formula unit, apfu) vs. P (apfu); (B) 3Ca (apfu) vs. 2(REE + Y) (apfu); (C) REE + Si (apfu) vs. Ca + P (apfu); and (D) Ca + Si vs. 2REE (apfu). Box in panels A and B indicates the region of ideal monazite formula. REE are La, Ce, Pr, Nd, Sm, Eu, Gd, and Tb.

2.3. Llallagua Monazite LA-ICP-MS Analyses

LA-ICP-MS major, minor, and trace element transects of monazite grains were performed at the University of Texas at Austin using a New Wave UP193fx (193 nm, 4–6 ns pulse width) excimer laser coupled to an Agilent 7500ce ICP-MS. Tracks for the laser pits were positioned proximal and parallel to the previously measured EPMA grain transects (Figure 2). Laser ablation parameters optimized from monazite test ablations were 45 s ablations using a 25 μm diameter spot size at 45% power (fluence of ~4.9 J/cm²), 10 Hz repetition rate, and a He cell flow of 250 mL/min. Pulse-to-pulse laser power variation was <3.5% over the analysis period. All spots were pre-ablated for 2 s using a 75 μm spot, 20% laser power, and 10 Hz repetition rate to remove surface contamination (i.e., EPMA carbon coat). The quadrupole time-resolved method involved measurement of 22 analytes at one point per spectral peak, using the integration times of 10 ms (31P and 89Y), 20 ms (23Na, 27Al, 47Ti, 55Mn, 57Fe, 75As, 137Ba, 153Eu, 157Gd, 159Tb, 163Dy, 165Ho, 166Er, 169Tm, 172Yb, and 175Lu) or 30 ms (204Pb, 208Pb, 232Th, and 238U). The resulting sampling period (0.5062 s) corresponded to >90% detection time, enabling 118 measurements to be made within the dwell interval (60 s), conditions suitable for robust measurement [32]. A 45 s gas blank interval was used between all laser measurements.

Monazite analyses were bracketed hourly by triplicate analyses of laser ablation standards NIST-612 and NIST-610 [33] and USGS MAPS-4. See [34,35] for evaluations of the quality of the NIST-612 and NIST-610 glasses. Elemental concentrations were derived with the Iolite software [36] using MAPS-4 as the primary calibration standard and 31P as the internal standard reference. Monazite P concentrations were assigned based on EPMA P₂O₅ analyses. MAPS-4 is a synthetic trace element-doped Ca₅(PO₄)₂ precipitate [37] with a P content (16.7 ± 1.7 wt %) reasonably similar to the monazite (11.94 wt % from EPMA). Average analyte recoveries were better for NIST-610 (128%)

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Grain 1 (n = 23)</th>
<th>Grain 3 (n = 25)</th>
<th>Grain 4 (n = 16)</th>
<th>All Grains (n = 64)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd</td>
<td>0.156 (0.011)</td>
<td>0.174 (0.010)</td>
<td>0.172 (0.010)</td>
<td>0.167 (0.013)</td>
</tr>
<tr>
<td>Sm</td>
<td>0.016 (0.002)</td>
<td>0.016 (0.003)</td>
<td>0.017 (0.002)</td>
<td>0.016 (0.003)</td>
</tr>
<tr>
<td>Eu</td>
<td>0.013 (0.003)</td>
<td>0.013 (0.002)</td>
<td>0.013 (0.001)</td>
<td>0.013 (0.002)</td>
</tr>
<tr>
<td>Gd</td>
<td>0.009 (0.001)</td>
<td>0.009 (0.002)</td>
<td>0.008 (0.002)</td>
<td>0.009 (0.002)</td>
</tr>
<tr>
<td>Ca</td>
<td>0.022 (0.013)</td>
<td>0.025 (0.019)</td>
<td>0.026 (0.013)</td>
<td>0.024 (0.016)</td>
</tr>
<tr>
<td>F</td>
<td>0.108 (0.011)</td>
<td>0.109 (0.013)</td>
<td>0.114 (0.011)</td>
<td>0.110 (0.012)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.004 (0.001)</td>
<td>0.004 (0.001)</td>
<td>0.004 (0.001)</td>
<td>0.004 (0.001)</td>
</tr>
<tr>
<td>Total</td>
<td>2.01 (0.01)</td>
<td>2.01 (0.01)</td>
<td>2.01 (0.005)</td>
<td>2.01 (0.005)</td>
</tr>
</tbody>
</table>

1 Measured but not detected: SO₃, PbO, FeO, MnO, MgO, Na₂O, ThO₂, and Al₂O₃ (wt%). Supplementary Materials, File S1 contains details regarding each analysis and standard data. See Figure 2 for locations. 2 n = number of spots on monazite grain; 3 Oxides and halogens in this groups reported in wt %; 4 Number in parentheses is 1σ standard deviation of the average in absolute values; 5 Atoms per formula unit (apfu) are normalized to four oxygens.
than NIST-612 (156%), but we consider these to be worst case estimates of accuracy considering that the P contents of these standards are ~5000 and ~30,000 times lower than MAPS-4. Analyte concentrations for monazite ablations were predominantly 100 to 1000 times higher than estimated detection limits, and signals for $^{204}$Pb were 40 to 155 times higher than detection limits.

Both the EPMA and LA-ICP-MS targeted a wide range of possible elements present in the monazite structure, and both approaches report As, Th, U, Al, Y, Pb, Eu, Gd, Tb, Fe, Mn, and Na contents. A direct comparison of the chemical data for these elements obtained using both LA-ICP-MS and EPMA is inappropriate, however, as significant differences exist in terms of sampling region and detection limits. The EPMA approach relies on the analysis of oxides and halides from the surface of the monazite using X-ray element lines emitted from the mineral structure as a region of the grain was targeted with a 2 $\mu$m electron beam, whereas the LA-ICP-MS obtained chemical data sputtered from a 25 $\mu$m-diameter circular spot following pre-ablation, and thus data arises from a deeper levels of the mineral not visible in BSE. In some cases, the laser spot overlaps zones of varying brightness or regions where more than one EPMA analysis was obtained (Figure 2). It is appropriate, however, to search for systematic variations. All compositional data and coordinates are available in Supplementary Materials, File S1

Following LA-ICP-MS, grains were re-imaged in secondary electrons (SE) using a JEOL JSM-6490LV SEM at the University of Texas at Austin, Dept. of Geological Sciences. This instrument operated at low vacuum mode, 15 kV accelerating voltage, and a 2 $\mu$m spot size. The goal was to identify any ablation craters that intersected secondary alteration features, deformation textures, or microcracks (defined as >5 $\mu$m in width). Regions that contain microcracks were examined to compare pre- and post-ablation to ascertain if their origin was due to the laser or are intrinsic to the grain. All imaged spots are seen in Figure 2D–F.

3. Results

3.1. Llallagua Monazite EPMA

Each grain shows oscillatory zoning in BSE (Figure 2), but grain 1 has a bright core, whereas grains 3 and 4 have darker cores. Note that what we define as the mineral core is our best approximation that represents the center of the grains, which may not be precisely exposed. The Llallagua monazite EPMA analyses support stoichiometry close to the ideal mineral formula (Figure 3A,B). The mineral contains Ce$_2$O$_3$ > La$_2$O$_3$ > Nd$_2$O$_3$ > Pr$_2$O$_3$ > Y$_2$O$_3$ > Sm$_2$O$_3$ > Eu$_2$O$_3$ > Gd$_2$O$_3$ > Tb$_2$O$_3$ (wt %). As expected, concentrations of ThO$_2$ and UO$_2$ (wt %) are below detection limits with the EPMA methods used (0.18 and 0.13 wt %, respectively). Other oxides present at or below detection are As$_2$O$_5$, TiO$_2$, Al$_2$O$_3$, SO$_3$, PbO, FeO, MnO, MgO, Na$_2$O, and Cl (Table 2).

Silicon is present in the Llallagua samples at levels <0.2 wt % SiO$_2$ (Table 2). The huttonite substitution mechanism for the incorporation of Th in monazite involves Si (ThSiREE$_{-1}$P$_{-1}$) [38]. However, this mechanism is inappropriate for these grains, as the Llallagua monazite contains undetectable amounts of radiogenic elements. Additionally, the monazite contains 0.58 ± 0.37 wt % CaO (Table 2; Figure 4A–C) suggesting a slight modification of the brabanite exchange vector (Ca$_3$REE$_{-2}$ vs. CaThUREE$_{-2}$) (Figure 3B). This substitution occurs in apatite with a vacancy [39]. Other substitutions that occur in apatite that also appear relevant to this monazite include CaPREE$_{-1}$Si$_1$ and CaSiREE$_{-2}$ (Figure 3C,D).

We detected higher amounts of fluorine in the monazite (average 0.88 ± 0.10 wt %) (Table 2, Figure 4A–C), an element commonly found in apatite [40–42]. We found no clear relationship between the amount of F and any cations, perhaps due to its substitution in the anion site or interstitial sites in the monazite structure, creating a degree of disorder. The amount of F does not vary significantly across the monazite grains (Figure 4A–C). We exclude the possibility that F is an analytical artifact, as a monazite grain from the Amelia pegmatite was analyzed using the exact procedure and did not detect F, which would be expected if problematic conditions arose with standards or choice of background
and peak [28]. Note that using the TAP monochromator, the F Kα line is effectively free of any overlaps among the analyzed elements.

Figure 4. Compositional transects across Llallagua monazite: (A) grain 1; (B) grain 3; and (C) grain 4 in Y2O3, Eu2O3, CaO and F obtained using EPMA. Approximate location of each monazite core is indicated; (D–F) Transects in Y (scale X 10,000 ppm) across Llallagua monazite grain 1, grain 3, and grain 4, respectively, obtained using LA-ICP-MS. See Figure 2 for locations of these transects.

Oscillatory zoning in the Llallagua monazite is seen using high contrast BSE and is controlled by an interplay of high Z and low Z elements (Figure 5). Darker regions are dominated by higher amounts of P, Si, Y, and Ca, whereas lighter regions contain higher amounts of REE. We found no correlation between a single specific element and brightness of zones within the grains. Although most monazite zoning in BSE is due to the higher atomic masses of Th and U, the Llallagua monazite BSE zoning appears controlled by REE contents. If monazite has REE/P + Si + Y + Ca < 0.85, the region appears darker on the BSE image. If it contains REE/P + Si + Y + Ca > 0.85, the area appears brighter. Using the electron microprobe compositions, the Llallagua monazite has CeN < LaN and a positive Eu anomaly (Figure 6A–C). Apatite from the Llallagua deposit also shows a positive Eu anomaly that has been linked to crystallization in a reservoir enriched in Eu [43]. Other monazite grains with positive Eu anomalies and low radiogenic elements have been suggested to be indicative of significant hydrothermal contribution [44]. The amount of Eu2O3 (0.99 ± 0.17 wt %, Table 2, Figure 4A–C) is present at levels similar to the amount of F. We see a slight increase in Eu2O3 from core to rim across the grains, which is not seen in other REEs or Y2O3 (Figure 4A–C).
Figure 5. Compositional transects across Llallagua monazite: (A) grain 1; (B) grain 3; and (C) grain 4 in lower atomic number (low Z, black circles) elements (P, Si, Y, and Ca) and high atomic number (high Z, open circles) elements (La, Ce, Pr, Nd, Sm, Eu, Gd, and Tb). Compositions obtained using the EPMA. Shaded areas are approximate regions that appear darker in BSE, whereas white regions are lighter (see Figure 2). Approximate location of each monazite core is indicated; (D) Plot of the low Z versus high Z elements for all Llallagua monazite EPMA compositions. Black spots correlate to regions that are darker in BSE, whereas open circles appear lighter in BSE.

Figure 6. Chondrite-normalized [45] REE plots of Llallagua monazite: (A) grain 1; (B) grain 3; and (C) grain 4 obtained using EPMA. Core regions are indicated by dark circles, mid-rim by grey circles, and rim by white circles. The grey square box indicates approaching instrument detection limits; (D–F) Chondrite-normalized middle and heavy REE patterns obtained using LA-ICP-MS. We include the EPMA analysis of Sm as a grey box.
No correlation exists between the chondrite-normalized REE patterns or REE contents of the Llallagua monazite and zoning in BSE. We explored numerous trends with REE compositional data and found general relationships between decreasing Y and increasing Ce, and decreasing La and increasing Nd + Pr (Figure 7A,B). This is likely due to ionic radii of these elements, with Y and heavier REE showing lower affinities for the monazite structure [46,47].

![Figure 7](image_url)

**Figure 7.** (A) Y (apfu) vs. Ce (apfu); and (B) La (apfu) vs. Pr + Nd (apfu) for individual spots on the Llallagua monazite obtained using EPMA; and (C,D) Yb (ppm) vs. Lu (ppm) and Gd (%) vs. Tb (ppm), respectively, for individual spots obtained using LA-ICP-MS data.

### 3.2. Llallagua Monazite LA-ICP-MS Analyses

Using LA-ICP-MS, we find the Llallagua monazite shows a wide range of concentrations for many minor and trace elements. The grains contain higher amounts of $^{238}\text{U}$ (123 ± 17 ppm) compared to Th (39 ± 20 ppm) (average of 56 analyses, including uncertainty, ±2σ; Table 3; Figure 8A–C), but a few spots do contain higher Th. The highest Th content we measured is located in the core of grain 1 (935 ± 107 ppm with 85.4 ± 9.9 ppm U, see Supplementary Materials, File S1; ±2σ, Figure 8A). This is also the brightest region in BSE seen in the monazite (Figure 2). We speculate that the higher % common Pb reported for the Llallagua monazite is likely due to the small amounts of radiogenic elements present in the mineral, and thus a lower amount of detectable radiogenic Pb (average $^{208}\text{Pb}$ is 0.5 ± 0.2 ppm) (see also [11]). Other approaches (Secondary Ion Mass Spectrometry) may be able to detect common Pb, and confirm this hypothesis. Other elements present below detection limits are $^{23}\text{Na}$, $^{27}\text{Al}$, $^{47}\text{Tl}$, $^{55}\text{Mn}$, $^{57}\text{Fe}$, and $^{137}\text{Ba}$. Arsenic-75 is present in the monazite at 195 ± 23 ppm (average of 56 analyses, including uncertainty, ±2σ, Table 3). This element has been correlated to monazite S contents [48], but $^{203}\text{S}$ was not detected using the electron microprobe and not measured using LA-ICP-MS. In addition, the tectonic setting may lend itself to higher amounts of common Pb.

In terms of REE, we find the LA-ICP-MS analyses show Gd > Dy > Eu > Er > Tb > Ho > Yb > Tm > Lu (ppm; Table 3). This differs from the EMP analyses, which yield $\text{Eu}_2\text{O}_3 > \text{Gd}_2\text{O}_3$ (wt %). This is likely due to differences in the area sampled during analysis and different detection limits for each approach. The general trends of EPMA and LA-ICP-MS results show overall similar patterns and are consistent with what is expected for the behavior or REE, lending confidence in the LA-ICP-MS results. For example, the amount of Lu (ppm) increases with increasing amounts of Yb (ppm) and Gd (ppm) increases with increasing amounts of Tb (ppm), a function of the atomic radii of these cations (Figure 7C–D). Transects in $\text{Y}_2\text{O}_3$ (wt %) and Y (ppm) (Figure 4) and $\text{Eu}_2\text{O}_3$ (wt %) and Eu (ppm) (Figure 4A–C and Figure 8D–F) show the same general trends. Overall, the amount of Eu (ppm) and U (ppm) increases from core to rim across the grains (Figure 8).

A major difference between the LA-ICP-MS and EPMA is seen with Eu (Figure 6). It is difficult to evaluate the Eu anomaly using LA-ICP-MS data, as we did not measure Sm. If we include Sm data from the EPMA with the LA-ICP-MS HREE data, the results suggests Eu anomaly is negative for core analyses and non-existent to positive at the rim (Figure 6D–F). The approaches do differ in terms of volume of material sampled and thus this trend may not be real. $\frac{\text{Eu}_{\text{measured}}}{\text{Eu}_{\text{chondrite}}}$ obtained using LA-ICP-MS increases from core or mid-rim to rim for all grains.
Table 3. Average Llallagua monazite LA-ICP-MS compositions.

<table>
<thead>
<tr>
<th>Isotope (ppm)</th>
<th>Grain 1 (n = 19)</th>
<th>Grain 3 (n = 22)</th>
<th>Grain 4 (n = 12)</th>
<th>All Grains (n = 56)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75 As</td>
<td>173 (21)</td>
<td>207 (23)</td>
<td>208 (27)</td>
<td>195 (23)</td>
</tr>
<tr>
<td>89 Y</td>
<td>24,119 (3008)</td>
<td>22,946 (2596)</td>
<td>23,808 (3348)</td>
<td>23,562 (2929)</td>
</tr>
<tr>
<td>153 Eu</td>
<td>3459 (507)</td>
<td>2429 (318)</td>
<td>2078 (339)</td>
<td>2719 (400)</td>
</tr>
<tr>
<td>157 Gd</td>
<td>14,344 (1774)</td>
<td>14,445 (1601)</td>
<td>14,291 (2012)</td>
<td>14,374 (1763)</td>
</tr>
<tr>
<td>159 Tb</td>
<td>1782 (210)</td>
<td>1720 (191)</td>
<td>1757 (248)</td>
<td>1751 (212)</td>
</tr>
<tr>
<td>163 Dy</td>
<td>8165 (982)</td>
<td>7635 (826)</td>
<td>8058 (1082)</td>
<td>7903 (945)</td>
</tr>
<tr>
<td>165 Ho</td>
<td>1038 (127)</td>
<td>1030 (107)</td>
<td>1057 (136)</td>
<td>1037 (121)</td>
</tr>
<tr>
<td>166 Er</td>
<td>2142 (261)</td>
<td>2099 (213)</td>
<td>2188 (289)</td>
<td>2134 (249)</td>
</tr>
<tr>
<td>169 Tm</td>
<td>167 (20)</td>
<td>162 (16)</td>
<td>169 (22)</td>
<td>165 (19)</td>
</tr>
<tr>
<td>172 Yb</td>
<td>682 (79)</td>
<td>653 (65)</td>
<td>686 (92)</td>
<td>671 (77)</td>
</tr>
<tr>
<td>175 Lu</td>
<td>59 (7)</td>
<td>51 (5)</td>
<td>55 (7)</td>
<td>55 (6)</td>
</tr>
<tr>
<td>204 Pb</td>
<td>5.2 (15.6)</td>
<td>1.2 (12)</td>
<td>3.0 (13)</td>
<td>3.0 (14)</td>
</tr>
<tr>
<td>208 Pb</td>
<td>0.5 (0.2)</td>
<td>0.6 (0.2)</td>
<td>0.3 (0.1)</td>
<td>0.5 (0.2)</td>
</tr>
<tr>
<td>232 Th</td>
<td>103 (33)</td>
<td>3.3 (1.9)</td>
<td>3.7 (1.9)</td>
<td>39 (20)</td>
</tr>
<tr>
<td>238 U</td>
<td>160 (22)</td>
<td>107 (12)</td>
<td>96 (13)</td>
<td>123 (17)</td>
</tr>
</tbody>
</table>

1 Measured but not detected: 23Na, 55Mn, 57Fe, and 137Ba. Supplementary Materials, File S1 contains details regarding each analysis and standard data; 2 Compositions reported in ppm; 3 n = number of spots on monazite grain; 4 Number in parentheses is 2σ standard deviation of the average in absolute values, taking into account analytical uncertainties.

Figure 8. Transects in 232Th (ppm) and 238U (ppm) across Llallagua monazite: (A) grain 1; (B) grain 3; and (C) grain 4. Location of core is indicated; (D–F) Eu (ppm) transects across grains 1, 3, and 4, respectively. Data obtained using LA-ICP-MS.
4. Discussion and Conclusions

4.1. Evidence for Hydrothermal Origin

We speculate that the Llallagua monazite precipitated directly from a fluid [15] or via the fluid-mediated replacement of apatite [49]. An alternative origin for these grains is either a primary igneous origin or metamorphism of pre-existing grains. Radiogenic element contents, geochemical signatures, local abundance, and common association with hydrothermal mineral assemblages have been suggested as a means to identify monazite that crystallized from hot, aqueous fluids [50]. We do not have direct field context from these grains, but the role of fluids in the formation of these monazites is supported by field observations by others [5,6,20]. Numerous other phosphate minerals have been reported from the deposit, including xenotime, pyromorphite, vanadinite, wavelite, vauxite, paravauxite, metavauxite, augelite, childrenite, diadochite, and florencite-Ce [5,6,15]. Based on their textural relationships observed by others in hand-sample, most of these phosphates are thought to have formed on the large scale via supergene solutions [15]. Monazite and florencite-Ce appear to be the only major sinks for REE in the Llallagua system [5,6], with radiogenic elements likely hosted primarily by zircon and thorite [6].

In addition, monazite grains with low U and/or Th are common in rocks that have experienced significant fluid involvement, including authigenic precipitation (e.g., [27,51–53]) or retrograde reactions [54–56]. These types of monazites are also found as hydrothermal precipitates [57–59] or in carbonatites (e.g., [60–63]). We would anticipate higher ThO$_2$ content in igneous monazite (3 to >5 wt % ThO$_2$) compared to hydrothermal (0–1 wt % ThO$_2$) [50] or authigenic grains (e.g., 0.63 wt % ThO$_2$, <0.18 wt % UO$_2$) [52]. Although the bright core in monazite grain 1 (Figure 2A) suggests a different origin from the rest of the grain, its sieve-like texture is commonly observed in monazite that has experienced significant fluid involvement [52]. This core may be the result of secondary alteration, but the oscillatory zoning that parallels its boundaries suggests it may be a primary feature. Oscillatory-zoned monazite is also reported primarily from igneous and/or fluid-rich systems (e.g., [12,13,64–66]). In both cases, its composition reflects local feedback between the monazite’s growth surface and the fluid supply of elements (e.g., [64]).

4.2. Insight from Compositional Data

The Llallagua monazite contains some of the highest amounts of F reported for the mineral (0.88 ± 0.10 wt % F, Table 2, Figure 4A–C). Fluorine is an unusual element to be found in monazite, with higher amounts being reported in grains affected by secondary fluid-mediated alteration (0.3–0.6 wt %) [67] as well as those found in rare metal ore deposits (0.48 ± 0.07 wt %) [68]. Fluorine is used to charge balance the huttonite substitution [69] and is thought to play a factor in the enrichment of high-Th monazites [70]. Fluorine-rich fluids are an effective medium for transporting Y and REE in a variety of geologic environments [67,68,71–73], and appear to have no effect on monazite stability [74]. These types of fluids appear to enhance the mobility of Th compared to U and contribute common Pb to monazite [75]. The Llallagua grains show both higher U/Th ratios and common $^{206}$Pb, consistent with this observation. We find F does not vary in concentration from core to rim across the grains (Figure 4A–C).

Fluorapatite is common in the Llallagua mine [5,6,15], and some have speculated that the presence of F in the Llallagua monazite may be due in part of the decomposition of fluorapatite during the final stages of hydrothermal deposition [6,66,76]. Phosphates suggested to form during the dissolution of apatite include wavelite, paravauxite, and childrenite [6]. This process wherein apatite plays a role in the formation of monazite is commonly observed in ore deposits world-wide and can yield monazite with distinctly low amounts of radiogenic elements and higher U/Th, as is observed in these samples [77–82]. Alternatively, the presence of F in monazite may be due to early stage crystallization in the presence of F-rich fluids. In the grains we analyzed, we do not see evidence for the direct replacement of apatite in the monazite textures or zoning.
Monazite BSE zoning is controlled by an interplay of high atomic number (Z, REE) and low Z (Si + Ca + P + Y) elements (Figure 5) and cannot be attributed to a single control. The bright core of monazite grain 1 (Figure 2A) has low CaO (0.2–0.4 wt %), which would not be expected if the grain directly replaced existing apatite. The darker cores in grains 3 and 4 have 1.30–1.05 wt % CaO and are surrounded by oscillatory zoning (Figure 2B,C), suggesting precipitation from a fluid containing in this phase. Monazite and apatite in the Llallagua deposit share substitution mechanisms, including Ca₃REE₂, Ca₃REE₋₁Si₁₋₁, and Ca₃Si₃REE₋₂ (Figure 3). Their SiO₂ (0.17 ± 0.03 wt %) and REE contents may also have been derived from apatite, which is seen in other settings (e.g., [77–79,83]). An Eocene Sm-Nd apatite age [24] is ~20 m.y. older than the monazite [7,11], lending support for the hypothesis of monazite precipitation via the dissolution of pre-existing apatite. Apatite and monazite have been shown to yield similar ages in metamorphic and igneous rocks with any age discrepancies associated with fluid-induced retrogression [84].

Apatite and monazite from the Llallagua deposit share positive Eu anomalies seen in the EPMA data set (Figure 6) [43]. If plagioclase was present in the system during a phase of apatite crystallization, the mineral would likely not show this characteristic [85]. Rare plagioclase phenocrysts are found in the volcanic porphyry, but are often replaced by tourmaline, sercite, quartz, kaolinite, cassiterite or pyrite [6,86]. The LA-ICP-MS data are difficult to evaluate due to the lack of the Sm measurement, but the electron microprobe results suggest the grains record a positive Eu anomaly. Monazite with positive Eu anomalies has been reported from banded iron formations [44], carbonatites [87], lower crustal rocks [88,89], and in metamorphic rocks as inclusions in plagioclase [90]. Fluids with strongly positive Eu anomalies are characteristic of highly reducing conditions [91–94], including back arc basin settings like the Llallagua deposit [95].

Both the EPMA and LA-ICP-MS analyses show the amount of Eu overall in the Llallagua monazite increases from core to rim (Figures 4 and 8), suggesting the mineral sequestered this element from the fluids in which it crystallized. The Eu contents of the monazite grains are high (0.99 ± 0.17 wt % Eu₂O₃, 2719 ± 400 ppm Eu; Tables 2 and 3) compared to those from metamorphic settings (<0.5 wt %) [90].

Overall, the monazite compositions reported here can constrain elements of the fluid chemistry, assist with tectonic interpretations, and suggest mineral reactions. We do not have key field or mineralogical contexts for the grains collected, and our comments regarding its tectonic setting should therefore be interpreted with caution. Despite this, the monazite chemistry reported here provides some clues that are useful for interpreting its origin and the origin of others like it. The results are consistent with the Llallagua monazite forming in a highly reducing environment via the direct precipitation of F- and Eu-rich hydrothermal fluids. These elements may have been supplied by the dissolution of fluorapatite that formed during an earlier tectonic episode. The positive Eu anomalies seen in the grains lend support for reducing conditions.

Monazite is an important REE ore [96–99]. Numerous technological devices are reliant on REE components and demand for these elements is projected to increase [99–101]. Identifying and characterizing known and potential REE sources are important issues facing the public and policy makers [101,102]. Most monazite ore deposits that are economically viable rare earth resources are placer [97,101,103], with rare primary deposits, which include the Van Rhynsdorp and Naboomspruit in South Africa [104], Front Range in Colorado [105], Mountain Pass in California [106], and Bayan Obo in China [107]. Comparisons of our compositional data with those from major monazite ore localities indicate the grains share characteristics (20–30% Ce₂O₃; 10% to 40% La₂O₃, significant amounts of Nd, Pr, and Sm, lesser amounts of Dy, Er, and Ho) [97]. A major environmental concern with the extraction of REEs from monazite is the presence of radiogenic elements [103,108–111]. Compositional analyses and attempts to date the Llallagua monazite have consistently reported its minor U and Th contents (this study, [5,7,11,15,20]). The low radiogenic element content of the Llallagua monazite may help minimize issues associated with waste management.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-9276/6/3/36/s1, Excel file of EPMA and LA-ICP-MS analyses of the monazite grains.
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Author Contributions: E.J.C. conceived and designed the experiments; N.R.M. performed the experiments; E.C. and N.M. analyzed the data; and E.C. wrote the paper.

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