IN SEARCH OF NEW MONAZITE AND TITANITE STANDARD MINERALS FOR *IN SITU* U-Pb GEOCHRONOLOGY.

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Introduction: Monazites and titanites are rare in planetary materials. However, when they do occur, they offer unique opportunities for precise age dating of planetary processes. Monazites occur in some lunar and martian samples [1-6], whereas titanites are relatively common in eucrites [7]. These minerals also occur in terrestrial impact craters [8-11], offering potential opportunity to date impact event with high precision. For some of these applications, a high spatial resolution is required, due to the rarity of the material and small mineral grain sizes (e.g., monazite in martian meteorites) or zoning of the minerals observed in shock metamorphism in terrestrial impact craters. For high spatial resolution techniques such as secondary ion mass spectrometry (SIMS), well-calibrated, homogeneous matrix matched standards are required with highly precise and ideally concordant ages independently dated by isotope dilution thermal ionization mass spectrometry (ID-TIMS). Currently, there are not many suitable standards that meet these criteria. Here we report our first results for two promising minerals, which can potentially serve as such standards for *in situ* U-Pb geochronology by SIMS and *in house* ID-TIMS standard to compare with unknown samples.

Materials and Methods: YQ-82 titanite was separated from an alkaline dyke located in Zhongtiao mountain, China. RW-1 is a gem quality monazite obtained from a mineral dealer, whereas the monazite standard 14-F-1 from Madagascar was kindly provided by L. M. Heaman.

All samples and mineral standards were cleaned in distilled acetone, followed by MilliQ water and 3 M HNO_3 and monazites were additionally cleaned in 0.5 M HCl. Two grains each of the monazite sample RW-1 and the standard 14-F-1 (Madagascar) [12, 13] were dissolved in a series of partial dissolution steps. These were performed in 2.5 M HCl with increasing temperature from 80 to 190°C in 3 ml vials stacked in a Parr dissolution vessel for 15 h each step [12]. The leachate was removed after each dissolution step, spiked with a ^{202}Pb-^{205}Pb-^{233}U-^{236}U spike and evaporated. The samples were redissolved in 6 M HCl and dried down again to ensure sample-spike equilibration. The remaining grain was rinsed three times in MilliQ water before the next leaching step.

Individual titanite grains for sample YQ-82 were selected, washed as described above and spiked with a ^{202}Pb-^{205}Pb-^{233}U-^{236}U spike. The titanites were dissolved on a hotplate in 3 ml Savillex vials in an HF-HNO_3 mixture at 100°C for four days. The solutions were evaporated and the sample redissolved in 6 M HCl, followed by evaporation. U and Pb were separated from the matrix elements using anion exchange resin with HCl based chemistry for monazites [14] and HCl-HBr based chemistry for titanites [15]. Pb isotopes were measured on a *Triton Plus* thermal ionization mass spectrometer in static mode on Faraday cups for monazites and on a MasCom secondary electron multiplier for titanites at UC Davis. During this study, the monazite standard 14-F-1 and a solution standard provided by the EARTHTIME community were monitored to ensure accuracy of the results. Uranium was measured on a *Neptune Plus* multi-collector inductively coupled plasma mass spectrometer in static mode on Faraday cups, coupled with 10^{11} Ω amplifiers except for the ^{235}U cup, which was paired with a 10^{12} Ω amplifier. Data was corrected for solution blank and instrumental mass dependent fractionation using an exponential law based on the known ^{233}U-^{236}U ratio of IRMM-3636 [16], which is the source of U in the U-Pb mixed spike. U-Pb dates were calculated using the algorithms of [17] using the decay constants of [18] and assuming a U/Th ratio of the source magma of 4. The ^{238}U/^{235}U ratio was assumed to be 137.818 for the titanites YQ-82 [19], whereas the measured ratio of 137.704 was used for monazite RW-1. As for monazite standard 14-F-1, the ^{238}U/^{235}U ratio of 137.818 was assumed for comparison with published results in addition to our own measured value of 137.715.

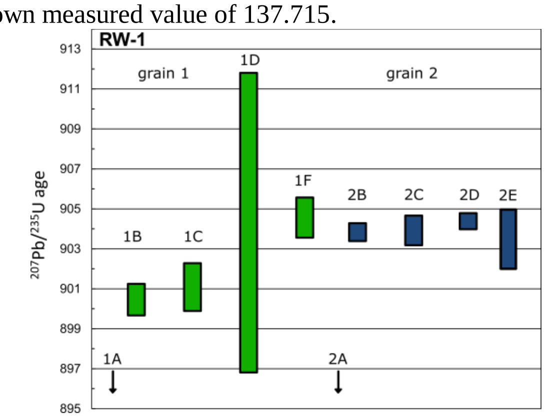

Fig. 1: Leaching steps for the two monazite grains of the sample RW-1 (first step is beyond the scale of the figure, step 1E did not yield usable data).

Results: For all monazites the first leaching step show a significantly different age from the remaining leaching steps. This first leaching step is far less radiogenic than the following steps, most likely removing surface contaminants. The leaching steps become increasingly more radiogenic, though the differences are minor after the third leaching step ($^{206}Pb/^{204}Pb$ >7,000 for RW-1 and >30,000 for 14-F-1). For RW-1, the results from the two grains comprises a total of six leaching steps (1D, 1F, 2B – 2E in Fig. 1), yielding a weighted average $^{207}Pb/^{235}U$ age of 904.15±0.26 (MSWD=1.03, Fig. 1).

For the standard 14-F-1, it was also observed that all Pb contamination was removed by leaching step three and all following steps showed similar radiogenic Pb content. For these monazite grains, however, different domains seem to have dissolved and no single age could be determined from the leaching steps (Fig. 2). Numerically recombining all leaching steps from the third to the last for both grains yield identical $^{207}Pb/^{235}U$ ages with an average of 512.82±0.44 (using a $^{238}U/^{235}U$ of 137.818), compared to 512.11±0.35 Ma of [12] and 512.7±1.8 of [13]. Using the measured $^{238}U/^{235}U$ the $^{207}Pb/^{235}U$ ages is 512.52±0.44. For these monazites only the $^{207}Pb/^{235}U$ ages are considered and no concordance is evaluated due to Th disequilibrium. Monazites incorporate excess ^{230}Th, during crystallization, which decays to ^{206}Pb. Thus monazites typically appear reversely discordant. A correction for this effect is possible if the Th/U ratio of the host rock is known [20].

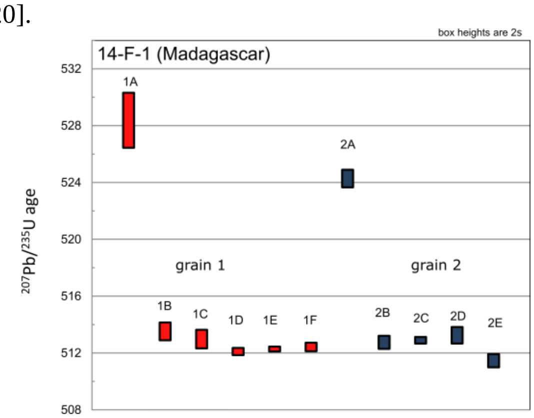

Fig. 2: $^{207}Pb/^{235}U$ ages for the leaching steps of the 14-F-1 monazite standard.

The titanite YQ-82 has very low to no initial common Pb content, which makes it an ideal candidate for a U-Pb standard. The six titanite grains of sample YQ-82 are concordant, when considering the uncertainty in the decay constants. Out of the six titanite grains four agree perfectly, with one being slightly younger and one slightly older grain (Fig. 3). The weighted average $^{206}Pb/^{238}U$ age of the four grains is 1837.6±1.0 Ma (MSWD=1.3), the $^{207}Pb/^{235}U$ age is 1840.93±0.91 Ma (MSWD=2.0) and the $^{207}Pb/^{206}Pb$ age is 1845.0±1.1 Ma (MSWD=2.0) (Fig. 3). During this study the EARTHTIME standard *ET-100* yielded a $^{206}Pb/^{238}U$ age of 100.15±0.06 Ma (n=2, MSWD=0.46).

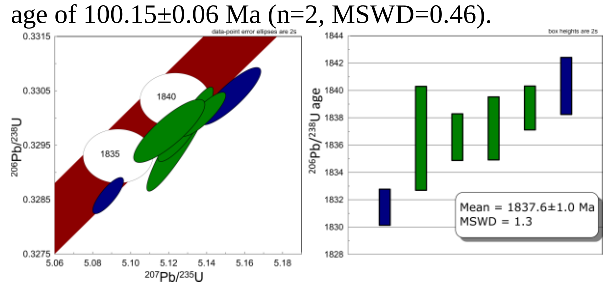

Fig. 3: Concordia diagram and weighted average diagram of the six dated titanite grains of YQ-82. The symbols marked in green were chosen for the age calculation.

Discussion and conclusion: Here we propose new mineral standards for U-Pb geochronology of monazite and titanite. For SIMS U-Pb geochronology, matrix matched standards are a prerequisite to obtain accurate ages. This is especially important for minerals that have a wide range of compositions such as monazites. The Pb/U ratio can be affected by as much as 30% due to differences in composition [21]. Therefore, a wide variety of mineral standards with differing compositions are advantageous.

The titanite YQ-82 is exceptional, due to the very low to non-existent initial Pb compared to other titanite standards [22], which reduces the correction for the initial Pb and therefore improves the precision on the calculated date.

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