U-Pb dating of titanite by LA-ICP-QQQ-MS

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Titanite has the ability to incorporate significant amounts of common Pb, which leads to uncertainty when applying the U-Pb decay series for geochronology. The isobaric interference of ^{204}Hg on ^{204}Pb poses an additional complexity in applying common Pb corrections. Here we investigate the removal of ^{204}Hg interferences during titanite U-Pb dating using reaction cell gas chemistry via triple quadrupole mass spectrometry. U-Pb dates were determined for the natural titanite reference materials MKED-1 and BLR1 using an ESI NWR193^{UC} excimer laser coupled to an Agilent 8900 'triple quad' mass spectrometer. The 8900 is equipped with an octopole collision/reaction cell, which enables online interference removal. Two experiments were run, one in which we collected data in NoGas mode, and one in which NH_3 was used as a reaction cell gas in MS/MS mode, in order to assess the feasibility of determining U/Pb ratios with mass shifted isotopes.

In all experiments, a signal smoothing device was placed inline just before the ICP-MS interface, downstream from the addition of the Ar nebulizer gas to the He carrier gas stream. For the NoGas experiment, titanite was ablated using a 25 μm spot, with a beam energy density of 3 J/cm^2, and a pulse rate of 4 Hz. In NoGas mode, signal intensities for the isotopes ^{201}Hg, ^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{232}Th, ^{235}U, and ^{238}U were counted. In MS/MS mode, titanite was ablated using a 40 μm spot, with a beam energy density of 5 J/cm^2, and a pulse rate of 4 Hz. A larger spot size in this experiment was used to counteract the decrease in signal intensity due to use of the reaction cell. In MS/MS mode, NH_3 was flowed through the reaction cell in order to enable a charge transfer reaction between NH_3 and Hg^+, effectively neutralizing Hg. The isotopes ^{201}Hg, ^{202}Hg, ^{204}Pb, ^{206}Pb, and ^{207}Pb were measured on-mass, as the isotopes of Pb are not affected by the NH_3 gas. Uranium and Th both exhibit partial reaction with NH_3 gas; therefore, the isotopes ^{232}Th, ^{235}U, and ^{238}U were measured mass-shifted up 15 mass units, at masses 247, 250, and 253 respectively.

Ratios of ^{207}Pb/^{235}U, ^{206}Pb/^{238}U, and ^{207}Pb/^{206}Pb were determined using the UPbGeochron4 DRS in Iolite (v.3.71) with MKED-1 as the primary reference material. Dates were calculated using IsoplotR by applying the Stacey-Kramers correction for common Pb. All isotopes of Hg were effectively neutralized by the NH_3 charge transfer reaction in MS/MS mode; zero counts were detected for Hg isotopes. Dates for the BLR-1 titanite were 1050.55 ± 2.72 (2σ, n=12) Ma in NoGas mode, and 1048 ± 1.88 (2σ, n=15) Ma in MS/MS mode. These dates are in excellent agreement with the TIMS ^{206}Pb/^{238}U date for the BLR-1 titanite of 1047.1 ± 0.4 Ma. This method has the potential to enable measurement of ^{204}Pb without needing to correct for Hg interferences.