

Using triple quadrupole interference removal to improve data quality in laser ablation ICP-MS for geochemical applications

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Uranium-lead dating

Goal

To demonstrate effective interference removal using the Thermo Scientific iCAP TQ ICP-MS and subsequent data quality improvements on geochemical samples analyzed by laser ablation ICP-MS.

Introduction

Geological samples are inherently complex matrices that are difficult to digest without using very aggressive acids and digestion techniques. Laser ablation overcomes sample preparation difficulties and makes it easier to analyze these samples by inductively coupled plasma mass spectrometry (ICP-MS). Another important advantage is the ability to perform spatially resolved analysis of specific areas in a sample, allowing visualization of the distribution of trace elements using elemental mapping (a.k.a. laser ablation imaging), which can provide insights into geological processes.

By its very nature, however, laser ablation sampling prohibits pre-analysis sample cleanup using techniques such as solid phase extraction or column separation. This means there is a high probability that matrix induced interferences on analytes of interest exist. Isobaric interferences, in particular, are difficult to overcome using either single quadrupole ICP-MS with kinetic energy discrimination (KED) or high resolution (HR) ICP-MS; however, triple quadrupole based ICP-MS instruments offer a new way to efficiently overcome isobaric interferences, based on selective chemical reactions inside a collision/reaction cell system (CRC).

This application note focuses on three geological systems in particular that can suffer from difficult isobaric interferences, namely uranium-lead geochronology, hafnium isotope analysis and rare earth element (REE) determination.

Uranium-lead geochronology

For this application, radiogenic lead isotopes are used to calculate the age of accessory minerals such as zircons. Zircon crystals incorporate uranium (and thorium) into their crystal lattices, which then radioactively decay to specific isotopes of lead. The decay chains are well understood, and the decay constants for conversion are known (see Table 1)¹.

Table 1. U-Th-Pb Geochronometer system decay constants and half-lives.

Parent Nuclide	Daughter Isotope	Decay Constant (yr ⁻¹)	Half Life (yr)
²³⁸ U	²⁰⁶ Pb	1.55 × 10 ⁻¹⁰	4.47 × 10 ⁹
²³⁵ U	²⁰⁷ Pb	9.85 × 10 ⁻¹⁰	7.04 × 10 ⁸
²³² Th	²⁰⁸ Pb	4.95 × 10 ⁻¹¹	4.95 × 10 ¹⁰

Zircon crystals are closed systems, and lead can only be incorporated through crystallization (or re-crystallization), so it is possible to assign amounts of ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb to decayed ²³⁸U, ²³²Th and ²³⁵U respectively and thus determine an accurate age for when the host rock cooled.

Any natural lead present in the system, either by contamination or during crystallization, needs to be accounted for. ²⁰⁴Pb is free from radiogenic sources, so can be used for so-called ‘common lead’ correction; however, ²⁰⁴Hg interferes with the ²⁰⁴Pb signal. Ammonia gas is effective at removing mercury from the ion beam through a charge transfer reaction, leaving lead ions unaffected. REEs in the sample can also react with ammonia and form ions on *m/z* 204, so additional mass filtration using Q1 is required to avoid potential formation of new interferences on the product ions (see Figure 1).

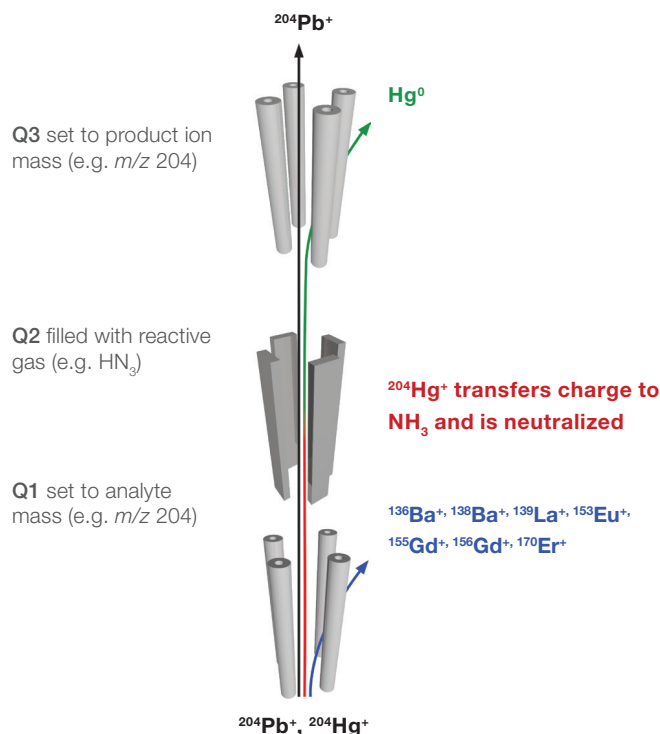


Figure 1. Schematic of triple-quadrupole interference removal of ²⁰⁴Hg from ²⁰⁴Pb signals. Q1 removes REE elements that can form interfering product ions and mercury is removed through charge transfer to ammonia.

Hafnium isotope petrogenesis

Hafnium isotopes are used to determine the petrogenesis of igneous rocks, and can be used to show crust or mantle mixing and weathering cycles. Changes in the hafnium 176/177 ratio show whether the host rock was formed in the Earth’s crust or in the mantle, all referenced to the Chondrite Uniform Reservoir (ChUR) meteorite reference ratio:

$$\epsilon_{\text{Hf}} = \left[\frac{\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}} \right)_{\text{Smpl}}}{\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}} \right)_{\text{ChUR}}} - 1 \right] \times 10^4$$

A negative value of ϵ suggests the igneous rock was formed in the Earth’s crust, whereas a positive value suggests a mantle source. Changes in this ratio can also show up migration or weathering cycles of heavy sediments. The ¹⁷⁶Hf/¹⁷⁷Hf ratio measurement is, however, complicated by isobaric interference on ¹⁷⁶Hf from ¹⁷⁶Lu and ¹⁷⁶Yb (see Figure 2).

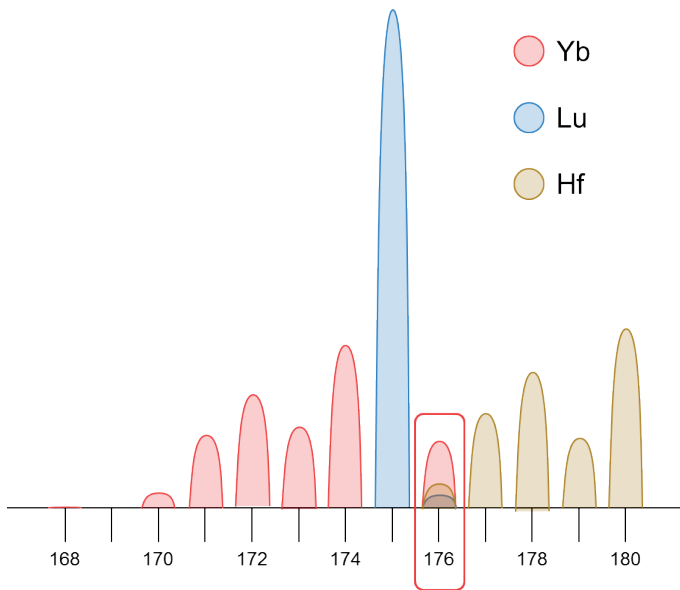


Figure 2. Schematic Spectra of Lu, Yb and Hf showing isobaric overlap at m/z 176.

Hafnium reacts with ammonia whereas lutetium and ytterbium do not, so hafnium can be measured directly using a mass shift reaction. REEs in the sample can potentially interfere through ammonia cluster formation, so these are filtered using Q1 (Figure 3). Since REEs are present in almost all samples where hafnium isotopes would be measured, single quadrupole ICP-MS systems, which do not have the ability to filter the ion beam prior to reaction, cannot do this application in this way.

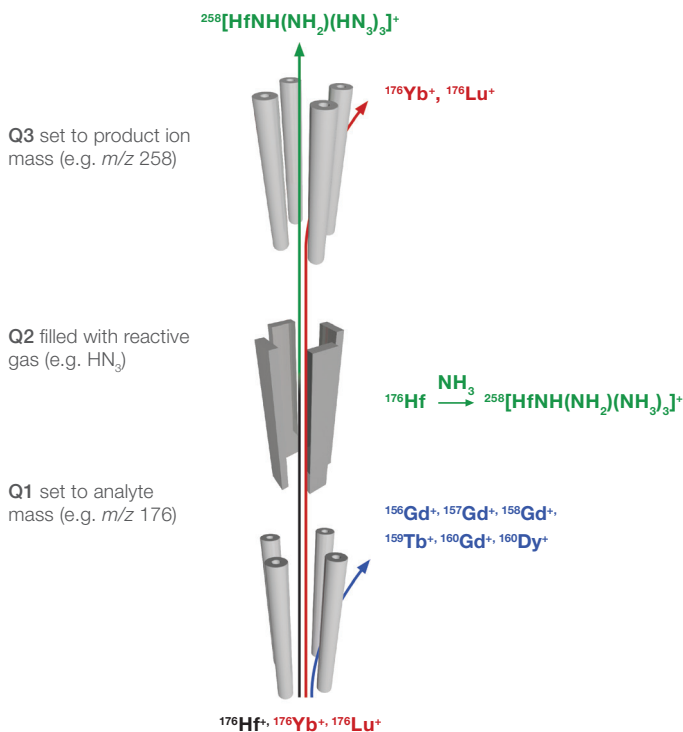


Figure 3. Schematic of triple-quadrupole interference removal of ^{176}Lu and ^{176}Yb from ^{176}Hf signals. Q1 removes REE elements that can form interfering product ions and hafnium is mass shifted with ammonia.

Rare Earth Element systems

During the birth of the planet, REEs were set at a particular concentration and distribution. Much like hafnium fractionation, the 'heavy rare earths' (Y, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) show less enrichment in the Earth's crust than the 'light rare earths' (Sc, La, Ce, Pr, Nd, Pm, Sm and Eu), relative to chondrite meteorite reference materials (which are taken as references for the original REE concentrations). Consequently, a material's REE composition is characteristic of a particular geological zone.

Laser ablation enables visualization of the REE distribution in mineral grains using elemental mapping. Time-resolved changes associated with initial growth or partial melting and re-crystallization can be seen, and tectonic or anthropogenic effects can be inferred.

Most polyatomic interferences in REE determinations can be removed using KED, which can obtain good results, but signal attenuation in this mode is a problem that is detrimental to detection limits. Oxygen mass shift, on the other hand, can be beneficial to a number of REEs and other trace metals and does not attenuate ion signals as much as KED.

Sample preparation

To assess U-Pb and Hf isotope performance, standard zircon grains (91500 and Plešovice) were mounted in a 1-inch circular epoxy puck and the surface polished flat. For REE distribution maps, thin sections of eclogite-blueschist rocks containing garnet grains were supplied pre-mounted and polished flat. The zircon standard puck, a polished NIST SRM 612 glass standard and the thin section were all mounted in a standard sample holder (supplied with the LA system) and placed into the LA sample chamber.

Instrumentation

A Thermo Scientific™ iCAP™ TQ ICP-MS was coupled to a Teledyne CETAC Technologies LSX-213 G2+ Laser Ablation System when used to analyze the U-Pb system and Hf isotopes in zircon grains, and coupled to a Teledyne CETAC Technologies Analyte G2 Excimer Laser Ablation System when used to map the REE distribution in garnet crystals. The choice of appropriate method settings (e.g. triple quadrupole vs. single quadrupole operation, reactive gas used and product ions to be analyzed in Q3) was accomplished using the Reaction Finder method development assistant in the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software. Reaction Finder selects optimum analysis conditions despite the many available options inherent when using a triple quadrupole ICP-MS, but also leaves flexibility for testing different settings for a particular analyte.

Thermo Scientific iCAP TQ ICP-MS

U-Pb Geochronology and Hf Isotopes

RF power	1100 W
Nebulizer gas	0.465 L·min ⁻¹
NH ₃ flow	0.280 mL·min ⁻¹
Dwell time per <i>m/z</i>	0.02 s

REE Mapping

RF Power	1550 W
Nebulizer gas	0.867 L·min ⁻¹
O ₂ flow	0.205 mL·min ⁻¹
KED He flow (for comparison)	4.18 mL·min ⁻¹
Dwell time per <i>m/z</i>	0.025 s

Teledyne CETAC Technologies LSX-213 G2+ LA System

Total He flow	0.92 L·min ⁻¹
Sample transfer kit	Standard Aerosol Transfer System
Laser fluence	~4 J·cm ⁻²
Spot size	50 μm
Repetition rate	20 Hz
Burst count	1200 Shots (60 secs)
Samples	Zircons (U-Pb Geochronology and Hf Isotopes)

Teledyne CETAC Technologies Analyte G2 LA System

Total He flow	0.75 L·min ⁻¹
Sample transfer kit	Aerosol Rapid Introduction System (ARIS)
Laser fluence	~4 J·cm ⁻²
Spot size	5 μm square
Repetition rate	100 Hz
Line Scan rate	23 μm·sec ⁻¹
Samples	Garnet grains (REE Distribution)

Data Processing

For zircon analyses, zircon 91500 was used as the reference material for both U-Pb ages and Hf mass bias correction. Results consequently reported are calculated from data obtained from the Plešovice zircon.

Data processing for U-Pb ages was performed using *iolite*™ Software, using a built-in data reduction scheme that corrects for gas blank baselines, downhole fractionation and common lead correction, according to the procedure developed by Paton *et al.*². Hf isotope data were processed manually using Microsoft™ Excel® software. Mass bias correction was performed using the exponential model detailed by Yang and Sturgeon³.

Garnet elemental distribution maps were baseline corrected and maps generated using the CellSpace™ procedure within the *iolite* Software, based on algorithms detailed by Paul *et al.*⁴.

Results

Uranium Lead Geochronology

Table 2. Results obtained for Plešovice zircon using zircon 91500 as a reference for downhole fractionation correction, common lead correction and age determination (TQ-NH₃ mode).

Value	Reference	Measured (±2σ)
$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	0.05372	0.05255 ± 0.00071
$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	0.395	0.391 ± 0.017
$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	0.05321	0.05372 ± 0.00084
206/238 Age		330.1 ± 4.3 Ma
207/235 Age	337 Ma	334 ± 12 Ma
207/206 Age		337 ± 32 Ma

The results shown in Table 2 show that by using TQ-NH₃ mode with the iCAP TQ ICP-MS, accurate isotope ratios and accurate age data can be easily achieved. Any mercury in the system has been effectively removed by reaction with NH₃, and the reaction chemistry has not adversely fractionated the signals. The ages calculated using *iolite* Software agree very closely to the accepted ages for the Plešovice zircon*, with good precision.

*Reference age data from www.plasmage.org/reference-materials

Hafnium Isotopes

The isotope pattern of the Hf-ammonia clusters shows that the mass shift reaction efficiently and effectively removed Yb and Lu interferences on ¹⁷⁶Hf and does not produce significant mass fractionation (Figure 4).

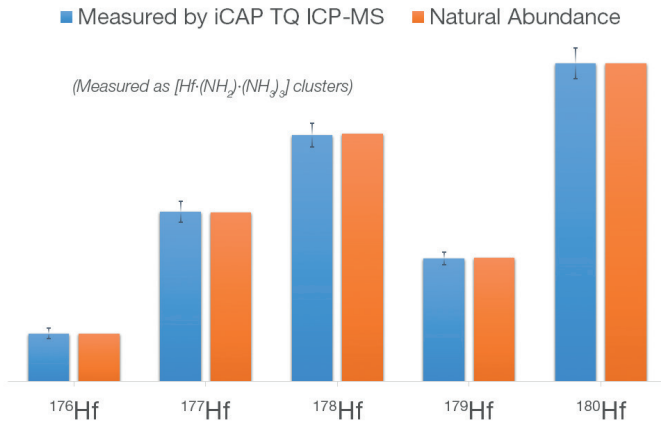


Figure 4. Isotope Pattern for $\text{Hf}(\text{NH}_2)(\text{NH}_3)_3$ clusters obtained using the iCAP TQ ICP-MS from Plešovice zircon grains (after mass bias correction using Zircon 91500 as a reference).

The results shown in Table 3 show that the isotope ratios measured have good accuracy; however, the precision is in the percent range. This is a general limitation of sequential scanning instruments (such as all quadrupole based ICP-MS systems) and the secondary electron multiplier (SEM) detectors used by them. The precision range observed in this study covers all known zircon standards for their hafnium isotope ratios.

No detailed conclusion on the sample's history can be drawn with this data alone, but the data shows the power of triple quadrupole ICP-MS as a tool for the removal of isobaric interferences affecting ^{176}Hf .

The approach demonstrated in this study using a mass shift is probably applicable for lutetium-hafnium isochrons for geochronology, but the Plešovice samples do not have enough variability in Lu to confirm this.

Table 3. Hf isotope ratios measured by the iCAP TQ ICP-MS using TQ- NH_3 mode, measuring $\text{Hf}(\text{NH}_2)(\text{NH}_3)_3$ clusters

Isotopes	Reference Ratio	Measured Ratio ($\pm 2\sigma$)	Relative Precision
$\frac{^{176}\text{Hf}}{^{177}\text{Hf}}$	0.282475	0.281939 ± 0.001767	$\pm 0.63\%$
$\frac{^{178}\text{Hf}}{^{177}\text{Hf}}$	1.46721	1.449725 ± 0.021585	$\pm 1.49\%$
$\frac{^{180}\text{Hf}}{^{177}\text{Hf}}$	1.886703	1.873135 ± 0.040113	$\pm 2.14\%$

For precise Hf isotope data, it is advisable to use a (simultaneously scanning) multicollector system such as the Thermo Scientific™ NEPTUNE™ Plus MC-ICP-MS, as the attainable precision with this instrument is significantly better than that which can be achieved with quadrupole instruments fitted with SEM detectors (highlighted in Figure 5).

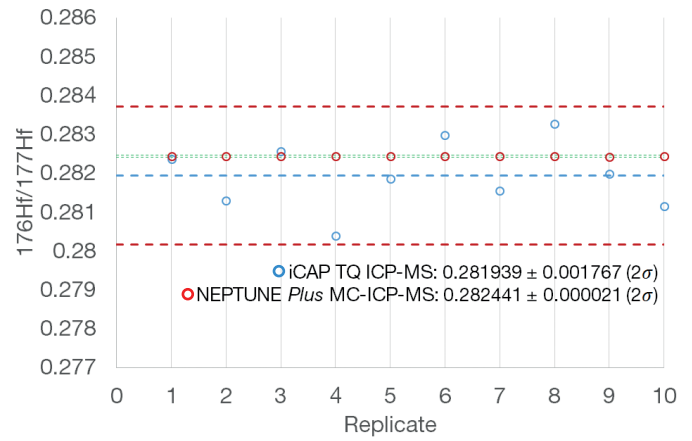


Figure 5. Attainable precision for a quadrupole instrument fitted with an SEM detector is not as precise as a multicollector ICP-MS, which is much better suited to high precision isotope ratio measurements.

REE Mapping

The garnet grains mapped were spessartine crystals, which means they are rich in manganese. Partial melt and re-crystallization shows up as clear zones in the Mn distribution. Sc and Y can be used as proxies for light and heavy REEs respectively, saving on scanning time and improving attainable map resolution. The maps generated by scanning these three elements are presented in Figure 6.

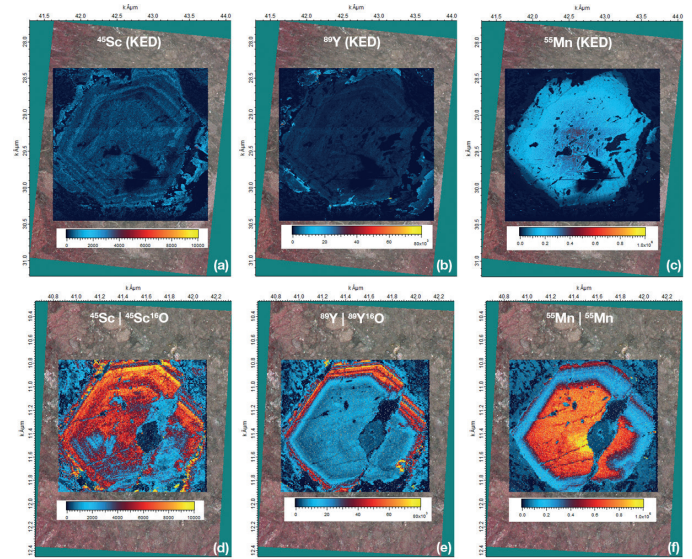


Figure 6. Element distributions maps for (a) ^{45}Sc by SQ-KED, (b) ^{89}Y by SQ KED, (c) ^{55}Mn by SQ KED, (d) ^{45}Sc in TQ- O_2 as $^{45}\text{Sc}^{16}\text{O}$, (e) ^{89}Y in TQ- O_2 as $^{89}\text{Y}^{16}\text{O}$ and (f) ^{55}Mn in TQ- O_2 as ^{55}Mn

Both grains are from the same thin section and should show similar zoning. TQ-O₂ has much higher sensitivity than SQ-KED, so the contrast is greater in the elemental maps and Mn zoning can be seen showing that these grains partially melted and re-crystallized in a manganese deficient geological environment. The Sc distribution remains equal, but the Y distribution is enriched suggesting the partial melt and re-crystallization occurred in a geological environment dominated by the Earth's mantle.

These maps also highlight that the design of the QCell in the iCAP TQ ICP-MS means that high transmission is maintained with TQ-O₂ mode for those elements where on mass analysis is appropriate; therefore, all REE elements can be measured in the same mode without compromising data quality.

Conclusion

Selective interference removal is easily achieved with the Thermo Scientific iCAP TQ ICP-MS, allowing accurate uranium-lead ages to be calculated, precise hafnium isotopes to be measured, and high contrast elemental maps to be generated.

Acknowledgments

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