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NEW FRONTIERS IN ISOTOPE RATIO MEASUREMENT USING COLLISION CELL, MULTI-COLLECTOR PLASMA MASS-SPECTROMETRY

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Tim Elliott was piqued by the potential of isotope geochemistry as an undergraduate in Geological Sciences in Cambridge in the mid-80s. The pleasing opportunity the discipline offered to make some big statements about the Earth was reinforced during a PhD with Chris Hawkesworth and Peter van Calsteren at the Open University, studying the melting behaviour of the mantle beneath the ocean islands of La Palma and Iceland. In 1991 Tim headed for the US on a NATO fellowship to work at Lamont Doherty Geological Observatory in the lab of Alan Zindler. This was an eye-opening experience into the wider world of isotope geochemistry and beyond, but with a more specific focus on element fluxes at the Marianas. Five years in Amsterdam saw Tim hone lab skills and write up data from years before- there was somewhat less immediate career pressure back then. Tim returned to the UK in 1999, to help form the Bristol Isotope Group and start a collection of mass-spectrometers in the Will Memorial basement. The latest of these is the subject of this presentation.

ABSTRACT

We present the design concept and capabilities of a novel isotope ratio mass-spectrometer. We have coupled components from a modern, inductively coupled plasma, quadrupole mass-spectrometer (Thermo Fisher Scientific iCAP Q) with a multi-collector, inductively coupled multi-collector (Thermo Fisher Scientific Neptune plus). This ‘tribrid’ instrument with a rapid scanning mass filter and collision cell placed before an independent double-focussing, sector mass-spectrometer is dubbed Proteus. The specificity of ion-gas reactions in the collision cell achieves results equivalent to very high mass resolution. The collision cell is operated together with quadrupole running in one of three modes i) full transmission, ii) mass window, transmitting only the ions of the target element, iii) single mass resolution either scanning or static. This arrangement is unique to sector, isotope ratio mass-spectrometers and makes possible a wide range of new measurements we describe.

1. INTRODUCTION

Multi-collector, inductively coupled plasma mass-spectrometers (MC-ICPMS) have transformed inorganic isotope ratio mass-spectrometry. The plasma source allows nearly all elements to be ionised sufficiently well to permit isotope ratio measurement and it can be readily attached to introduction devices enabling rapid throughput of purified samples or *in situ* analyses using laser ablation. Yet unselective ionisation and ready aspiration also lead to unwanted effects of interferences from matrix and gas species (derived from the plasma, air and sample solution). While some interferences can be avoided using prior chemical separation, careful control of tuning conditions and moderate mass resolution (M/ΔM to ~10,000), others are unavoidable and limit the full potential of MC-ICPMS.

An important solution to these problems has been developed in the form of collision cells. These are gas-filled ion-guides, in which ions react with the gas, either removing the interferences from the target ions or vice versa. Despite the success and wide application of these devices in single collector, quadrupole mass-spectrometers [1], their combination with MC-ICP-MS has been very limited. A notable exception was the Micromass Isoprobe, which used a gas filled hexapole as both a focussing component (to thermalise the ion beam before a sector mass analyser) and collision cell. This instrument is no longer manufactured, but the use of a collision cell with MC-ICP-MS remained an attractive prospect. To this end we built a new collision cell sector mass-spectrometer, Proteus, with wider capabilities and building on some lessons from Isoprobe.

2. INSTRUMENT DESIGN

The Proteus comprises a low energy (500V) ‘front end’ dominantly composed of components from the Thermo Fisher Scientific iCAP Q (coloured parts of Fig. 1) and a high energy (10 kV), standard

Thermo Fisher Scientific Neptune Plus MC-ICPMS collector end (grey parts in Fig. 1). The plasma torch (blue, Fig 1) and 90° bend (to remove neutrals, yellow in Fig. 1) deliver ions to the RF quadrupole (purple, Fig 1). The beam then passes through a rapidly switchable, electrostatic lens to either the collision cell (red, Fig 1) or secondary electron multiplier (green, Fig 1). Initially a standard iCAP Q collision cell was used but this was subsequently changed to a 'drag cell', in which an electric field can be applied along the axis of the cell to enhance extraction of ions. In order to minimise possible generation of organic interferences within the collision cell, the device is bakeable and the gas feed lines are made from high grade steel with getters and low polymer mass-flow controllers (Fig. 2). A transfer lens couples the 'front end' to the 'collector end'.

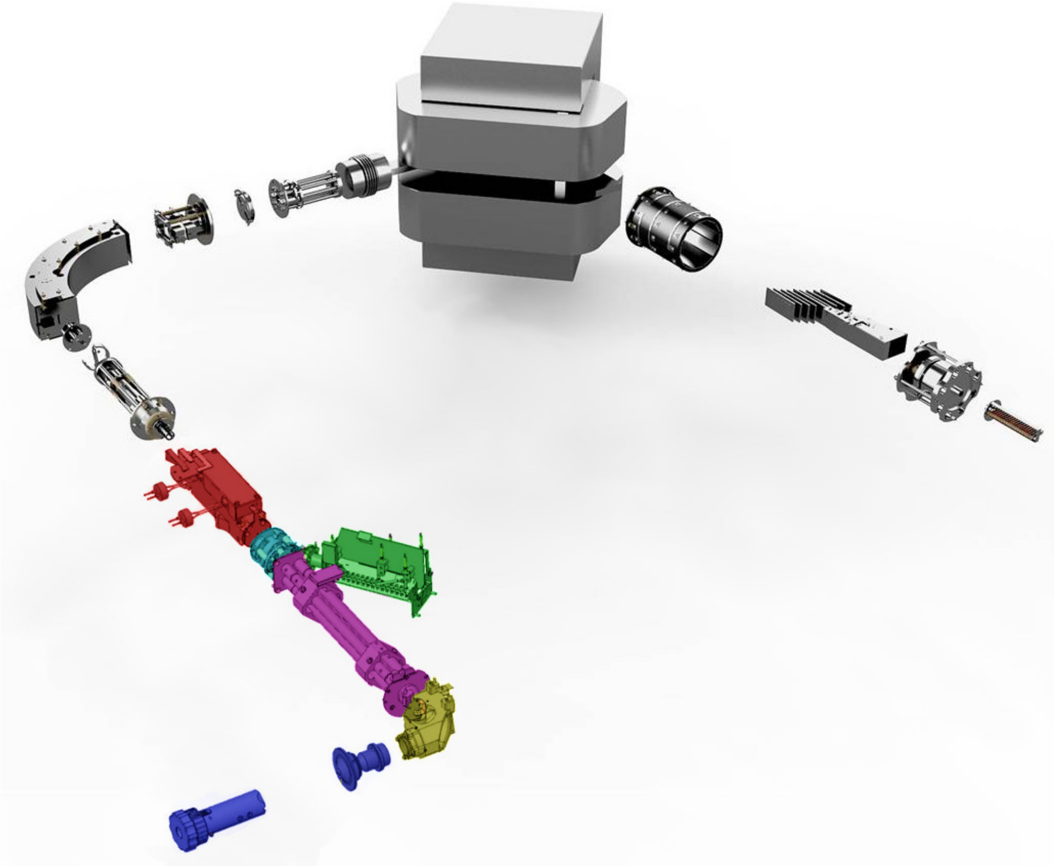

Figure 1. Schematic of Proteus (see text for details).

Using a term from organic mass-spectrometry, we describe Proteus as a 'tribrid' to distinguish the arrangement of ion-optical devices from other MC-ICP-MS (Micromass Isoprobe, a rare option on the Fisons Axiom and most recently the Nu Sapphire). The combination of quadrupole mass filter with collision cell before the collector end allows three main modes of operation, for this tandem mass-spectrometer.

Figure 2. Photograph showing ‘front end’ of Proteus (top of screen), with sample line leading from Apex desolvator to torch, and gas delivery controls to collision cell (bottom of screen).

i) Full transmission, where the quadrupole is set to give no mass-filtering. This mode is used for conventional isotope ratio measurements (with the collision cell is filled with He to provide collisional focussing but no specific reactions) or for measurements in which the interference is removed from the target mass spectrum (e.g., $^{40}Ar^+$ removed from $^{40}Ca^+$).

ii) Wide Window, where the quadrupole is set to transmit only a given mass range (typically ± 8 amu around a central mass). In this mode, the target ions are allowed into the collision cell but the rest of the mass-spectrum is removed (Fig. 3). This is useful for schemes in which the target ions react with the collisional gas to produce new, higher mass molecular ion species (e.g., $^{86}Sr^+$ reacts with CH_3F to produce $^{86}SrF^+$). The quadrupole windowing ensures that the reacting ions are ‘promoted’ as molecular ions into an interference free part of the mass spectrum.

iii) Single mass resolution, where the quadrupole runs with a conventional single mass unit window. In this mode, either the quadrupole can make a rapid mass scan (as in traditional ICP-MS) or remain static. The former can be used to analyse or characterise the beam before the collision cell, in conjunction with the switching lens, which causes the beam to be deflected ~150° into an off-axis secondary electron multiplier (Fig. 1). The latter routine excludes all ions other than a single target mass from the collision cell. This can notably reduce interfering secondary ions produced by an adjacent beam entering the collision cell, e.g., hydrides and helps achieve high abundance sensitivity.

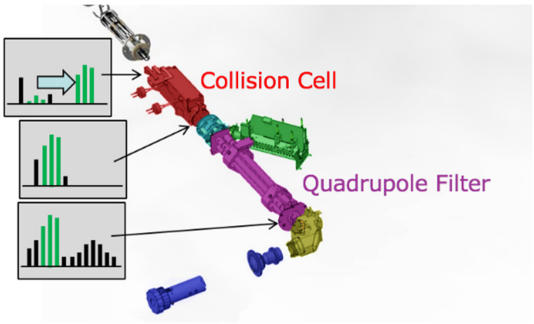

Figure 3. Cartoon of window mode, showing full spectrum entering quadrupole with target ions in green. Quadrupole removes isotopes at masses higher (and lower, not shown) than window around masses of interest. In collision cell, target ions react with gas to produce heavier molecular ion species that are 'promoted' to the clean part of the mass spectrum.

An example of each of these measurement modes is given below.

3. *APPLICATIONS*

3.1. Ca isotope measurements

An $^{40}Ar^+$ interference many times greater than potential sample $^{40}Ca^+$ ions is an inevitable consequence of using an Ar plasma on conventional MC-ICP-MS. Yet $^{40}Ar^+$ ions can be very effectively charge neutralised with H_2 ($^{40}Ar^+ + H_2 \rightarrow {}^{40}Ar + H_2^+$) and, therefore, removed from the spectrum [2]. A few ml/min H_2 supplied to the collision cell, as part of a H_2/He mix, is sufficient to near quantitatively remove the $^{40}Ar^+$ signal. This enables measurement of Ca isotope ratios, either for determination of radiogenic $^{40}Ca/^{44}Ca$ (internally normalised to $^{42}Ca/^{44}Ca$) or double-spiked analysis for mass-dependent Ca isotope fractionation. Although thermal ionisation mass-spectrometry is an alternative, it is both slow and has proven surprisingly difficult to obtain reproducibility <100 ppm (2 sd) [3].

We have analysed samples in full transmission mode, with a He/H_2 reaction gas. A 5µg/g Ca solution yields ~1.1 nA Ca beam (aspirating at ~50 µl/min) and we obtain measurements reproducible to <50 ppm (2 sd) when bracketed and normalised to standard solutions. This work documents that despite the more complex ion-optics of the low energy front end, high precision isotope ratio measurements can be obtained. Similarly, measurements of Nd isotope ratios over a year were within the standard Neptune specifications.

3.2. Laser ablation $^{87}Sr/^{86}Sr$ measurements

There are several important beta decay systems in geology that make valuable chronometers, perhaps most notably $^{87}Rb \rightarrow {}^{87}Sr$. Analysing phases with high Rb/Sr should yield precise ages, but this requires time-consuming mineral separation, as well as dissolution and chromatographic separation of Rb and Sr. *In situ* approaches to make this process more time efficient seem precluded because the best samples to be dated inevitably have the largest interference of parent on daughter (for beta decay systems, in contrast U-Pb chronology used in zircons). An extreme mass resolution of 280,000 (M/ΔM) would be required to magnetically separate ^{87}Rb from ^{87}Sr sufficiently for measurement. Collision cell mass-spectrometry makes such measurements possible using ion-specificity.

Appropriate collision gas reaction for a range of geologically interesting examples are documented by Bandura et al. [4]. There are several options for Sr but we have initially used SF_6, which efficiently produces SrF^+ ions with Sr^+ but leaves Rb^+ ions unreacted. A spectrum produced by aspirating a 6 µg/g Rb solution with a 200 ng/g Sr solution (NIST 987) shows that Sr is quantitatively removed from interfering Rb by reaction with SF_6 and promoted to a clear part of the spectrum produced by quadrupole windowing around the Sr^+ masses (Fig. 4). Measurements of this experiment yielded $^{87}Sr/^{86}Sr$ measurements within error of accepted NIST 987 values.

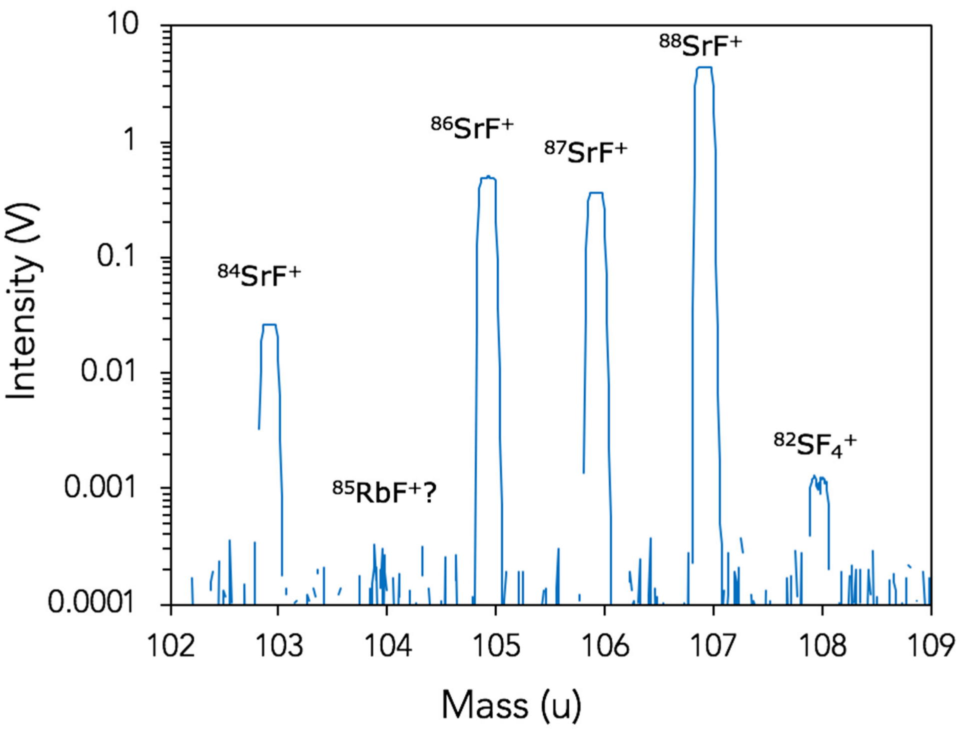

Figure 4. Spectrum of SrF with negligible Rb interference from an initial solution with initially 30x more Rb than Sr (see text). Note the logarithmic y-axis scale of beam intensity (V using amplifiers with 10^{11} ohm resistors).

This lays the way for laser ablation measurements. The potential of this approach has explored using single collector mass-spectrometers [5, 6], but multi-collection on Faraday cups, possible on Proteus, offers much higher accuracy and precision.

3.3. *High abundance sensitivity tandem mass-spectrometry*

Compared to thermal ionisation mass-spectrometers, the scatter and energy spread in MC-ICP-MS results in poorer abundance sensitivity and greater difficulty in accurate measurement of minor isotopes next to major ones. Thermalisation of the ion beam in the collision cell (using He as the cell gas) improves the abundance sensitivity of Proteus relative to a standard Neptune (for example 12 ppb at 1 amu for Proteus in with ± 8 amu quadrupole window versus ~500 ppb for Neptune, both instruments using a final retarding filter before collection on axial secondary electron multiplier, SEM). However this can be further improved by decreasing the quadrupole window to allow only single masses through and sequentially measuring major and minor beams using different quadrupole settings (collecting the beams on Faraday and SEM respectively).

We have explored this approach for ^{210}Pb, of interest as a part of the ^{238}U decay chain with a typical secular equilibrium ^{210}Pb/^{238}U ratio ~1x10^{-9}. We have obtained a 5 ± 1ppt abundance sensitivity at mass 210 relative to an intense ^{208}Pb beam. From scanning the spectrum, it is clear than this value represents a discrete peak (^{208}PbH$_2^+$ created in the plasma?) and so is not the ultimate abundance sensitivity achievable. This capability is of interest to monitoring dangerous short-lived radio nuclides in the environment (e.g., ^{129}I, ^{133}Cs), cosmogenic nuclides (e.g., ^{10}Be) as well as providing a mass-spectrometric means to measure ^{210}Pb for dating sedimentation and volcanic degassing.

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