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Applications of a high performance ion detection system to the analysis of geological samples by sector field ICP-MS

Authors

L. Rottmann,
Thermo Fisher Scientific,
Bremen, Germany;
A. Klügel, H. Anders, H. Kuhnert,
University Bremen, Department of
Geosciences, Bremen, Germany

Keywords

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Goal

To demonstrate the
ideal suitability of the
Thermo Scientific™
Element 2™ High Resolution
ICP-MS for trace metals
analysis in high purity samples,
related to the manufacture of
semiconductors.

Introduction

The ion detection system of an ICP-MS plays an important role in the automated (user interaction-free) determination of unknown samples containing trace and major elements.

The use of the high performance ion detection system of the Thermo Scientific™ Element 2™ High Resolution ICP-MS is demonstrated here in two different geological applications with a wide range of concentrations within the sample.

1. The Ion Detection System

There are several challenges in designing a modern ion detection system for an ICP-MS. The following criteria should be fulfilled:

- Fast and reliable

- Low Dead Time

- Detection of ultra-traces and major elements in unknown samples in a single analysis

- Detection of transient signals

- Automatic detection without user interaction

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The detection system of the Element 2 HR-ICP-MS consists of a conversion dynode, a discrete dynode SEM and reliable detection electronics.
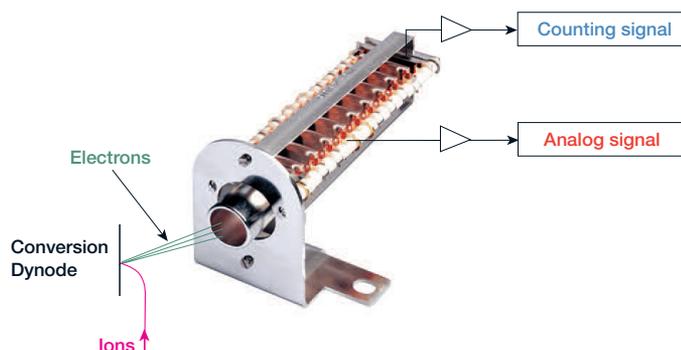
Figure 1. Element 2 HR-ICP-MS Ion Detection System.

Properties of the Element 2 HR-ICP-MS detection system:

- Acquisition time down to 100 µs in counting mode

- Dead time ~ 25 ns

- Dynamic range > 10^9

- Simultaneous determination of analog and counting signal (< $5 \cdot 10^6$ cps)

- "Both" mode that allows the detection system to choose the correct detector mode based upon the signal detected

- Automatic cross calibration for each spectrum

- Mass independent detector response (due to high kinetic energy of the ions)

- Automatic protection of the SEM (counting part)
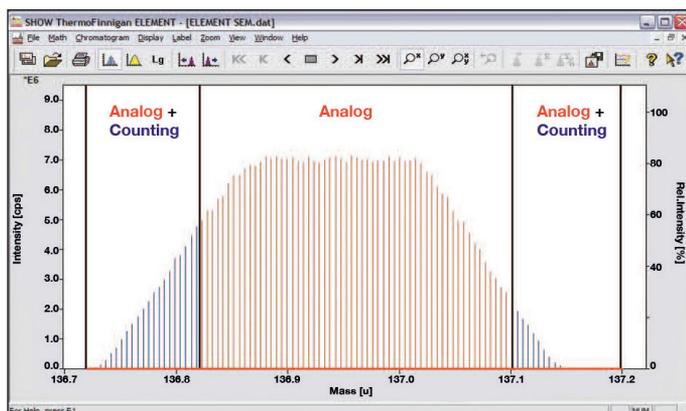
Figure 2. Spectrum measured in "Both" mode.

2. Trace element analyses of volcanic rocks from Madeira

The Madeira Archipelago consists of five volcanic islands reflecting plate motion over a hot spot. The concentrations of thirty-seven trace elements in basalts from four islands were determined in order to reconstruct their geochemical evolution and to constrain the nature of the mantle source.

Experimental Data
Sample preparation:
- Digestion of rock powders (HF / aqua regia)

- Dilution with HNO_3 (final dilution factor = 5000)

- Addition of internal standard (In).

Analysis:
- Instrument: Element 2 HR-ICP-MS

- 15 isotopes in low-resolution (LR)

- 8 isotopes in medium-resolution (MR)

- 16 isotopes incl. rare earth elements (REE) in high-resolution (HR)

Intensity range:
- 300 – $1.1 \cdot 10^8$ cps (up to 10^5 in a single sample).

Results
The element concentrations determined ranged from <0.02 µg/g in the solid (Thallium) to >1000 µg/g (Strontium) (Figure 3). The REE spectra show smooth curves in chondrite normalized diagrams (Figure 4). Analytical precision is better than 3% for most elements in LR and MR modes and 5% in HR mode. Replicate analyses of USGS reference materials yielded accuracies of >95% for most elements (Figure 5).

Interpretation
The strong enrichment of the light relative to the heavy REE (Figure 4) is typical of oceanic island basalts (OIB). It indicates garnet as a residual phase in the source of the basalts, implying melting depths of >80 km. Variations between the samples are attributed to varying degrees of olivine and clinopyroxene fractionation, but not plagioclase since negative Eu anomalies are not observed.
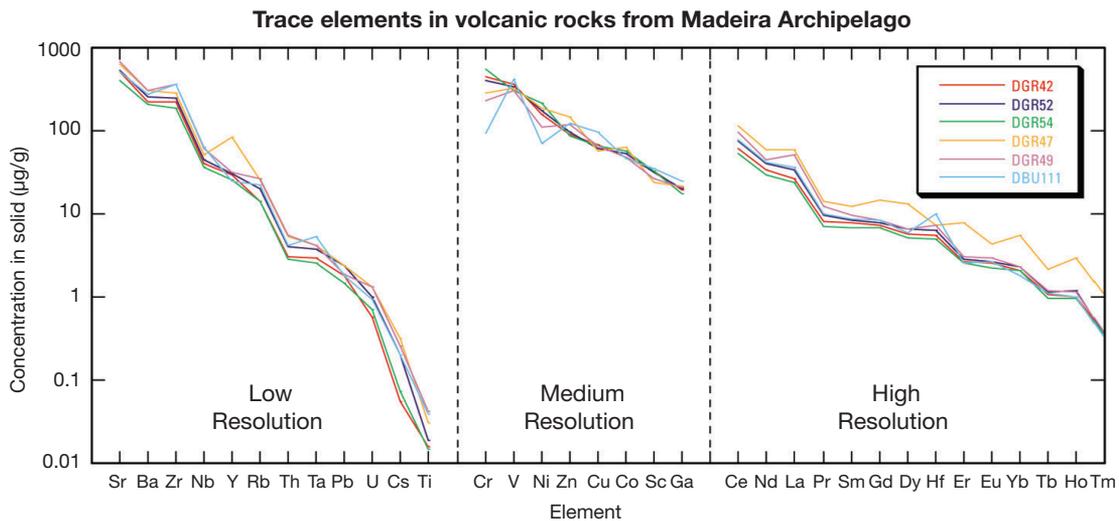
Figure 3. Trace element concentrations of selected samples, ordered by overall abundance and resolution chosen for analysis. Measured concentrations span a range of almost five orders of magnitude.
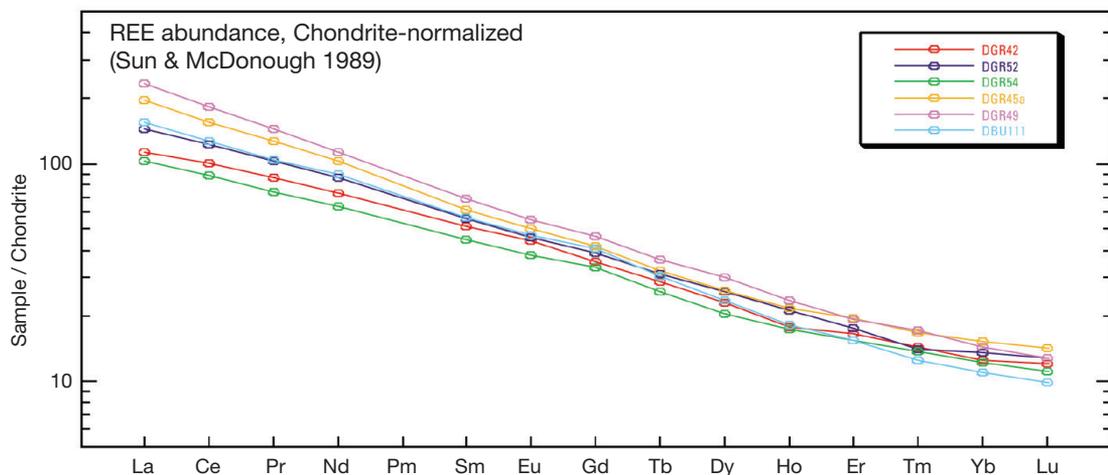
Figure 4. Chondrite normalized REE plots show smooth patterns with decreasing abundances from the light to the heavy REE indicating residual garnet in the mantle source of Madeira basalts.
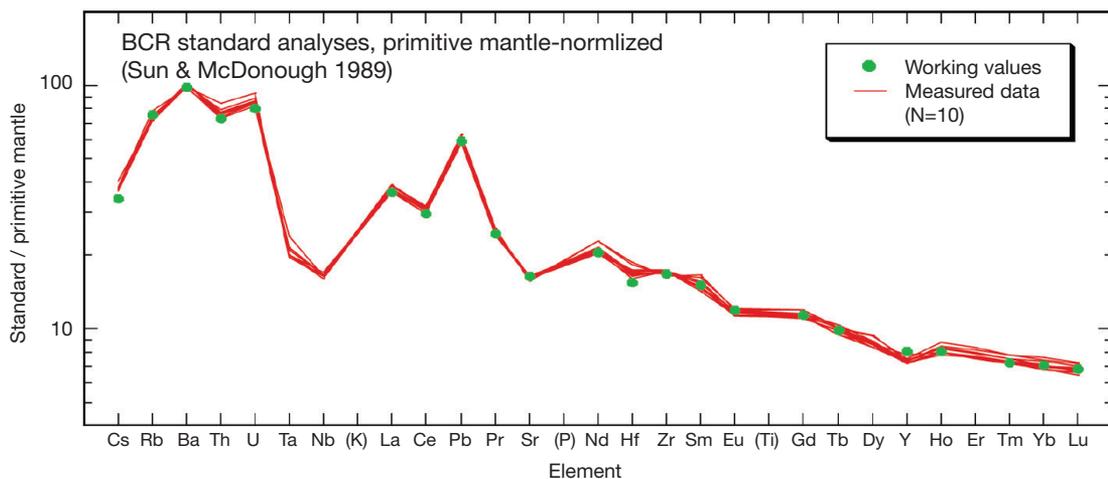
Figure 5. Normalized incompatible element diagram (Sun and McDonough 1989) with 10 analyses of USGS Columbia River basalt standard BCR-2. The data set (from six sample preparations) indicates accuracy of >95% for most elements.

3. Determination of Sr/Ca and U/Ca in corals

Background and Scope

Massive stony corals form skeletons of calcium carbonate (aragonite). During growth, new material is accreted at the outer surface resulting in a layered, tree-ring-like structure (Figure 6). The amount of trace and minor elements incorporated into the skeleton is largely determined by environmental parameters during skeletal formation. Sr/Caratios, and more recently U/Ca-ratios, determined in these layers have emerged as measures of water temperature, where (due to thermodynamics) high concentrations of Sr and U correspond to low temperatures.
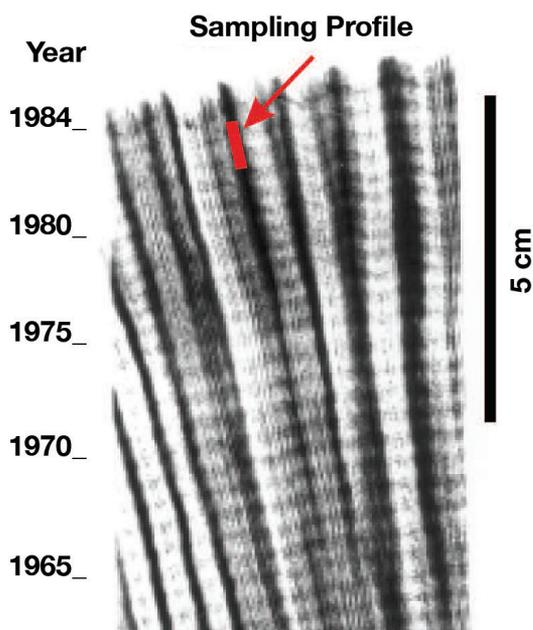
Figure 6. X-radiography of the carbonate skeleton of the reef-building coral Diploria strigosa. The horizontal bands are due to variations in skeletal density. Each couplet of one dark (summer) and one light (winter) band represents one year of growth. The sampling profile is marked as a red line.

Compared to Sr/Ca ratios, the U/Ca-ratios are about six times more sensitive to temperature (relative change is ~ 3.7% /K compared to 0.7 %/K for Sr/Ca), but the concentration of U is low (about 2.5 ppm in dry mass).

The requirements therefore for the simultaneous measurement of Ca, Sr, and U are:

- A detection range of at least 5 orders of magnitude.
- High precision (<< 1% RSD).
- Low detection limits (low ppt-range).

Experimental Data

Sample:
- Diploria strigosa from Bermuda (12 m depth)

Sample Preparation:
- Slice of coral
- Sample drilled out
- Digestion of 100-300 µg in 25 ml 1.3% HNO_3
- Addition of internal standard (Y)

Instrument:
- Element 2 HR-ICP-MS with 100 µl/min microflow nebulizer fitted to a Cyclone-Scott-double spray chamber

Analysis Time:
- 5 min

Results

The data span shown represents two years of coral skeletal growth with sampling intervals equivalent to one month. A well structured, temperature-driven seasonality is evident in both Sr/Ca and U/Ca ratios (Figure 7) resulting in a high correlation (r=0.89) between the two parameters. The seasonal amplitudes are approx. 2.5 ˚C. In contrast, the inter-annual trends are opposed, reflecting differences in the biological fractionation of the elements and possible changes in the local seawater composition.
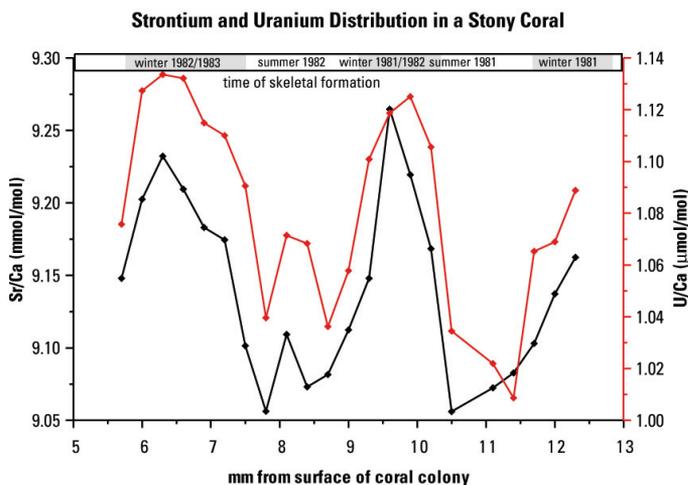
Isotope	Average conc.	Average RSD (%)
Ca-48	3 ppm	0.25
Sr-87	60 ppb	0.28
U-238	19 ppt	0.56

RSD's are based on 10 runs

Figure 7. Depth profile of Sr/Ca and U/Ca ratios from the coral shown in Figure 6. The sinusoidal variations in elemental composition are driven by the seasonal cycle of water temperature.

4. Conclusions

The Element 2 HR-ICP-MS is well suited for the determination of unknown samples containing major, minor and trace elements in a wide range of sample types. This wide range in signals can be handled by the high performance ion detection system of the Element 2 HR-ICP-MS without user interaction. All elements required in geological applications can be measured with high accuracy and reproducibility, independent of sample matrix.

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