In-situ Sr isotope Studies - LA-MC-ICP-MS
Applications

• Tracing magma/mantle processes
• Tracing ancient civilization migrations in sites of Archaeological interest
• Hydrothermal activity/diagenetic processes
• Groundwater research – e.g., Godomey Well Field, Benin
Radioactive Decay - The Basic Equations

Total number of daughter atoms in system undergoing decay is:

\[ D = D_o + D^* \]

where \( D = \) total; \( D_o = \) original; \( D^* = \) number produced by decay

As \( D^* = N (e^{\lambda t} - 1) \), then:

\[ D = D_o + N (e^{\lambda t} - 1) \]

\( \lambda = \) decay constant
\( t = \) age of rock, mineral

Basic equation for age determination of rocks & minerals.
Radioactive Decay - The Basic Equations

Writing decay equation using a ‘real’ example, such as the decay of $^{87}\text{Rb}$ to $^{87}\text{Sr}$:

$$^{87}\text{Sr} = ^{87}\text{Sr}_0 + ^{87}\text{Rb} \ (e^{\lambda t} - 1)$$

However:

Much easier and more meaningful to measure the ratio of two isotopes rather than the absolute abundance of one (using a MC-ICP-MS instrument).
Therefore, $^{87}\text{Sr}$ is normalized to a non-radiogenic isotope, i.e. $^{86}\text{Sr}$.

Thus, the useful form of the decay equation is:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_{\text{Initial}} + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} (e^{\lambda t} - 1)$$
Sr isotope compositions – *terrestrial reservoirs*

- $^{87}\text{Sr}/^{86}\text{Sr}$ isotope compositions of:
  - Present-day MORB (*Mid-Ocean Ridge Basalt*) = $0.7020 – 0.7025$
  - Old (>2.7 billion year-old) granite = $>0.7200$
  - Present-day seawater has a $^{87}\text{Sr}/^{86}\text{Sr}$ value of $0.7092$
Measuring $^{87}\text{Sr}/^{86}\text{Sr}$ variations in minerals and groundmass from basalts using LA-MC-ICPMS

Frank C. Ramos\textsuperscript{a,\,*}, John A. Wolff\textsuperscript{b}, Darren L. Tollstrup\textsuperscript{a}

\textsuperscript{a}Department of Earth Sciences, University of California, Santa Cruz, Santa Cruz, CA, 95064, USA
\textsuperscript{b}Department of Geology, Washington State University, Pullman, WA 99164-2812, USA

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• Ramos et al. (2004) undertook a thorough evaluation of potential elemental and molecular interferences including Ca dimers and Ca argides, Fe dioxides, Ga and Zn oxides, doubly charged REEs and Hf, and singly charged Kr and Rb.

• Critical interferences include Kr, Rb, and doubly charged Er and Yb ions, while molecular species have only a limited impact on Sr isotope ratios.

• Demonstrate the accuracy with analyzed minerals, including marine carbonate, plagioclase, and clinopyroxene, which offer differing concentrations of interfering elements.

• Address potential complications and pitfalls associated with the technique and LA-MC-ICPMS in general.
Table 3
Collector block configuration of the ThermoFinnigan Neptune™ MC-ICPMS used for both solution and LA-MC-ICPMS Sr isotope analysis

<table>
<thead>
<tr>
<th>Collector</th>
<th>L4</th>
<th>L3</th>
<th>L2</th>
<th>L1</th>
<th>C</th>
<th>H1</th>
<th>H2</th>
<th>H3</th>
<th>H4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>83</td>
<td>83.5</td>
<td>84</td>
<td>85</td>
<td>85.5</td>
<td>86</td>
<td>86.5</td>
<td>87</td>
<td>88</td>
</tr>
<tr>
<td>Isotope of interest</td>
<td>³⁸Kr11.5%</td>
<td>¹⁶⁷Er²⁺</td>
<td>⁸⁴Sr0.56%</td>
<td>⁸⁵Rb72.2%</td>
<td>¹⁷¹Yb²⁺</td>
<td>⁸⁶Sr98.6%</td>
<td>¹⁷³Yb²⁺</td>
<td>⁸⁷Sr7.00%</td>
<td>⁸⁸Sr82.6%</td>
</tr>
<tr>
<td>Isobaric interferences</td>
<td>¹⁶⁶Er²⁺</td>
<td>¹⁶⁸Er²⁺</td>
<td>¹⁶⁸Yb²⁺</td>
<td>¹⁷⁰Er²⁺</td>
<td>¹⁷⁰Yb²⁺</td>
<td>¹⁷²Yb²⁺</td>
<td>¹⁷⁴Yb²⁺</td>
<td>¹⁷⁶Yb²⁺</td>
<td></td>
</tr>
</tbody>
</table>

Monitored species and interferences affecting the Sr masses are also illustrated along with natural abundances for Sr, Rb and Kr.
**Table 3.**
Nu Plasma collector array, incorporating the distribution and magnitude of relevant elemental and molecular interferences (adapted from Ramos et al. 2004)

<table>
<thead>
<tr>
<th>Collector</th>
<th>L3</th>
<th>L2</th>
<th>Axial</th>
<th>H2</th>
<th>H3</th>
<th>H4</th>
<th>H5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>83</td>
<td>84</td>
<td>85</td>
<td>86</td>
<td>86.5</td>
<td>87</td>
<td>88</td>
</tr>
<tr>
<td>Double mass</td>
<td>166</td>
<td>168</td>
<td>170</td>
<td>172</td>
<td>173</td>
<td>174</td>
<td>176</td>
</tr>
<tr>
<td>Analyte isotopes</td>
<td><strong>-</strong></td>
<td><strong>-</strong></td>
<td><strong>-</strong></td>
<td><strong>-</strong></td>
<td><strong>-</strong></td>
<td><strong>-</strong></td>
<td><strong>-</strong></td>
</tr>
<tr>
<td>Singly-charged interferences</td>
<td><strong>Kr11.55%</strong></td>
<td><strong>Kr56.90%</strong></td>
<td><strong>Rb72.15%</strong></td>
<td><strong>Sr0.86%</strong></td>
<td><strong>Sr70.82%</strong></td>
<td><strong>Yb31.84%</strong></td>
<td><strong>Yb12.73%</strong></td>
</tr>
<tr>
<td>Doubly-charged interferences</td>
<td><strong>Er33.41%</strong></td>
<td><strong>Er27.07%</strong></td>
<td><strong>Er14.88%</strong></td>
<td><strong>Kr173.77%</strong></td>
<td><strong>Rb27.85%</strong></td>
<td><strong>Yb31.84%</strong></td>
<td><strong>Yb12.73%</strong></td>
</tr>
<tr>
<td>Molecular interferences</td>
<td><strong>43Ca40Ar0.13%</strong></td>
<td><strong>44Ca40Ar2.13%</strong></td>
<td><strong>46Ca40Ca</strong></td>
<td><strong>46Ca40Ar0.003%</strong></td>
<td><strong>48Ca40Ca</strong></td>
<td><strong>48Ca40Ca</strong></td>
<td><strong>48Ca40Ca</strong></td>
</tr>
</tbody>
</table>

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*a* Only molecules containing either $^{40}\text{Ca}$ or $^{40}\text{Ar}$ are considered of any influence, as such all other combinations are omitted. Percentages indicated are the combined abundances of Ca dimers and Ca argides.
Collector Configuration – *In-situ* Sr, University of Notre Dame
Methodology
(Ramos et al. 2004)

• UP213 nm laser ablation system coupled to Neptune MC-ICP-MS

• Employed rastering – troughs of 160 x 500 microns, or 80 x 500 microns (using a 80 micron spot size)

• Depth of penetration ~ 70 to 130 microns

• He gas was flushed into laser ablation cell at a rate of ~0.90 L/min
Methodology  
(Ramos et al. 2004)

- Sample (Ar) gas flow rate was ~0.7 L/min

- $^{88}$Sr ion signal – minimum value of ~1.0 volt

- Generate precision of <0.00005 – standard error 2 sigma level on the $^{87}$Sr/$^{86}$Sr ratio

- Baseline measurements were conducted “on-peak” for 180 seconds
Interferences

• **Ca dimers (e.g., $^{44}\text{Ca}^{43}\text{Ca}^+$)** have been shown to interfere with Sr isotope masses during secondary ionization mass spectrometry (SIMS) measurements of carbonate and aragonite (Weber et al., 2004).

• Waight et al. (2002) suggest that **Ca argides (e.g., $^{44}\text{Ca}^{40}\text{Ar}^+$)**, present as a result of Ca ionization in the argon plasma, also interfere with Sr isotope masses when analyzing materials characterized by high Ca/Sr ratios such as carbonate (~500) and plagioclase (~50–200).
Ramos et al. (2004)
Interferences

- **Erbium (Er):**
- Forms singly- (Er\(^+\)) and doubly-charged (Er\(^{2+}\)) ions in plasma; the latter are problematic since mass (m)/charge (z) of Er\(^{2+}\) ions overlaps that of Rb, Sr and Kr
  
  - \(^{168}\text{Er}^{2+}\) overlaps \(^{84}\text{Sr}\) and \(^{170}\text{Er}^{2+}\) overlaps \(^{85}\text{Rb}\)
Interferences

- Ytterbium (Yb):