Mineral Chemistry: Modern Techniques and Applications to Exploration

Simon Jackson
Geological Survey of Canada
Ottawa, ON
Introduction

Mineral Chemistry and Indicator Mineral Exploration
- Must use in situ analytical techniques – speed and cost effectiveness
- Wide range of techniques: widely variable cost, value/$$
- Focus on most widely used, cost-efficient in situ technologies

Instrumentation, figures of merit, major applications of:
- Major and minor elements by EPMA
- Trace elements by LA-ICP-MS
- Low precision isotopic analysis (U-Pb) by LA-ICP-MS, Ion Probe
- High precision isotopic analysis by LA-MC-ICP-MS
- Integration of multiple techniques
In Situ Major Element Analysis:
Electron Probe Micro-Analyzer (EPMA)

- Electron microprobe
- Mature technology (from 1960s)
- Collimated electron beam → X-ray generation
- Spot sizes 1-2 µm x few µm
- Sequential WDS crystal spectrometers
- Simultaneous EDS spectrometer
- High continuum background → major elements (%)
- Minor elements (200-500 ppm)
- Imaging - BSE, CL, SEM
- Mapping (major elements)
**Calibration**

- Calibration against mineral standards
- ZAF matrix correction

**WDS: wavelength dispersive analysis (crystal spectrometers)**

- one element at a time, on each (~5 spectrometers)
- 10 min analysis $\rightarrow$ detection limits of 200-500 ppm
- lower detection limits require very long count times
- higher resolution, higher intensity with larger crystals ($\$$)
- precise - data quality depends on counts (time)
- element mapping ($\leq$5 elements)

**EDS: energy-dispersive analysis (Si(Li) detector)**

- simultaneous energy spectrum $\rightarrow$ rapid phase identification
- analysis of major elements (use as extra spectrometer)
- rapid multi-element mapping
Electron MicroProbe: Imaging

BSE/CL Imaging of Zircons

Imaging to assess growth history of zircon for later trace element/U-Pb/Hf isotope analysis


X-ray mapping (Ca)

Gt growth in pressure shadows in Stewart River metapelite → 2 deformation events (courtesy: R. Berman)
Applications of EPMA in Indicator Mineral Analysis

- Typing garnets and ilmenites in diamond exploration; e.g., ‘G10’ Garnet
- Discriminating sources of Fe-Ox minerals
- Discriminating sources of placer gold
- Providing major element data for calibrating LA-ICP-MS trace analysis

Grutter et al. (2004)
Beaudoin et al. (2009)
In Situ Trace Element Analysis - Laser Ablation (LA)-ICP-MS

Sample = thin section, polished block, grain mount, rock sample
The Plasma-based instrument family
- ICP-AES/OES (atomic/optical emission spectroscopy)
- ICP-MS – ion detection method:
  - Quadrupole
  - Magnetic sector single collector
  - Magnetic sector multi-collector
  - (Time of flight)

Sequential

Simultaneous
Which ICP-MS?

**Quadrupole ICPMS:**
- Rapid scanning of whole mass spectrum
- High sensitivity
- Reaction/collision cell reduces some overlaps
- Relatively low cost (<US 200,000)

**Magnetic Sector (High-Resolution) ICPMS:**
- Higher sensitivity than most quadrupole systems
- High resolution resolves overlaps for special applications (e.g., ArO on Fe), but at reduced sensitivity – fewer applications in dry plasma work (LA)
- Scans limited portions of spectrum rapidly, whole spectrum more slowly
- High cost (>US 300,000)

*Quadrupole ICP-MS: faster, more versatile and economic – preferred for LA work*
LA-ICP-MS Set Up

LASER

Laser pit

ICP-MS
Sample Cell

- Sample outlet
- Standard
- Sample
- He gas inlet
Time Resolved Analysis and Data Processing

- Often complex signals – zoning etc., esp. hydrothermal minerals
- Provides valuable information on distribution of trace elements in ablation volume
- Signals must be selectively integrated
  - specialized software
  - difficult to automate
**LA-ICP-MS - Calibration and Figures of Merit**

**LAM-ICP-MS DETECTION LIMITS**

- Robust relatively matrix-intolerant calibration with synthetic glasses
- Requires concn. of 1 (major) element in sample

**LAM-ICP-MS PRECISION**

- rapid - 3-5 min per analysis (manual); 2-3 minutes (automated) – 500 analyses/day
- spatially resolved (<10 - >100 µm resolution)
- depth profiling (1 µm resolution)
- multi-element (40-50 elements)
- precise (ca. 2%)
- detection limit to low ppb at 30-40 µm resolution
  (spot size dependent)
- ‘accurate’ (see fine print for conditions)
- individual fluid and melt inclusions
- isotope ratios, esp. U/Pb (down to 0.1-1% RSD)
Applications of LA-ICP-MS in Indicatory Mineral Analysis

Diamond Exploration
- Garnets: Ni geothermometry
- Garnet/ilmenite geochemistry

Regional exploration
- Zircon, apatite geochemistry

Belousova et al. (2002)

Courtesy: M. Escayola
Applications of LA-ICP-MS in Indicatory Mineral Analysis

Porphyry Cu-Au
- Zircon REE geochemistry

Gold
- Detrital gold discrimination

REE in Zircons

GOLD

Natural Resources Canada
Ressources naturelles Canada
In-situ Dating: U-Pb in Zircon, Monazite

TIMS single-grain analysis:
- benchmark technique
- ultimate precision (~0.1%)
- but slow, complex chemistry
- zircons may be multistage
  - requires in situ techniques
  - 20-50 µm resolution

1-2% precision very useful:
- Ion microprobe
  - SHRIMP
  - CAMECA
- LA-ICPMS

Concordia age = 415.1 ± 1.3 Ma
MSWD (of concordance) = 0.53
IDTIMS age (206/238) = 416.8 ± 1.1 Ma
Ion Microprobe
(SHRIMP)
# Comparison of Ion Probe and LA-Q-ICP-MS

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<tr>
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<th>SHRIMP</th>
<th>LA-Q-ICP-MS</th>
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<tr>
<td>Precision (2 σ)</td>
<td>ca. 1-2%</td>
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<td>Spatial resolution</td>
<td>5-35 µm diameter, 1-2 µm deep (slow drilling rate, minimal sample consumption)</td>
<td>15-60 µm diameter, &gt;15 µm deep (1 µm/s drilling rate, moderate sample consumption)</td>
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<td>Relative throughput - analyses</td>
<td>10-30 min/analysis</td>
<td>3-5 min (manual) = 60-80 per day 1-2 min (automated) = 500-1000 per day!</td>
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<td>Common Pb correction</td>
<td>$^{204}$Pb correction</td>
<td>$^{204}$Pb correction compromised by Hg</td>
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<td>Other capabilities</td>
<td>O, S, C isotopes; traces elements (matrix sensitive $\rightarrow$ mineral standards)</td>
<td>Trace elements (relatively matrix insensitive $\rightarrow$ glass standards)</td>
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<td>Capital Costs</td>
<td>High (&gt;$1M)</td>
<td>Moderate (&lt;$500,000)</td>
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High Precision Isotopic Analysis by MC-ICP-MS

- MC $\rightarrow$ *high precision* isotopic analysis
- Radiogenic isotope analyses (e.g., Sr, Nd, Hf, Os, Pb) with ppm precision
- ICP $\rightarrow$ *“Non-traditional”* stable isotope analysis (e.g., Mg, Fe, Cu, Zn, Ni, Sb)
- ICP $\rightarrow$ *LA in situ* isotopic analysis; e.g., Hf in zircon, Pb in feldspar, Cu in cpy, Fe in magnetite – 0.1 ‰ in 3-5 minutes

### METAL ISOTOPES

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<tr>
<th>ATOMIC MASS</th>
<th>Cu</th>
<th>Zn</th>
<th>Ni</th>
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\[\text{ISOTOPIC ABUNDANCE (\%)}\]
Applications of LA-MC-ICP-MS in Indicator Mineral Analysis

- Fe isotopes in Fe-Ox minerals
  - Combined with elemental analyses
- Si isotopes in resistate silicates
- Hf isotopes in zircon
  - Combined with trace element and U-Pb data

Graham et al. (2004)
The ‘TerraneChron’ Approach (http://www.es.mq.edu.au/gemoc/)

- Traditional heavy mineral separation
- Zircon grain picking (Leica UV binocular)
- Mounting of grains in polished blocks
- EPMA: BSE/CL imaging, Hf+Y+U+Th
- LA-ICPMS: U-Pb dating
- LA-MC-ICPMS: Hf isotope analysis
- (LA-ICP-MS REE provides more information; e.g., oxidation state)
Four major stages of crustal evolution
Each stage has a distinct pattern of crustal recycling and juvenile mantle input
Each stage (apart from the last) ends with a period of crustal homogenisation
Some very depleted mantle sources
Much of the Signature is actually derived from inherited zircons in metasediments - not outcropping geology!
In-situ microanalysis: Essential for applications of RIM technology to mineral exploration

Major (minor) elements: EPMA
- offers best spatial resolution and accuracy
- provides major element data required for LA-ICP-MS

Trace (minor) elements: LA-ICP-MS
- most rapid, cost-effective

U-Pb dating
- LA-ICP-MS quickest and cheapest
- Ion microprobe provides best spatial resolution

Isotopic analysis – LA-MC-ICP-MS
- many new applications (Hf, Sr, Nd ……) for tracers
- stable isotopes of metals - new and promising field
- integration with chemical and dating adds an extra dimension
Acknowledgements

- Geological Survey of Canada, particularly
  - Beth McClenaghan
  - Bill Davis
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  - Rob Berman

- GEMOC, Macquarie University, especially:
  - Bill Griffin
  - Norman Pearson
  - Elena Belousova
Shorter wavelength:
✓ increased absorption
✓ reduced optical penetration
✓ more controlled ablation
✓ smaller particle size
✓ reduced matrix effects
✓ smaller spot size
x greater cost and complexity

213 nm is the current “industry standard”:
• solid state laser
• short wavelength
• short pulse width (metals)

193 nm required for the most demanding applications
• fluid inclusion analysis in quartz
Ar or He in UV laser to ICP torch

TV

Lens

Mirror

Sample
Schematic of a Nd:YAG LA System
Northparkes Porphyry Cu-Au Deposit, N.S.W.

Cross section through E26 porphyry deposit

- Isotopically heavy Cu in propylitic halo

Cu grade (wt%)
- >1
- 1~0.3

δ^{65}Cu (per mil)

Cu grade (wt.%)
Application Of Metal Isotopes In Mineral Exploration

Cu isotopes in SE Australian granites

- Local anomalous Cu isotope values identified in Yeoval granite
- Macroscopically “fresh” outcrops possess microveinlets containing chalcopyrite

Natural Resources Canada
Ressources naturelles Canada
Cu isotopes are sensitive indicators of cryptic hydrothermal activity
e.g., distal portions of hydrothermal Cu deposits, margins of porphyry systems
can be more sensitive than element geochemistry
Zircon REE as a Proxy for Magma Oxidation State

- zircon REE systematics (esp. Ce*/Ce) are a sensitive proxy for magma oxidation state, and, therefore,
- prospectivity of intrusive rocks for associated mineralization
Fundamentals of Sequential ICP-MS

Quadrupole-ICP-MS

Detector
System control
Interface
Torch
Quadrupole mass filter
Ion lens system

Canada