Investigation of Mocs and Pleșcoi meteorites using inductively coupled plasma mass spectrometry (ICP-MS):

elemental composition and Pb isotopic ratios

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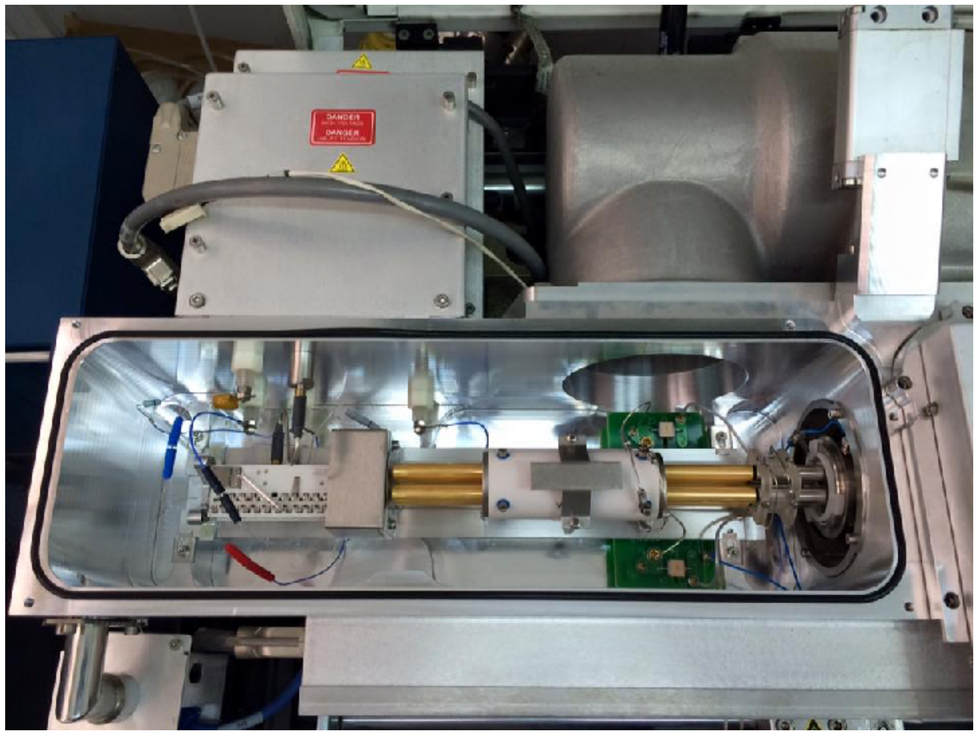
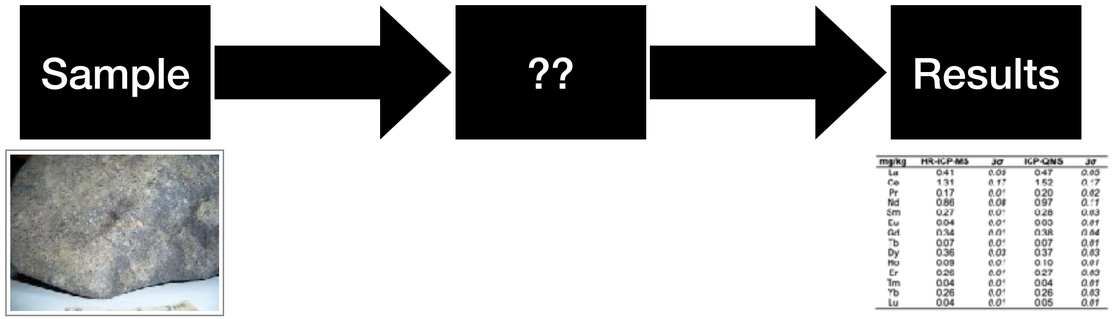
Inductively coupled plasma mass spectrometry

- **Mass spectrometer** (**MS**)
  - identifying components (elements)
- **Inductively coupled plasma** (**ICP**)
  - from *atoms* to *ions*



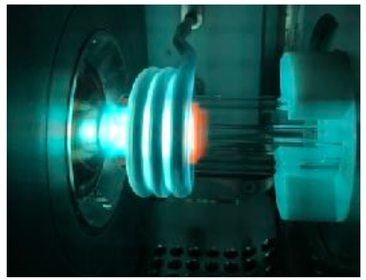


mg/kg	HR-ICP-MS	2σ	ICP-QMS	2σ
La	0.41	0.03	0.47	0.03
Ce	1.31	0.17	1.52	0.17
Pr	0.17	0.01	0.20	0.02
Nd	0.86	0.08	0.97	0.11
Sm	0.27	0.01	0.28	0.03
Eu	0.04	0.01	0.03	0.01
Gd	0.14	0.01	0.18	0.04
Tb	0.07	0.01	0.07	0.01
Dy	0.36	0.03	0.37	0.03
Ho	0.09	0.01	0.10	0.01
Er	0.26	0.01	0.27	0.03
Tm	0.04	0.01	0.04	0.01
Yb	0.26	0.01	0.26	0.03
Lu	0.04	0.01	0.05	0.01

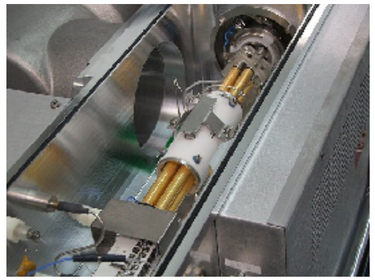
Inductively coupled plasma mass spectrometry

Sample introduction system

Ion source (plasma)



Ion filter (quadrupole)



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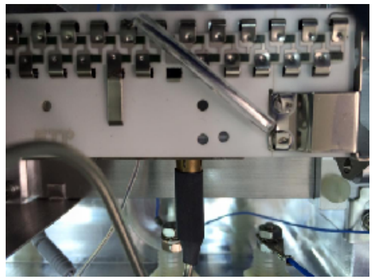

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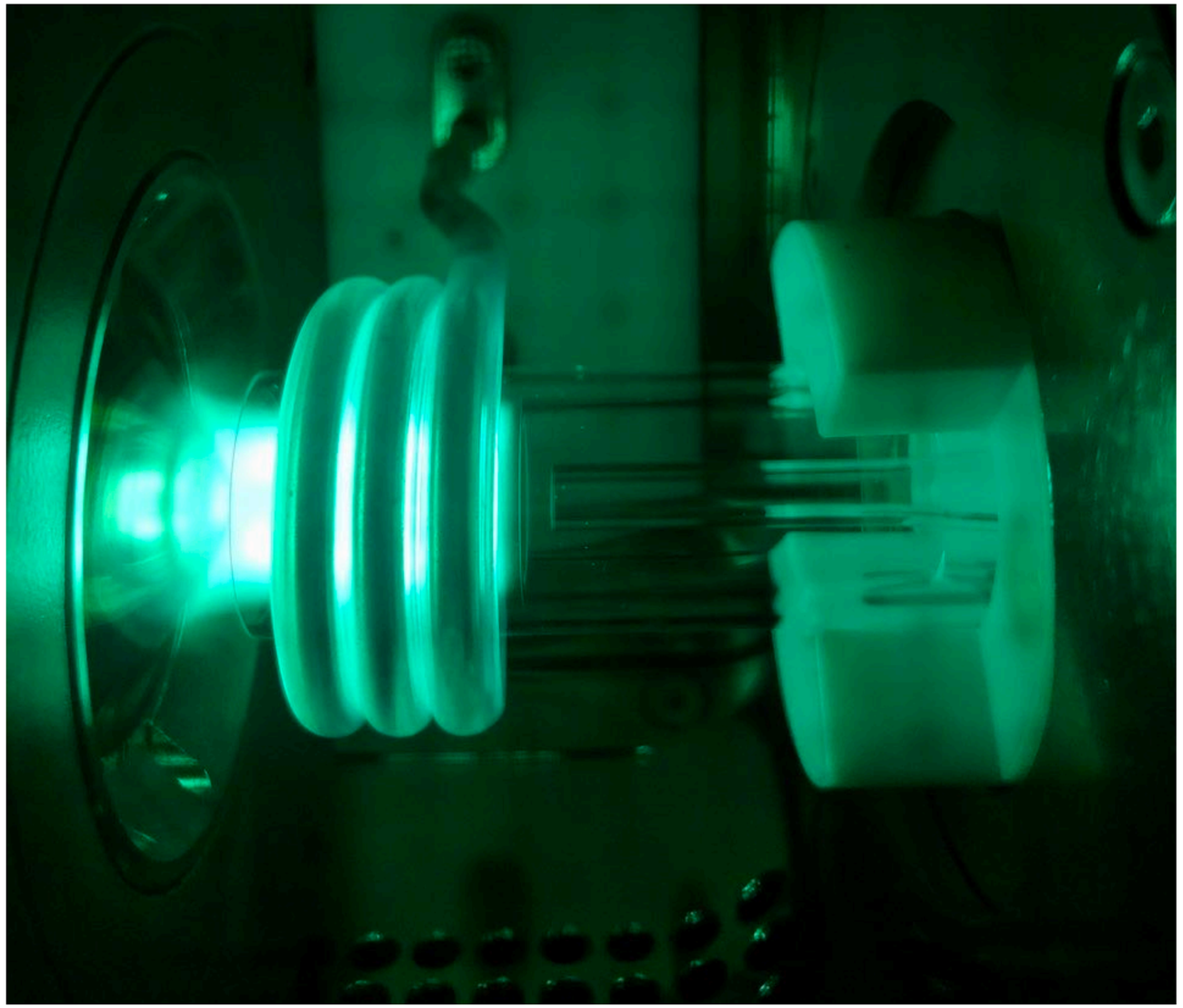
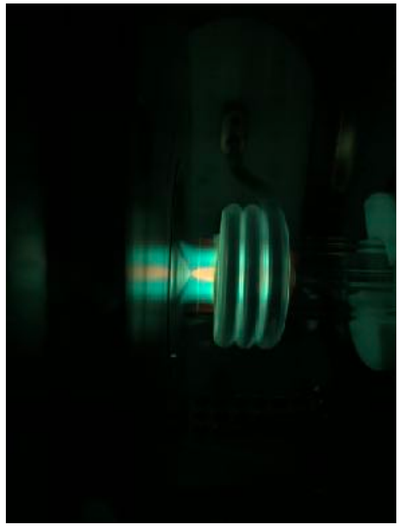
Inductively coupled plasma mass spectrometry



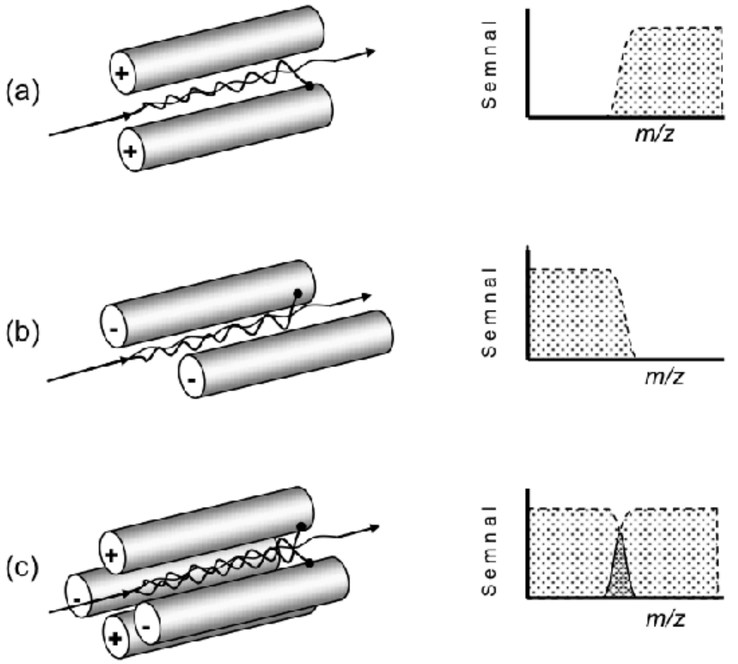


Inductively coupled plasma mass spectrometry

- **Mass filter: quadrupole**
  - m / z (z=1)
  - R = m / Δm
  - R ~400, Δm ~0.5

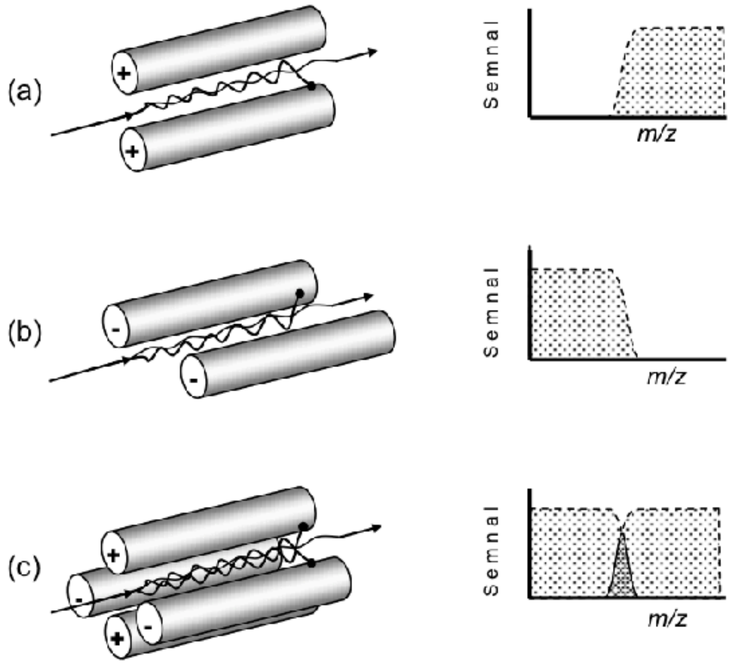
21	22	23	24	25
Sc	Ti	V	Cr	Mn
Scandium	Titanium	Vanadium	Chromium	Manganese
44.956	47.867	50.942	51.996	54.938

  - Interferences
    - isobaric: (^{204}Hg, ^{204}Pb), (^{64}Ni, ^{64}Zn)
    - polyatomic: (^{56}Fe, ^{40}Ar^{16}O), (^{75}As, ^{40}Ar^{35}Cl)



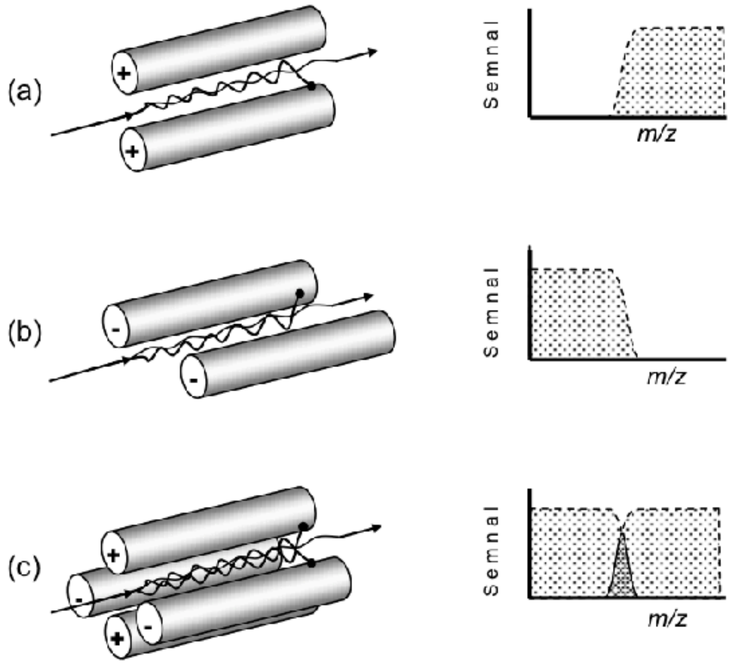
Inductively coupled plasma mass spectrometry

- **Mass filter: quadrupole**
  - R = m / Δm
  - Vanadium: m=50.942 amu
  - Cromium: m=51.996 amu
  - Δm=1.054 amu, R=48 (<400) 😊



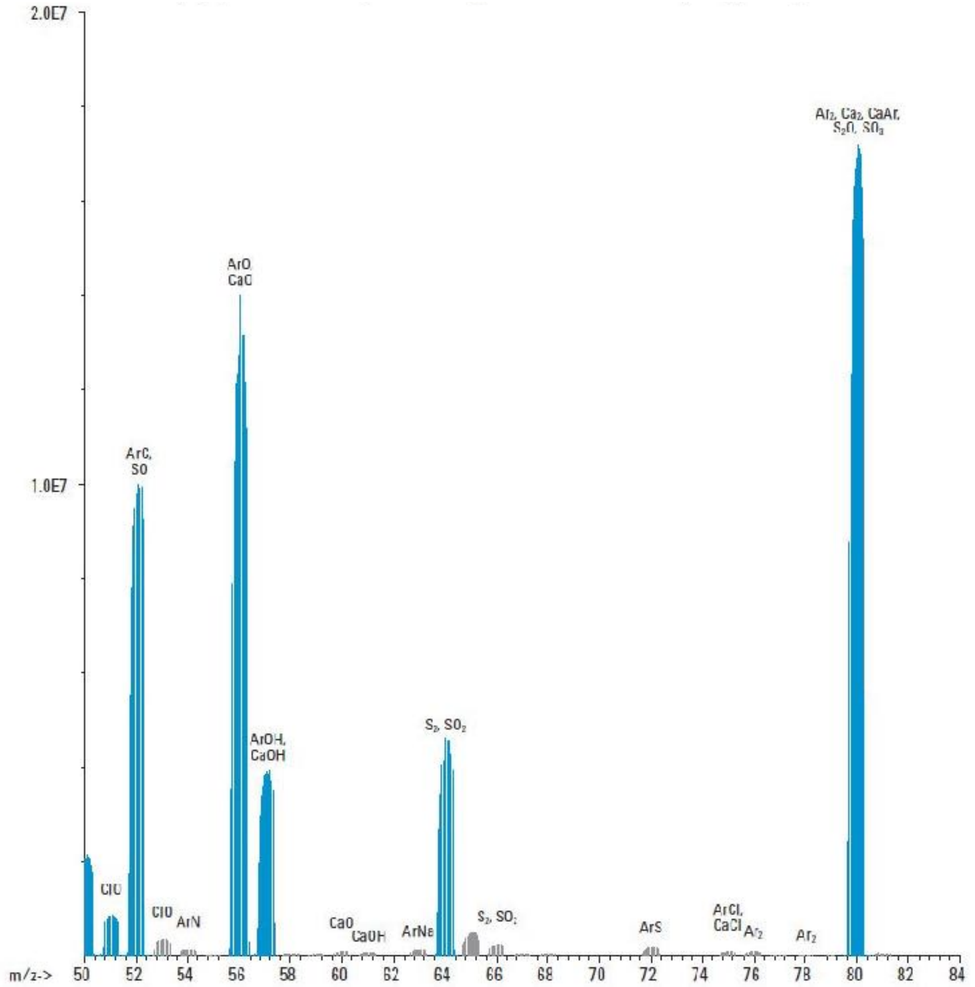
Inductively coupled plasma mass spectrometry

- **Mass filter: quadrupole**
  - R = m / Δm
  - ^{64}Ni: m=63.927966 amu
  - ^{64}Zn: m=63.929142 amu
  - Δm(^{64}Ni^{64}Zn)=0.001176 amu, R=54360 (>400) 😓
  - Δm(^{204}Hg^{204}Pb)=0.00045 amu, R=451111 (>400) 😓



Inductively coupled plasma mass spectrometry

- **Inteferences mitigation techniques**
  - pick another isotope (*if possible*)
  - correction equations (*based on natural abundances*)
  - mass-shift *(dynamic reaction cell* —DRC)
    - e.g. $^{75}As = {}^{40}Ar + {}^{35}Cl = {}^{75}(ArCl)$
  - kinetic energy discrimination (KED, using He)
    - e.g. $^{56}Fe = {}^{40}Ar + {}^{16}O = {}^{56}(ArO)$



Inductively coupled plasma mass spectrometry

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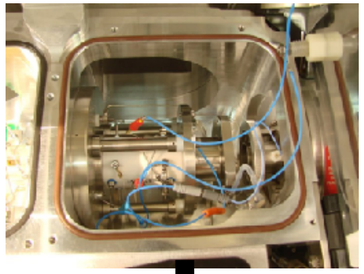

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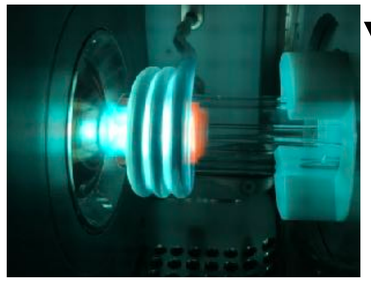

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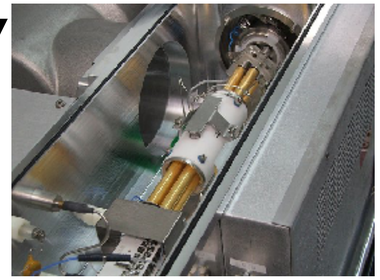

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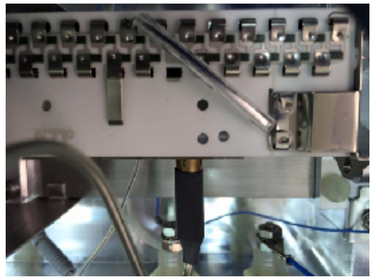

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Inductively coupled plasma mass spectrometry

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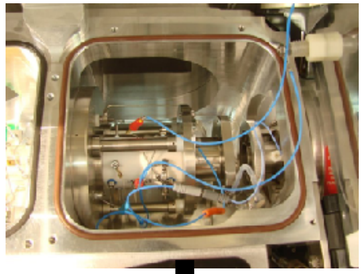

$^{75}As \xrightarrow{^{16}O_2} {}^{91}(AsO)$

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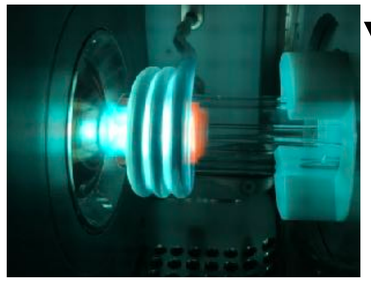

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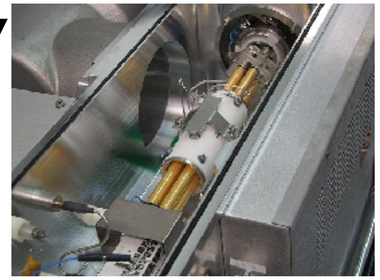

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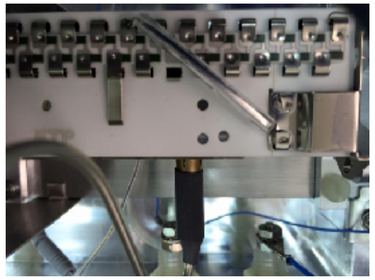

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Inductively coupled plasma mass spectrometry

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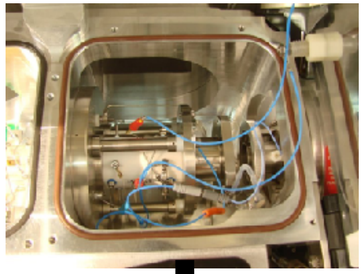

$^{56}Fe + ^{56}(ArO) \xrightarrow{He} {}^{56}Fe$

Sample introduction system

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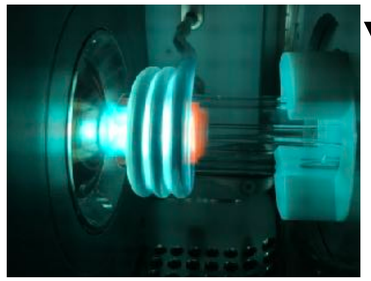

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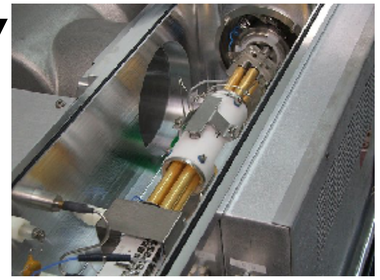

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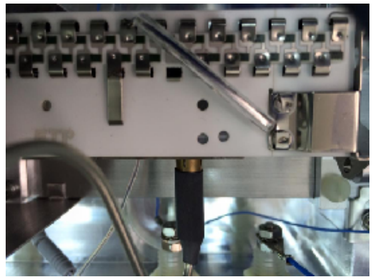

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- **Inteferences mitigation techniques**
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  - mass-shift *(dynamic reaction cell* —DRC)
    - e.g. 75As = 40Ar + 35Cl (ArCl)
  - kinetic energy discrimination (KED)
    - e.g. 56Fe = 40Ar + 16O (ArO)
  - triple quadrupole system

Inductively coupled plasma mass spectrometry

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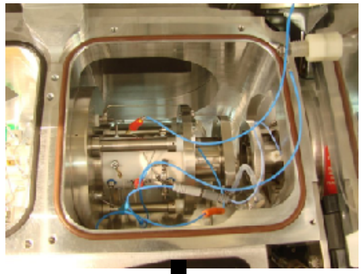

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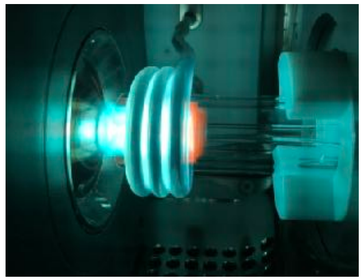

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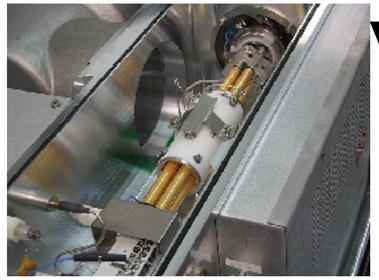

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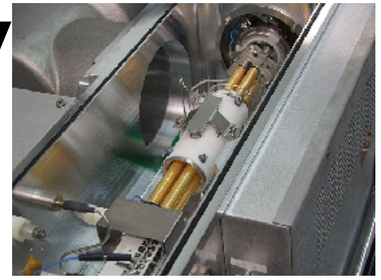

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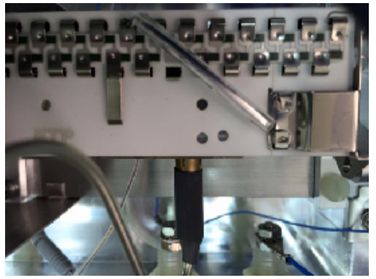

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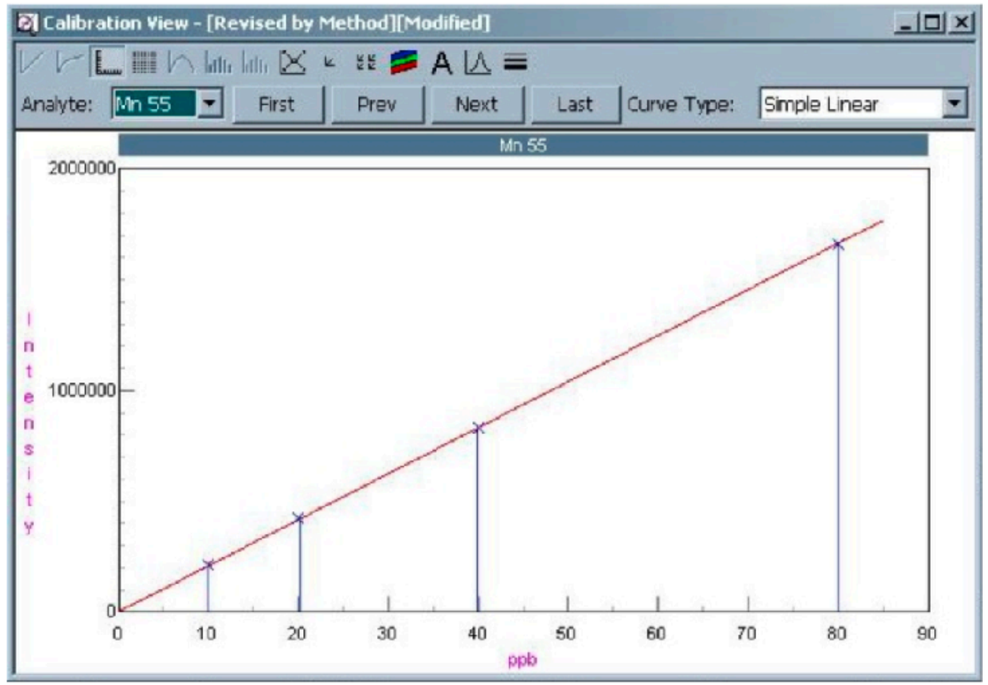
Inductively coupled plasma mass spectrometry

- **Calibration**
  - Measure calibration standards (known concentration)
  - Build calibration curve
  - Measure unknown sample
  - Use the calibration curve cu get the concentration
  - Calibration curve is actually a line (detector is usually linear for ~9 orders of magnitude)



Meteorites

- Over **76000** identified meteorites
- Classification
  - Chondrites (~86%)
  - Iron (~5%)
  - Stony-iron (~1%)
  - Achondrites
    - Moon, Mars etc

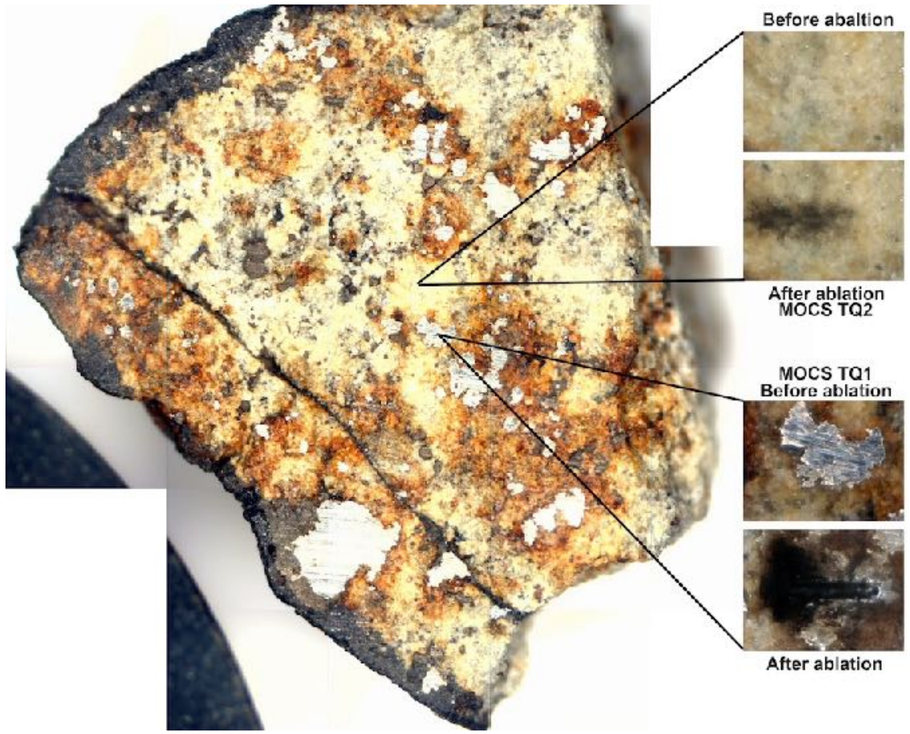
Romanian meteorites

Nr.	Nume	An	Localitate	Coordonate	Tip	Masă	Obs.
1	Mezö-Madaras	1852	Mădăraș, MS	46°36’N, 24°26’E	L3.7	22.70 kg	*fall*
2	Ohaba	1857	Ohaba, AB	46°04’N, 23°47’E	H5	16.25 kg	*fall*
3	Kakowa	1858	Grădinari, CS	45°08’N, 21°40’E	L6	577 g	*fall*
4	Mocs	1882	Mociu, CJ	46°48’N, 24°02’E	L5-6	300 kg	*fall*
5	Zsadany	1875	Cornești, TM	45°55’N, 21°13’E	H5	552 g	*fall*
6	Tuzla	1920	Tuzla, CT	44°01’N, 28°38’E	L6	236 g	*find*
7	Sopot	1927	Sopot, DJ	44°25’N, 23°30’E	OC	958 g	*fall*
8	Tauti	1937	Tauti, AR	46°43’N, 23°30’E	L6	21 kg	*fall*
9	Gresia	1990	Gresia, TR	44°10’N, 24°55’E	H4	26.9 kg	*find*
10	Pleșcoi	2008	Pleșcoi, BZ	45°16’N, 26°42’E	L5-6	6.91 kg	*fall*

- **Mocs**
  - Fall date: 03.02.1882 over **Mocs** (azi Mociu), Cluj
  - Total mass: ~300 kg, 100+ fragments
- **Pleșcoi**
  - Fall date: 12.06.2008 over **Pleșcoi**, Buzău
  - Total mass: 6.91 kg, 1 fragment

Isotopic ratio measurements (phase 1)

Calibration for laser ablation



	literature data		measured values	
	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
NIST 610	**0.9096**	**2.167**	**0.9165**	**2.1895**
SD	*0.0008*	*0.0018*	*0.0063*	*0.0269*
RSD	*0.088*	*0.0831*	*0.6852*	*1.2189*

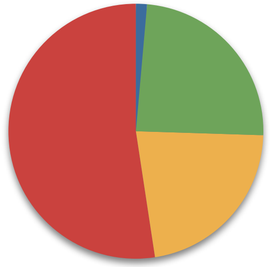
Isotopic ratio measurements (phase 2)

Calibration for liquid sample

NIST 981	Measured values	Certified values
$^{204}Pb/^{207}Pb$	0.0591 ± 0.0001	0.059042 ± 0.000037
$^{207}Pb/^{206}Pb$	0.9137 ± 0.0013	0.9146 ± 0.00033
$^{208}Pb/^{206}Pb$	2.1653 ± 0.0031	2.1681 ± 0.0008

	$^{207}Pb/^{206}Pb$	*SD*	*RSD*	$^{208}Pb/^{206}Pb$	*SD*	*RSD*
Mocs S	0.8656	*0.0084*	*0.97*	2.1011	*0.0036*	*0.17*
Plescoi S	0.8610	*0.0092*	*1.07*	2.1329	*0.0041*	*0.19*
Mocs LA	0.8564	*0.0135*	*1.58*	2.1092	*0.0432*	*2.05*
Plescoi LA	0.8576	*0.014*	*1.63*	2.1349	*0.0561*	*2.63*

Lead (Pb) natural abundance



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 981

Common Lead Isotopic Standard

This Standard Reference Material (SRM) is intended primarily for use as an isotopic standard. SRM 981 consists of 1 gram of a commercially available, high purity lead metal, of 99.9+ percent purity, that was extruded into wire form. The atomic weight of the material is calculated to be 207.215 using the nuclidic masses 203.973044, 205.974468, 206.975903, and 207.976650. The certified isotopic compositions are given below.

Atomic Abundance Ratio, Lead-204/Lead-206 ... 0.059042 ± 0.000037

Atomic Abundance Ratio, Lead-207/Lead-206 ... 0.91464 ± 0.00033

Atomic Abundance Ratio, Lead-208/Lead-206 ... 2.1681 ± 0.0008

Lead-204, atom percent ... 1.4255 ± 0.0012

Lead-206, atom percent ... 24.1442 ± 0.0057

Lead-207, atom percent ... 22.0833 ± 0.0027

Lead-208, atom percent ... 52.3470 ± 0.0086

Overall limits of error are based on 95 percent confidence limits for the mean of the ratio measurements and on allowances for the known sources of possible systematic error.

Measurements for certification were by triple filament solid-sample mass spectrometry. Mixtures with known $^{208}Pb/^{206}Pb$ ratio, prepared from high-purity separated isotope solutions, were used as comparison standards. Details of the preparation and measurements were published by E.J. Catanzaro, T.J. Murphy, W.R. Shields, and E.L. Garner, J. Research NBS 72A, No. 3,261 (1968).

The analytical measurements leading to the certification of this material were performed in the NIST Inorganic Analytical Research Division.

The overall coordination of efforts leading to the update and revision of this certificate was coordinated through the Standard Reference Materials Program by T. E. Gills.

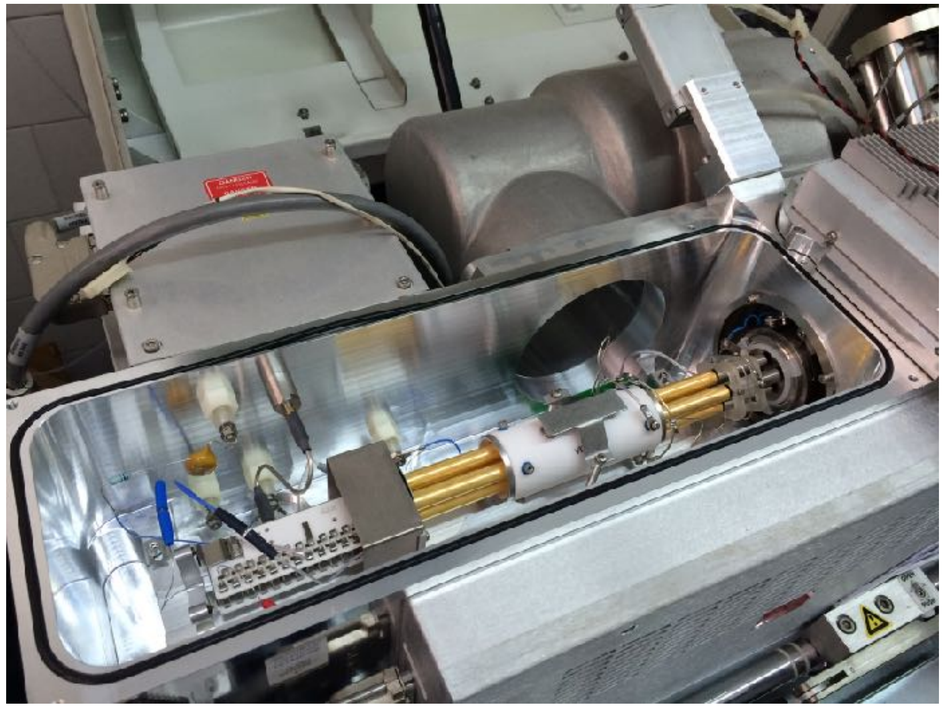
Gaithersburg, MD 20899
March 25, 1992
(Revision of certificate dated 4-10-73)

William P. Reed, Chief
Standard Reference Materials Program

Rare earth elements (REE) for Mocs

Sample preparation

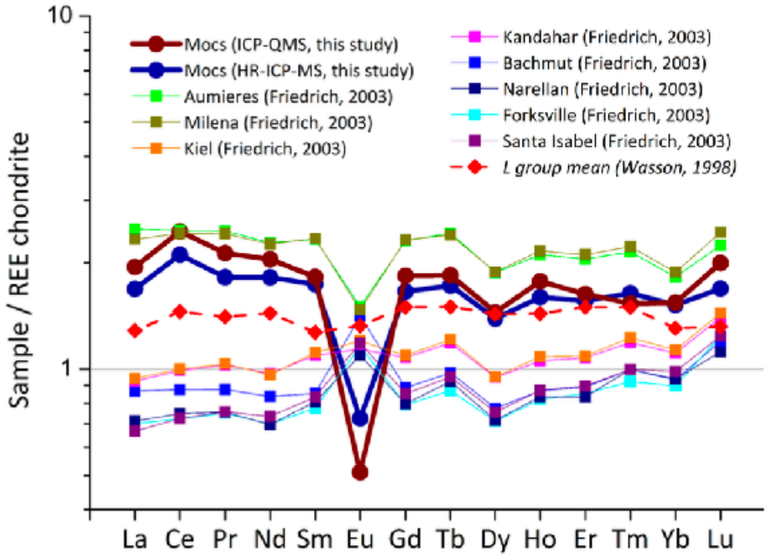
- Mocs fragment was grounded to very fine powder; 100 mg of Mocs and Allende meteorites were used for analysis;
- 3 mL HNO3, 3 ml HF and 2 mL H2O were added to the sample and then placed in the microwave oven for 30 minutes (up to 22°C in the first 10 minutes, no change for another 10 minutes, then up to 240°C for the remaining time).
- After cooling, the digested solutions were evaporated and dried down on a hot plate.
- The second stage of acid treatment consisted on 1 mL HNO3, 2 mL HCL and 5 mL H2O and placed again in the microwave oven for 35 minutes (up to 200°C in the first 15 minutes, then the temperature was kept constant).
- After cooling, the final solution was brought to a total volume of 50 mL with deionized water in a volumetric flask, ready for direct ICP-MS analysis.
- A blank solution was prepared and its contribution was extracted from samples detector counts (cps level).



Rare earth elements (Mocs)

Instrumentation and results

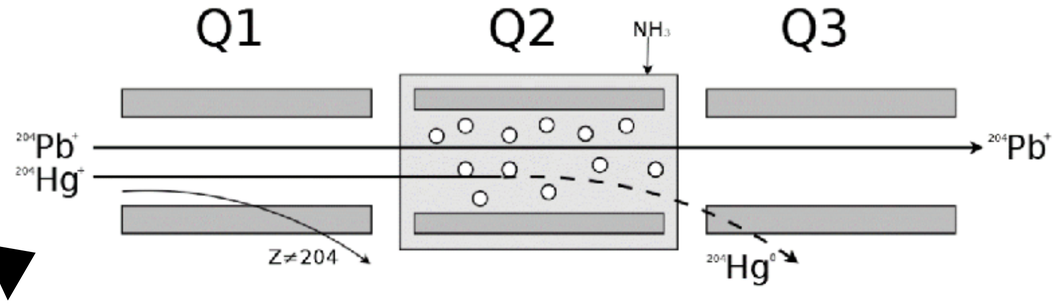
- Perkin-Elmer Multi-Element Standard II used for calibration
- Allende reference material (obtained from Smithsonian Museum)
- *Perkin-Elmer* **Elan DRC II** quadrupole ICP-MS from INCDO INOE2000 Research Institute for Analytical Instrumentation (ICIA) Cluj-Napoca
- *Nu Instruments* **AttoM** high-resolution ICP-MS (HR-ICP-MS) from Department of Geology, Faculty of Biology and Geology, Babeș-Bolyai University, Cluj-Napoca



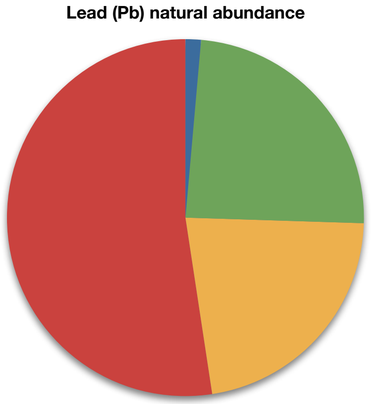
mg/kg	HR-ICP-MS	3σ	ICP-QMS	3σ
La	0.41	*0.05*	0.47	*0.05*
Ce	1.31	*0.17*	1.52	*0.17*
Pr	0.17	*0.01*	0.20	*0.02*
Nd	0.86	*0.08*	0.97	*0.11*
Sm	0.27	*0.01*	0.28	*0.03*
Eu	0.04	*0.01*	0.03	*0.01*
Gd	0.34	*0.01*	0.38	*0.04*
Tb	0.07	*0.01*	0.07	*0.01*
Dy	0.36	*0.03*	0.37	*0.03*
Ho	0.09	*0.01*	0.10	*0.01*
Er	0.26	*0.01*	0.27	*0.03*
Tm	0.04	*0.01*	0.04	*0.01*
Yb	0.26	*0.01*	0.26	*0.03*
Lu	0.04	*0.01*	0.05	*0.01*

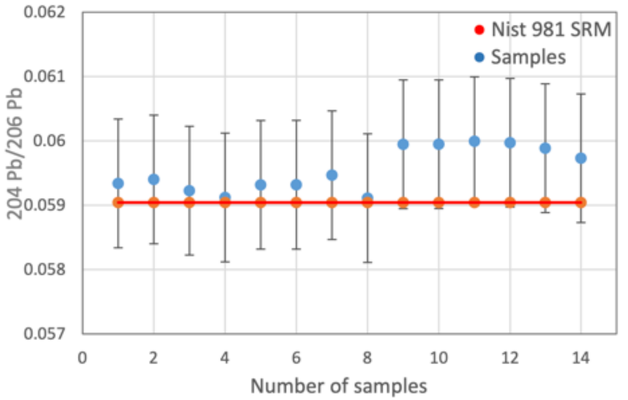
Future plans

- Plești RRE data
- Revisiting isotopic measurements for Mocs and Plești (Allende?) including ^{204}Pb isotope using *Thermo Fisher Scientific* **iCAP TQ** ICP-MS triple-quadrupole, initial trials are encouraging



- List for Santa Claus:
  - Geochronology…
  - More precise isotopic ratio data (MC-ICP-MS)…





Thank you!