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Magnesium hydroxide coprecipitation for separation of trace elements from calcium matrix of fish otoliths and biominerals for ICP-MS determination

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U.S. Geological Survey

ICP-MS overview

CONS

- Relatively high capital cost (~2-3x ICP-OES)
- Require more operator experience
- TDS < 0.2%
- Matrix interferences
- Isobaric interferences
- Relatively high running cost

PROS

- Routine trace element analysis (ppb and below)
- Fast multi element analysis
- Wide range of elements (>75)
- Analysis of a wide variety of samples
- A wide variety of sample introduction methods
- High sensitivity
- DL's of <1ppt for some elements in solution
- Large linear dynamic range (9 orders)
- Few spectral interferences
- Simple spectra produced
- Isotopic analysis capability
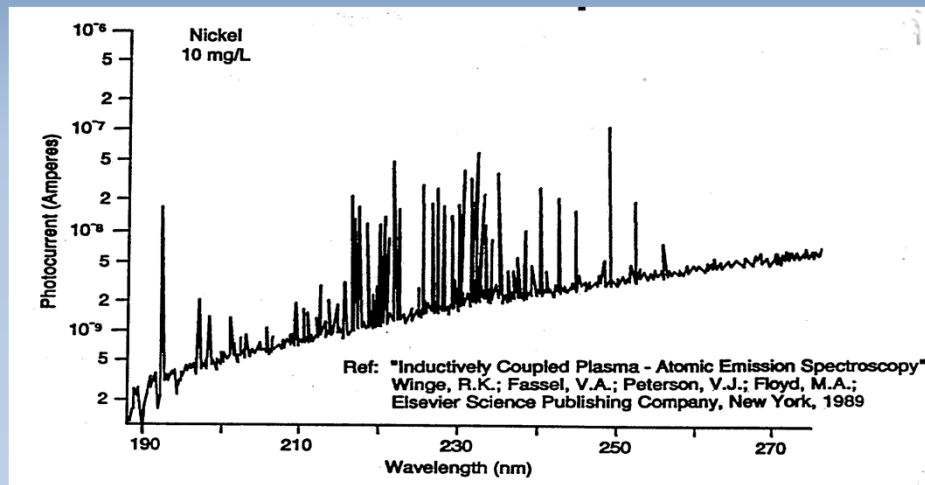
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How sensitive is ICP-MS?
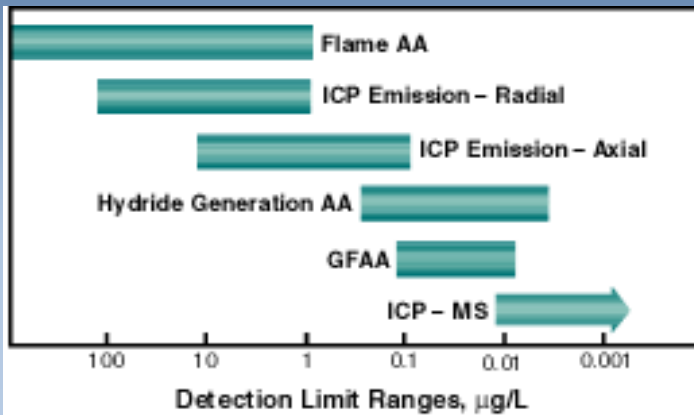
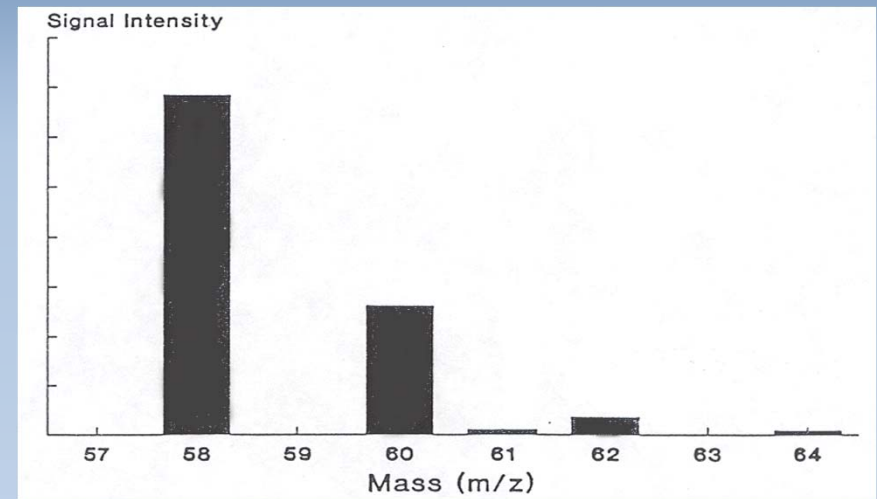ICP-MS provides the lowest detection limits for most elements.

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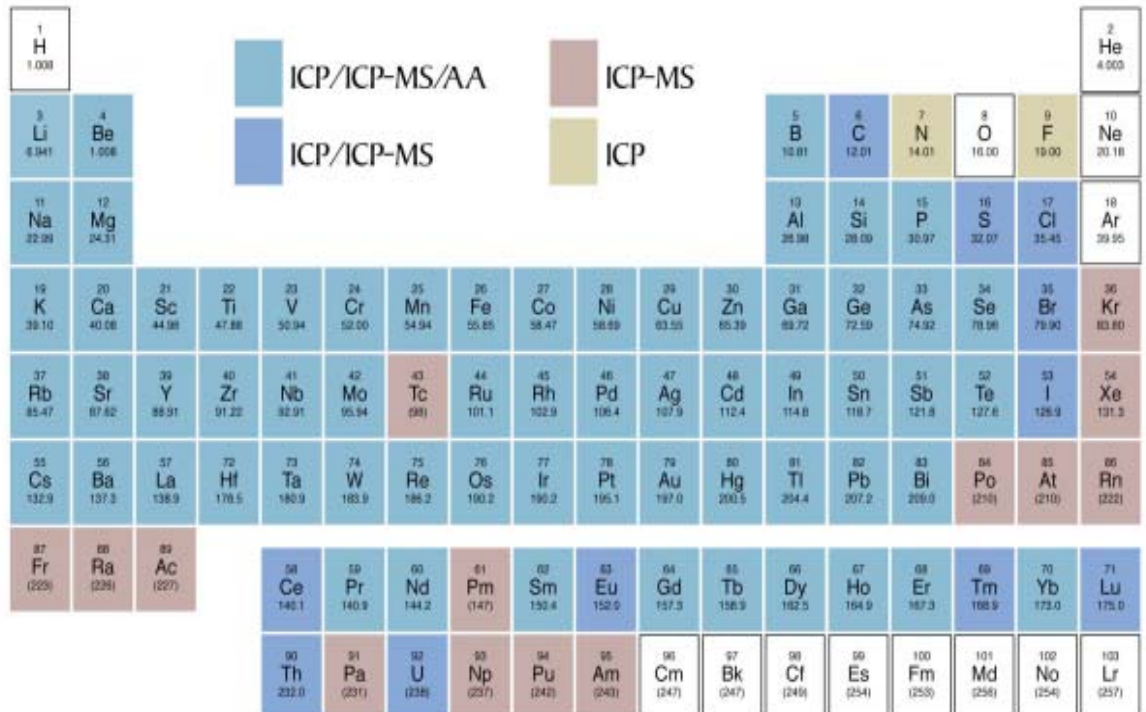
ICP-MS vs ICP-OES spectra
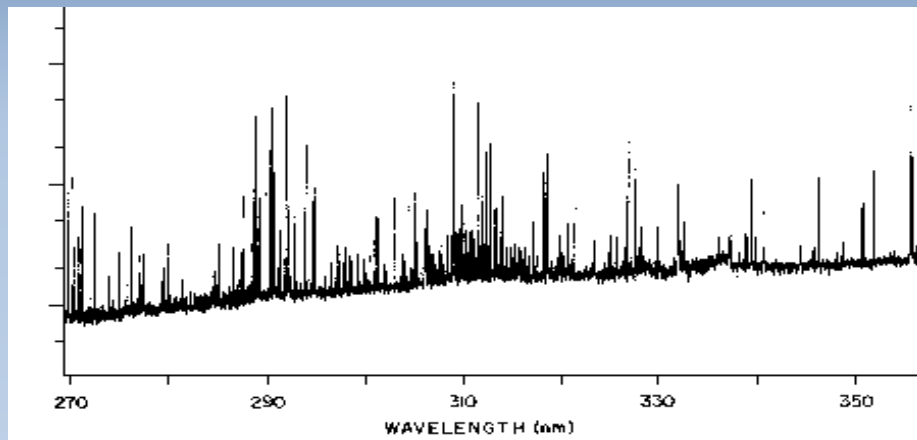
ICP-OES Spectra

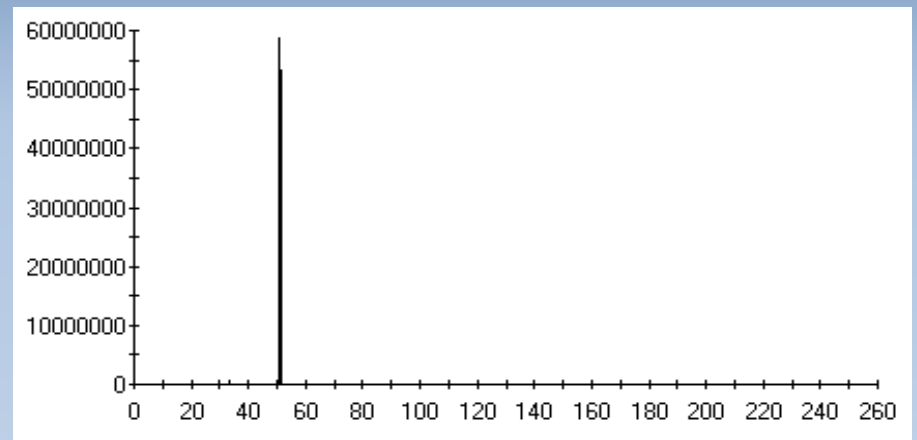## ICP-MS Spectra – Nickel

ICP-MS vs ICP-OES spectra

ICP-OES Spectra - Vanadium 10 mg/L

ICP-MS Spectra - Vanadium 10 mg/L

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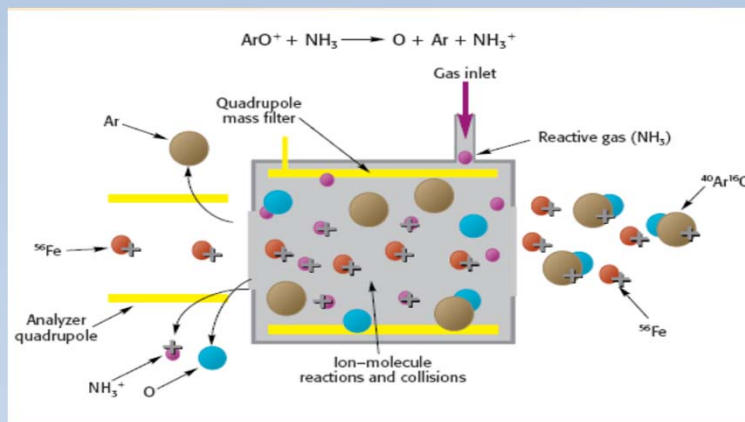# Means for eliminating spectral interferences

Standard mode

CCT, DRC or CRI mode
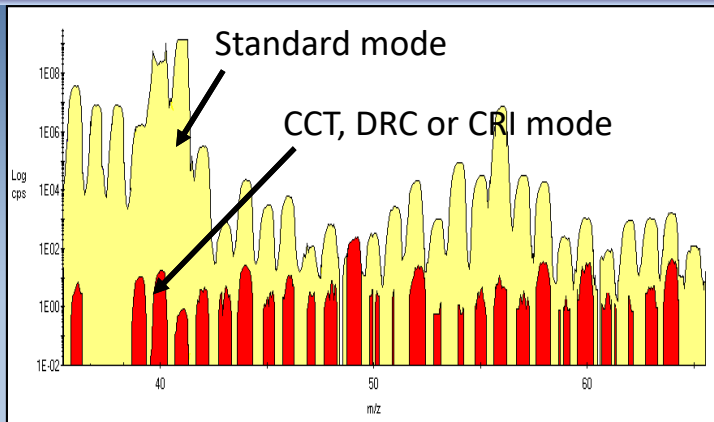
Cell gases for reducing some potential interferences

56	Fe	ArO	H_2 or NH_3 / He
63	Cu	ArNa	H_2 / He
66	Zn	ArMg	H_2 / He
72	Ge	ArAr	H_2 / He
75	As	ArCl	H_2 / He
77	Se	ArCl	H_2 / He
78	Se	ArAr	H_2 / He
80	Se	ArAr	H_2 / He
82	Se	ArHArH	H_2 / He

$ArO^+ + NH_3 \longrightarrow O + Ar + NH_3^+$

Collision Cell technology (CCT)
Dynamic Reaction Cell (DRC)
Collision Reaction Interface (CRI)

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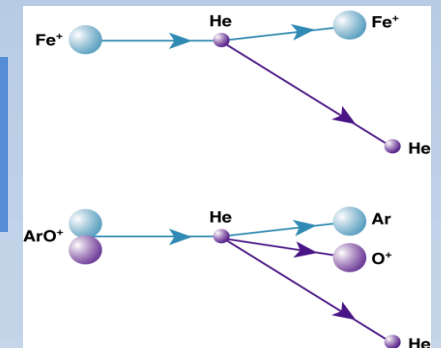
Challenges in seawater measurements

Dissolved Ion	Concentration mg/kg (ppm)
Chloride (Cl^-)	19,345
Sodium (Na^+)	10,752
Sulfate (SO_4^{2-})	2701
Magnesium (Mg^{2+})	1295
Calcium (Ca^{2+})	416
Potassium (K^+)	390
Bicarbonate (HCO_3^{2-})	145
Bromide (Br^-)	66
Borate (BO_3^{2-})	27
Strontium (Sr^{2+})	13
Fluoride (F^-)	1
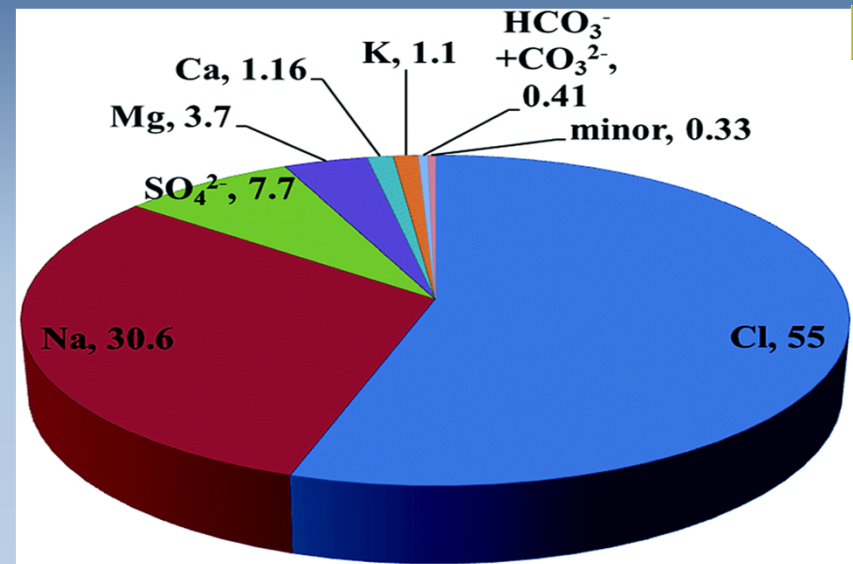
AZ1

Seawater composition (%)

- **Very low concentrations of trace elements require judicious analytical separation**
- **High salinity of seawater hampers detection limits and accuracy of ICPMS measurements**

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AZ1   Arslan, Zikri, 7/20/2020

Literature: Mg(OH)₂ coprecipitation for seawater analysis

Literature: Mg(OH)$_2$ coprecipitation for seawater analysis

Contents lists available at ScienceDirect

Talanta

Determination of rare earth elements and other trace elements (Y, Mn, Co, Cr) in seawater using Tm addition and Mg(OH)$_2$ co-precipitation

Nicolas Freslon[a,b,c], Germain Bayon[a,*], Dominique Birot[a], Claire Bollinger[b,c], Jean Alix Barrat[b,c]

[a] Département Géosciences Marines, IFREMER, 29280 Plouzané, France
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[c] CNRS UMR6538, IUEM, Université de Brest, 29280 Plouzané, France

ARTICLE INFO

ABSTRACT

This paper reports on a novel procedure for determining trace element abundances (REE and Y, Cr, Mn, Co) in seawater by inductively coupled plasma sector field mass spectrometry (ICP-SFMS). The procedure uses a combination of pre-concentration using co-precipitation onto magnesium hydroxides and addition of thulium spike. The validity of the method was assessed onto 25 ml volumes of certified reference materials (NASS- and CASS-4) and in house seawater standard. Procedural blanks were determined by applying the same procedure to aliquots of seawater previously depleted in trace elements by successive Mg(OH)$_2$ co-precipitations, yielding estimated contributions to the studied samples better than 1.1% for all elements, with the exception of Cr (<3.3%) and Co (up to 8%). The reproducibility of the method over the six month duration of the study was smaller than 11% RSD for all the studied elements. Results obtained for NASS-5 and CASS-4 agree well with published working values for trace elements.

Contents lists available at ScienceDirect

Analytica Chimica Acta

Determination of ultratrace levels of dissolved metals in seawater by reaction cell inductively coupled plasma mass spectrometry after ammonia induced magnesium hydroxide coprecipitation

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ARTICLE INFO

ABSTRACT

A method for the determination of ultratrace amounts of Cr, Fe, Mn, Pb and Zn in seawater has been developed. It combined the low-blank magnesium hydroxide coprecipitation procedure with quadrupole inductively coupled plasma mass spectrometry and used the dynamic reaction cell technique to resolve the polyatomic interferences arising from the residual matrix, the solvent and plasma gases. Detection limits ($3\sigma_B$, $n=10$) for Cr, Fe, Mn, Pb and Zn were 0.02, 0.10, 0.01, 0.002 and 0.19 nM, respectively, using 50 mL of seawater sample. The accuracy of the analytical procedure was verified by the analysis of the seawater reference materials CASS-4, NASS-5, SAFe D2 and SAFe S. The analytical precision ranged from 3% to 16% ($n=6$), with a sample throughput of about 6 samples h^{-1}.

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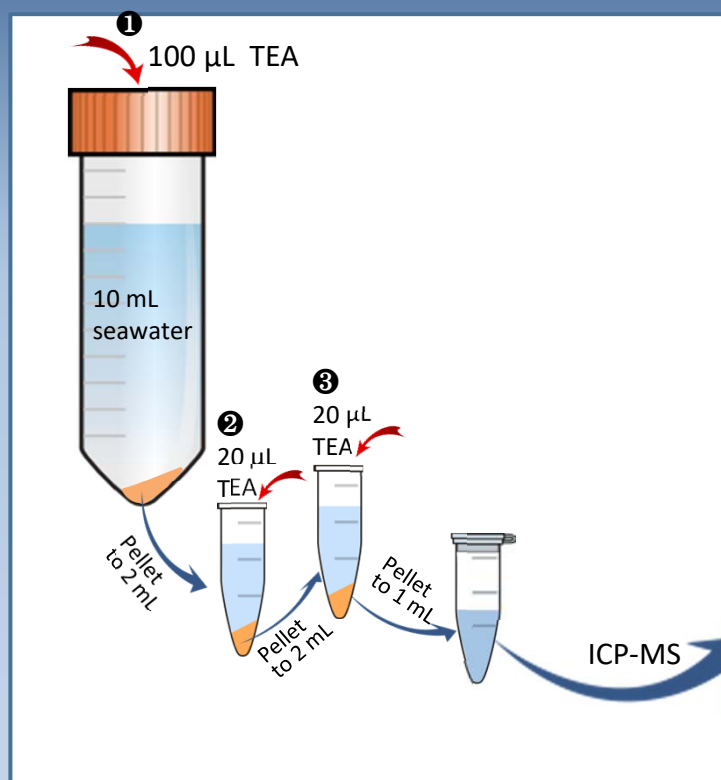
Can TEA improve Mg(OH)$_2$ coprecipitation?
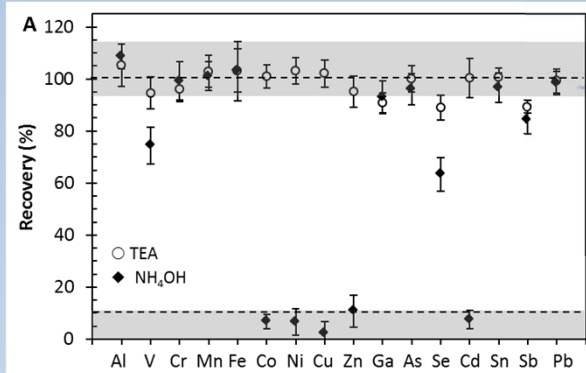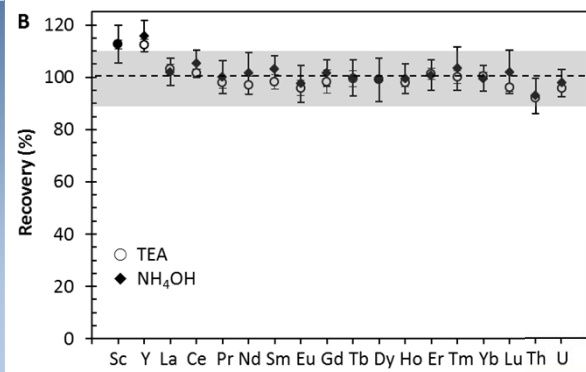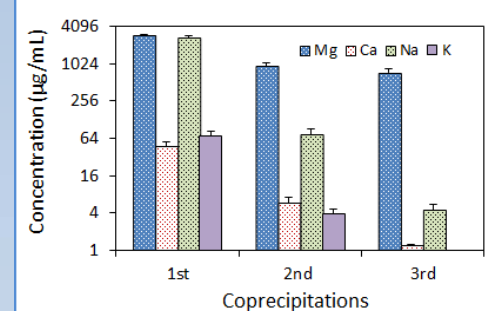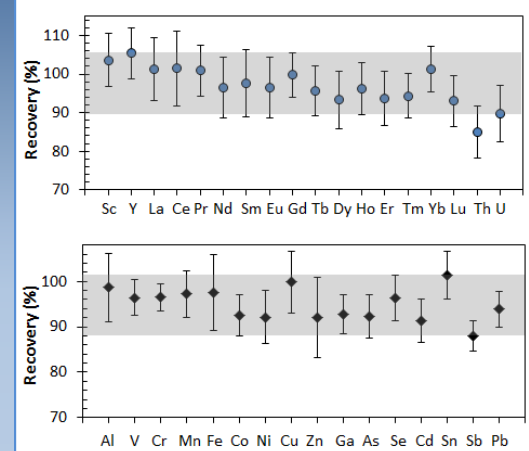
Scavenging of elements from seawater via TEA and NH$_4$OH: *TEA is more effective on V, Co, Ni, Cu, Cd, Zn and Se*

Improved Mg(OH)$_2$ coprecipitation

ICP-MS in otolith microchemical analysis

What is an otolith?

- White, bone-like structures in the head of a fish providing sense of balance to the fish in much the same way the inner ear provides balance in humans.

- Otoliths are composed of $CaCO_3$-protein matrix deposited in layers that grow as the fish grows. $CaCO_3$ is in aragonite crystal form.

Atlantic salmon   Pollock   Swordfish   Herring
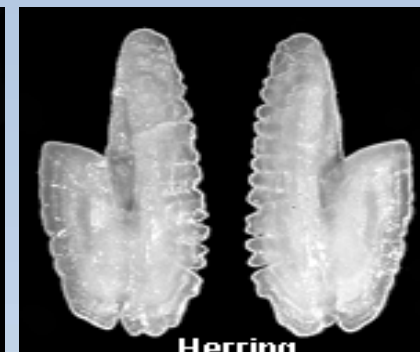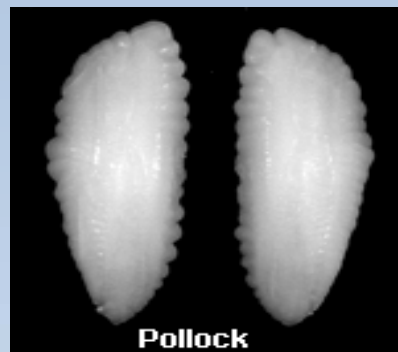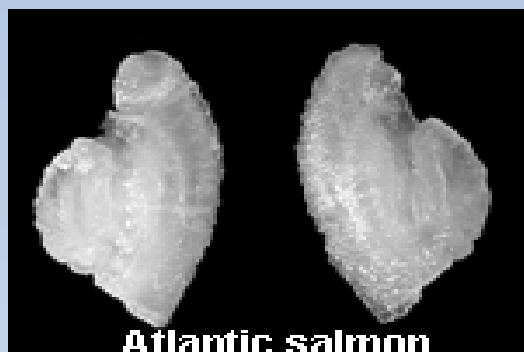
Unlike bones and scales, aragonite structure remains unaltered after deposition

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Elemental composition of otoliths
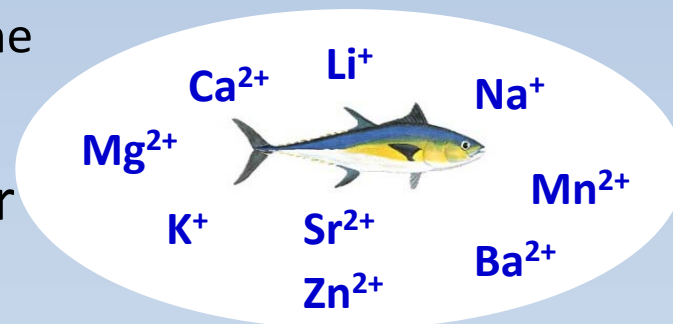
- Elemental composition of otoliths derives from the fish's aqueous environment.

- Trace elements comprise 1% of an otolith and are derived from water (96% $CaCO_3$, 3% protein).

- Composition varies with salinity, temperature, water chemistry, fish physiology and diet, and reflect the chemistry of the aqueous environment in which the fish resides.

Seawater

Ca^{2+} Li^+ Na^+

Mg^{2+}

Mn^{2+}

K^+ Sr^{2+}

Ba^{2+}

Zn^{2+}
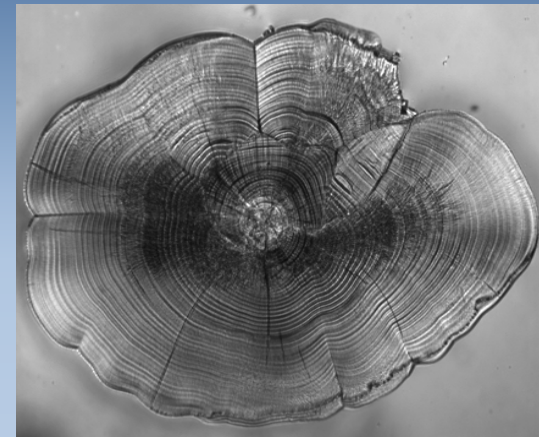
Mg(OH)$_2$ coprecipitation in simulated otolith solution

1 100 μL TEA

- 5,000 ppm Ca(II) as nitrate
- 10 ppb ME + 1ppb REE spike
- **200 ppm Mg(II)** (added as precipitant)

2 100 μL TEA

Pellet to ca. 2 mL

Pellet to 2 mL

ICP-MS
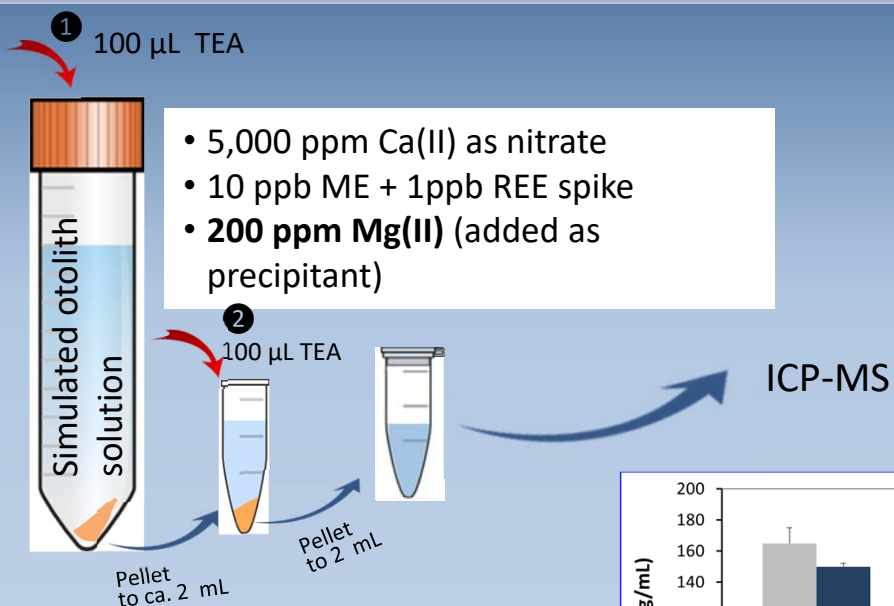
5000 ppm Ca(II) matrix is reduced to ~12 ppm
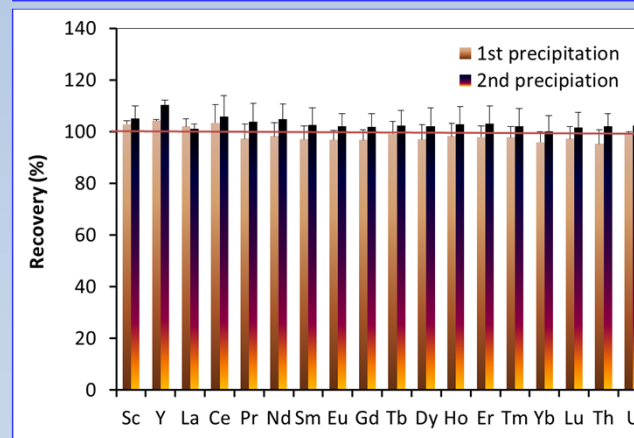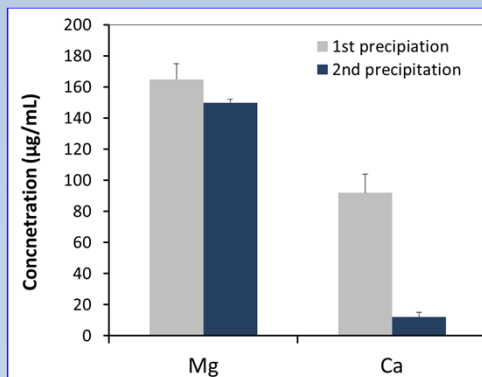
Optimization of Mg(II) for quantitative coprecipitation

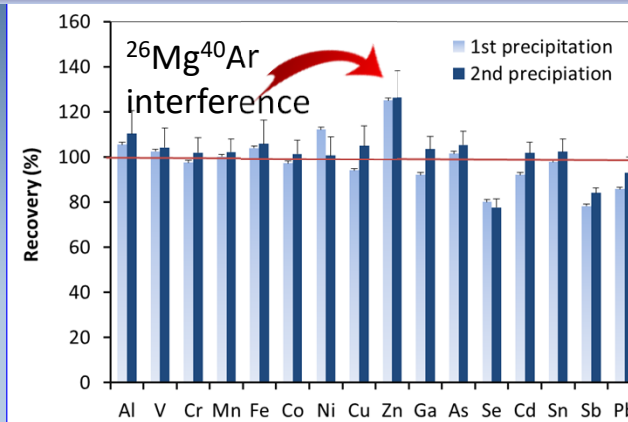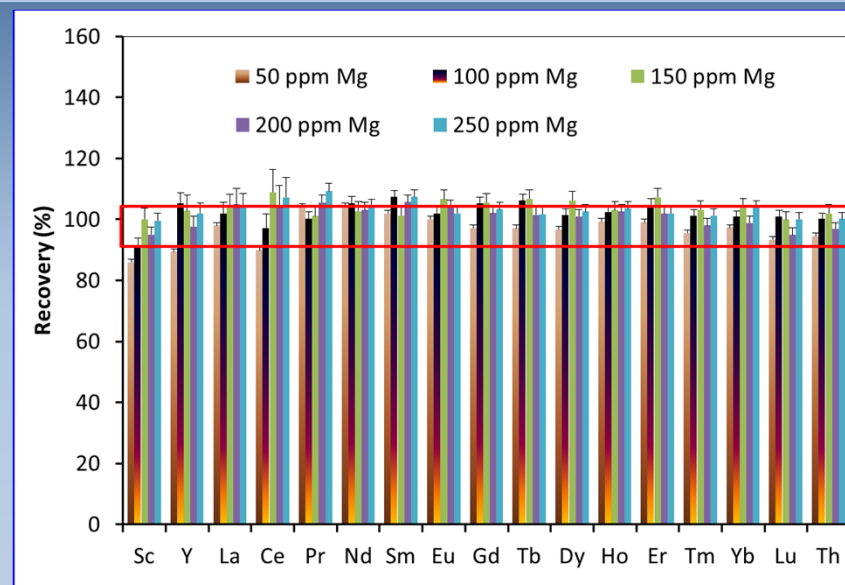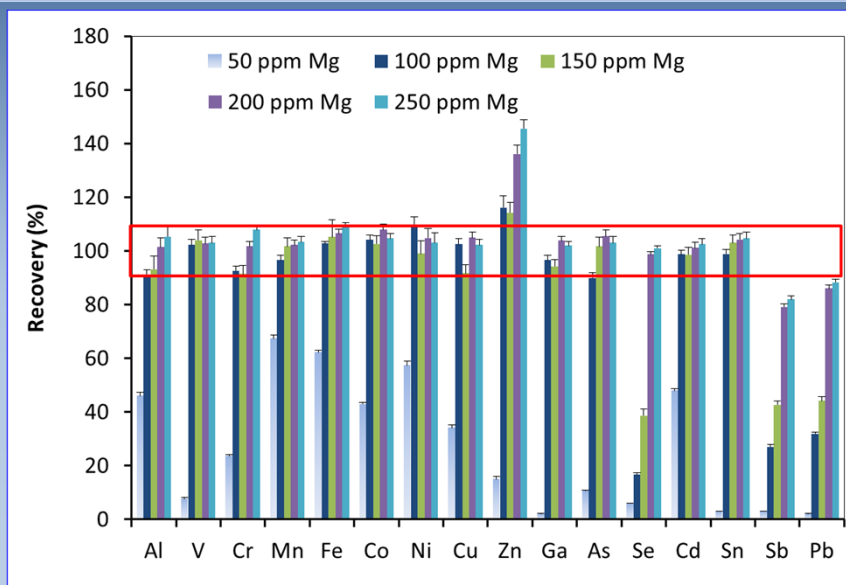- Otoliths contains marginal levels of Mg, approximately 20 to 30 µg/g (or 1 to 4 µg/mL in solution).
- Mg(OH)$_2$ coprecipitation requires at least 150 µg/mL Mg(II) present in solution for quantitative scavenging of most trace elements.
- REEs are quantitively precipitated at lower Mg(II) levels - approximately 50 µg/mL Mg(II).

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Summary / Conclusion

- A new approach for separation of trace elements and rare earth elements from calcium carbonate matrix of otoliths and other biominerals was developed.

- $Mg(OH)_2$ coprecipitation demonstrated for seawater analysis appears to be attractive and simple approach for complete elemental analysis of fish otoliths and biomineral by ICP-MS.

- Ca matrix of solutions can be reduced to trace levels (from 5000 µg/mL to around 10 µg/mL) making solutions more suitable for ICP-MS analysis.

- Additional Mg is required for initiation of $Mg(OH)_2$ precipitation. Optimum levels vary between 50 and 150 µg/mL depending on type of analysis and elements of interest.

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Summary / Conclusion

- Additional Mg levels lead to MgAr interferences on Zn determinations. These could be resolved by HR-ICP-MS, DRC technique or separate analysis of dissolved otoliths prior to $Mg(OH)_2$ coprecipitation.

- This is a work in progress and validation of the approach will be completed with relevant otolith reference materials and biominerals.

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