Calcite Chemistry: matrix independent analysis?
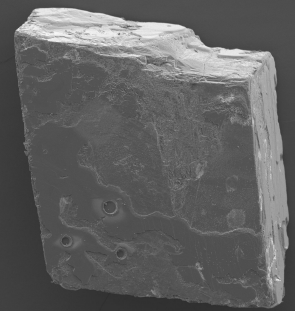
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HV 10.0 kV | Spot 3.0 | WD 10.1 mm | Tilt -0.0 ° | Mag 104x | Sig SE | 3/15/2006 9:58:13 AM | 1.0mm | 016

Introduction

We routinely analyze calcite and aragonite in our laboratory from fossil and cultured foraminifera using NIST SRM 610 for calibration. We use a GeoLas 200Q Excimer 193 nm laser coupled to a Micromass Platform ICP-MS. Ablation craters are typically 40-80 μm in diameter. Different fluences are applied to the glass standards (12 Jcm^{-2}) and samples (2 Jcm^{-2})

Key problems

1. How well do $CaCO_3$ materials ablate at 193 nm?

2. Can we get accurate results for Mg/Ca, Sr/Ca and Mn/Ca in calcite using NIST glasses for calibration?

3. What was the long term reproducibility of these ratios over a four year period?
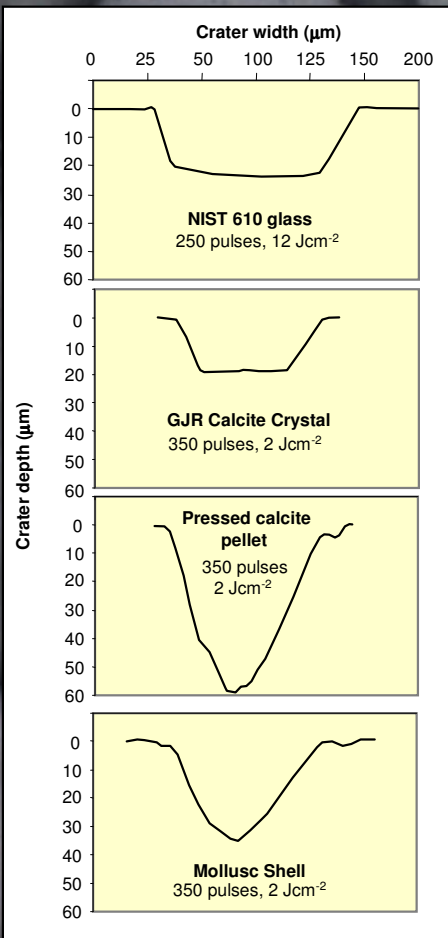
Crater Profiles

NIST 610 glass
250 pulses, 12 Jcm^{-2}

GJR Calcite Crystal
350 pulses, 2 Jcm^{-2}

Pressed calcite pellet
350 pulses
2 Jcm^{-2}

Mollusc Shell
350 pulses, 2 Jcm^{-2}

NIST 610 is used for calibration. The ablation rate is approximately 80 nm/pulse. The sloping walls on the figure are a function of the profilometer measurement. In reality the walls are close to vertical
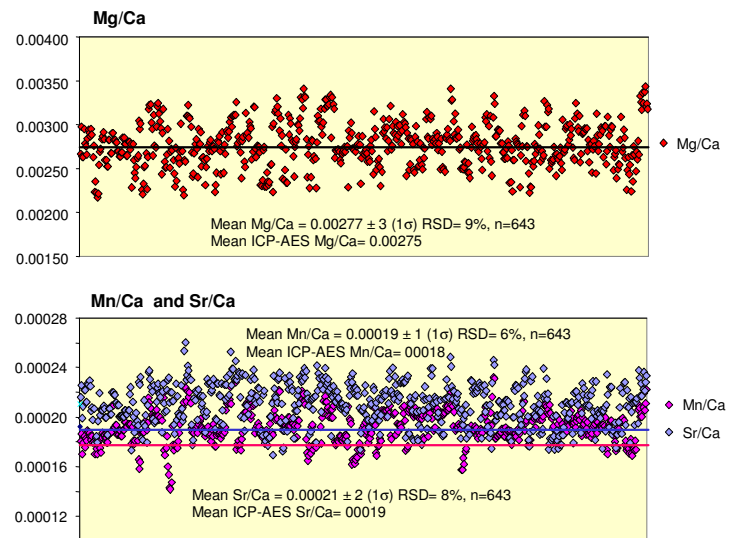
Crater in our in-house calcite reference standard (GJR). The ablation rate is 60 nm/pulse. The calcite ablates more reproducibly at lower fluence

Pressed pellets could be useful as standards. However they ablate more erratically and liberate much more sample per pulse. The ablation rate is about 130 nm/puls

In the biogenic $CaCO_3$ sample ablation was also surprisingly erratic. The ablation rate is now about 80 nm/pulse.

4-year long term precision & accuracy

Mg/Ca

Mean Mg/Ca = 0.00277 ± 3 (1σ) RSD= 9%, n=643
Mean ICP-AES Mg/Ca= 0.00275

Mn/Ca and Sr/Ca

Mean Mn/Ca = 0.00019 ± 1 (1σ) RSD= 6%, n=643
Mean ICP-AES Mn/Ca= 00018

Mean Sr/Ca = 0.00021 ± 2 (1σ) RSD= 8%, n=643
Mean ICP-AES Sr/Ca= 00019

Magnesium to calcium and strontium to calcium ratio's (in mMol/Mol) are important in paleo-climate studies. The figures above show excellent long-term reproducibility for data collected from from 2004 to present. The Mg concentration in the GJR is 673.6 ±56.7 ppm. Sr is 184.3±7.2 ppm and Mn is 105.6±5.7 ppm. This values fall within 7% of ICP-AES bulk digest data.

Line-scan measurements indicate homogeneity in GJR reference calcite crystal

- Mn ppm
- Moving avarage Mn
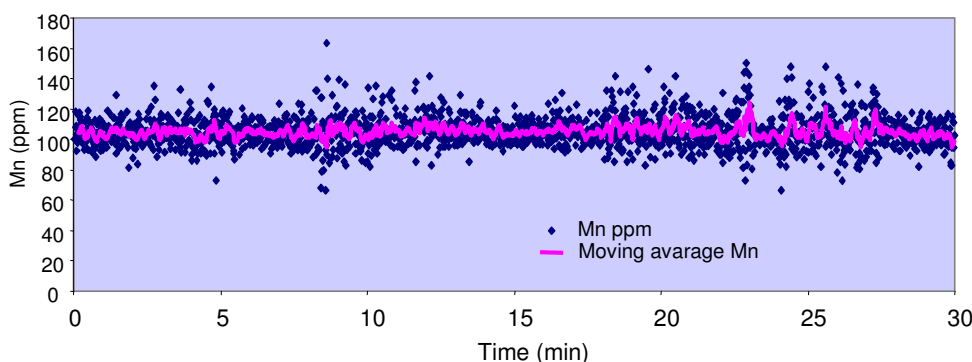
Conclusions

1. NIST 610 can be used to calibrate calcite matricies at 193 nm with different fluences applied to samples and standards

2. Long term reproducibility is excellent (within 10%)

3. GJR is a good candidate as a secondary standard