

"Bleaching" of biogenic carbonates – beware of changes in trace element concentrations!



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#6



Conclusion

Target trace element (TE) determines sample pre-treatment:

Avoid sample treatment when analyzing low concentration TEs (e.g. Mn/Ca)
=> contamination or reallocation

If necessary, apply NaOCl treatment prior to Sr/Ca measurements
=> efficient removal of the organic matrix without
=> alteration of Sr/Ca ratios and/or the carbonate structure

Rationale

Numerous attempts to correlate trace element (TE) concentrations in biogenic carbonates with environmental parameters led to contradictory results. Proxy analyses imply that physical processes control TE incorporation in biogenic carbonates. Incorporation of TEs into the organic matrix, however, is also controlled by physiological processes – **that is the problem!**

One approach to improve the correlation is to chemically remove the organic matrix prior to TE measurements. We use inorganic carbonate and bivalve shell powder (*Arctica islandica*) to examine the effect of 12 treatments on:

- organic matter (N) content
- trace element ratios (Mg/Ca, Sr/Ca, Ba/Ca, Mn/Ca)
- structure and composition of the carbonate

Method

Inorganic carbonate powder

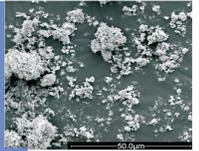
6 subsamples

Treatment 1 to 5 + control

Measurements of:

- N content => CN Analyzer
 - TE ratios => ICP-MS
 - crystallographic structure => XRD
- of the carbonate

A. islandica shell >> one valve



13 subsamples

Treatment 1 to 12 + control

0	No treatment (control)
1	Washing only
2	Acetone
3	H ₂ O ₂
4	NaOH
5	NaOCl
6	Mucosal
7	Acetone+H ₂ O ₂ +Acetone
8	Acetone+NaOH+Acetone
9	Acetone+NaOCl+Acetone
10	Acetone+Mucosal+Acetone
11	Acetone+H ₂ O ₂ +NaOH+Acetone
12	Acetone+H ₂ O ₂ +NaOH+NaOCl+Mucosal+Acetone

Results

Inorganic carbonate powder

sample treatment causes changes of TE/Ca ratios

AND

NaOH treatment alters the crystallographic structure of the carbonate

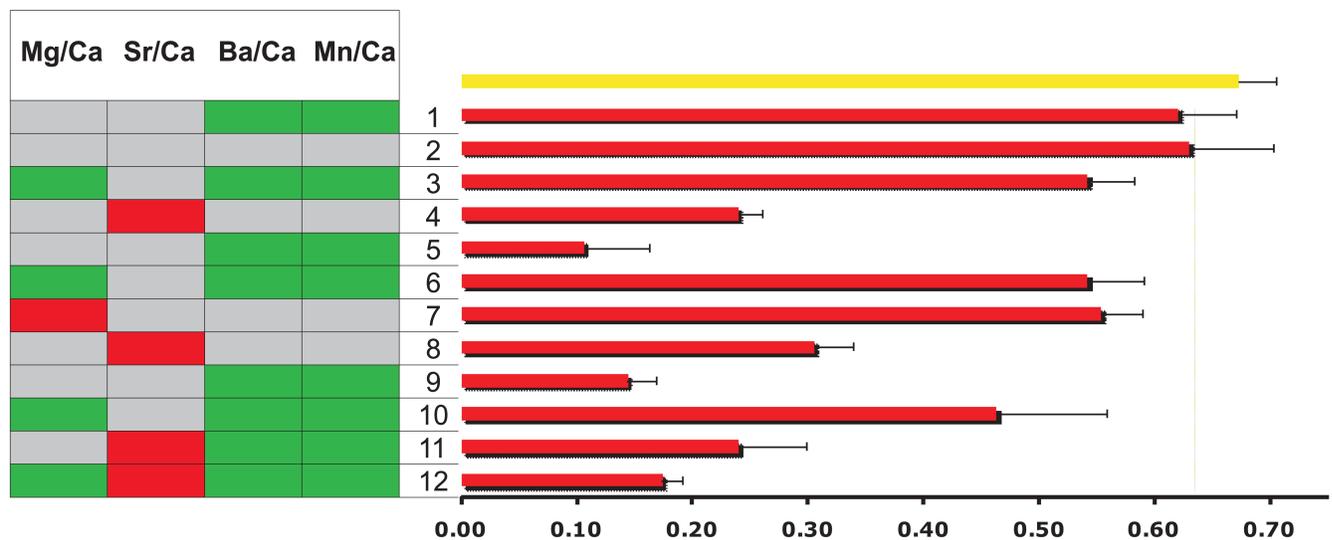
Mg/Ca	Sr/Ca	Ba/Ca	Mn/Ca		% calcite	other constituents after sample treatment
				1	100	
				2	100	
				3	100	
				4	0	Ca(OH) ₂ , Na ₂ CO ₃ , Na ₂ Ca(CO ₃) ₂ ·5H ₂ O, NaOH
				5	75	NaCl

A. islandica shell powder

most efficient N removers:
=> NaOCl (# 5,9,12)
=> NaOH (# 4,8,11,12)

BUT

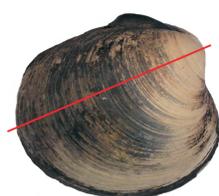
Sr/Ca: NaOH treatment => significant decrease
Mg/Ca, Ba/Ca, Mn/Ca: => no clear pattern
=> tendency to increase



No treatment without side effects! The different treatments (i) vary in their efficiency to remove organic matter, (ii) cause treatment and element specific changes in trace element ratios, and (iii) can even alter the structure and composition of the carbonate.

What's next

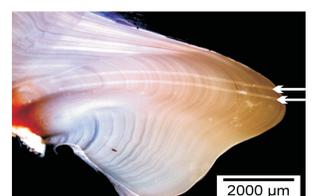
Combine spatial TE map (LA-ICP-MS, microprobe) with spatial mapping of organic matter (Raman)



A. islandica shell



cross-section of the shell



umbo with LA-ICP-MS tracks