

Supplementary Information

1. The procedure of determination of inorganic magnesium content in coccolithophore calcite

The organically bound magnesium in the sample was initially dissociated and measured. Then nitric acid ($0.1 \text{ mol}\cdot\text{L}^{-1}$) was used to completely dissolve the sample, resulting to both organically bound and inorganic magnesium dissociation and then the magnesium concentration was remeasured. The inorganic magnesium was quantitated by the subtraction of organically bound magnesium from the total magnesium. This involved firstly weighing the samples, followed by dilution with deionised water. After 20 minutes of ultra-sonication, the sample suspension was homogeneous and the alkaline-earth metal ions in sample suspension could be detected. Then Cu^{2+} solution (20 mg mL^{-1}) was added to the sample suspension. After 30 minutes of ultra-sonication, the alkaline-earth metal ions in the sample suspension were quantified again. The pH of the suspension was then adjusted to about 2.0 using nitric acid ($0.1 \text{ mol}\cdot\text{L}^{-1}$). This was enough to dissolve all of the carbonates (CaCO_3 , SrCO_3 and MgCO_3) and to release all the Mg^{2+} from the organic phase. The alkaline-earth metal ions in the sample solution were then quantified. All the measurements were performed by a developed HPCIC method.

For each HPCIC measurement, samples were prepared by the following procedure: after the sample suspension became completely homogeneous by ultra-sonication, a certain amount (1 - 5 mL) of suspension was taken and centrifuged. After centrifugation, the supernatant was filtered ($0.22 \mu\text{m}$ syringe filter) and adjusted to $\text{pH} \sim 2.0$ using nitric acid ($0.1 \text{ mol}\cdot\text{L}^{-1}$). The acidic conditions prevented the precipitation of Ca^{2+} or Mg^{2+} . Then chromatography was performed on the filtered supernatant.

2. The list of specified impurities in laboratory grade CaCO₃ samples from different suppliers

Component	Content, %		
	BDH chemicals (Poole, UK)	AJAX chemicals (Sydney, Australia)	Strem Chemicals (Miami, USA)
CaCO ₃	> 99.0	> 99.0	> 99.5
Chloride (Cl)	0.001	0.001	no data
Sulphate (SO ₄)	0.01	0.01	no data
Ammonium (NH ₄)	0.05	0.003	no data
Heavy Metals (Pb)	0.002	0.001	no data
Magnesium (Mg)	0.02	0.02	no data
Iron (Fe)	0.001	0.003	no data
Potassium (K)	0.05	0.01	no data
Sodium (Na)	(sum of Na and K)	0.1	no data
Silicate (SiO ₂)	0.01		no data
Nitrate (NO ₃)	0.02		no data
Phosphate (PO ₄)	0.002		no data
Barium (Ba)	no data	0.005	no data
Strontium (Sr)	no data	0.1	no data

3. The HR-ICP-MS procedure and data

Samples analysed using magnetic sector ICP-MS with medium spectral resolution employed. Samples analysed after dilution 10x, with Indium added as internal standard (at 100 ng L⁻¹), and nitric acid added to final concentration 1%. Quantitation via comparison to external aqueous calibration standards also prepared in 1% nitric acid. All values in measured samples as ng L⁻¹. Scaled up and blank adjusted samples as µg L⁻¹.

The analysed solutions

QC1 and QC2: Quality Control, using 100 ng L⁻¹ of Na, Mg, Ca and K standard solution.

Rinse: Rinsed the machine by ultra-pure water

NIST: SRM 1640a - Trace Elements in Natural Water Reference Material

A1: 53.61 mg of standard reference material (limestone)

A2: 49.20 mg of standard reference material (limestone)

A3: 50.58 mg of standard reference material (limestone)

D1: 51.61 mg of calcium carbonate (Strem Chemicals)

F1: 51.03 mg of calcium carbonate (Strem Chemicals)

Samples **A1, A2, A3, D1** and **F1** were dissolved in 50 mL of 0.03 mol L⁻¹ HNO₃.

Before analysis tests, ng L ⁻¹						
	QC1	Rinse1	Rinse1a	NIST	Rinse1b	Rinse1c
Dilution factor	1	1	1	2	1	1
²³ Na (MR)	103.7	4.6	4.3	1493.5	5.4	5.1
²⁴ Mg (MR)	101.5	0.3	0.3	498.6	0.2	0.3
⁴² Ca (MR)	95.4	3.5	2.7	2688.5	4.3	2.8
³⁹ K (HR)	98.2	1.3	1.1	286.9	1.1	1.0

Analysis of calcium carbonate sample, ng L ⁻¹						
	Blank	A1	A2	A3	D1	F1
Dilution factor	10	10	10	10	10	10
²³ Na (MR)	928.5	117.3	129.3	664.4	8864.3	17114.2
²⁴ Mg (MR)	1.2	159.2	143.3	152.5	529.7	523.4
⁴² Ca (MR)	31.4	37117.1	34427.4	35873.0	33592.6	38418.0
³⁹ K (HR)	5.1	489.8	693.4	260.3	187.5	105.5

After analysis tests, ng L⁻¹			
	Rinse2	QC2	Rinse2a
Dilution factor	10	10	10
²³ Na (MR)	21.3	118.5	16.4
²⁴ Mg (MR)	0.5	101.3	0.2
⁴² Ca (MR)	4.3	104.1	2.5
³⁹ K (HR)	1.4	97.9	1.1

Suggested target concentrations, µg L⁻¹					
	A1	A2	A3	D1	F1
²⁴ Mg (MR)	1.6	1.5	1.5	5.0	5.0