PNAS
www.pnas.org

Supplementary Information for

Global variability in seawater Mg:Ca and Sr:Ca ratios in the modern ocean

Mario Lebrato[1,*,§], Dieter Garbe-Schönberg[1], Marius N. Müller[2], Sonia Blanco-Ameijeiras[3], Richard A. Feely[4], Laura Lorenzoni[5], Juan-Carlos. Molinero[6,†], Karen Bremer[1], Daniel O. B. Jones[7], Debora Iglesias-Rodriguez[8], Dana Greeley[4], Miles D. Lamare[9], Aurelien Paulmier[10], Michelle Graco[10], Joan Cartes[11], Joana Barcelos e Ramos[12], Ana de Lara[13], Ricardo Sanchez-Leal[14], Paz Jimenez[14], Flavio E. Paparazzo[15], Susan E. Hartman[7], Ulrike Westernströer[1], Marie Küter[1], Roberto Benavides[6], Armindo F. da Silva[16], Steven Bell[17], Chris Payne[18], Solveig Olafsdottir[19], Kelly Robinson[20], Liisa M. Jantunen[21], Alexander Korablev[22], Richard J. Webster[23], Elizabeth M. Jones[24], Olivier Gilg[25], Bailly du Bois Pascal[26], Jacek Beldowski[27], Carin Ashjian[28], Nejib D. Yahia[29], Benjamin Twining[30], Xue-Gang Chen[31], Li-Chun Tseng[32], Jiang-Shiou Hwang[32,33], Hans-Uwe Dahms[34] and Andreas Oschlies[6]

[1] Institute of Geosciences, Kiel University, 24118, Kiel, Germany
[2] Oceanography Department, Federal University of Pernambuco, 50670-901, Recife, Brazil
[3] Earth Sciences Department, ETH Zürich, 8092, Zürich, Switzerland
[4] Ocean Climate Department, Pacific Marine Environmental Laboratory/NOAA, 98115, Seattle, USA
[5] Remote Sensing Department, University of South Florida, 33701, Florida, USA
[6] Ecology Department, GEOMAR Helmholtz Centre for Ocean Research Kiel, 24148, Kiel, Germany
[7] Ocean Biogeochemistry and Ecosystems Department, National Oceanography Center, SO14 3ZH, Southampton, UK
[8] Ecology, Evolution and Marine Biology Department, University of California Santa Barbara, 93106, Santa Barbara, USA
[9] Department of Marine Science, University of Otago, 9016, Dunedin, New Zealand
[10] Biogeosciences Department, Laboratoire d´Etudes en Geophysique et Oceanographie Spatiales (LEGOS), IRD/CNRS/CNES/UPS, University of Toulouse, 31000, Toulouse, France
[11] Renewable Marine Resources Department, Institute of Marine Sciences at Spanish National Research Council, 08003, Barcelona, Spain
[12] Climate, Meteorology and Global Changes Department, University of the Azores, 9501-855, Ponta Delgada, Portugal
[13] Organisms & Systems Biology Department, University of Oviedo, 33003, Oviedo, Spain
[14] Physical Oceanography Department, Spanish Institute of Oceanography (IEO), 11006, Cadiz, Spain

[15] Biological Oceanography, CESIMAR-CONICET, 2915, Chubut, Argentina
[16] Marine Biogeochemistry Department, Bazaruto Center for Scientific Studies (BCSS), Benguerra Island, 1304, Vilankulos, Mozambique
[17] Marine Chemistry Department, Bermuda Institute of Ocean Sciences (BIOS), GE 01, St. George, Bermuda
[18] Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, BC V6T 1Z4, Vancouver, Canada
[19] Marine Environment Department, Marine and Freshwater Research Institute, 101, Reykjavic, Iceland
[20] Department of Biology, University of Louisiana at Lafayette, 70503, Louisiana USA
[21] Air Quality Processes Research Department, Environment and Climate Change Canada, L0L 1N0, Ontario, Canada
[22] Geophysics Department, University of Bergen, 5007, Bergen, Norway
[23] Clinical Research Unit, CHEO Research Institute, K1H 8L1, Ottawa, Ontario, Canada
[24]Oceanography and Climate Department, Institute of Marine Research, Fram Centre, Hjalmar 9007 Tromsø, Norway
[25] Chrono-Environnement Department, Université de Bourgogne Franche-Comté, 21078, Dijon, France
[26] Radioecology Department, IRSN - Cherbourg Radioecology Laboratory (LRC), 50130, Octeville, France
[27] Marine Chemistry and Biochemistry Department, Polish Academy of Sciences, 81-712, Sopot, Poland
[28] Biology Department, Woods Hole Oceanographic Institution, 02543, Massachusetts, USA
[29] Biological and Environmental Sciences Department, Qatar University, 2713, Doha, Qatar
[30] Center for Ocean Biogeochemistry and Climate Change, Bigelow Laboratory for Ocean Sciences, ME 04544, USA
[31] Department of Ocean Science and Engineering, Zhejiang University, 316021, Zhoushan, China
[32] Marine Biology Institute, National Taiwan Ocean University, 20224, Keelung City, Taiwan
[33] Center for Excellence for the Oceans, National Taiwan Ocean University, 20224, Keelung City, Taiwan
[34] Department of Biomedical Science and Environmental Biology, Kaohsiung Medical University, 807, Kaohsiung, Taiwan

[*]*Corresponding Author*
Institute of Geosciences, CAU Kiel University, Ludewig-Meyn-Strasse 10, 24118, Kiel, Germany
E-mail: mlebrato13@gmail.com
Telephone: +34 610 67 77 42

[§]*Present Address*
Bazaruto Center for Scientific Studies (BCSS), Benguerra Island, Inhambane Province, Mozambique

[†]*Present address*
Marine Biodiversity, Exploitation and Conservation (MARBEC), IRD/CNRS/IFREMER/University of Montpellier, CS 30171 - 34203, Sète cedex, France

This PDF file includes:

Methods S1
Supplementary Text S1
Fig. 2
Figs. S1 to S5
Captions for Figs. S1 to S5
Tables S1 to S3
Captions for Tables S1 to S3

Other supplementary materials for this manuscript include the following:

Appendix 1 to 6
References

Supplementary Information

Materials and Methods S1

Global sampling program

Sampling efforts from 2009 until 2017 combined ongoing research cruises, official programs and time-series with citizen science initiatives, recreational boats and fellow scientific volunteers to reach globally to as many remote locations and ecosystems as possible (Fig. 1; SI Appendix 1, 3, 4). Agreements were established between the PI and all participants to collect seawater samples following a strict protocol (see SI Appendix Text S1) along with the sample metadata (latitude, longitude, temperature, salinity, depths, and CTD data). Sampling was organized either by direct contact with existing projects/surveys/programs/oceanographic lines/buoys or by posting announcements in group emails/lists and institutions around the world. We accessed samples in a total of 79 programs/cruises/initiatives worldwide, and we were directly involved/present in at least 15 cruises. Sampling effort covered all possible locations at low/temperate/high latitudes, open ocean, and coastal regions with emphasis on the euphotic (0-300 m), mesopelagic (300-1000 m), and abyssal zones (+1000 m) using transects, stations and vertical CTD profiles. The baseline strategy was to sample horizontally (transects) and vertically (CTD rosette) from coastal regions to the open ocean to monitor variability at large, expanding also to the shelves, the neritic zones, river mouths, the intertidal/subtidal and the ice sheets. Number of samples and locations were pre-arranged with participants but a large number of expeditions changed their plans, thus sampling occurred on opportunity (see SI Appendix Fig. S3 for examples). All participants were provided exactly with the same sampling kit to maximize sampling homogeneity, which consisted in 15/50 ml sterile tubes, 50 ml sterile syringes, 0.20 µm sterile filters (to retain particles and bacteria), plastic gloves, and *Parafilm*® (see SI Appendix Text S1 for details).

Seawater sampling procedure

All research cruises had a Niskin-type bottle, a CTD rosette array or a scientific-grade sampling device available to recover seawater samples at surface and depth. Other participants (surface samples) used a bucket or directly collected the sample with a plastic tube. Right after sampling, all samples were gently filtered through a 0.22 µm sterile filter using a sterile syringe and stored into 15/50 ml polyethylene tubes with *Parafilm*® wrapped around the cap, preventing thus contamination and evaporation. All samples were stored in the fridge (4 to 8 °C) and sent for analysis to the ICP-MS lab at Institute of Geosciences, Christian-Albrechts-Universität zu Kiel, Germany, between 6 to 12 months after collection. After 1 year in storage in a cold place, no signs of seawater evaporation or leaks were observed (< 0.05% Mg/Ca and Sr/Ca ratios variability n = 30) (*1*). All our samples were measured within 12 months after collection to guarantee data quality and comparability, minimizing any % change over time.

Seawater analytical procedures

In the laboratory at Institute of Geosciences, Kiel University, Germany, samples were divided into three splits (A, B, C) and only split A was analyzed. Splits B and C were stored as a back-up in cases of analytical bias, or re-sampling/verification. All split A samples were analyzed in the same laboratory and machine by the same person, for Ca, Mg, Sr with truly simultaneous data acquisition using an inductively coupled plasma – optical emission spectrometer (ICP-OES) SPECTRO Ciros™ CCD SOP with radial viewing optics. Samples were 50-fold diluted with 2% (v/v) freshly subboiled in HNO_3 and introduced with a GE Seaspray™ micro-nebulizer and thermostatized Cinnabar™ cyclonic spray chamber. All sample preparation work, and storage of sample solutions in the auto-sampler during analysis, was performed under Class-100 clean bench conditions by the same person. Only all-plastic lab ware was used for handling and treatment of the samples, avoiding storage in polypropylene mini-vials having elevated Mg. Only ultrapure reagents and ultrapure water (Elga Labwater) were used. The following emission lines were selected for quantification: Ca: 317.933 (II); Mg: 279.553nm (II); Sr: 407.771nm (II), 421.552nm (II) and measured simultaneously within the same pre-selected acquisition interval ("Phase 3"). In addition, Ar: 597.159nm (I) was used as a monitor line for plasma temperature. Three pixels were summarized for peak area integration of the respective emission line (Smart Analyzer 3.30 Software, Spectro A.I.). Total analysis time per sample with 5 replicate measurements including sample take-up and washout was roughly 6 minutes consuming about 2 ml of measuring solution. A combined intensity calibration and drift correction procedure using IAPSO standards (*2*, *3*) was applied for data processing (SI Appendix 4). Calibration solutions were matrix matched with NaCl to 50-fold diluted normal seawater salinity covering the range of seawater Mg:Ca 4.10-5.80 (mol:mol), and Sr:Ca 7.70-8.80 (mmol:mol). Raw data (in cps) was exported from the instrument into spreadsheet software for post-processing. Average raw counts from 5 runs for *Blank-00* (blank for Ca) and *Blank-0* (matrix-matched with 10 mg l^{-1} Ca as a blank for Mg, Sr) were subtracted from all subsequent measurements. From blank-subtracted raw intensities, ratios were calculated for all combinations of selected Mg and Sr wavelengths with the selected Ca line in order to determine the most robust wavelength pairs. A linear least-square regression function was applied for the calculation of molar ratios (in mmol:mol) from intensity ratios of the calibration standards (*2*). Then, the obtained results were normalized to an external standard (IAPSO, ORIL, U.K. using Mg:Ca = 5.140 mol:mol, Sr:Ca = 8.481 mmol:mol) in a way commonly used in isotope studies. This approach minimizes variability and uncertainties, respectively, resulting from both instrument drift during the day and instrument set-up between different days. Every batch of 6 samples was bracketed by the IAPSO normalization standard that was also used for linear drift correction. For estimating short term reproducibility every 11th sample was reanalyzed, and so were the first 5 samples from a session reanalyzed at the end of the session with e.g. 352 samples. Mean uncertainty estimated from duplicate measurements per sample on 33 randomly chosen samples was 0.35 and 0.85 % relative SD (1 SD) for seawater Mg:Ca and Sr:Ca while measurement uncertainty (5 runs) was 0.16 and 0.37 % RSD, respectively (SI Appendix 4). The expanded uncertainties including uncertainty of the true values for IAPSO are 3.30 % for seawater Sr:Ca and 0.5 % for seawater Mg:Ca. Uncertainty as estimated from measurement reproducibility that is important for detecting small differences even in our open ocean sample suite, was well below 0.40 % for seawater Mg:Ca and 0.90 % for seawater Sr:Ca. When averaging only the first three measurements for our IAPSO reference sample right after initial calibration of all three analytical sessions where the samples were run, then the measured

IAPSO average was Sr:Ca = 8.481 ±0.068 mmol:mol. Comparing data routinely obtained for multi-element analyses of seawater, then we find measured IAPSO averages ranging from Sr:Ca = 8.273 to 8.555 mmol:mol. It is always the Ca that is making the difference: we measure around 409 mg L^{-1} Ca (10.20 mM Ca) while ODP-TAMU reported 422 mg L^{-1}, 10.55 mM Ca. Our Sr results are identical with ODP_TAMU: 7.62 mg L^{-1} Sr (86.97 µM Sr).

Literature data and information use

Our new measured dataset was complemented with a seawater Mg:Ca and Sr:Ca ratios literature survey (Fig. 4c for comparison with this study data; SI Appendix 2) to expand on the global horizontal and vertical coverage, to consolidate and compare with the work of earlier researchers at a regional scale. Hundreds of publications and reports were screened for data quality and analytical clarity to mine data comparable to our measured dataset (analytical methods varied from ICP-AES/-OES to gravimetric titration and to TIMS). The methods section for each publication/report were also carefully inspected for analytical accuracy. We also put together a table on the historical use of seawater Mg:Ca and Sr:Ca ratios in all marine science disciplines in the last 100 years (Table S3). This served to put in perspective the significance of the new dataset results for the scientific community to foresee if the implications apply to a certain discipline.

Public datasets use

The newly measured seawater Mg:Ca and Sr:Ca ratios dataset (SI Appendix 3) was combined with seawater environmental metadata mined from GLODAPv2 (*4*, *5*), and used to analyze and classify seawater Mg:Ca and Sr:Ca ratios as a function of environmental variables (SI Appendix 3). ArcGIS 10.0 (ESRI 2011) and the 3-D analytical tool "NEAR 3-D analysis" were used to link environmental seawater conditions with the sample's seawater ratios. This approach permitted evaluation of the diagonal distance between each ratio input parameter (latitude, longitude, and depth) and the nearest seawater datum (temperature, salinity, Total Alkalinity - TA, dissolved inorganic carbon - DIC, pH_{total} and pCO_2) at a specific latitude, longitude, and depth. The prerequisite for data adoption was a matching data set XYZ (including ratio parameter) versus $X_iY_iZ_i$ (including ambient seawater property). Both datasets were plotted on a 2-D field and merged into a single 3-D field, and then the nearest seawater datum to the ratio was determined using a diagonal line in a 3-D matrix. Additionally, each datum was individually checked to verify that the NEAR 3-D approach worked correctly. When the prediction was not sufficiently accurate, the closest value was manually selected. This procedure ensured selection of the most relevant seawater parameters for a given ratio. The GEMS-GLORI database was used to provide a distribution map of seawater Mg:Ca ratios from river mouths/plumes around the world (SI Appendix 6; SI Appendix Fig. S1), but these data were not used in the overall analysis, and are reported merely for comparison purposes. Lastly, various paleo proxies' global databases were mined to provide distribution maps of paleo reconstructions and understand the relevance of our database results for the scientific community (SI Appendix Fig. S2). Our published databases are deposited at the NOAA National Center for Environmental Information (NCEI) under Accession Number 0171017 in http://accession.nodc.noaa.gov/0171017 (DOI:10.7289/V5571996).

Data analysis and statistics

The final seawater Mg:Ca and Sr:Ca ratios were classified by Ocean, Longhurst Province, Ecosystem type, Latitude, Longitude, Depth (in 5 intervals to facilitate analyses) (SI Appendix 3) and then by all the metadata (chemistry) to facilitate interpretation of results and statistical analyses. Ratios were mapped globally (Fig. 1; SI Appendix S1), versus. Depth, and by ecosystem

(Fig. 1, 3) to understand ratios spatial and vertical distributions. Ratios were also plotted against each property to understand individual processes/mechanisms and to monitor variability (Fig. 2). A Generalized Linear Model (GLM) using forward stepwise selection was applied to the ratios vs. 5 depth intervals to understand complexity and individual parameter significance with depth (SI Appendix 5; SI Appendix Table S2). All analyses and graphical work were performed in Statistica 13.0 (StatSoft), SigmaPlot 12.0 (Systat Software Inc.), ArcGIS (ESRI 2011), SURFER (Golden Software, LLC.), and Corel Draw X3 (Corel Corp.).

Text S1

The following instructions were sent to each project participant and PI along with the same 15 ml falcon tubes, 0.20 µm filters, Parafilm, and 50 ml syringes and gloves to ensure reproducibility and minimize handling errors. A PDF was emailed and a printed version was included in the boxes with the consumables.

Sampling for the determination of seawater composition in terms of Mg/Ca and Sr/Ca (PI: Mario Lebrato)

Sampling

Note: use gloves during sampling procedure

1. Sample along the agreed transect/station using a Niskin-type bottle, a bucket or any means to get seawater in a clean way. Use only the lab gear/consumables we provide.
2. Samples must be stored cool and dry place.
3. Avoid touching or contaminating the sample before or after the procedure.

Laboratory

1. Filter through a fresh sterile 0.20 µm filter using a syringe for each sampling station/sample.
2. Rinse the syringe 3 times with seawater that is going to be filtered (mounting and dismounting the syringe).
3. Dismount the back part of the syringe.
4. Pour 40 ml of seawater.
5. Mount back the syringe.
6. Filter gently, but discard the initial 2 to 5 ml of seawater.
7. Store 15 ml of the sample in a Falcon tube**.**
8. Close the cap with Parafilm if possible or close very tight.
9. Store in a cool and dry place until shipping to us.

Labelling

Samples label and ID should be easily linked with the Excel sheet and metadata.

Metadata

Collect for each sample: Date, Latitude/Longitude, Sample depth, Temperature, and Salinity only with calibrated or trusted sensors. Please include notes on metadata errors, inaccuracies or any relevant issue. If needed discussion, please email the project PI.

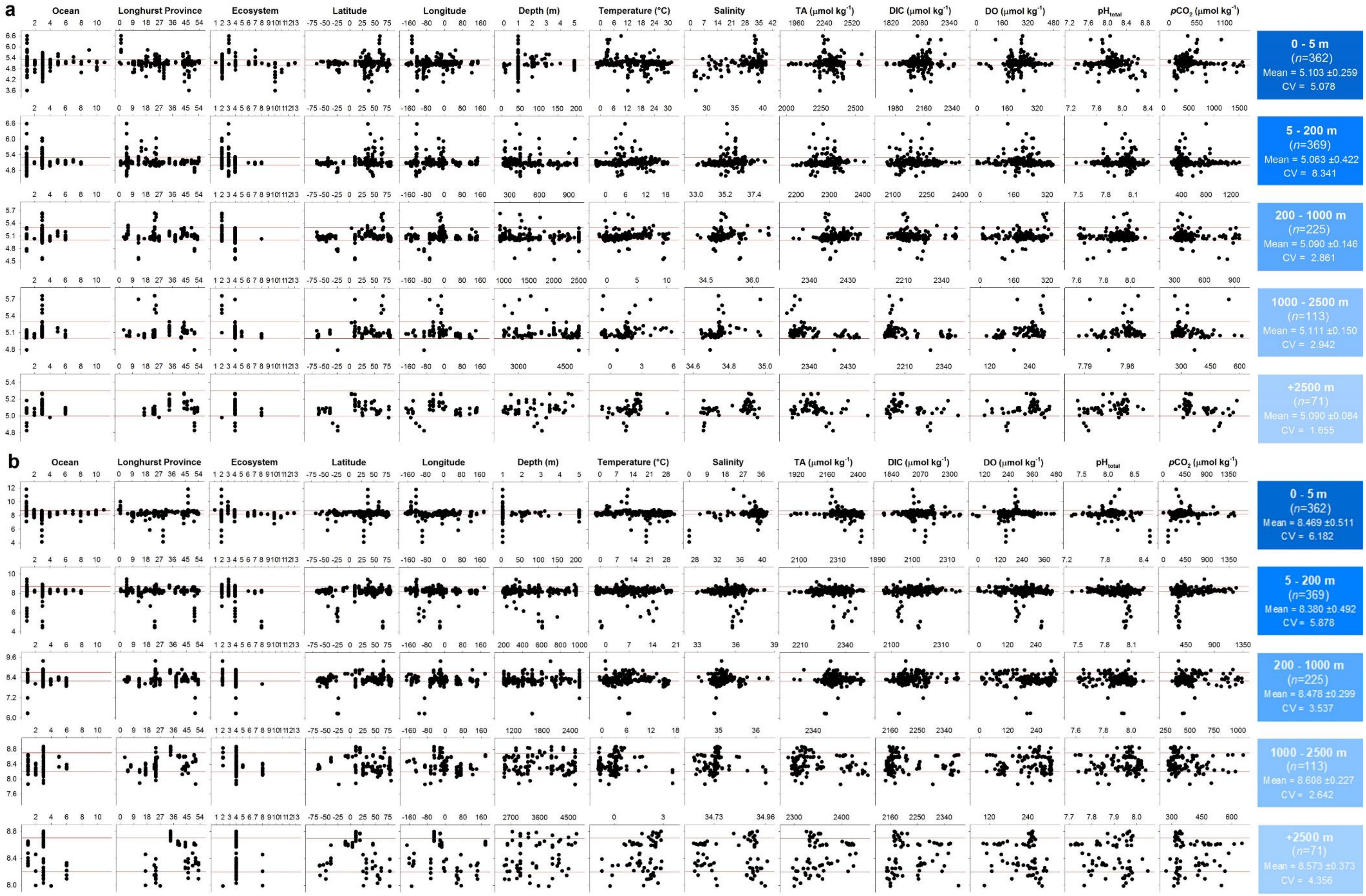

a
b
Ocean
Longhurst Province
Ecosystem
Latitude
Longitude
Depth (m)
Temperature (°C)
Salinity
TA (μmol kg-1)
DIC (μmol kg-1)
DO (μmol kg-1)
pHtotal
pCO2 (μmol kg-1)
Mg:CaSW (mol:mol)
Sr:CaSW (mmol:mol)
0 - 5 m
(n=362)
Mean = 5.103 ±0.259
CV = 5.078
5 - 200 m
(n=369)
Mean = 5.063 ±0.422
CV = 8.341
200 - 1000 m
(n=225)
Mean = 5.090 ±0.146
CV = 2.861
1000 - 2500 m
(n=113)
Mean = 5.111 ±0.150
CV = 2.942
+2500 m
(n=71)
Mean = 5.090 ±0.084
CV = 1.655
0 - 5 m
(n=362)
Mean = 8.469 ±0.511
CV = 6.182
5 - 200 m
(n=369)
Mean = 8.380 ±0.492
CV = 5.878
200 - 1000 m
(n=225)
Mean = 8.478 ±0.299
CV = 3.537
1000 - 2500 m
(n=113)
Mean = 8.608 ±0.227
CV = 2.642
+2500 m
(n=71)
Mean = 8.573 ±0.373
CV = 4.356

Fig. 2. Modern ocean seawater Mg:Ca and Sr:Ca ratios versus environmental parameters. Data horizontally classified for seawater Mg:Ca (a) and Sr:Ca (b) ratios as a function of environmental variables (GLODAPv2; *41, 42*) from the largest to the smallest dimension, and vertically in five depth intervals of 0-5 m, 5-200 m, 100-1000 m, 1000-2500 m, and +2500 m. Data within the red lines represent literature assumed knowledge of modern seawater ratios. Code for “Ocean” is: 1=Pacific, 2=Indian, 3=Atlantic, 4=Arctic, 5=Mediterranean, 6=Southern, 7=Red Sea, 8=China Sea, 9=Arabian Sea, 10=Baltic Sea, 11=IAPSO. Code for “Longhurst Province” is in SI Appendix Table S1 and Vliz (2009): http://www.marineplan.es/ES/fichas_kml/biogeog_prov.html. Code for “Ecosystem” is: 1=IAPSO (This study), 2=Coastal Sea, 3=Coastal Upwelling, 4=Open Ocean, 5=Open Ocean Upwelling, 6=Shallow Hydrothermal Vent, 7=Coral Reef, 8=Deep Hydrothermal Vent, 9=Glacier Seawater, 10=Estuary, 11=Mudflats, 12=Mangroves, 13=Seagrass. Extended analysis of seawater Mg:Ca ratios data from river mouths to assess coastal waters can be found in SI Appendix Fig. S1.

Supplementary Figures & Captions

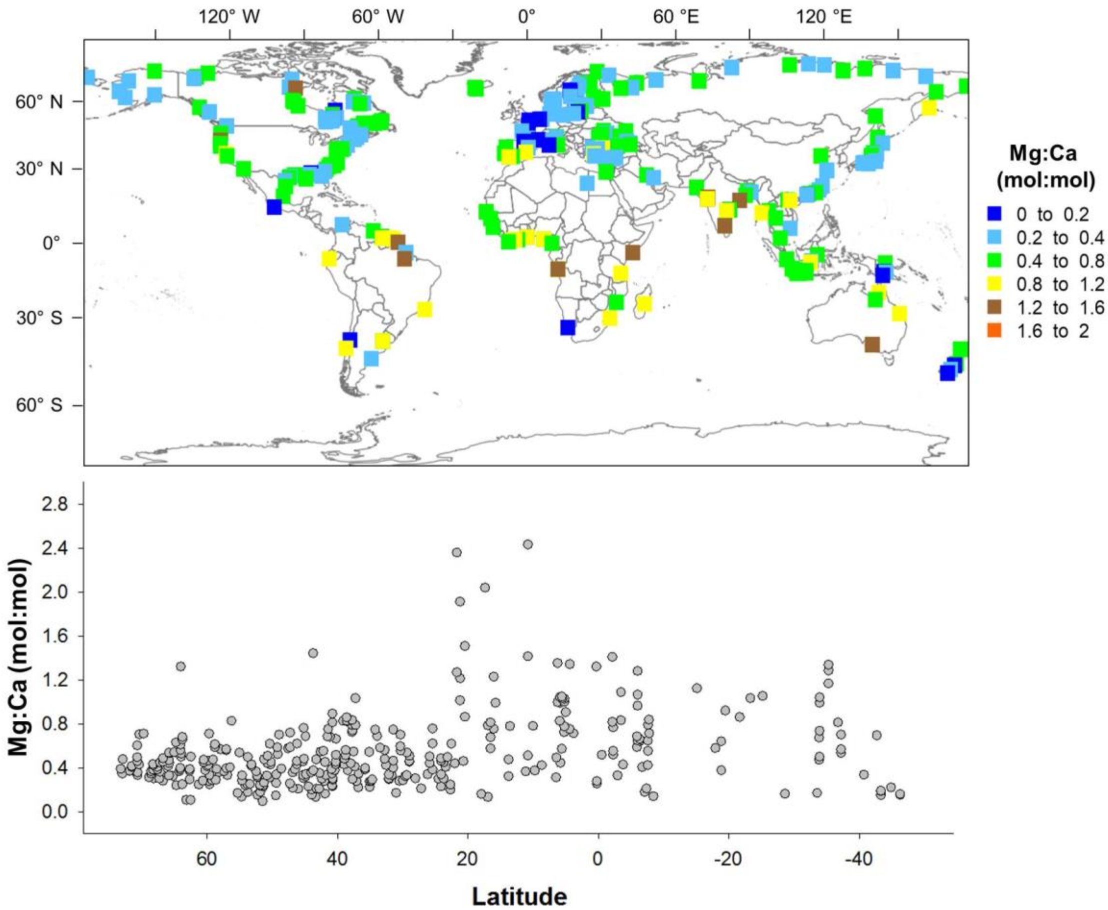


Fig. S1. River mouth seawater Mg/Ca ratios. Compilation of seawater Mg and Ca concentrations along with seawater Mg/Ca ratios of major river mouths globally. River mouth data help to understand coastal anomalies in seawater composition and can be treated as "caution areas" for paleo research aiming to reconstruct more open ocean settings for certain properties. Original data belong to the GEMS-GLORI database (*6*), which can be accessed at https://doi.pangaea.de/10.1594/PANGAEA.804574.

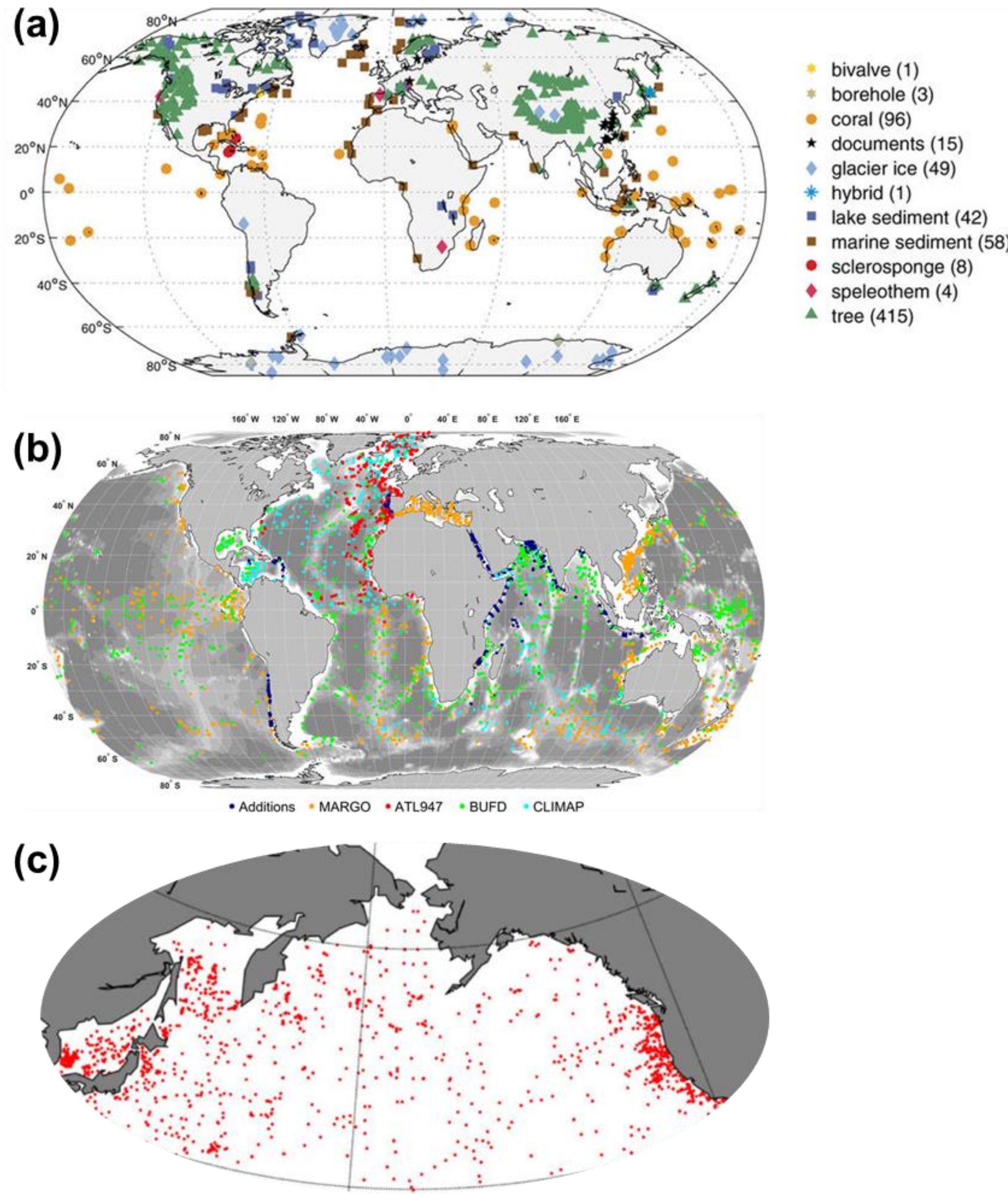
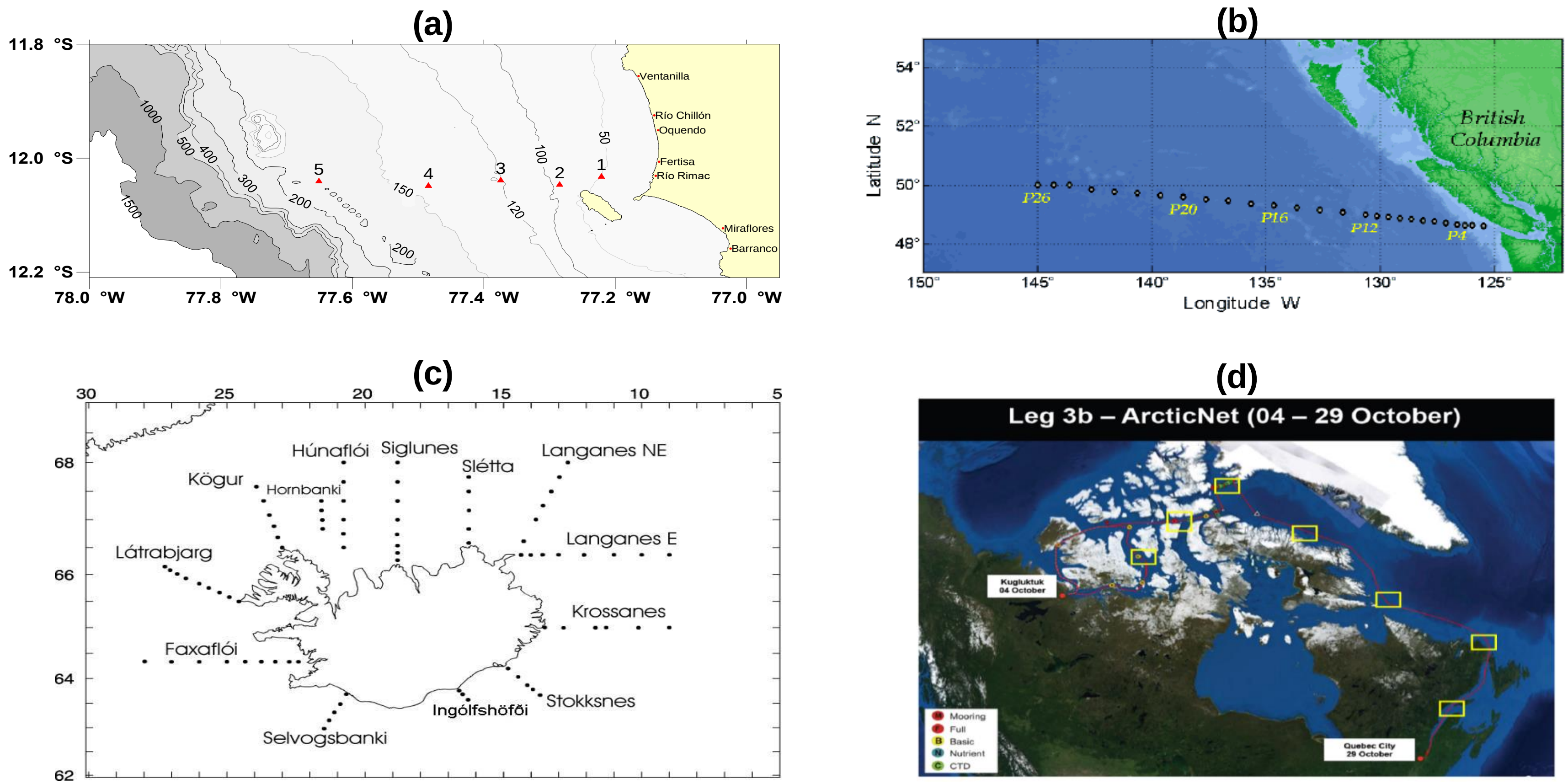
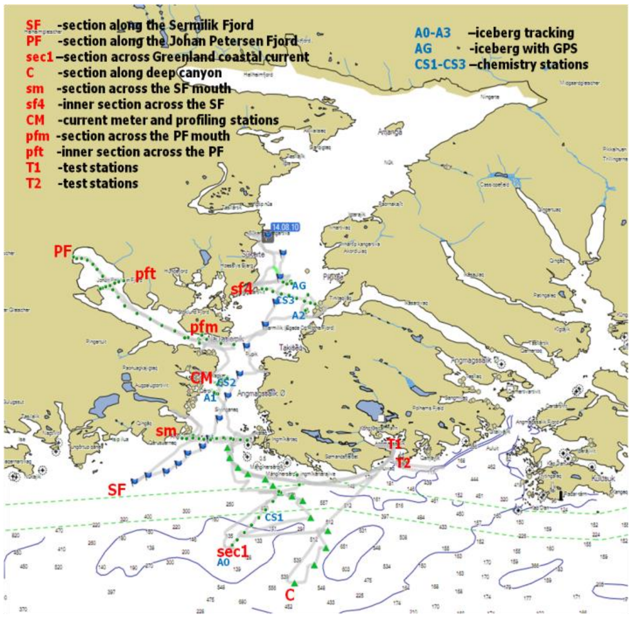


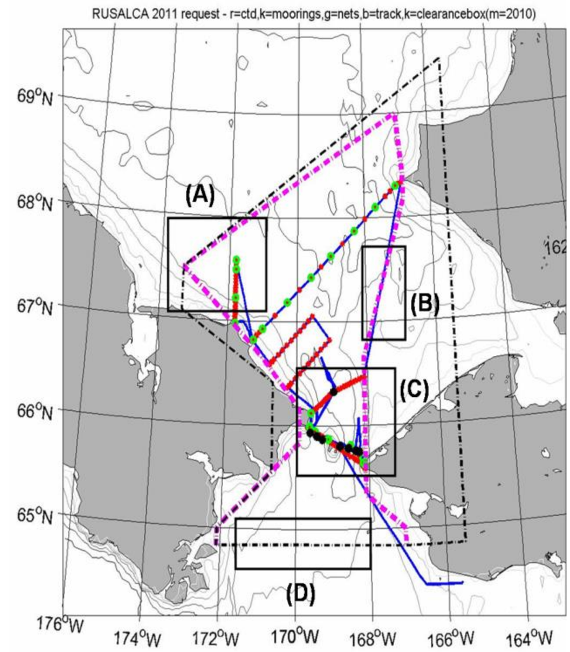
Fig. S2. Examples of databases used in paleo research. A good understanding of modern seawater Mg:Ca and Sr:Ca ratios divided by Ocean, Longhurst Province, Ecosystem and region comes into perspective in paleo research depending on the type of reconstruction being conducted. Nowadays, efforts to develop paleo proxies have reached a global scale but still rely on local and regional samples: (a) Geographical distribution by archive type in the proxy records from the PAGES2k initiative (*7*), (b) Census of planktonic foraminifera in surface sediment samples (*8*), and (c) Paleoceanographic sediment cores from the North Pacific, 1951-2016 (*9*). All figures are used as published under a Creative Commons CC-BY license and a Creative Commons Attribution 3.0 License to M. Lebrato.


(a)
11.8 °S
12.0 °S
12.2 °S
78.0 °W
77.8 °W
77.6 °W
77.4 °W
77.2 °W
77.0 °W
Ventanilla
Río Chillón
Oquendo
Fertisa
Río Rimac
Miraflores
Barranco
1
2
3
4
5
1000
1500
500
400
300
200
150
120
100
50
(b)
British Columbia
Latitude N
Longitude W
54°
52°
50°
48°
150°
145°
140°
135°
130°
125°
P26
P20
P16
P12
P4
(c)
30
25
20
15
10
5
68
66
64
62
Húnaflói
Siglunes
Slétta
Langanes NE
Kögur
Hornbanki
Langanes E
Látrabjarg
Krossanes
Faxaflói
Stokksnes
Ingólfshöfði
Selvogsbanki
(d)
Leg 3b – ArcticNet (04 – 29 October)
Kugluktuk 04 October
Quebec City 29 October
Mooring
Full
Basic
Nutrient
CTD

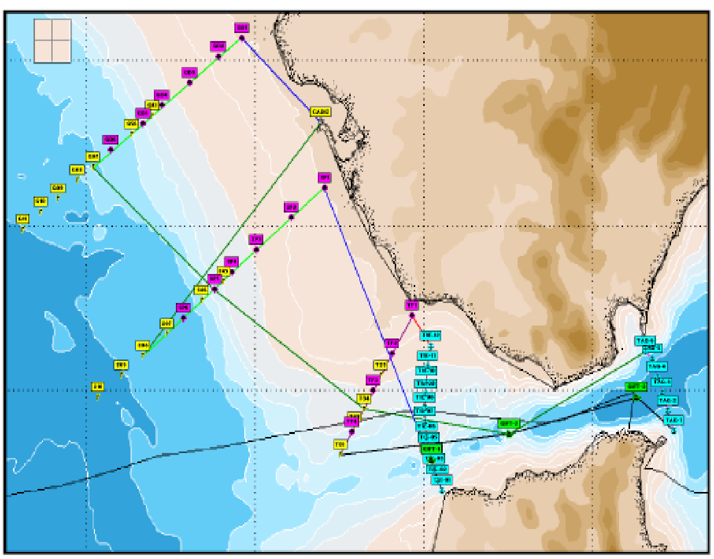
(e)


SF -section along the Sermilik Fjord
PF -section along the Johan Petersen Fjord
sec1 -section across Greenland coastal current
C -section along deep canyon
sm -section across the SF mouth
sf4 -inner section across the SF
CM -current meter and profiling stations
pfm -section across the PF mouth
pft -inner section across the PF
T1 -test stations
T2 -test stations
A0-A3 -iceberg tracking
AG -iceberg with GPS
CS1-CS3 -chemistry stations
PF
pft
sf4
pfm
CM
sm
SF
T1
T2
sec1
C

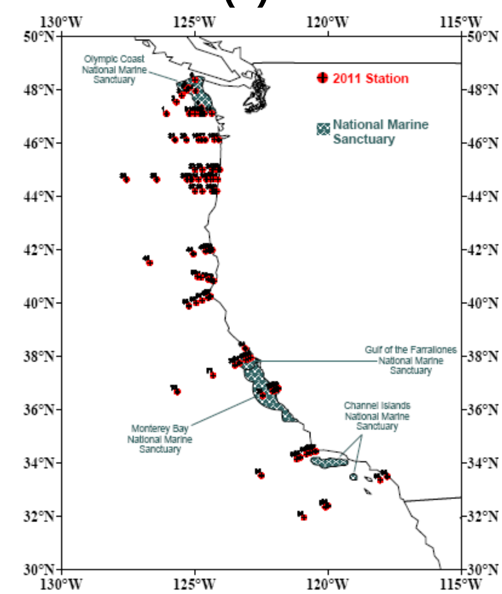
(f)


RUSALCA 2011 request - r=ctd,k=moorings,g=nets,b=track,k=clearancebox(m=2010)
69°N
68°N
67°N
66°N
65°N
(A)
(B)
(C)
(D)
176°W
174°W
172°W
170°W
168°W
166°W
164°W

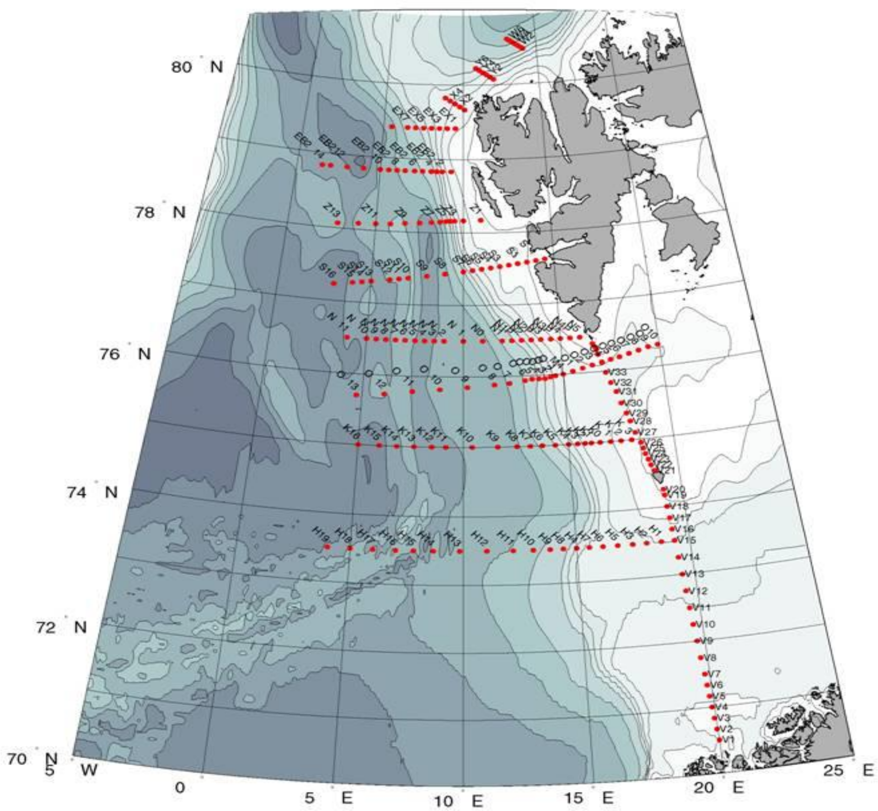
(g)



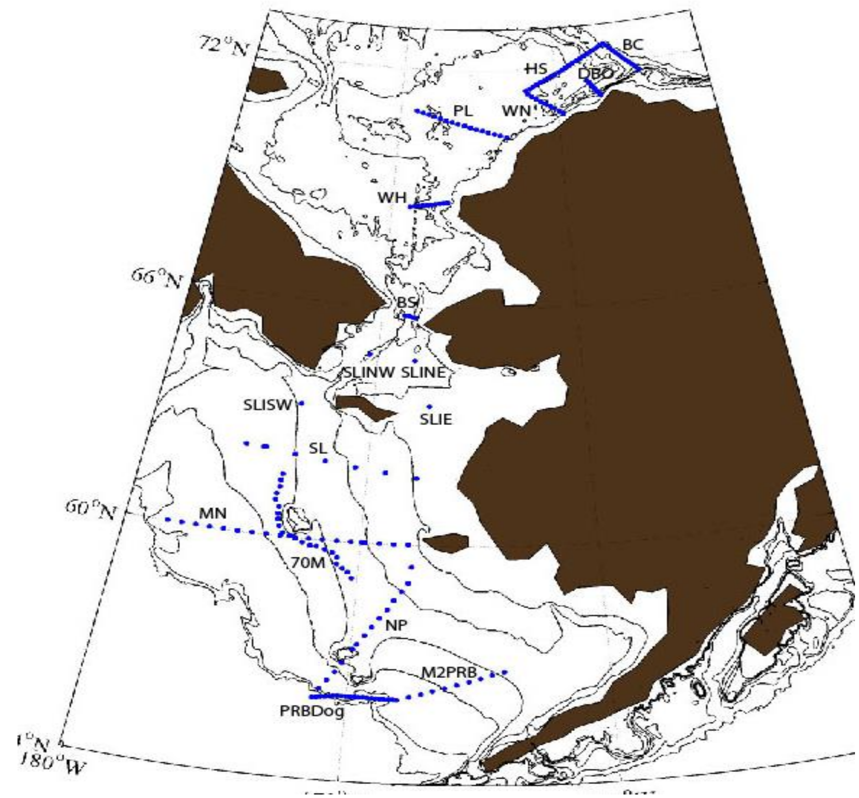
(h)


130°W
125°W
120°W
115°W
50°N
48°N
46°N
44°N
42°N
40°N
38°N
36°N
34°N
32°N
30°N
Olympic Coast National Marine Sanctuary
2011 Station
National Marine Sanctuary
Gulf of the Farallones National Marine Sanctuary
Monterey Bay National Marine Sanctuary
Channel Islands National Marine Sanctuary

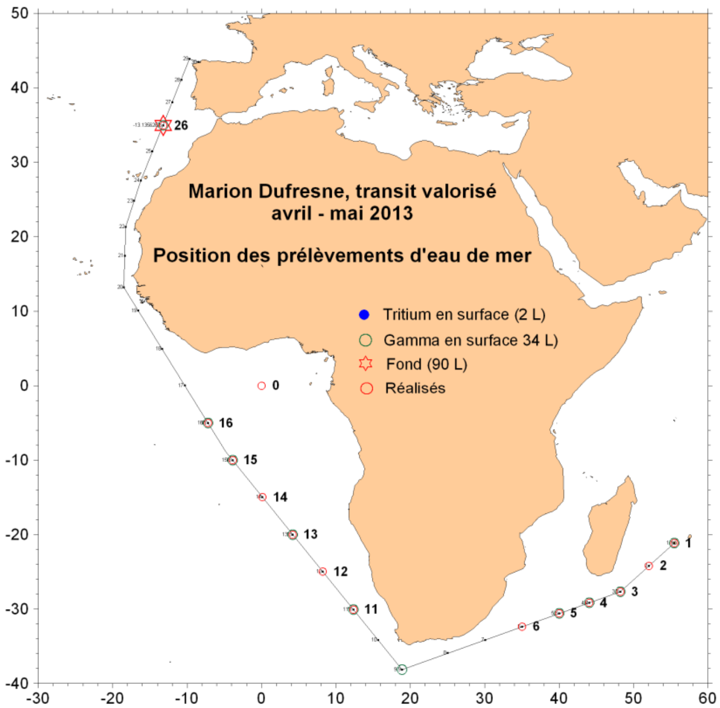
(i)


80 N
78 N
76 N
74 N
72 N
70 N
5 W
0
5 E
10 E
15 E
20 E
25 E

(j)


72°N
66°N
60°N
180°W
BC
HS
DBO
PL
WN
WH
BS
SLINW
SLINE
SLISW
SLIE
SL
MN
70M
NP
M2PRB
PRBDog

(k)


Marion Dufresne, transit valorisé
avril - mai 2013
Position des prélèvements d'eau de mer
Tritium en surface (2 L)
Gamma en surface 34 L)
Fond (90 L)
Réalisés

(l)

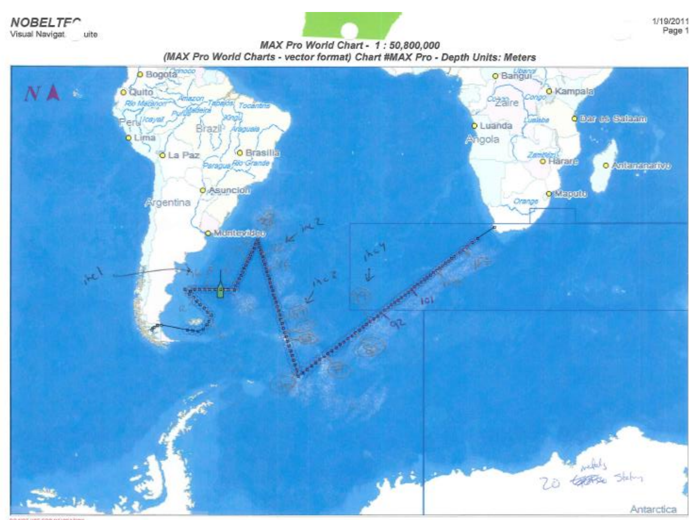

NOBELTEC
1/19/2011
Page 1
MAX Pro World Chart - 1 : 50,800,000
(MAX Pro World Charts - vector format) Chart #MAX Pro - Depth Units: Meters
Antarctica

Fig. S3. Examples of cruises, surveys, and stations where seawater Mg:Ca and Sr:Ca ratios samples were obtained. Maps were provided by PI and collaborators from the corresponding cruise, and have not been modified. (a) Transect in the Peru Oxygen Minimum Zone (OMZ) at Callao (Lima) (PI. A.P.). (b) Transect on the Line P programme (NOAA) off Vancouver (Pacific Ocean) (PI: C.P.). (c) Radials in the Iceland Sea from a permanent programme held by the Marine Research Institute of Iceland (PI: S.O.). (d) Cruise track around the Canadian Archipelago (PI: L.J.). (e) Work done in the Sermilik fjord and the close shelf in the southern Greenland Sea (PI: A.K.). (f) Transects available in the Russian-American Long-term Census of the Arctic (RUSALCA) around the Bering Strait (PI: R.H.). (g) Radials in the INGRES3-02 (200108)/STOCA 2011 08 research cruise in the Strait of Gibraltar (PI: R.S.L.). (h) Radial surveys in a carbonate chemistry cruise along the California Current (PI: R.A.F) (i) Radials in a cruise around Svalbard in the sub-Arctic Ocean (PI: J.B.). (j) Cruise track of stations in a cruise from Woods Hole Oceanographic Institution around the Bering Strait (PI: C. A.). (k) Long-cruise from La Reunion to Spain (PI: P.B.D.B). (l) Long-cruise from South Africa to South America (PI: B.T.). Not all cruises maps and tracks are included here, just a subset for showing this study collaborative approach.

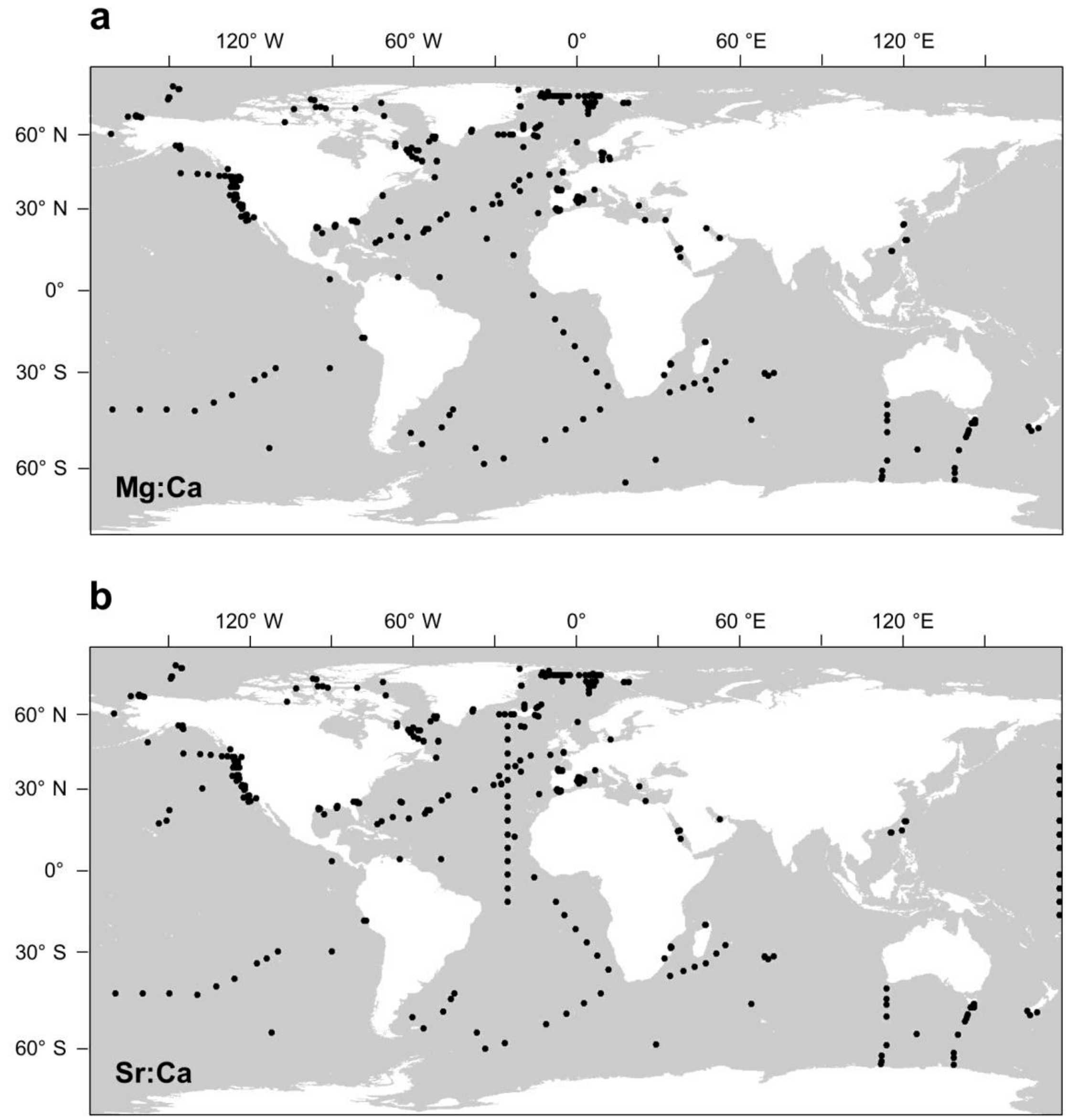


Fig. S4. Global sampling effort of seawater Mg:Ca and Sr:Ca ratios used in this study. Sampling stations used to average seawater Mg:Ca (a) and Sr:Ca (b) ratios at all depths in 5x5 quadrats to show global sampling effort. Note that many stations have also a vertical component with samples down to 6000 m (see Fig. 1, 4)

Supplementary Tables & Captions

Table S1. Mean seawater Mg:Ca and Sr:Ca values divided by Ocean/Sea, Longhurst Province and Ecosystem. Data are classified using mean and standard deviation in the five depth intervals used for the analysis using as major divisions Ocean/Sea, Longhurst Province and Ecosystem. Note that a IAPSO seawater sample is derived from the literature (*10*), and also from our measurements.

Ocean/Sea	**0-5 m**		**5-200 m**		**200-1000 m**		**1000-2500 m**		**2500+ m**	
	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca
1. Pacific	5.165 ±0.482	9.084 ±1.650	5.244 ±0.317	8.366 ±0.605	5.061 ±0.122	8.467 ±0.591	5.048 ±0.088	8.611 ±0.219	5.017 ±0.110	8.517 ±0.567
2. Indian	5.074 ±0.130	8.439 ±0.249	5.074 ±0.029	8.393 ±0.079	5.029 ±0.000	8.209 ±0.000	5.041 ±0.027	8.431 ±0.111	5.044 ±0.040	8.418 ±0.236
3. Atlantic	5.085 ±0.192	8.357 ±0.524	5.038 ±0.541	8.381 ±0.502	5.104 ±0.162	8.500 ±0.224	5.134 ±0.172	8.639 ±0.240	5.124 ±0.069	8.654 ±0.260
4. Arctic	5.051 ±0.097	8.440 ±0.133	5.021 ±0.045	8.377 ±0.107	5.019 ±0.031	8.372 ±0.098	5.165 ±0.034	8.731 ±0.138	4.982 ±0.000	8.088 ±0.000
5. Mediterranean	5.139 ±0.142	8.451 ±0.120	5.117 ±0.036	8.467 ±0.065	5.133 ±0.051	8.513 ±0.070	5.063 ±0.045	8.519 ±0.045	5.066 ±0.026	8.446 ±0.087
6. Southern	5.129 ±0.072	8.798 ±0.000	5.077 ±0.038	8.395 ±0.100	n/a	n/a	n/a	n/a	n/a	n/a
7. Red Sea	5.266 ±0.152	8.400 ±0.023	5.146 ±0.036	8.487 ±0.047	n/a	n/a	n/a	n/a	n/a	n/a
8. China Sea	4.938 ±0.313	8.711 ±0.171	5.067 ±0.031	8.269 ±0.109	n/a	n/a	n/a	n/a	n/a	n/a
9. Arabian Sea	5.511 ±0.439	8.385 ±0.000	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
10. Baltic Sea	4.993 ±0.197	8.370 ±0.000	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
11. IAPSO Literature (Atlantic)	5.137 ±0.000	9.031 ±0.000	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
12. IAPSO This study (Standard)	5.155 ±0.035	8.428 ±0.062	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Longhurst Province	**0-5 m**		**5-200 m**		**200-1000 m**		**1000-2500 m**		**2500+ m**	
	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca
0. IAPSO (Westerlies - N. Atlantic Drift(WWDR)	5.137 ±0.000	9.031 ±0.000	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
1. Coastal - Alaska Downwelling Coastal	5.892 ±0.551	9.262 ±0.508	5.074 ±0.065	8.543 ±0.119	n/a	n/a	n/a	n/a	n/a	n/a
3. Coastal - Benguela Current Coastal	n/a	n/a	5.066 ±0.000	8.373 ±0.000	5.069 ±0.000	8.450 ±0.000	5.148 ±0.000	8.784 ±0.000	n/a	n/a
4. Coastal - Brazil Current Coastal	n/a	n/a	5.104 ±0.000	8.360 ±0.000	5.018 ±0.001	8.390 ±0.073	n/a	n/a	n/a	n/a
5. Coastal - California Upwelling Coastal	n/a		5.503 ±0.357	8.471 ±0.345	5.086 ±0.047	8.515 ±0.127	5.046 ±0.004	8.415 ±0.025	n/a	n/a
6. Coastal - Canary Coastal (EACB)	5.091 ±0.000	8.446 ±0.000	5.143 ±0.089	8.477 ±0.119	5.180 ±0.077	8.527 ±0.058	n/a	n/a	n/a	n/a
7. Coastal - Central America Coastal	n/a	n/a	n/a	n/a	n/a	n/a	5.074 ±0.044	8.541 ±0.023	n/a	n/a
8. Chile-Peru Current Coastal	n/a	n/a	5.101 ±0.025	8.545 ±0.085	n/a	n/a	n/a	n/a	n/a	n/a
9. Coastal - China Sea Coastal	5.072 ±0.107	8.402 ±0.135	5.081 ±0.025	8.384 ±0.116	n/a	n/a	n/a	n/a	n/a	n/a
10. Coastal - E. Africa Coastal	5.033 ±0.167	8.376 ±0.200	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
13. Coastal - Guianas Coastal	5.113 ±0.110	8.339 ±0.112	4.917 ±0.707	8.251 ±0.400	4.934 ±0.217	8.295 ±0.198	4.714 ±0.328	8.299 ±0.195	n/a	n/a
15. Coastal - NE Atlantic Shelves	5.025 ±0.165	8.317 ±0.044	5.705 ±0.200	8.043 ±0.236	n/a	n/a	n/a	n/a	n/a	n/a
17. Coastal - NW Arabian Upwelling	5.104 ±0.008	8.449 ±0.078	5.074 ±0.029	8.393 ±0.079	5.029 ±0.000	8.210 ±0.000	5.041 ±0.027	8.431 ±0.111	5.044 ±0.040	8.418 ±0.236
18. Coastal - NW Atlantic Shelves	5.058 ±0.341	8.385 ±0.413	5.291 ±0.290	8.534 ±0.171	n/a	n/a	n/a	n/a	n/a	n/a
19. Coastal - Red Sea, Persian Gulf	5.364 ±0.279	9.086 ±0.000	5.146 ±0.036	8.487 ±0.047	n/a	n/a	n/a	n/a	n/a	n/a
21. Coastal - SW Atlantic Shelves	5.006 ±0.094	7.402 ±1.291	5.056 ±0.056	8.154 ±0.760	5.046 ±0.026	8.342 ±0.136	n/a	n/a	n/a	n/a

23. Polar - Antarctic	5.078 ±0.094		5.081 ±0.052		5.073 ±0.065	8.415 ±0.165	5.063 ±0.045	8.519 ±0.045	5.055 ±0.038	8.457 ±0.074
24. Polar - Atlantic Arctic	5.116 ±0.139	n/a	5.071 ±0.092	8.387 ±0.090	5.103 ±0.178	8.475 ±0.208	5.107 ±0.135	8.516 ±0.183	5.057 ±0.027	8.370 ±0.103
25. Polar - Atlantic Subarctic	5.232 ±0.189	8.475 ±0.189	5.630 ±0.360	8.330 ±0.602	5.403 ±0.176	8.741 ±0.199	5.517 ±0.096	8.779 ±0.013	n/a	n/a
27. Polar - Boreal Polar (POLR)	5.065 ±0.144	8.623 ±0.173	4.978 ±0.085	8.787 ±0.271	4.987 ±0.056	8.372 ±0.098	n/a	n/a	4.982 0±0.000	8.181 ±0.000
29. Trades - Archipelagic Deep Basins	5.048 ±0.000	8.443 ±0.128	5.067 ±0.031	8.377 ±0.107	n/a	n/a	n/a	n/a	n/a	n/a
30. Trades - Caribbean	4.862 ±0.293	8.711 ±0.171	5.092 ±0.025	8.269 ±0.109	n/a	n/a	n/a	n/a	n/a	n/a
31. Trades - Eastern Tropical Atlantic	5.109 ±0.042	7.542 ±1.319	n/a	8.374 ±0.070	n/a	n/a	n/a	n/a	n/a	n/a
32. Trades - Indian Monsoon Gyres	5.116 ±0.076	8.460 ±0.154	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
33. Trades - Indian S. Subtropical Gyre	5.117 ±0.115	8.499 ±0.319	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
34. Trades - N. Atlantic Tropical Gyral (TRPG)	n/a	8.823 ±0.000	5.158 ±0.074	n/a	5.130 ±0.039	8.995 ±0.072	5.169 ±0.060	8.991 ±0.068	5.152 ±0.049	8.986 ±0.049
36. Trades - N. Pacific Tropical Gyre	n/a	8.783 ±0.024	n/a	8.881 ±0.095	n/a	n/a	n/a	n/a	n/a	n/a
38. Trades - South Atlantic Gyral (SATG)	5.135 ±0.023	8.740 ±0.041	5.049 ±0.038	n/a	5.058 ±0.042	8.458 ±0.169	n/a	n/a	n/a	n/a
39. Trades - W. Pacific Warm Pool	n/a	8.555 ±0.033	n/a	8.363 ±0.142	n/a	8.847 ±0.005	n/a	8.824 ±0.007	n/a	8.834 ±0.021
40. Trades - Western Tropical Atlantic	n/a	8.735 ±0.012	n/a	8.788 ±0.000	n/a	8.849 ±0.000	n/a	8.811 ±0.019	n/a	8.803 ±0.010
42. Westerlies - Kuroshio Current	n/a	8.739 ±0.037	5.076 ±0.022	8.808 ±0.043	5.081 ±0.080	8.536 ±0.246	5.012 ±0.011	8.390 ±0.102	n/a	n/a
43. Westerlies - Mediterranean Sea, Black Sea	5.139 ±0.142	n/a	5.117 ±0.036	8.392 ±0.055	5.133 ±0.051	8.513 ±0.070	5.165 ±0.034	8.731 ±0.138	n/a	n/a
44. Westerlies - N. Atlantic Drift (WWDR)	5.075 ±0.154	8.451 ±0.120	5.075 ±0.059	8.467 ±0.065	5.186 ±0.055	8.543 ±0.156	5.158 ±0.071	8.608 ±0.171	5.199 ±0.074	8.648 ±0.181
45. Westerlies - N. Atlantic Subtropical Gyral East (STGE)	5.141 ±0.036	8.379 ±0.235	5.097 ±0.000	8.405 ±0.232	5.140 ±0.000	8.640 ±0.000	5.115 ±0.029	8.584 ±0.051	n/a	n/a
46. Westerlies - N. Atlantic Subtropical Gyral (West) (STGW)	5.166 ±0.245	8.495 ±0.033	5.139 ±0.025	8.412 ±0.000	5.129 ±0.025	8.409 ±0.044	5.109 ±0.024	8.478 ±0.113	5.102 ±0.039	8.450 ±0.105
47. Westerlies - N. Pacific Polar Front	4.910 ±0.654	8.486 ±0.255	n/a	8.419 ±0.065	n/a	n/a	n/a	n/a	n/a	n/a
48. Westerlies - N. Pacific Subtropical Gyre (West)	n/a	11.082 ±2.349	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
49. Westerlies - Pacific Subarctic Gyres (East)	5.086 ±0.108	8.706 ±0.017	5.115 ±0.063	n/a	5.164 ±0.109	8.561 ±0.019	5.147 0±0.000	8.650 ±0.000	5.132 ±0.069	8.583 ±0.135
50. Westerlies - Pacific Subarctic Gyres (West)	n/a	8.805 ±0.000	n/a	8.503 ±0.053	n/a	8.839 ±0.010	n/a	8.846 ±0.011	n/a	8.816 ±0.008
51. Westerlies - S. Pacific Subtropical Gyre	4.981 ±0.217	8.829 ±0.000	4.995 ±0.135	8.819 ±0.000	4.968 ±0.125	8.164 ±0.901	4.991 ±0.137	8.537 ±0.325	4.930 ±0.091	8.079 ±0.740
52. Westerlies - S. Subtropical Convergence	n/a	6.884 ±3.205	5.101 ±0.025	7.779 ±1.257	5.086 ±0.021	8.445 ±0.043	n/a	n/a	n/a	n/a
53. Westerlies - Subantarctic	5.190 ±0.013	n/a	5.061 ±0.019	8.393 ±0.047	5.051 ±0.033	8.337 ±0.132	n/a	n/a	5.077 ±0.020	8.435 ±0.108
54. Westerlies - Tasman Sea	5.174 ±0.047	8.667 ±0.233	5.187 ±0.060	8.404 ±0.135	n/a	n/a	n/a	n/a	n/a	n/a

Ecosystem	**0-5 m**		**5-200 m**		**200-1000 m**		**1000-2500 m**		**2500+ m**	
	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca	Mg:Ca	Sr:Ca
1. IAPSO (Open Ocean)	5.137 ±0.000	9.031 ±0.000	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
2. Coastal Sea	5.087 ±0.190	8.508 ±1.093	5.178 ±0.263	8.455 ±0.273	5.165 ±0.281	8.550 ±0.264	5.581 ±0.115	8.867 ±0.116	n/a	n/a
3. Coastal Upwelling	6.044 ±0.399	9.330 ±0.476	5.434 ±0.366	8.500 ±0.316	n/a	n/a	n/a	n/a	n/a	n/a
4. Open Ocean	5.115 ±0.110	9.538 ±0.493	5.061 ±0.175	8.379 ±0.414	5.067 ±0.086	8.463 ±0.305	5.084 ±0.113	8.618 ±0.231	5.083 ±0.097	8.580 ±0.377
5. Open Ocean Upwelling	n/a	n/a	n/a	n/a	n/a	n/a	5.074 ±0.044	8.541 ±0.023	n/a	n/a
6. Shallow Hydrothermal Vent	5.087 ±0.042	8.402 ±0.135	5.089 ±0.000	8.411 ±0.000	n/a	n/a	n/a	n/a	n/a	n/a
7. Coral Reef	5.268 ±0.205	8.367 ±0.101	5.067 ±0.031	8.269 ±0.109	n/a	n/a	n/a	n/a	n/a	n/a
8. Deep Hydrothermal Vent	5.104 ±0.008	8.449 ±0.078	5.333 ±0.261	6.596 ±1.979	5.029 ±0.000	8.209 ±0.000	5.041 ±0.027	8.431 ±0.111	5.044 ±0.040	8.418 ±0.236
9. Glacier Seawater	4.932 ±0.106	8.384 ±0.004	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
10. Estuary	4.564 ±0.633	9.378 ±2.294	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
11. Mudflats	4.680 ±0.110	7.990 ±0.161	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
12. Mangroves	5.034 ±0.047	8.515 ±0.024	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
13. Seagrass	5.116 ±0.025	8.551 ±0.048	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
EXTRA DATA - River mouths	0.092 - 2.430	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Table S2. Generalized Linear Model (GLM) results using forward stepwise regression. Results of the GLM for seawater Mg:Ca and Sr:Ca ratios using the 5 depth intervals to understand the complexity of the ratios vs. the environmental variables (full results in SI Appendix 5). Significant results are bold. Also included is an indication of the system complexity with depth.

Depth interval	**Variable**	**Mg:Ca**	**Sr:Ca**	**N° of variables**		**Complexity**	
		p-level		**Mg:Ca**	**Sr:Ca**	**Mg:Ca**	**Sr:Ca**
	Ocean/Sea	0.116	0.279			Ocean/Sea	Ocean/Sea
	Longhurst	**0.000**				Longhurst	
	Ecosystem	**0.000**	0.194			Ecosystem	Ecosystem
	Latitude	0.174				Latitude	
	Longitude	**0.000**	0.159			Longitude	Longitude
0 - 5 m	Depth	**0.020**	**0.016**			Depth	Depth
	Temperature	0.360	**0.011**	12	8	Temperature	Temperature
	Salinity	**0.000**	**0.000**			Salinity	Salinity
	TA	**0.025**	**0.000**			TA	TA
	DIC	**0.010**				DIC	
	DO	**0.000**	**0.003**			DO	DO
	pH_{total}						
	CO_2	**0.004**				CO_2	
	Ocean/Sea		**0.012**				Ocean/Sea
	Longhurst	0.112				Longhurst	
	Ecosystem	**0.000**	**0.000**			Ecosystem	Ecosystem
	Latitude		0.064				Latitude
	Longitude	**0.001**	0.082			Longitude	Longitude
	Depth						
5 - 200 m	Temperature	0.297	**0.000**	7	11	Temperature	Temperature
	Salinity		0.136				Salinity
	TA	**0.018**	**0.000**			TA	TA
	DIC		**0.000**				DIC
	DO	**0.013**	**0.001**			DO	DO
	pH_{total}		**0.000**				pH_{total}
	CO_2	**0.047**	**0.048**			CO_2	CO_2
	Ocean/Sea	**0.024**	0.239			Ocean/Sea	Ocean/Sea
	Longhurst	**0.018**	0.138			Longhurst	Longhurst
	Ecosystem	**0.000**	**0.003**			Ecosystem	Ecosystem
	Latitude	0.166	0.126			Latitude	Latitude
	Longitude	**0.000**	**0.002**			Longitude	Longitude
	Depth						
200 - 1000 m	Temperature			6	6		
	Salinity						
	TA	**0.011**				TA	
	DIC		**0.005**				DIC
	DO						
	pH_{total}						
	CO_2						
	Ocean/Sea						
	Longhurst		0.106				Longhurst
	Ecosystem	**0.001**	**0.001**			Ecosystem	Ecosystem
	Latitude		**0.063**				Latitude
	Longitude						
	Depth						
1000 - 2500 m	Temperature		0.010	2	8		Temperature
	Salinity						
	TA	0.171	0.177			TA	TA
	DIC		**0.045**				DIC
	DO		**0.001**				DO
	pH_{total}						
	CO_2		0.674				CO_2
	Ocean/Sea	**0.013**				Ocean/Sea	
	Longhurst						
+ 2500 m	Ecosystem	0.286		6	4	Ecosystem	
	Latitude						
	Longitude	0.124	**0.019**			Longitude	Longitude
	Depth		0.118				Depth

	Temperature	0.067	0.091		Temperature	Temperature
	Salinity		**0.031**			Salinity
	TA					
	DIC					
	DO	**0.043**			DO	
	pH_{total}					
	CO_2	**0.006**			CO_2	

Table S3. Historical use of seawater Mg:Ca and Sr:Ca ratios. Summary of ratios use in various marine science disciplines in the last 100 years.

Year	Reference	Location	Mg:Ca	Sr:Ca	Category
1938	*11*	Atlantic Ocean	No	Yes	Analytic method development
1955	*12*	Artificial Seawater	No	Yes	Analytic method development
1956	*13*	Atlantic Ocean	No	Yes	Analytic method development
1992	*14*	Atlantic Ocean	No	Yes	Biological effect
1999	*15*	Pacific Ocean	Yes	Yes	Biological effect
1999	*16*	Atlantic Ocean, Pacific Ocean, Indian Ocean	No	Yes	Biological effect
2003	*17*	China Sea	Yes	No	Biological effect
2010	*18*	Atlantic Ocean	Yes	No	Biological effect
2011	*19*	Standard seawater manipulation	Yes	No	Biological effect
2011	*20*	Atlantic Ocean	Yes	No	Biological effect
2012	*21*	UK coastal waters (Plymouth), Atlantic Ocean	Yes	Yes	Biological effect
2014	*22*	Atlantic Ocean	Yes	No	Biological effect
2014	*23*	Artificial Seawater	Yes	Yes	Biological effect
1999	*24*	Pacific Ocean	Yes	Yes	Hydrothermal fluxes
2011	*25*	Mediterranean Sea, Arabian Gulf (Kuwait)	Yes	No	Industrial Desalination plants
1982	*26*	Gulf of Mexico, Pacific Ocean, Atlantic Ocean	Yes	Yes	Paleoceanography
1994	*27*	Pacific Ocean	No	Yes	Paleoceanography
1995	*28*	Pacific Ocean	No	Yes	Paleoceanography
1996	*29*	China Sea	No	Yes	Paleoceanography
1998	*30*	Pacific Ocean	Yes	Yes	Paleoceanography
1998	*31*	Worldwide	Yes	No	Paleoceanography
2000	*32*	Open Ocean (various)	Yes	No	Paleoceanography
2005	*33*	Atlantic Ocean, Pacific Ocean	Yes	No	Paleoceanography
2010	*34*	Atlantic Ocean, Pacific Ocean	Yes	Yes	Paleoceanography
2013	*35*	Mathematical model	Yes	No	Paleoceanography
2013	*36*	Mathematical model	Yes	No	Paleoceanography
1819	*37*	Open Ocean (various)	Yes	No	Seawater composition
1938	*38*	Pacific Ocean	Yes	Yes	Seawater composition
1951	*39*	Atlantic Ocean	No	Yes	Seawater composition
1956	*40*	English channel, Atlantic Ocean	No	Yes	Seawater composition
1966	*41*	Gulf of Mexico, Atlantic Ocean	No	Yes	Seawater composition
1966	*42*	Southern Ocean, Pacific Ocean, Atlantic Ocean, Red Sea, Persian Gulf,	Yes	Yes	Seawater composition
1966	*42*	Atlantic Ocean, Pacific Ocean, Indian Ocean, Southern Ocean	Yes	Yes	Seawater composition
1967	*43*	Atlantic Ocean	Yes	Yes	Seawater composition
1967	*44*	Atlantic Ocean, Pacific Ocean, North Sea, Indian Ocean, Mediterranean	Yes	Yes	Seawater composition
1972	*45*	Pacific Ocean, Mediterranean Sea	No	Yes	Seawater composition
1973	*46*	Atlantic Ocean	Yes	No	Seawater composition
1974	*47*	Atlantic Ocean, Pacific Ocean	No	Yes	Seawater composition
1999	*48*	Atlantic Ocean, Pacific Ocean transect	No	Yes	Seawater composition
2006	*49*	Antarctica, South Madagascar	Yes	No	Seawater composition
2008	*50*	Atlantic Ocean	Yes	Yes	Seawater composition

2010	*51*	Standard SSW76, North Atlantic	Yes	No	Seawater composition

Supplementary Databases

Appendix 1. Database used to classify and coordinate each individual research cruise/expedition. Excel file providing details of how each cruise and expeditions was planned and organized to recover seawater samples to measure seawater Mg:Ca and Sr:Ca ratios. This file belongs to the start of this project. The final database is in SI Appendix 3.

Appendix 2. Database with the raw literature data. Excel file with all the literature data selected for this study that were found comparable to our samples. The original database is permanently deposited at the NOAA National Center for Environmental Information (NCEI) under Accession Number 0171017 in http://accession.nodc.noaa.gov/0171017 (DOI:10.7289/V5571996).

Appendix 3. Database with the raw and classified data per depth band. Excel file with all the measured and the literature data compiled in this study. Also included are all environmental metadata mined from GLODAPv2 (*4*, *5*), and used to analyze and classify seawater Mg:Ca and Sr:Ca ratios as function of environmental variables. The original database is permanently deposited at the NOAA National Center for Environmental Information (NCEI) under Accession Number 0171017 in http://accession.nodc.noaa.gov/0171017 (DOI:10.7289/V5571996).

Appendix 4. ICP-OES quality control data and measurements replication. Details on the ICP-OES laboratory quality and replicability that guarantees the high precision results presented in this study.

Appendix 5. General Linear Model (GLM) results using forward stepwise regression. Full results of the GLM for seawater Mg:Ca and Sr:Ca ratios using the 5 depth intervals to understand the complexity of the ratios vs. the environmental variables (summary in SI Appendix Table S2).

Appendix 6. Summarized river mouth seawater Mg:Ca ratios. Compilation of seawater Mg and Ca concentrations along with seawater Mg/Ca ratio of major rivers globally for comparison purposes (the data were not used in this dataset analysis). Original data belong to the GEMS-GLORI database of Meybeck and Alain (2012) which can be accessed at https://doi.pangaea.de/10.1594/PANGAEA.804574.

References

1. J. B. Ries, Seawater Mg/Ca controls polymorph mineralogy of microbial $CaCO_3$: a potential proxy for calcite-aragonite seas in Precambrian time. *Geobiology* **6**, 106-119 (2008)

2. DeVilliers S., M. Greaves, H. Elderfield H, An intensity ratio calibration method for the accurate determination of Mg/Ca and Sr/Ca of marine carbonates by ICP-AES. *Geochem. Geophys. Geosys.* **3**, 1001 (2002)

3. Schrag D. P., Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates. *Paleoceanogr.* **14**, 97-102 (1999)

4. R. M. Key et al., A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP). *G. Biogeochem. Cy.* **18**, GB4031 (2004)

5. R. M. Key et al., Global ocean data analysis project, version 2 (ORNL/CDIAC-162 NDP-093, 2015)

6. M. Meybeck, R. Alain, GEMS-GLORI world river discharge database. Laboratoire de Géologie Appliquée, Université Pierre et Marie Curie, Paris, France, PANGAEA, https://doi.org/10.1594/PANGAEA.804574 (2012)

7. J. Emile-Geay et al., A global multiproxy database for temperatura reconstructions of the Common Era. *Sci. Data* **4**, 170088 (2017)

8. M. Siccha, M. Kucera, ForCenS, A curated database of planktonic foraminifera census counts in marine surface sediment samples. *Sci. Data* **4**, 170109 (2017)

9. M. Borreggine, S. E. Myhre, K. A. S. Mislan, C. Deutsch, C. Davis, A database of paleoceanographic sediment cores from the North Pacific, 1951-2016. *Earth System Sci. Data* **9**, 739-749 (2017)

10. R. A. Pawlowicz, The absolute salinity of seawater diluted by river water. *Deep-Sea Res.* **101**, 71-79 (2015)

11. D. A. Webb, Strontium in seawater and its effect on calcium determination. *Nature* **142**, 751-752(1938)

12. T. J. Chow, T. G. Thompsok, Flame photometric determination of strontium in seawater. *Anal. Chem.* **27**, 18-21 (1955)

13. R. W. Hummel, A. A. Smales, Determination of strontium in sea water by using both radioactive and stable isotopes. *Analyst* **81**, 110-113 (1956)

14. R. E. Bernstein, R. H. Byrne, P. R. Betzer, A. M. Greco, Morphologies and transformations of celestite in seawater: The role of acantharians in strontium and barium geochemistry. *Geochim.Cosmochim. Ac.* **56**, 3273-3279 (1992)

15. D. W. Lea, T. A. Mashiotta, H. J. Spero, Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing. *Geochim.Cosmochim. Ac.* **63**, 2369-2379 (1999)

16. H. M. Stoll, D. P. Schrag, S. C. Clemens, Are seawater Sr/Ca variations preserved in Quaternary foraminifera? *Geochim.Cosmochim. Ac.* **63**, 3535-3547 (1999)

17. W. Zang et al., The influences of Mg, Ca and Mg/Ca ratios in mixed seawater on the emergence rate of Penaeus japonicas postlarva. *Chinese J. Oceanol. Limnol.* **21**, 78-85 (2003)

18. J. B. Ries, Review: Geological and experimental evidence for secular variation in seawater Mg/Ca (calcite-aragonite seas) and its effects on marine biological calcification: *Biogeosciences* **7**, 2795-2849 (2010)

19. M. N. Müller et al., Response of the coccolithophores *Emiliania huxleyi* and *Coccolithus braarudii* to changing seawater Mg2+ and Ca2+ concentrations: Mg/Ca, Sr/Ca ratios and δ44/40Ca, δ26/24Mg of coccolith calcite. *Geochim. Cosmochim. Ac.***75**, 2088-2102 (2011)

20. N. Suarez-Bosche, thesis, Acclimation and phenotypic plasticity of echinoderm larvae in a changing ocean, University of Southampton (2011)

21. S. Blanco-Ameijeiras et al., Removal of organic magnesium in coccolithophore calcite. *Geochim.Cosmochim. Ac.* **89**, 226-239 (2012)

22. A. Mewes, G. Langer, L. J. de Nooijer, J. Bijma, J. G. Reichart, Effect of different seawater Mg2+ concentrations on calcification in two benthic foraminifers. *Mar. Micropal*. **113**, 56-64 (2014)

23. M. N. Müller et al., Influence of temperature and CO_2 on the strontium and magnesium composition of coccolithophore calcite. *Biogeosciences* **11**, 1065-1075 (2014)

24. S. de Villiers, B. K. Nelson, Detection of low-temperature hydrothermal fluxes by seawater Mg and Ca anomalies. *Science* **285**, 721-723 (1999)

25. Lenntech, Inc. https://www.lenntech.com/ (2018)

26. J. R. Dodd, E. L. Crisp, Non-linear variation with salinity of Sr/Ca and Mg/Ca ratios in water and aragonitic bivalve shells and implications for paleosalinity studies. *Palaeogeogr. Palaeocl.* **38**, 45-56 (1982)

27. S. de Villiers, G. T. Shen, B. K. Nelson, The Sr/Ca-temperature relationship in coralline aragonite: influence of variability in (Sr/Ca) seawater and skeletal growth parameters. *Geochim. Cosmochim. Ac.* **58**, 197-208 (1994)

28. S. de Villiers, B. K. Nelson, A. R. Chivas, Biological controls on coral Sr/Ca and δ18O reconstructions of sea surface temperatures. *Science* **269**, 1247-1249 (1995)

29. C-C, Shen et al., The calibration of D[Sr/Ca] versus sea surface temperature relationship for Porites corals. *Geochim. Cosmochim. Ac.* **60**, 3849-3858 (1996)

30. B. L. Ingram, P. De Deckker, A. R. Chivas, M. E. Conrad, A. R. Byrne, Stable isotopes, Sr/Ca, and Mg/Ca in biogenic carbonates from Petaluma Marsh, northern California, USA: *Geochim. Cosmochim. Ac.* **62**, 3229-3237 (1998)

31. S. M. Stanley, L. A. Hardie, Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry. *Palaeogeogr. Palaeocl.* **144**, 3-19 (1998)

32. D. W. Lea, D. K. Pak, H. J. Spero, Climate impact of Late Quaternary equatorial Pacific sea surface temperature variations. *Science* **289**, 1719-1724 (2000)

33. S. de Villiers et al., The composition of the continental river weathering flux deduced from seawater Mg isotopes. *Chem. Geol.* **216**, 133-142 (2005)

34. R. M. Coggon, D. A. H. Teagle, C. E. Smith-Duque, J. C. Alt, M. J. Cooper, Reconstructing past seawater Mg/Ca and Sr/Ca from mid-ocean ridge flank calcium carbonate veins. *Science* **327**, 1114-1117 (2010)

35. M. Ligi, E. Bonatti, M. Cuffaro, D. Brunelli, Post-Mesozoic rapid increase of seawater Mg/Ca due to enhanced mantle-seawater interaction. *Sci. Reports* **3**, 1-8 (2013)+

36. R. Muller, A. Dutkiewicz, M. Seton, C. Gaina, Seawater chemistry driven *by*supercontinent assembly, breakup, and dispersal. *Geology* **41**, 907-910 (2013)

37. A. Marcet, On the specific gravity and temperature in different parts of the ocean and in particular seas, with sorne account of their saline contents. *Philos. Trans. Roy. Soc. London* **109**, 161-208 (1819)

38. Y. Miyake, 1939. Chemical studies of the Western Pacific Ocean. *Bull. Chem. Soc. Japan* **14**, 29-55 (1939)

39. H. T. Odum, Note on the strontium content of sea water, celestite Radiolaria, and strontianite snail shells. *Science* **114**, 211-213 (1951)

40. H. J. M. Bowen, Strontium and barium in sea water and marine organisms. *J. Mar. Bio. Assoc. U.K.* **36**, 451-460 (1956)

41. E. E. Angino, G. K- Billings, N. R. Axdersen Observed variations in the strontium concentration of seawater. *Chem. Geol.* **1**, 145-153 (1966)

42. F. Culkin, R. A. Cox, Sodium, potassium, magnesium, calcium and strontium in seawater. *Deep-Sea Res.* **13**, 789-804 (1966)

43. B. P. Fabricand, E. S. lmbimbo, M. E. Brey, Atomic absorption analyses for Ca, Li, Mg, K, Rb and Sr at two Atlantic Ocean stations. *Deep-Sea Res.* **14**, 785-789 (1967)

44. J. P. Riley, M. Tongudai, The major cation chlorinity ratios in seawater. *Chem. Geol.* **2**, 263-269 (1967)

45. M. Bernat, T. Church, J. Allegre, Barium and Strontium concentrations in Pacific and Mediterranean seawater profiles by direct isotope dilution mass spectrometry. *Earth Planet. Sc. Lett.* **16**, 75-80 (1972)

46. J. H. Carpenter, M. E. Manella, Magnesium to chlorinity ratios in sea water. *J. Geophys. Res.* **78**, 3621-3626 (1973)

47. G. W. Brass, K. K. Turekian, Strontium distribution in GEOSECS oceanic profiles. *Earth Planet. Sc. Lett.* **23**, 141-148 (1974)

48. S. de Villiers, Seawater strontium and Sr/Ca variability in the Atlantic and Pacific oceans. *Earth Planet. Sc. Lett.* **171**, 623-634 (1999)

49. S. Naik, R. J. Noronha, P. V. Shirodkar, R. Sen Gupta, On the distribution of Calcium, Magnesium, Sulphate and Boron in the South-Western Indian Ocean region of the Southern Ocean. *Sci. report first Indian Exp. Antarctica* **1983**, 87-94 (2006)

50. F. J. Millero, R. Feistel, D. G. Wright, T. J. McDougall, The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale. *Deep-Sea Res.* **55**, 50-72 (2008)

51. R. A. Pawlowicz, Model for predicting changes in the electrical conductivity, practical salinity, and absolute salinity of seawater due to variations in relative chemical composition. *Ocean Science* **6**, 361-378 (2010)