



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

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Seawater Mg:Ca and Sr:Ca ratios are biogeochemical parameters reflecting the Earth–ocean–atmosphere dynamic exchange of elements. The ratios' dependence on the environment and organisms' biology facilitates their application in marine sciences. Here, we present a measured single-laboratory dataset, combined with previous data, to test the assumption of limited seawater Mg:Ca and Sr:Ca variability across marine environments globally. High variability was found in open-ocean upwelling and polar regions, shelves/neritic and river-influenced areas, where seawater Mg:Ca and Sr:Ca ratios range from ~4.40 to 6.40 mmol:mol and ~6.95 to 9.80 mmol:mol, respectively. Open-ocean seawater Mg:Ca is semi-conservative (~4.90 to 5.30 mol:mol), while Sr:Ca is more variable and nonconservative (~7.70 to 9.10 mmol:mol); both ratios are nonconservative in coastal seas. Further, the Ca, Mg, and Sr elemental fluxes are connected to large total alkalinity deviations from International Association for the Physical Sciences of the Oceans (IAPSO) standard values. Because there is significant modern seawater Mg:Ca and Sr:Ca ratios variability across marine environments we cannot absolutely assume that fossil archives using taxa-specific proxies reflect true global seawater chemistry but rather taxa- and process-specific ecosystem variations, reflecting regional conditions. This variability could reconcile secular seawater Mg:Ca and Sr:Ca ratio reconstructions using different taxa and techniques by assuming an error of 1 to 1.50 mol:mol, and 1 to 1.90 mmol:mol, respectively. The modern ratios' variability is similar to the reconstructed rise over 20 Ma (Neogene Period), nurturing the question of semi-nonconservative behavior of Ca, Mg, and Sr over modern Earth geological history with an overlooked environmental effect.

The first global approximation of modern seawater composition and elemental ratios was conducted by Marcet, Forchhammer, and Dittmar more than 130 y ago, concluding that elemental proportions were almost identical (seawater Ca, Mg, and Sr, and their ratios). This assumption of near-constant seawater Mg:Ca and Sr:Ca ratios is historically known as the Forchhammer's Principle, the Principle of Constant Proportions, or simply, the Marcet's principle. Over the last decades, this principle has not been revisited and therefore remains a pivotal textbook dogma in the current understanding of ancient and modern ocean chemistry. The lack of solid evidence for the near-constant seawater Mg:Ca

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Significance

Seawater elemental composition, namely Mg:Ca and Sr:Ca ratios are widely used in marine sciences. Our new single-laboratory global dataset, combined with past data of seawater Mg:Ca and Sr:Ca ratios, suggests that modern ocean variability is significant across different environments, being similar to the changes during the Neogene Period (20 Ma). Because there is large variability in seawater ratios, we cannot assume that secular changes derived from fossilized taxa with varied ecological niches and from diverse ecosystems provide an unbiased representation of past global seawater chemistry. We suggest that the problem of inconsistencies in previous studies of, for example, paleo conditions from different fossil taxa may be reduced by accounting for taxonomic differences, ecosystems, and abiotic processes to overcome the regional environmental effect.

and Sr:Ca ratios, except in the open ocean, is surprising given the importance of this assumption for reconstructing ancient ocean seawater chemistry, its use as a proxy for temperature, or global biogeochemical modeling input parameter needs.

The Principle of Constant Proportions for marine elemental ratios seems intuitive based on the a priori conservative behavior of these elements. Calculations of residence times tend to rely on the mean ocean residence time (MORT) concept, assuming a perfect and instantaneous mixed ocean, with inputs and outputs being at steady state (1). Modern seawater elemental composition is governed by dissolved inputs, outputs, chemical exchanges, and interactions with major Earth system compartments and oceanic cycles. Elements with long MORTs and strong internal cycling can show more variability than expected. At the macro scale, Mg from terrestrial igneous rock weathering and Ca and Sr from limestone dissolution and dolomitization are mainly added to coastal waters by rivers, continental runoff, and midocean ridges (MORs). Sinks for Mg are removal at MORs via interaction with basalt, dolomitization, and biogenic calcification and particulate export where Ca is removed as sinking carbonates. Removal of Sr occurs during substitution of Ca in biogenic calcite and via carbonate export and uptake into planktonic organisms (foraminifera, acantharians, and coccolithophores). The residence times of Mg, Ca, and Sr are ~13, 1, and 4 My, respectively, and these a priori conservative behaviors following the MORT concept are the basis of the application of the respective elemental ratios in many marine science disciplines (2). Evidence from paleo reconstruction suggests that the seawater Mg:Ca (mol:mol) ratio oscillated over the past 541 My (Phanerozoic Eon) from 1.00 to 5.10–5.20 (3, 4), mainly driven by changes in global oceanic crust production, mixing rate of MORs hydrothermal fluxes, and mixing with brines and rivers (5). Changes in seawater Mg:Ca ratios are especially critical to correctly interpret past and modern mineralogy of biogenic living and deposited carbonates. The seawater Sr:Ca ratio (mmol:mol) has been relatively constant during the last 60 My, ranging between 7.50 and 10.00, decreasing from 14 to 16 around 70 to 80 Ma (6), but with few reliable assessments published (7). Given that no modern global ocean seawater survey of elemental proportions has been conducted, constant elemental ratios have always been assumed based on these characteristics and the MORT concept, but without rigorous assessments in terms of spatiotemporal variability or changes at the macro or meso scale or ecosystem level.

Recent regional biogeochemical investigations include seawater Mg:Ca and Sr:Ca ratios as well as individual element concentrations in vertical profiles, horizontal distributions, and meridional transects in mostly open-ocean surface environments (8–10). The latest studies in salinity and the standard for the calculation of the thermodynamic properties of seawater [thermodynamic equation of seawater - 2010 (TEOS-10) (11, 12)] include coastal and river mouth

seawater ratios measurements (e.g., GEMS-GLORI database) (13). In marine sciences, seawater Mg:Ca and Sr:Ca ratios are useful to identify biogeochemical processes such as precipitation, dissolution, or consumption that alter the physicochemical properties of seawater. The ratios reflect the dynamic exchange of important elements between the solid Earth, ocean water masses, the atmosphere, and processes such as biological consumption and dissolution. Prior to our study, there was no comprehensive global survey of marine elemental ratios, but several local and regional studies using different analytical laboratories and techniques providing limited evidence to question the constant proportion assumption. An up-to-date single-laboratory assessment of modern seawater Mg:Ca and Sr:Ca ratios is timely and critical across chemical oceanography, paleoclimatology, oceanic circulation, water masses tracking, and the seawater chemical evolution of the ocean, to ensure the underlying assumptions of using elemental ratios are met and to reassess the validity of conservative behavior beyond the MORT premises. Deviations from seawater Ca, Mg, and Sr conservative behavior are known to exist owing to physical changes in the water masses, biological uptake, chemical buffering and dissolution, precipitation, evaporation, dilution, ice melt, groundwater/lacustrine discharges, aeolian inputs, and ocean mixing (14). The fragmented knowledge of these deviations leads to modern experimental and laboratory work being conducted under the assumption that the seawater origin retains constant seawater Mg:Ca and Sr:Ca ratios with oceanic values around 5.00 to 5.12 mol:mol and 8.40 to 8.64 mmol:mol, respectively (3, 9, 10). However, estuaries, marshes, river mouths, and coastal river mouth plumes deviate considerably from these ratios (15), from ~2.00 to 5.00 mol:mol in the case of Mg:Ca and < 8.00 mmol:mol in the case of Sr:Ca (16). Likewise, transects from shelf to oceanic waters in the Atlantic show a larger seawater Mg:Ca ratio of 5.40 to 5.60 mol:mol in coastal waters than offshore 5.10 to 5.20 mol:mol (17). Samples in open-ocean waters of the Red Sea and the Mediterranean Sea indicate variations from 5.40 to 5.80 mol:mol, likely following high surface ocean evaporation rates in enclosed seas. Hence, seawater Mg:Ca in continental margins and oceanic regions can be spatially heterogeneous owing to variable Mg concentrations (10).

The most recent seawater Sr:Ca ratio assessment at large scale excludes continental margins, concentrating on meridional transects in oceanic Atlantic and Pacific surface waters, suggesting a variability of 1 to 3% around 8.50 mmol:mol (9). This fluctuation is higher than Quaternary seawater Sr:Ca paleo reconstructions uncertainty/confidence intervals (e.g., using coccoliths and foraminifera). Depth is assumed to exert a control on elemental composition: In the Pacific, the euphotic zone is depleted in seawater Ca by ~1% relative to deep waters below 1,000 m in depth (18), and the opposite occurs in the Atlantic both for Ca and Mg (19). In the Indian Ocean, seawater Mg:Ca ratios vary with depth depending on location (10), and in the Pacific surface seawater Sr:Ca is reduced by ~1 to 3% compared to deep waters below 1,000 m (9, 20), while seawater Sr:Ca gradients increase in other ocean basins (21). Ca and Mg are crucial elements for biological functioning at the cellular, membrane, and molecular levels, while Sr is not considered to be an essential element for photosynthetic organisms (22). Therefore, the trends are attributed to pelagic Sr utilization in the euphotic zone by coccolithophores via SrCO₃, and acantharians via SrSO₄ (also observed for nutrient depth profiles) and redissolution below their respective saturation horizons. Dissolved Sr is assumed to be a highly conservative element below the euphotic zone, but it is subjected to large variability in the upper ocean.

Numerous scientific studies around seawater Mg:Ca and Sr:Ca ratios in the modern ocean target local or regional process-orientated reconstructions of seawater Mg:Ca and Sr:Ca ratios throughout Earth's history without considering differences in ranges, biogeographical provinces, or ecosystem criteria, often assuming that

fixed-location estimations reflect the global ocean in general. This has contributed to the broad assumption that these elements have long residence times and conservative behavior and, hence, constant ratios, with few exceptions. Namely, reconstructions of seawater Mg:Ca and Sr:Ca ratios using different taxa and techniques at different laboratories have concluded that the ratios increased during the last 66 My (Cenozoic) with large variability/uncertainty depending on the approach used. However, the reconstructions contrast on the magnitude of change/increase and they diverge on the variability in the modern era beyond the consensus around open-ocean/deep-sea values of Mg:Ca = 5.10 mol:mol (3, 7) and Sr:Ca = 8.20 mmol:mol (7). Considering that no detailed global survey of modern seawater Mg:Ca and Sr:Ca ratios has been conducted in the last 130 y with fragmented pieces of evidence in different oceans and environments, but modern analytical techniques progressed toward high analytical precision, a reassessment is timely. This can help to reconcile earlier results and to advance our understanding of the distribution patterns of major seawater ions. The process-orientated strategy presented here was used to answer relevant biological, paleoceanographic, empirical, and modeling questions related to modern seawater Mg:Ca and Sr:Ca ratios at a global scale.

These questions include the following:

- 1) How do these elemental ratios vary with ocean habitat, province, ecosystem, depth, latitude, and seawater chemistry?
- 2) What is the true modern variability across the global ocean and how conservative are present-day elemental ratios?
- 3) How does this variability affect the interpretation of paleo estimations, and can estimations based on different techniques and taxa be reconciled?

Results

The present study measured modern seawater Mg:Ca and Sr:Ca ratios in more than 1,100 samples from 79 research cruises and expeditions worldwide, which were compared with published data and then merged into a master databank deposited at the National Oceanic and Atmospheric Administration (NOAA) National Center for Environmental Information (NCEI) under accession number 0171017 at <https://data.nodc.noaa.gov/cgi-bin/iso?id=gov.noaa.nodc:0171017> (*SI Appendix*, Fig. S1 and S2). The seawater Ca, Mg, Sr, Mg:Ca, and Sr:Ca data followed normal distribution curves (Anderson–Darling $P < 0.005$). The following ranges and observations emerged from separating the data using quartiles and confidence intervals, as well as graphical representations. The distribution of seawater Mg:Ca in the euphotic zone varied between 4.95 and 5.30 mol:mol with some peaks up to 5.40 mol:mol in all open-ocean settings at all latitudes, while seawater Sr:Ca was more variable, from 7.70 to 9.10 mmol:mol (Figs. 1 and 2). However, there were many deviations from these ranges for seawater Mg:Ca, mostly coinciding with coastal, shelf, and upwelling regions (down to 4.50 and up to 6.60 mol:mol), and especially in neritic and river-influenced areas (0.40 and 2.40 to 4.50 mol:mol) (Figs. 3 and 4 and *SI Appendix*, Fig. S1 and Dataset S6). Seawater Sr:Ca showed slight variation beyond 7.70 to 9.10 mmol:mol, with some exceptions around this range mostly in upwelling areas (Figs. 1 and 4). The spatial distribution of the two ratios in different depth ranges showed significantly less complexity (Fig. 2 and the generalized linear model [GLM] in *SI Appendix*, Table S2), particularly below 200 m (Fig. 1), but several regions with greater heterogeneity (e.g., coastal/open-ocean upwelling regions, polar seas, several shelf environments) were found in all oceans. The limited number of samples obtained below 1,000 m weakens a general extrapolation for the deep ocean in general, but a higher variability was certainly observed in the upper 1,000 m, and especially in the first 200 m, where numerous environmental variables and processes (e.g., calcification

and dissolution) are governing biogeochemical processes and occurring simultaneously (Fig. 2 and *SI Appendix*, Table S2).

When seawater Mg:Ca and Sr:Ca ratios were averaged by ocean/sea, Longhurst Province, and ecosystem (*SI Appendix*, Table S1), it emerged that the high number of open-ocean samples lowered the averages to “homogeneity” reducing the SE, which would suggest a conservative behavior if a grand mean was calculated across all data. The largest deviations from assumed homogeneity for both ratios around mean values (seawater Mg:Ca ~ 5.10 mol:mol, Sr:Ca ~ 8.50 mmol:mol) were observed as a function of ocean, Longhurst Province, ecosystem, latitude, salinity, total alkalinity (TA), dissolved inorganic carbon (DIC), and dissolved oxygen (DO) (Fig. 2 and *SI Appendix*, Table S1). These deviations were heavily dependent on depth band with a decreasing coefficient of variation with increasing depth. Of particular interest were the ratios distribution with respect to TA, DIC, and DO showing a decreasing complexity with depth, following the high interaction with biological processes in the upper ocean, and carbonate dissolution at depth linked to seawater Mg:Ca and Sr:Ca ratios fluctuations (Figs. 2 and 3). Salinity only had a major effect on the ratio’s distribution up to ~28 (mostly in the upper ocean), then the ratios behaved in a cloud mode, reflecting mostly the impact of biological processes. Cross plots of Ca, Mg, and Sr vs. TA reflected the ocean water masses and interior processes shifting the ratios via the hydrothermal, calcification, and dissolution effects at large (Fig. 3A). Cross plots of Mg and Sr vs. Ca and of Sr vs. Mg showed how all elements correlated with each other (r values between 0.60 and 0.97 in all cases; Fig. 3B), with deviations being explained by the different ecosystems’ water masses and processes such as river discharge (dilution and minerals addition), glacier impact (meltwater discharge, leading to dilution but also weathered minerals), hydrothermal impact (heavy metals and minerals addition), coastal processes (consumption/dissolution), and upwelling (minerals addition and consumption/dissolution) (Fig. 4D).

In general, the newly measured dataset greatly expanded literature data in the ranges, with no major disagreements, in terms of values around the same Longhurst provinces/regional areas and processes (Fig. 4). Most published data analyzed to date, except around river mouths/brackish waters, fall in the vicinity of the International Association for the Physical Sciences of the Oceans (IAPSO) standard (Fig. 4D), while our data showcase many wide linear extensions of the IAPSO values, for both ratios, along a greater range of variability. We observed most deviations along the biological calcification-favored line (Fig. 4D), except in instances when melting of ice-water dominated, or when a marked hydrothermalism effect was present. Variability in modern seawater Mg:Ca and Sr:Ca ratios was visualized by depth, ecosystem, and major regions/division (Fig. 4 A–C), treating all samples equally weighted despite the extended volume of the open ocean. The ratios range not only prevailed in the upper ocean but also continued within most of the depth profiles, although the range decreased with depth. This was very obvious when classifying data as “inshore” and “offshore” to show the broad vs. narrow ranges, and the ratios’ nonconservative vs. semiconservative behavior (Fig. 4C). The ratio groupings were compared to recent reconstructions of seawater Mg:Ca and Sr:Ca ratios (3, 7) from younger Earth history suggesting that the increase in ratios during the Neogene (20 Ma) is roughly within the same range of variability shown in modern ocean elemental ratios of most regions investigated here (Fig. 5). Surprisingly, our dataset ranges agreed well with the range calculation using tropical shelf echinoderms ossicles (23), where it was concluded that modern seawater Mg:Ca ranged from 4.0 to 6.4 mol:mol. This is in total agreement with our measurements (Figs. 4 and 5), despite the published study (23) using only one group of organisms. Additionally, our dataset ranges also agreed with a model estimation based on modified equations from foraminifera calibrations (24), which shows that modern seawater Mg:Ca ranges from 4.60 to 5.70 mol:mol. When

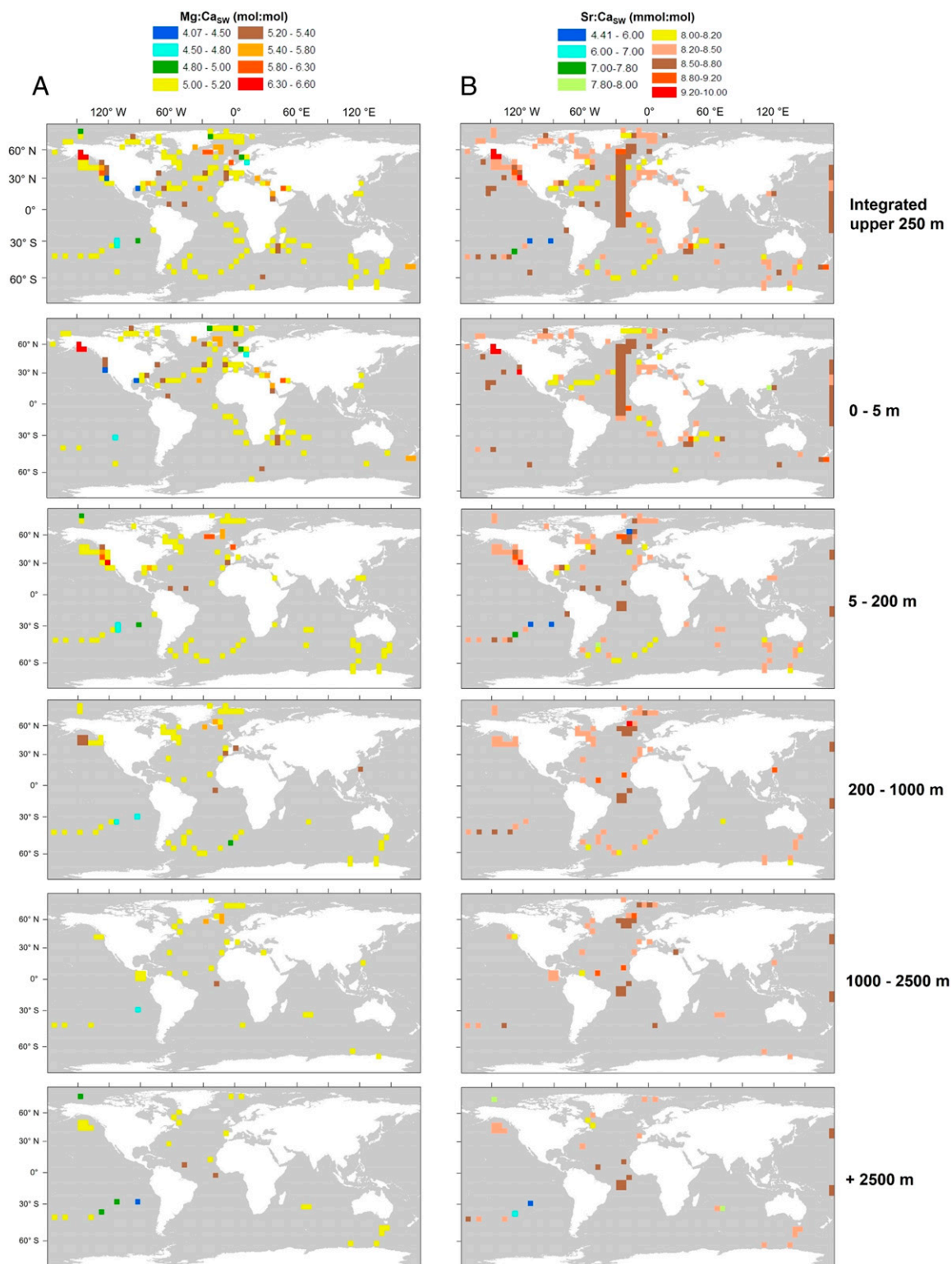


Fig. 1. Modern ocean global variability in seawater Mg:Ca and Sr:Ca ratios. Averaged global seawater Mg:Ca (A) and Sr:Ca (B) ratios from the upper 250 m and separated in five depth intervals (0 to 5 m, 5 to 200 m, 200 to 1,000 m, 1,000 to 2,500 m, and +2,500 m), overlaid in $5^\circ \times 5^\circ$ latitude/longitude quadrats (see *SI Appendix, Fig. S4* for sampling effort). Extended seawater Mg:Ca ratios data from river mouths can be found in *SI Appendix, Fig. S1*. The final databases are deposited at the NOAA NCEI under accession number 0171017 at <https://data.nodc.noaa.gov/cgi-bin/iso?id=gov.noaa.nodc:0171017> (DOI: 10.7289/N5571996).

we compared the modern ocean seawater Mg:Ca variability to experimental data describing the correlation between seawater and biogenic carbonate Mg:Ca ratios (Fig. 5A), it emerged that the natural variability of seawater Mg:Ca can be responsible for

significant changes in the Mg:Ca ratio of biogenic carbonates. For example, carbonates of scleractinian corals doubled their skeleton Mg:Ca ratio from 0.15 to 0.30 mol:mol when seawater Mg:Ca increased from 3.80 to 6.70 mol:mol (Fig. 5A), while other

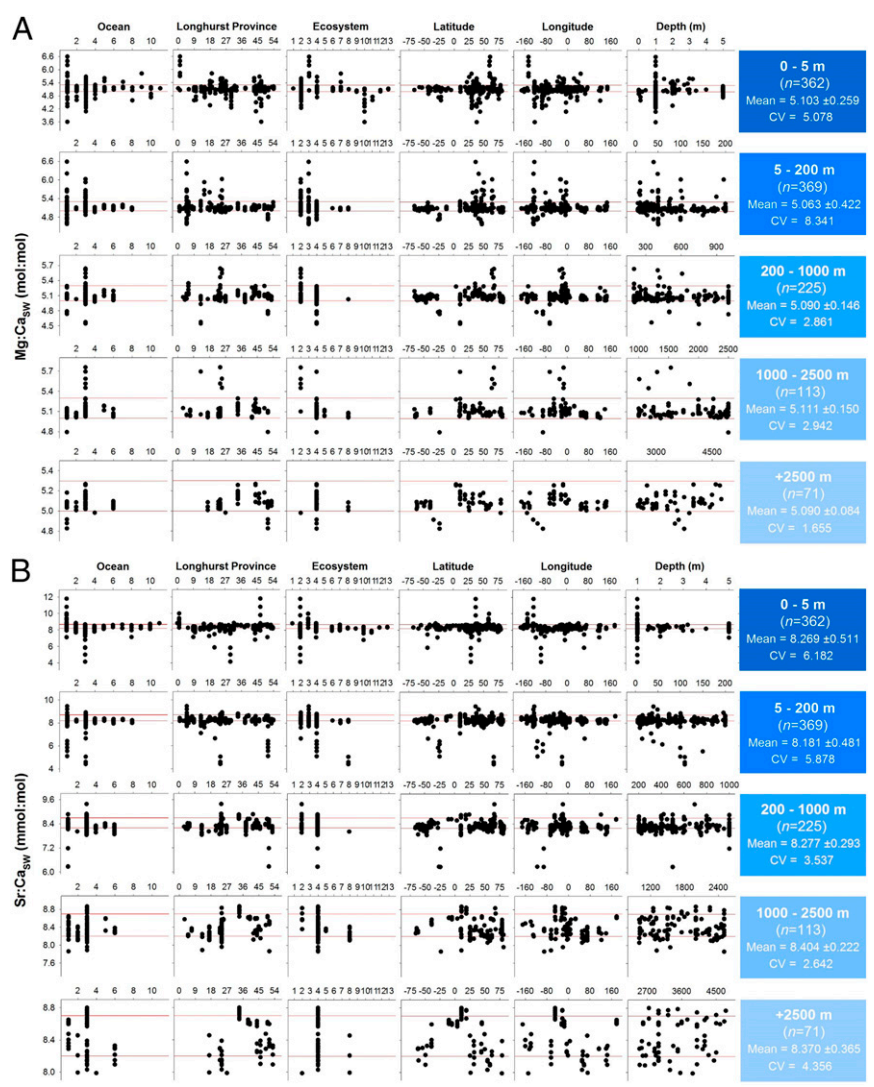


Fig. 2. Modern ocean seawater Mg:Ca and Sr:Ca ratios vs. environmental parameters. Data horizontally classified for seawater Mg:Ca (A) and Sr:Ca (B) ratios as a function of environmental variables (GLODAPv2; refs. 41 and 42) from the largest to the smallest dimension, and vertically in five depth intervals of 0 to 5 m, 5 to 200 m, 100 to 1,000 m, 1,000 to 2,500 m, and +2,500 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*. 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*. The full figure is available in the *SI Appendix*.

organisms also had significant increases. This can be further related to physiological traits, organism adaptation, enhancing uptake, and skeletal growth with reduction in the consumed element in the surrounding seawater.

Discussion

Modern Ocean Variability of Seawater Mg:Ca and Sr:Ca Ratios. The substantial spatial horizontal/vertical deviations from homogeneity, and the natural variability in modern seawater Mg:Ca and Sr:Ca ratios presented in this study, are in line with several local and regional studies that document deviations from the accepted average oceanic values (Mg:Ca ~ 5.10 mol:mol, Sr:Ca ~ 8.50 mmol:mol). Higher deviations from the means are expected in areas with active processes along the dissolution and calcification lines (Fig. 4), as well as near hydrothermal vents, regions of sea-ice formation, anoxic basins, coastal areas, and river mouths (12). Nevertheless, paleo-proxy model calibrations and experimental laboratory work

tend to assume conservative behavior, homogeneity, and steady state of modern ocean seawater Mg:Ca and Sr:Ca ratios following the MORT concept. Our results suggest that modern ocean variability (Figs. 3 and 4) should be considered, and that caution should be taken when reconstructing past seawater conditions, paying attention to the ecosystem from which the sample is being recovered. The inclusion of confidence intervals based on modern ocean elemental ratios’ variability (Fig. 5 and *SI Appendix, Fig. S2*) could offer a valid tool to communicate past seawater Mg:Ca and Sr:Ca ratios’ uncertainty. Yet, it is true that most reconstructions (7) reflect open-ocean bottom water masses appropriately, with a possible extrapolation to surface waters if corrections for biological activity are considered. Our results also support published discussions (4) suggesting that there is a need in the scientific community to have a detailed and better understanding of the variability in seawater Mg:Ca and Sr:Ca ratios from the past, and thus more detailed research needs to be conducted at the ecosystem

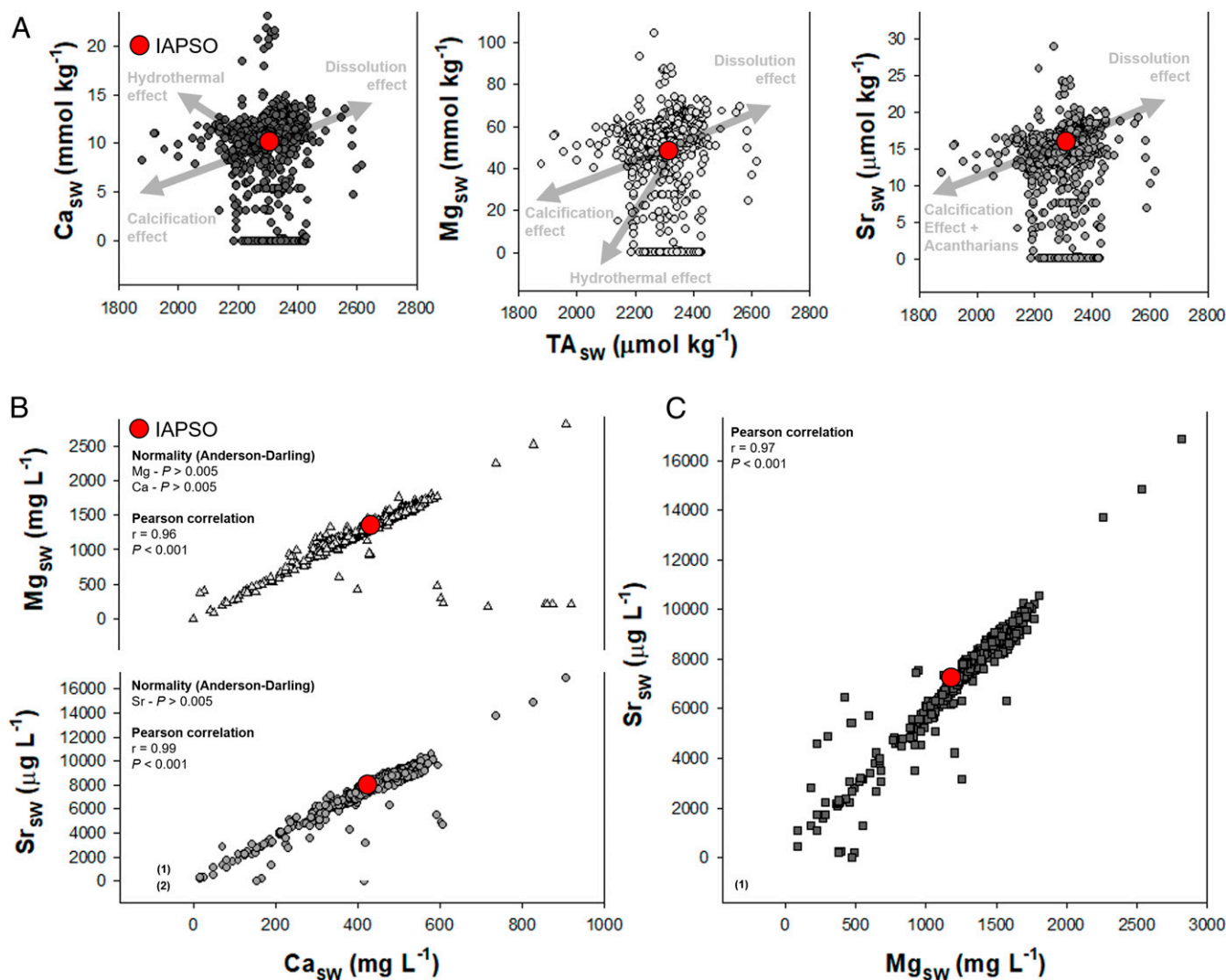


Fig. 3. Modern ocean seawater Ca, Mg, and Sr vs. TA; Mg and Sr vs. Ca; and Sr vs. Mg. Cross plots indicating the relations of seawater ions with TA (A) and between each other (B and C). TA is used to identify biogeochemical processes that could be impacting deviations from the ratios. (A–C) IAPSO (this study) seawater composition is used for comparison. Normality test results, and Pearson correlation coefficients are included in the graphs.

and habitat level (Figs. 3 and 4). The assumption of homogeneity in elemental ratios as currently used in marine sciences is mostly applicable to open-ocean conditions (but not in all cases), additionally to the deep ocean, and, in particular, to bottom water masses or at MOR flanks. Yet, many samples used in, for example, paleo-reconstruction studies have been obtained in shelves and marginal seas aiming to reconstruct open ocean or extrapolating results to the global ocean (SI Appendix, Fig. S2). These studies are mostly focused on temporal variability around a fixed location, while our dataset sheds light on the spatial ratios' variability at a fixed point in time, to then consider the likely variability that occurred in the past. The open and deep ocean represent the majority of the oceanic water by volume, but many key biogeochemical processes impacting the ratios directly or indirectly take place in continental margins, including slope, shelf, and neritic areas, where, for example, large TA fluxes and consumption occur, coupled to anoxia events, nutrient loads, freshwater mixing, and ice melting. Previously reported results on seawater Mg:Ca and Sr:Ca ratio reconstruction should strictly correspond to the water masses and the biogeographical region where the samples formed or the processes took place (7, 22, 23). The further we go back in time, the less reliable measurements are, and fewer data

are available, and thus it seems optimistic to extrapolate these data to the various past ocean regions/areas and ecosystems as a whole. This becomes obvious when considering that the variability in modern oceanic seawater Mg:Ca and Sr:Ca ratios ranges more than 2 units, which is large compared to the low variability needed for paleo reconstructions, depending on the reconstructed ecosystem and habitat of interest. It is reasonable to assume that a similar variability occurred throughout the past 600 My depending on the prevailing conditions and processes (Fig. 5), which could be one of the reasons why different ratio reconstructions, based on different taxa, techniques, and environments, do not agree on the end result/secular trend (discussed below).

Mechanisms Underlying Modern Ocean Variability in Seawater Mg:Ca and Sr:Ca Ratios. It is of critical importance to understand at a global level what is causing the variability in the ratios, what the implications are, and what can be learned from a deeper understanding of the underlying mechanisms to improve their use in marine sciences. It has been previously reported that anomalies in seawater Ca concentrations are due to removal from the upper ocean via calcification, enrichment from carbonate dissolution during sinking, dissolution in surface layers in regions of

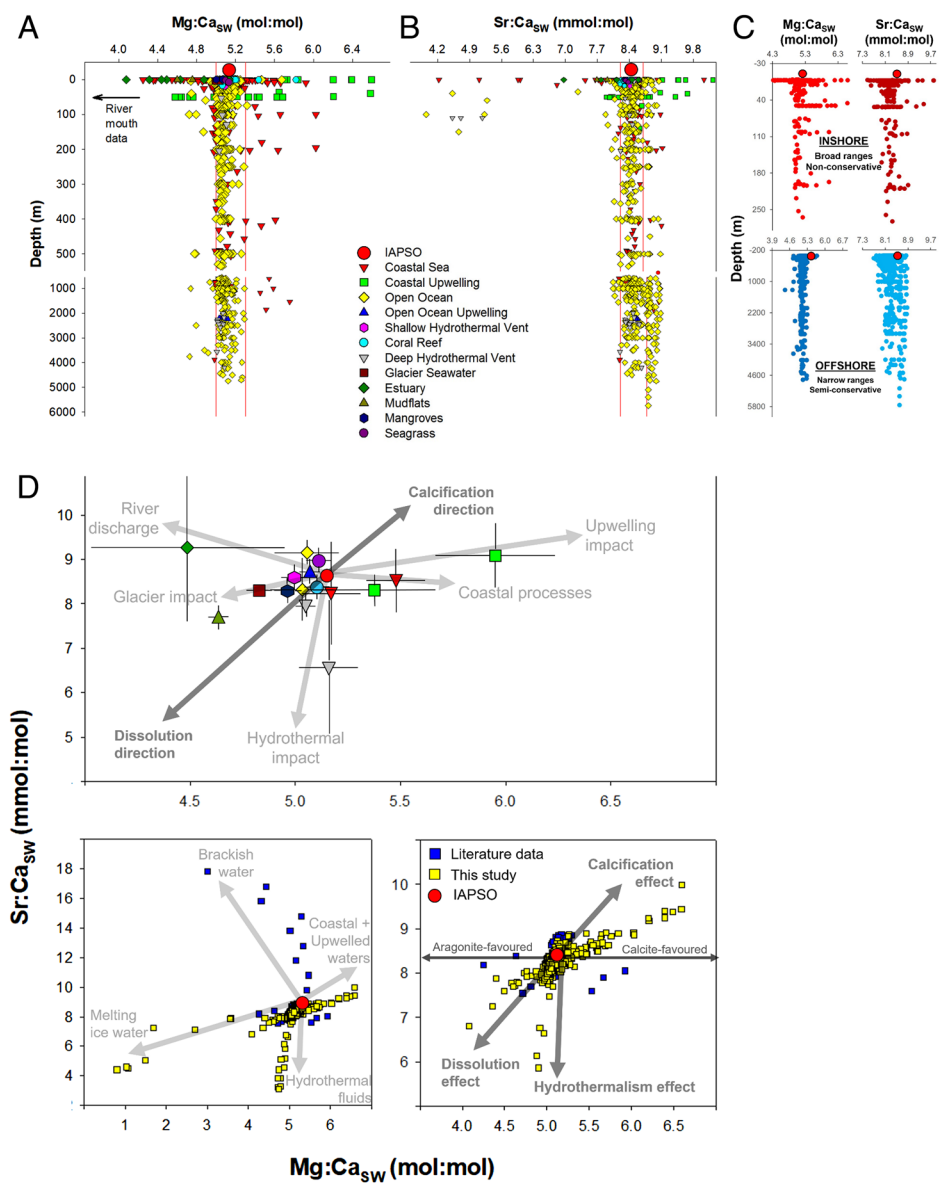


Fig. 4. Modern ocean seawater Mg:Ca and Sr:Ca ratios vs. depth, and conceptual diagrams of Sr:Ca vs. Mg:Ca to identify processes. Data classified horizontally for seawater Mg:Ca (A) and Sr:Ca (B) ratios per ecosystem, and vertically with depth. Seawater Mg:Ca ratios data from river mouths can be found in *SI Appendix, Fig. S1*. Data within the red lines represent literature assumed knowledge of modern seawater ratios. (C) A selection of curated seawater Mg:Ca and Sr:Ca ratios vs. depth, classified as “coastal seas” and “open ocean” to distinguish variability at large, separating the two major environments where marine science disciplines obtain samples/data. (D) Cross plots of averages and SDs of modern seawater Mg:Ca vs. Sr:Ca ratios with arrows indicating the direction of change for ocean processes. Also included are individual data points cross plots comparing literature vs. this study data. In all figure panels, IAPSO (this study) seawater Mg:Ca and Sr:Ca ratios are used for comparison.

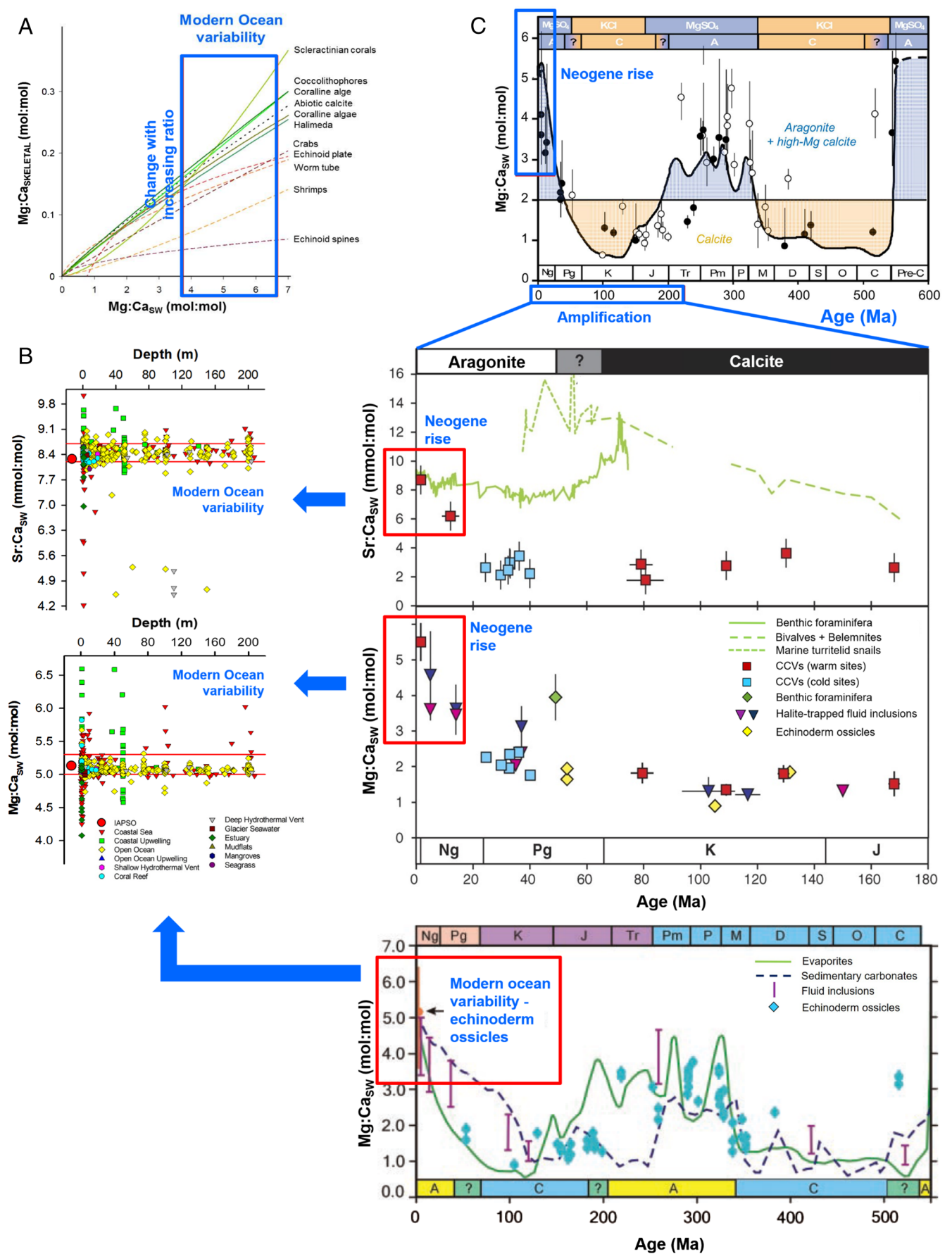


Fig. 5. Modern ocean seawater Mg:Ca and Sr:Ca ratios compared to reconstructions over geological time intervals. (A) Relation between seawater Mg:Ca and organism skeletal Mg:Ca, indicating the effect of modern seawater Mg:Ca natural variability on marine calcification. Reprinted from ref. 3, which is licensed under [CC BY 3.0](https://creativecommons.org/licenses/by/3.0/). (B) Upper ocean integrated 250-m modern ocean values for seawater Mg:Ca and Sr:Ca in various ecosystems showing that variability is similar to the reconstructed Neogene Period (23.03 Ma). From refs. 7 and 23. Reprinted with permission from AAAAS. (C) Phanerozoic Period (541 Ma) values for seawater Mg:Ca and the last 200 My of seawater Mg:Ca and Sr:Ca ratios are presented for comparison with modern ocean variability. Aragonite and calcite seas periods are included, and the geological periods: J, Jurassic; K, Cretaceous; Pg, Paleogene; and Ng, Neogene. Data, boxed and within the red lines, represent literature assumed knowledge of modern seawater ratios. Reprinted from ref. 3, which is licensed under [CC BY 3.0](https://creativecommons.org/licenses/by/3.0/). In all figure panels, "IAPSO (this study)" seawater Mg:Ca and Sr:Ca ratios are used for comparison. The raw data used in the geological time reconstructions can be checked in the figure legends in the corresponding papers (8, 12, 23).

low pH, associated with terrestrial inputs, and groundwater Ca fluxes (also observed in this study; Figs. 3 and 4). How these essential processes drive the elemental concentrations and ratios can be observed in the cloud dispersion around the IAPSO reference point along the TA gradient, considering all data points together (Fig. 3). The TA is of crucial importance in this study because it represents the charge balance in seawater and the buffer capacity to resist changes in pH. Thus, it has a strong relationship with salinity, being indirectly related to the seawater elemental composition. Dissolution of carbonates forms Ca^{2+} and CO_3^{2-} ; Ca^{+2} does not influence TA, but CO_3^{2-} increases TA by 2 units, and thereby shows an indirect relationship between seawater Ca^{2+} concentrations and TA (Fig. 3A). For example, in tropical regions of the Indian Ocean, Ca anomalies arise due to direct consumption by coral reefs during biogenic calcification (25), but it is unknown if the anomalies prevail over time or if they remain transient in nature. This process was observed in our data from the coral reefs in the Mozambique Channel, with anomalies driving a higher seawater Mg:Ca ratio despite the reefs being located in semi open ocean areas with continuous water exchange (Fig. 4A and B, light blue dots). Additionally, the cycling of Ca due to dissolution and precipitation of calcium carbonates modifies the TA in the surrounding seawater within coral reef lagoons (26, 27) but also in the open ocean and coastal environments via the carbonate/TA relation (Fig. 3A). The TA and DIC relation, in particular with seawater Mg:Ca, was magnified in continental margin upwelling areas, which in this dataset correspond to the east Pacific in the California Current system (NOAA cruises) (Figs. 3 and 4). In this particular case, seawater has a higher acidity (higher DIC and CO_2 , lower pH), which in turn dissolves carbonates faster due to a shallower saturation horizon for calcite and aragonite. This results in very high seawater Mg:Ca (> 6 mol:mol) and Sr:Ca (> 9 mmol:mol) ratios with respect to the reference IAPSO standard, with a few exceptions (Fig. 4A and B). As a general rule, coastal seas water masses in the Indian, Pacific, and Atlantic Oceans exhibited higher seawater Mg:Ca and Sr:Ca ratios than open ocean regions, driven by a combination of biological and chemical processes (Fig. 4C).

Regions of riverine and glacial meltwater input influence TA concentrations as well as seawater elemental cycling, acting as competing sources and sinks. Freshwater discharges act to dilute seawater carbonate and bicarbonate (the principal components of seawater TA), lowering salinity and thus reducing TA. However, these water sources supply dissolved minerals that increase TA and indirectly shift seawater Mg:Ca and Sr:Ca ratios, as seen in this dataset, for example in the river discharge and glacial melting samples around the Atlantic Ocean continental margins (Fig. 3). In polar regions, carbon cycling in sea-ice brines leads to the abiotic precipitation of carbonates in the ice, which are released to the upper ocean during ice melt, shifting also seawater Mg:Ca and Sr:Ca ratios. This, at the local/regional level, is an additional TA source when the precipitated carbonate is also dissolved. TA is semiconservative and can be used as a tracer for ocean circulation and mixing as different water masses have different TA signatures as well as seawater Mg:Ca and Sr:Ca ratios (assuming semiconservative behavior in the open ocean). Deep and bottom waters are typically TA-rich from remineralization and dissolution of carbonate/organic sinking particles and sediment resuspension. The Ca concentration in seawater is also modified via the production and dissolution of biogenic carbonates from several calcareous organisms, for example foraminifera tests, pteropod shells, and coccoliths (28) that mainly inhabit open-ocean water masses and upwelling regions. This induces further variability in seawater Mg:Ca and Sr:Ca ratios in spatiotemporal terms (Figs. 3 and 4). The fundamental reasons for Mg and Sr anomalies at the elemental level are more complex. Their variability is linked to profiles of phosphate (PO_4^{3-}) and nitrate (NO_3^-) that reflect biological consumption patterns

(3), mostly in the open ocean and upwelling regions (e.g., in meridional transects in the Atlantic and Pacific Ocean, as well as the California Current), accounting for up to 5% of the variation in the seawater Mg:Ca and Sr:Ca ratios (29). In continental margins, the ratios are mainly governed by regional upwelling and mixing of different water masses with riverine and groundwater/lacustrine inputs, which usually exhibit different elemental concentrations than the surface/surrounding waters (30) (SI Appendix, Table S1 and Figs. 1 and 3C). Our results indicate greater variability (above 5%) for seawater Sr:Ca compared to previous work (8) (2 to 3% change), which is attributed to the inclusion of more data encompassing a wider spatial scale. Open-ocean surface seawater Sr:Ca ratios are overall more variable than Mg:Ca ratios. This may be explained by the abundance of acantharians and Sr use, in contrast to the relatively small amount of Mg that is used by coccolithophores and foraminifera during biogenic calcification (31). Frequently, the maximum density of acantharians in the oceans is found between 50- and 200-m depth (32). This accounts for changes in seawater Sr composition in the upper ocean since acantharians utilize a substantial fraction of Sr to produce their tests. Sinking tests of upper ocean organisms provide a continuous vertical flux of Mg and Sr particulates out of the surface ocean, which dissolve while sinking, enriching the pool of dissolved Mg and Sr in deeper waters. If these enriched deep waters are upwelled, anomalies in the ratios occur (e.g., California Current; Fig. 3). Similarly, aeolian inputs induce variations in dissolved mineral ion fluxes (33). Mg can be enriched in dust of African, Asian, or North American origin, being deposited in all oceans by between 0.5 and 2.3 g/100 g (34). Also abundant in dust are other metals, specifically iron (Fe-compounds), which can fertilize phytoplankton blooms and enhance further biological uptake of Ca, Mg, and Sr, shifting the seawater ratios. At large, the trade-off between input and consumption processes affects the final seawater Mg:Ca and Sr:Ca ratios. Overall, Ca, Mg, and Sr are taken up during biological processes in the surface ocean and then dissolve as they sink through the water column. Below 1,000 m, ratio changes are a function of water mass circulation and deep carbonate dissolution, which is driven by the saturation horizons.

Processes related to the removal and addition of seawater Ca, Mg, and Sr, as well as the relation to TA, work at different spatiotemporal scales, including the ecosystem and habitat levels (Figs. 3 and 4). At large, riverine discharge in continental shelves, hydrothermalism, and MORs in the deep ocean dominate elemental (Ca, Mg, and Sr) fluxes. In certain ecosystems such as coral reefs or calcifying planktonic communities, organisms may significantly influence these fluxes and the ratios via calcification, dissolution, presence of calcite/aragonite/Mg-calcite, and the relation with TA (via hydrothermalism or neritic interactions, for example mangroves and seagrass meadows fluxes). The relation of TA to the elements is particularly important because TA fluxes are indirectly balanced via Ca increase owing to the CO_3^{2-} and also Mg from rock weathering (35). An increased sink flux of Ca during the last 30 My rather than changes in Mg and Sr is viewed as the force driving correlated increases of seawater Mg:Ca and Sr:Ca ratios (Fig. 3). Yet, this does not prevent local and regional processes from impacting the ratios on shorter time scales at the ecosystem and habitat levels.

Implications of Modern Ocean Variability in Seawater Mg:Ca and Sr:Ca Ratios. While the importance of organisms' carbonate Mg:Ca and Sr:Ca composition has been previously noted, less considered are the effects of in situ modern seawater Mg:Ca and Sr:Ca ratios on the calcification process and carbonate composition (35, 36). In coccoliths, a change of seawater Mg:Ca values from 5.10 to 5.90 mol:mol changes calcite Mg:Ca from 0.05 to 0.25 mmol:mol, which can override paleothermometry reconstructions based on them, or ancient seawater proxies on the

assumption of constant seawater ratios (17). Similarly, changes in seawater Sr:Ca from 4.00 to 10.00 mmol:mol increases the calcite Sr:Ca from 1.3 to 3.5 mmol:mol, depending on the seawater ratio (36–38), which challenges the application as paleo-productivity proxy (39, 40), because the modern variability exceeds the reconstructed one. This demonstrates the necessity for routinely incorporating a normalization of carbonate elemental ratios to seawater elemental ratios, which corresponds to the partitioning coefficient (comparison of the solubilities of two solutes in a solution) for each element (D_{Mg} and D_{Sr}) (3, 5). This is especially relevant for the comparison of carbonate samples from different ocean regions, ecosystems, habitats, and taxa, which is often needed in global studies.

The response of carbonate Mg:Ca and Sr:Ca ratios of benthic organisms to changes in seawater Mg:Ca and Sr:Ca ratios was recently assessed (3) (Fig. 5) to study taxa-specific calcification processes during Earth geological times. In experimental work, a source of error can be introduced when an organism with a fast generation/reproduction time is isolated from an estuary, a neritic/subtidal setting, shelf, or oceanic environment, and is then placed into experimental incubation media that use the locally available seawater or a source that is not the organism's original habitat. Thus, the newly precipitated carbonate structures may considerably differ from the previously formed carbonate that was precipitated under the seawater source of differing elemental composition. This effect may significantly alter the bulk carbonate Mg:Ca and Sr:Ca ratios. Organisms inhabit regions with seawater Mg:Ca and Sr:Ca ratios that sometimes are different from those assumed in empirical work and are used for extrapolation in paleo reconstructions or, for example, experiments to test the effects of ocean acidification. Hence, when other variables are modified (e.g., temperature or CO_2) results may also incorporate a response to an a priori believed conservative property like seawater Mg:Ca and Sr:Ca ratios, confounding the meaning of the response. For many organisms, changes within the observed range of modern seawater ratios impact physiology, mineralogy, reproduction, skeleton stiffness, growth rate, and productivity (3), which, in turn can affect the skeletal carbonate ratios. Our dataset suggests that the application of constant seawater elemental ratios needs to be carefully considered and could be a confounding factor in experimental work, if the regional and ecosystem dimensions are not considered.

Another challenge is that modern interpretations of past seawater conditions rely on the fossil carbonate record's being related to a homogeneous seawater composition (23, 24, 41), but they do not account for the environmental conditions and variability experienced by those organisms. Factors such as a life history in varying seawater ratios, or organisms living in ancient coastal regions or estuaries with seawater elemental ratios different from the assumed open-ocean conditions, are two examples where fossil signals could be potentially misinterpreted. For instance, the projected variability of calcite Mg:Ca and Sr:Ca ratios in many organisms over the range of modern ocean seawater ratios is between 1 and 2 units, which is equivalent to a temperature range greater than 5 °C for foraminifera (3) (Fig. 5). There are numerous examples of the use of calcite Mg:Ca to reconstruct paleo-environmental parameters. Foraminifera calcite Mg:Ca and Sr:Ca ratios have been calibrated vs. temperature using linear equations (42) and isotopic signatures (43), as well as molluscs' aragonite Mg:Ca ratios vs. temperature, also using linear equations (44). Echinoderms have been used to reconstruct seawater Mg:Ca ratios based on fossilized ossicles, using an exponential equation with respect to the skeleton mole percent $MgCO_3$ and the calcite Mg:Ca ratio (23). In a recent review (3), numerous benthic and planktonic organisms' calcite Mg:Ca ratios were compared to seawater Mg:Ca to discuss the use of their skeletons to reconstruct past seawater conditions, focusing on the fractionation coefficient and temperature. Other techniques use calcium carbonate vein (CCV) fluids plotted against temperature to reconstruct seawater Mg:Ca and Sr:Ca ratios. The seawater ratios

from which the fluids originated are determined from the fluid evolution trend. Finally, the CCV age is determined from the isotopic curves (7). In these cases, the reconstructed seawater does reflect regional and local conditions, and extrapolations were always transferred to the global ocean. Elemental ratios from foraminifera represent open-ocean water-column and seabed conditions, those from mollusks reflect continental shelf and neritic areas, those from echinoderms (tropical) reflect continental shelf and neritic areas, except if there is evidence that they were deep-sea mollusks/echinoderms, CCVs represent open ocean, MORs, and deep seabed water masses. In the case of the echinoderm's reconstruction, ossicles were treated individually, and then a pooled number of tropical species were used to represent the modern ocean, giving a seawater Mg:Ca range. Our global seawater Mg:Ca range down to 4,000 m varies from 4.80 to 5.60 mol:mol, which surprisingly agrees with the range in seawater Mg:Ca ratios determined using tropical echinoderms ossicles, where it was concluded that modern seawater Mg:Ca ratios range from 4.00 to 6.40 mol:mol (23). This is in total agreement with our measurements (Figs. 4 and 5) and in line with our suggestion that even if the averaged reconstructed seawater ratios are reliable they must include an error similar to that estimated from the modern ocean ratios and can only act as an approximation. In a recent study, model equations on foraminiferal calcite were adjusted to improve seawater Mg:Ca reconstructions, and it was proposed that a seawater Mg:Ca error of 0.5 mol:mol could be applied for the last 60 My. This correction would mostly agree with other paleo reconstructions based on different organisms and techniques (24). Based on our dataset, we support this error correction and further propose that a seawater Mg:Ca ratio confidence interval of between 1 and 1.5 mol:mol may be more appropriate to include most environmental and ecosystem-based variability. For the seawater Sr:Ca ratio, this goes up to 1.9 mmol:mol (Fig. 5) to account for possible environmental variability.

The notion that different procedures to reconstruct seawater ratios resulted in secular variability for different ecosystems seems logical when comparing the various methods and marine taxa, which consequently reflect the inhabited environment (Fig. 5). Published studies and equations use benthic/planktonic foraminifera, bivalves and belemnites, turrillid snails, CCVs, halite fluid inclusions, and echinoderm ossicles to reconstruct seawater ratios. There are also reliable linear equations for echinoid spines and plates, worm tubes, crabs, Halimeda algae, coralline algae, coccolithophores, and scleractinian corals (3). Considering the life history, ecological, and geochemical differences associated with the taxa and the reconstruction techniques, we suggest that there is nothing substantially erroneous with the way equations and proxies have been used, except in the assumption of homogeneous seawater ratios in all ecosystems and habitats that may lead to oversimplified estimations. If the reconstruction of secular changes requires assumptions of homogenous global elemental distribution, it is necessary to identify the potential source of error related to the environment/ecosystem/habitat being reconstructed. A separation of the ratios gives a range that does not sustain the notion of constant ratios, except in the open ocean, and even there not in all areas. In the open-ocean environment, paleothermometry and paleoproductivity proxies are robust because seawater Mg:Ca and Sr:Ca ratios are well constrained with depth, ranging from 4.80 to 5.30 mol:mol and 7.70 to 8.70 mmol:mol (Fig. 4), respectively, with some exceptions. However, if a research study requires low variability/constant ratios, which does not happen in the modern ocean and likely did not happen in the ocean over Earth geological times (Fig. 5), the results need to clearly indicate error ranges and potential environmental variability associated with the organisms and method used for the reconstruction. The narrowest variability we detected, even in the open and deep ocean, is seawater Mg:Ca from 4.95 to 5.25 mol:mol and Sr:Ca 7.90 to 8.50 mmol:mol. This means that even the open ocean experiences major deviations from homogeneity. Changes in the ratios in the modern ocean are

similar to the reconstructed Neogene rise (20 Ma), and well above Quaternary changes (2.5 Ma), because they could be reflecting environmental variability. This suggests that Neogene records and samples could also reflect to a certain extent local/regional conditions, being an artifact of depositional environments, with variable seawater ratios, similar to the modern ocean. The problem is not related to the marine archives themselves but to the proxy being used and how it is interpreted in relation to the reconstructed environment. For example, some of the most reliable seawater ratio reconstruction records are derived from halite fluid inclusions, which are formed under abnormal marine conditions. This begs the question whether they reflect global oceanic conditions or only those of the open ocean; we suggest they reflect the nearby environment from where they were isolated. The question remains as to how spatial variability in seawater ratios compares to temporal variability of the ratios within individual ecosystems and habitats. This research subject needs urgent attention, in particular in continental margins, where unknowns on how different taxa, ecosystems, and environmental variability may play a role in proxy estimations.

The general assumption of conservative and constant seawater ratios in the fossil record and sediment samples (45) comes into question, especially when considering that the variability of seawater Mg:Ca and Sr:Ca ratios in the modern ocean is in the same range as the reconstructed rise of these ratios over 20 Ma in the Neogene Period. Consequently, it should be acknowledged that in Earth geological time periods the oceanic seawater Mg:Ca and Sr:Ca ratios also exhibited larger variability than commonly presumed. We suggest that different seawater Mg:Ca and Sr:Ca reconstructions based on different taxa, techniques, and abiotic processes, which have given rise to different results, do not necessarily contradict each other but show potential environmental paleo variability, with potential ranges similar to those of the observations made in the modern ocean.

Materials and Methods

Sampling surveys were conducted from 2009 until 2017 in as many global locations as possible (Fig. 1, *SI Appendix*, Figs. S3 and S4, and Dataset 1), sampling in 79 cruises, with emphasis on the euphotic (0 to 300 m), mesopelagic (300 to 1,000 m), and abyssal zones (>1,000 m) including continental margins and open-ocean locations. For seawater sampling we used 15/50-mL sterile tubes, 50-mL sterile syringes, 0.20- μ m sterile filters, plastic gloves, and Parafilm (*SI Appendix*, Text S1). Most samples were recovered using a Niskin-type bottle. Samples were filtered through a 0.22- μ m sterile filter and stored in 15/50-mL polyethylene tubes with Parafilm wrapped around the cap to prevent any evaporation/contamination. Samples were stored in a refrigerator (4 to 8 °C) and sent for analysis to the inductively coupled plasma mass spectrometry laboratory at the Institute of Geosciences, Christian-Albrechts-Universität zu Kiel, Germany, between 6 and 12 mo after collection. After 1 y in storage, no signs of seawater evaporation were observed (< 0.05% seawater Mg:Ca and Sr:Ca ratios variability) (3). At the Institute of Geosciences, Kiel University, Germany, all samples were analyzed in the same laboratory and machine by the same person for Ca, Mg, and Sr, as well as other elements (*SI Appendix*), with simultaneous data acquisition using an inductively coupled plasma optical emission spectrometer SPECTRO Ciros charge-coupled device standard operating procedure. Samples were 50-fold diluted with 2% (vol/vol) freshly subboiled in HNO₃ and introduced with a GE Seaspray micronebulizer and thermostated Cinnabar cyclonic spray chamber. Sample preparation was performed under class-100 clean bench conditions with ultrapure reagents (Elga Labwater). The following emission lines were selected: Ca: 317.933nm (II); Mg: 279.553nm (II); Sr: 407.771nm (II), 421.552nm (II), and measured simultaneously within the same preselected acquisition interval ("Phase 3"). A combined intensity calibration and drift-correction procedure using IAPSO standards (46, 47) was applied for data processing (Dataset S4). 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. 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 (Dataset S4). 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 is well below 0.40% for seawater Mg:Ca and 0.90% for seawater Sr:Ca.

The measured dataset was complemented with a seawater Mg:Ca and Sr:Ca ratios literature survey (Fig. 4D and Dataset S2). Publications and reports methods sections were screened for data quality and analytical clarity to mine data comparable to our dataset based on standards used and analytical method/accuracy. We also put together a table on the historical use of seawater Mg:Ca and Sr:Ca ratios in the last 100 y (*SI Appendix*, Table S3). The final seawater Mg:Ca and Sr:Ca ratios database (Dataset S3) was combined with seawater environmental metadata mined from GLODAPv2 (48, 49) and used to analyze and classify seawater Mg:Ca and Sr:Ca ratios as a function of environmental variables (Dataset S3). ArcGIS 10.0 (ESRI 2011) and the three-dimensional analytical tool "NEAR 3-D analysis" were used to link environmental seawater conditions with the sample's seawater ratios. When the prediction was not sufficiently accurate, the closest value was manually selected. For comparison purposes, the GEMS-GLORI database, despite being compiled from primary and secondary sources, was used to provide a distribution map of seawater Mg:Ca ratios from river mouths/plumes around the world (*SI Appendix*, Fig. S1 and Dataset S6), but it was not added to the statistical analyses or mechanistic assessments. Finally, various paleo proxies' global databases were mined to provide distribution maps of paleo reconstructions (*SI Appendix*, Fig. S2), to identify where the majority of the paleo work has been conducted around the world.

The seawater Mg:Ca and Sr:Ca ratios were classified by ocean, Longhurst Province, ecosystem type, latitude, longitude, and depth (in five intervals) (Dataset S3) and then by all of the metadata (chemistry). Ratios were mapped globally (Fig. 1 and Dataset S1), vs. depth, and by ecosystem (Figs. 1 and 3). Ratios were also plotted against each property (Fig. 2). Data were tested for normality using the Anderson–Darling test (95% confidence), and element correlations were assessed using Pearson coefficients. The ratios data ranges used were decided using normality curves quartiles Q2 and Q3. If Q1 and Q4 quartiles were to be used, the ranges would be even larger, thus we decided to remain conservative to be fair with the data distribution and the field observations. A GLM using forward stepwise selection was applied to the ratios vs. five depth intervals (*SI Appendix*, Table S2 and Dataset S5). All analyses and graphical work were performed in Statistica 13.0 (StatSoft), SigmaPlot 12.0 (Systat Software Inc.), ArcGIS (ESRI), SURFER (Golden Software, LLC.), and Corel Draw X3 (Corel Corp.). A full version of Materials and Methods can be found in *SI Appendix*.

Data Availability. Our published databases are publicly accessible for readers, and they are deposited at the NOAA NCEI at <https://data.nodc.noaa.gov/cgi-bin/iso?id=gov.noaa.nodc:0171017> (50).

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