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► **To cite this version:**

Mario Lebrato, Dieter Garbe-Schönberg, Pascal Bailly Du Bois. Global variability in seawater Mg:Ca and Sr:Ca ratios in the modern ocean. Proceedings of the National Academy of Sciences of the United States of America, 2020, pp.201918943. 10.1073/pnas.1918943117 . hal-03118124

HAL Id: hal-03118124

<https://hal.science/hal-03118124>

Submitted on 21 Jan 2021

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3 Main text for

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

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79 **PHYSICAL SCIENCES**

80 Earth, Atmospheric, and Planetary Sciences
81

82 **BIOLOGICAL SCIENCES**

83 Environmental Sciences
84

85 **Abstract**

86
87 Seawater Mg:Ca and Sr:Ca ratios are biogeochemical parameters reflecting the Earth-ocean-
88 atmosphere dynamic exchange of elements. The ratios dependence on the physical and chemical
89 environment, facilitates their use as tools in marine sciences. It has been ~130 years since the last
90 global survey. Here, we present a new measured single-laboratory global dataset, combined with
91 previous data, to test the assumption of limited seawater Mg:Ca and Sr:Ca variability across marine
92 environments. There is high variability in open ocean upwelling and polar regions, shelves, neritic, and
93 river-influenced areas, where Mg:Ca and Sr:Ca range ~4.40-6.40 mmol:mol and ~6.95-9.80 mmol:mol,
94 respectively. Open-ocean seawater Mg:Ca is semi-conservative (~4.90 to 5.30 mol:mol), while Sr:Ca is
95 more variable and non-conservative (~7.70 to 8.80 mmol:mol); both ratios are non-conservative in
96 coastal seas. Further, the Ca, Mg and Sr elemental fluxes are connected to total alkalinity (TA)
97 deviations from IAPSO standard values. Because there is significant seawater Mg:Ca and Sr:Ca
98 variability across marine environments we cannot absolutely assume that fossil archives secular
99 changes using taxa-specific proxies reflect true global seawater chemistry, but taxa- and process-
100 specific ecosystem variations, reflecting regional conditions. This variability could reconcile secular
101 seawater Mg:Ca and Sr:Ca ratios reconstructions using different taxa, techniques, and processes, by
102 assuming an error of 1-1.50 mol:mol, and 1-1.90 mmol:mol, respectively. The modern ratios variability
103 is similar to the reconstructed rise over 20 million years (Neogene period), nurturing the question of
104 semi non-conservative behavior of Ca, Mg, and Sr over modern Earth geological history with an
105 overlooked environmental effect.

106

107 **Key words**

108

109 Seawater, Ratios, Mg:Ca, Sr:Ca, geochemistry, Neogene, Global

110

111 **Significance Statement**

112

113 Modern seawater Mg:Ca and Sr:Ca ratios are important tools in marine sciences. Our contemporary
114 new single-laboratory global dataset, combined with past data of Mg:Ca and Sr:Ca ratios, suggests that
115 ocean variability is substantial across different environments, being similar to the changes during the
116 Neogene period (20 million years). Because there is large variability in seawater ratios, we cannot
117 assume that secular changes derived from fossilized species with varied ecological niches and from
118 diverse ecosystems provide an unbiased representation of past global seawater chemistry. We suggest
119 that the problem of inconsistencies in previous studies of e.g. paleo conditions from different fossil taxa
120 may be reduced by accounting for species differences, ecosystems and abiotic processes, to overcome
121 the regional environmental effect.

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134 Introduction

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136 The first global approximation of modern seawater composition and elemental ratios was conducted by
137 Marcet, Forchhammer, and Dittmar more than 130 years ago, concluding that elemental proportions
138 were almost identical (seawater calcium – Ca, magnesium – Mg, and strontium – Sr, and their ratios).
139 This assumption of near-constant seawater Mg:Ca and Sr:Ca ratios is historically known as the
140 Forchhammer's Principle, the Principle of Constant Proportions, or the Marcet's principle. Over the
141 last decades, this principle has not been revisited, and therefore remains a pivotal dogma in the current
142 understanding of ancient and modern ocean chemistry. The lack of solid evidence for the near-constant
143 seawater Mg:Ca and Sr:Ca ratios except in the open ocean is surprising given the importance of this
144 assumption for e.g. reconstructing ancient global ocean seawater chemistry, its use as a proxy for
145 temperature, or biogeochemical modelling input parameter needs.

146

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

172

173 Recent regional biogeochemical investigations include Mg:Ca and Sr:Ca ratios as well as individual
174 element concentrations in vertical profiles, horizontal distributions, and meridional transects in mostly
175 open ocean surface environments (8-10). The latest studies in salinity and the standard for the
176 calculation of the thermodynamic properties of seawater (Thermodynamic Equation Of Seawater -
177 2010 [TEOS-10] 11, 12) include coastal and river mouth seawater ratios measurements (e.g. GEMS-
178 GLORI database) (13). In marine sciences, seawater Mg:Ca and Sr:Ca ratios are useful to identify
179 biogeochemical processes such as precipitation, dissolution, or consumption that alter the physical
180 properties of seawater. The ratios reflect the dynamic exchanges of important elements between the
181 solid Earth, ocean water masses, the atmosphere, and processes such as biological consumption and
182 dissolution. Prior to our study, there was no comprehensive global survey of marine elemental ratios,

183 but several local and regional studies using different analytical laboratories and techniques, providing
184 limiting evidence to question the constant proportion assumption. An up to date single-laboratory
185 assessment of modern seawater Mg:Ca and Sr:Ca ratios is timely and critical across chemical
186 oceanography, paleoclimatology, oceanic circulation, water masses tracking, and the seawater chemical
187 evolution of the ocean, to ensure the underlying assumptions of using elemental ratios are met, and to
188 re-assess the validity of conservative behavior beyond the MORT premises. Deviations from seawater
189 Ca, Mg, and Sr conservative behavior are known to exist owing to physical changes in the water
190 masses, biological uptake, chemical buffering and dissolution, precipitation, evaporation, dilution, ice
191 melt, groundwater/lacustrine discharges, aeolian inputs, and ocean mixing (14). The fragmented
192 knowledge of these deviations leads to modern experimental and laboratory work being conducted
193 under the assumption that the seawater origin retains constant seawater Mg:Ca and Sr:Ca ratios with
194 oceanic values around 5.00-5.12 (mol:mol), and 8.40-8.64 (mmol:mol), respectively (3, 9, 10).
195 However, estuaries, marshes, river mouths and coastal river mouth plumes deviate considerably from
196 these ratios (15), from ~ 2.00 to 5.00 (mol:mol) in the case of Mg:Ca, and < 8.00 (mmol:mol) in the
197 case of Sr:Ca (16). Likewise, transects from shelf to oceanic waters in the Atlantic show a larger
198 seawater Mg:Ca ratio 5.40-5.60 (mol:mol) in coastal waters than offshore 5.10-5.20 (mol:mol) (17).
199 Samples in open ocean waters of the Red Sea and the Mediterranean Sea indicate variations from 5.40
200 to 5.80 (mol:mol) likely following high surface ocean evaporation rates in enclosed seas. Hence,
201 seawater Mg:Ca in margins and oceanic regions can be spatially heterogeneous owing to variable Mg
202 concentrations (10).

203
204 The most recent seawater Sr:Ca ratios assessment at large scale, excludes continental margins,
205 concentrating on meridional transects in oceanic Atlantic and Pacific surface waters, suggesting a
206 variability of 1 to 3 % around 8.50 (mmol:mol) (9). This fluctuation is higher than Quaternary seawater
207 Sr:Ca paleo reconstructions uncertainty/confidence intervals (e.g. using coccoliths and foraminifera).
208 Depth is assumed to exert a control on elemental composition: in the Pacific the euphotic zone is
209 depleted in seawater Ca by ~ 1 % relative to deep waters below 1000 m depth (18); the opposite occurs
210 in the Atlantic both for Ca and Mg (19). In the Indian Ocean, seawater Mg:Ca ratios vary with depth
211 depending on location (10), and in the Pacific, surface seawater Sr:Ca is reduced by ~ 1 to 3 %
212 compared to deep waters below 1000 m (9, 20), while seawater Sr:Ca gradients increase in other ocean
213 basins (21). Ca and Mg are crucial elements for biological functioning at the cellular, membrane and
214 molecular level, while Sr is not considered to be an essential element for photosynthetic organisms
215 (22). Therefore, the trends are attributed to pelagic Sr utilization in the euphotic zone by
216 coccolithophores via SrCO₃, and acantharians via SrSO₄ (also observed for nutrient depth profiles), and
217 re-dissolution below their respective saturation horizons. Dissolved Sr is assumed to be a highly
218 conservative element below the euphotic zone, but it is subjected to large variability in the upper ocean.

219
220 Numerous scientific studies around seawater Mg:Ca and Sr:Ca ratios in the modern ocean target local
221 or regional process-orientated reconstructions of seawater Mg:Ca and Sr:Ca ratios throughout Earth
222 history without considering differences in ranges, biogeographical provinces, or ecosystem criteria,
223 often assuming that fixed-location estimations reflect the global ocean in general. This has contributed
224 to the broad assumption that these elements have long residence times and conservative behavior and,
225 hence, constant ratios, with few exceptions. Namely, reconstructions of seawater Mg:Ca and Sr:Ca
226 ratios using different taxa and techniques at different laboratories have concluded that the ratios
227 increased during the last 66 million years (Cenozoic) with large variability/uncertainty depending on
228 the approach used. However, the reconstructions contrast on the magnitude of change/increase and they
229 diverge on the variability in the modern era beyond the consensus around open ocean/deep-sea values
230 of Mg:Ca = 5.10 mol:mol (3, 7), and Sr:Ca = 8.20 mmol:mol (7). Considering that no detailed global
231 survey of modern seawater Mg:Ca and Sr:Ca ratios has been conducted in the last 130 years with

232 fragmented pieces of evidence in different oceans and environments, but modern analytical techniques
233 progressed towards high analytical precision, a re-assessment is timely. This can help to reconcile
234 earlier results and to advance our understanding of the distribution patterns of major seawater ions. The
235 process-orientated strategy presented here was used to answer relevant biological, palaeoceanographic,
236 and modelling questions related to modern seawater Mg:Ca and Sr:Ca ratios at a global scale.

237

238 These questions include:

239

240 (1) How do these elemental ratios vary with ocean habitat, province, ecosystem, depth, latitude,
241 seawater chemistry?

242

243 (2) What is the true modern variability across the global ocean and how conservative are present-
244 day elemental ratios?

245

246 (3) How does this variability affect the interpretation of paleo estimations, and can
247 estimations based on different techniques and taxa be reconciliated?

248

249 **Results**

250

251 The present study measured modern seawater Mg:Ca and Sr:Ca ratios in more than 1100 samples from
252 79 research cruises and expeditions worldwide, which were compared with published data, and then
253 merged into a master databank deposited at the NOAA National Center for Environmental Information
254 (NCEI) under Accession Number 0171017 in <http://accession.nodc.noaa.gov/0171017> (SI Appendix 1,
255 2). The seawater Ca, Mg, Sr, Mg:Ca, and Sr:Ca data followed normal distribution curves (Anderson-
256 Darling $P < 0.005$). The following ranges and observations emerged from separating the data using
257 quartiles and confidence intervals, as well as graphical representations. The distribution of seawater
258 Mg:Ca in the euphotic zone varied between 4.95 and 5.30 mol:mol with some peaks up to 5.40
259 mol:mol in all open ocean settings at all latitudes, while seawater Sr:Ca was more variable, from 7.70
260 to 8.80 mmol:mol (Fig. 1, 2). However, there were many deviations from these ranges for seawater
261 Mg:Ca, mostly coinciding with coastal, shelves, and upwelling regions (down to 4.50 and up to 6.60
262 mol:mol), and especially in neritic and river-influenced areas (0.40 and 2.40 to 4.50 mol:mol) (Fig. 3,
263 4; SI Appendix Fig.S1, Appendix 6). Seawater Sr:Ca showed slight variation beyond 7.70-8.80
264 mmol:mol, with some exceptions around this range mostly in upwelling areas (Fig. 1, 4). The spatial
265 distribution of the two ratios in different depth ranges showed significantly less complexity (Fig. 2;
266 GLM in SI Appendix Table S2), particularly below 200 m (Fig. 1), but several regions with greater
267 heterogeneity (e.g. coastal/open ocean upwelling regions, polar seas, several shelf environments), were
268 found in all oceans. The limited number of samples obtained below 1000 m weakens a general
269 extrapolation for the deep ocean, but a higher variability was certainly observed in the upper 1000 m,
270 and especially in the upper 200 m, where numerous environmental variables and processes (e.g.
271 calcification, dissolution) are governing biogeochemical processes (Fig. 2; SI Appendix Table S2).

272

273 When seawater Mg:Ca and Sr:Ca ratios were averaged by Ocean/Sea, Longhurst Province, and
274 Ecosystem (SI Appendix Table S1), it emerged that the high number of open ocean samples lowered
275 the averages to “homogeneity” reducing the standard error, which would suggest a conservative
276 behavior if a grand mean was calculated across all data. The largest deviations from assumed
277 homogeneity for both ratios around mean values (Mg:Ca ~ 5.10 mol:mol, Sr:Ca ~ 8.50 mmol:mol),
278 were observed as a function of Ocean, Longhurst Province, Ecosystem, Latitude, salinity, total
279 alkalinity (TA), dissolved inorganic carbon (DIC), and dissolved oxygen (DO) (Fig. 2; SI Appendix
280 Table S1). These deviations were heavily dependent on depth band with a decreasing coefficient of

281 variation (CV) with increasing depth. Of particular interest were the ratios distribution with respect to
282 TA, DIC, and DO showing a decreasing complexity with depth, following the high interaction with
283 biological processes in the upper ocean, and carbonate dissolution at depth linked to seawater Mg:Ca
284 and Sr:Ca ratios fluctuations (Fig. 2, 3). Salinity only had a major effect on the ratio's distribution up to
285 ~ 28 (mostly in the upper ocean), then the ratios behaved in a cloud-mode, reflecting mostly biological
286 processes. Cross plots of Ca, Mg, and Sr vs TA reflected the ocean water masses and interior processes
287 shifting the ratios via the hydrothermal, calcification, and dissolution effects at large (Fig. 3a). Cross
288 plots of Mg and Sr vs Ca, and of Sr vs Mg showed how all elements correlated with each other (r^2
289 values between 0.60 and 0.97 in all cases; Fig. 3b), with deviations being explained by the different
290 ecosystems water masses and processes such as river discharge (dilution and minerals addition), glacier
291 impact (meltwater discharge, leading to dilution but also weathered minerals), hydrothermal impact
292 (heavy metals and minerals addition), coastal processes (consumption/dissolution), and upwelling
293 (minerals addition, consumption/dissolution) (Fig. 4d).

294
295 In general, the newly measured dataset greatly expanded literature data in the ranges, with no major
296 disagreements, in terms of values around the same Longhurst provinces/regional areas, and processes
297 (Fig. 4). Most published data analyzed to date, except around river mouths/brackish waters, fall in the
298 vicinity of the IAPSO standard (Fig. 4d), while our data showcases multiple linear extensions of this
299 value, for both ratios, along a greater range of variability. We observed most deviations along the
300 biological calcification-favored line (Fig. 4d), except in instances when melting of ice water dominated,
301 or when a marked hydrothermalism effect was present. Variability in modern seawater Mg:Ca and
302 Sr:Ca ratios was visualized by depth, ecosystem, and major regions/division (Fig. 4a, b, c), treating all
303 samples equally weighted despite the extended volume of the open ocean. The ratios range not only
304 prevailed in the upper ocean, but continued within most of the depth profiles, though the range
305 decreased with depth. This was very obvious when classifying data as "Coastal Seas" and "Open
306 Ocean" to show the broad vs narrow ranges, and the ratios non-conservative vs semi-conservative
307 behavior (Fig. 4c). The ratio groupings were compared to recent reconstructions of seawater Mg:Ca
308 and Sr:Ca ratios (3, 7) from younger Earth history suggesting that the increase in ratios during the
309 Neogene (20 million years) is within the same range of variability shown in modern ocean elemental
310 ratios of most regions investigated here (Fig. 5). Surprisingly, our dataset ranges agreed well with the
311 range calculation using tropical shelf echinoderms ossicles (23), where it was concluded that modern
312 seawater Mg:Ca ranged from 4.0 to 6.4 mol:mol. This is in total agreement with our measurements
313 (Fig. 4, 5), despite the published study (23) using only one group of organisms. Additionally, our
314 dataset ranges also agreed with a model estimation based on modified equations from foraminifera
315 calibrations (24), which shows that modern seawater Mg:Ca ranges from 4.60 to 5.70 mol:mol. When
316 we compared the modern ocean Mg:Ca variability to experimental data describing the correlation
317 between seawater and biogenic carbonate Mg:Ca ratios (Fig. 5a), it emerged that the natural variability
318 of seawater Mg:Ca can be responsible for significant changes in the Mg:Ca ratio of biogenic
319 carbonates. For example, carbonates of scleractinian corals doubled their skeleton Mg:Ca ratio from
320 0.15 to 0.30 mol:mol when seawater Mg:Ca increases from 3.80 to 6.70 mol:mol (Fig. 5a), while other
321 organisms also had significant increases. This can be further related to physiological traits, organism
322 adaptation, enhancing uptake and skeletal growth with reduction in the consumed element in the
323 surrounding seawater. **Discussion**

324 325 **Modern ocean variability of seawater Mg:Ca and Sr:Ca ratios**

326
327 The substantial spatial horizontal/vertical deviations from homogeneity, and the natural variability in
328 modern seawater Mg:Ca and Sr:Ca ratios presented in this study, are in line with several local and
329 regional studies that document deviations from the accepted average oceanic values (Mg:Ca ~ 5.10

330 mol:mol, Sr:Ca ~ 8.50 mmol:mol). Higher deviations from the means are expected in areas with active
331 processes along the dissolution and calcification lines (Fig. 4), as well as near hydrothermal vents,
332 regions of sea ice formation, anoxic basins, coastal areas and river mouths (12). Nevertheless, paleo-
333 proxy model calibrations and experimental laboratory work tend to assume conservative behavior,
334 homogeneity, and steady state of modern ocean Mg:Ca and Sr:Ca ratios following the MORT concept.
335 Our results suggest that modern ocean variability (Fig. 3, 4) should be considered, and that caution
336 should be taken when reconstructing past seawater conditions, paying attention to the ecosystem from
337 which the sample is being recovered. The inclusion of confidence intervals based on modern ocean
338 elemental ratios variability (Fig. 5; SI Appendix Fig. S2) could offer a valid tool to communicate past
339 seawater Mg:Ca and Sr:Ca ratios uncertainty. Yet, it is true that most reconstructions (7) reflect open
340 ocean bottom water masses appropriately, with a possible extrapolation to surface waters if corrections
341 for biological activity are considered. Our results also support published discussions (4) suggesting that
342 there is a need in the scientific community to have a detailed and better understanding of the variability
343 in Mg:Ca and Sr:Ca ratios from the past, thus, more detailed research needs to be conducted at the
344 ecosystem and habitat level (Fig. 3, 4). The assumption of homogeneity in elemental ratios as currently
345 used in marine sciences is mostly applicable to open ocean conditions (not in all cases), additionally to
346 the deep ocean, and, in particular, to bottom water masses or at mid-ocean ridge flanks. Yet, many
347 samples used in e.g. paleo-reconstruction studies have been obtained in shelves and marginal seas
348 aiming to reconstruct open ocean or extrapolating results to the global ocean (SI Appendix Fig. S2).
349 These studies are mostly focused on temporal variability around a fixed location, while, our dataset,
350 sheds light on the spatial ratios' variability at a fixed point in time, to then consider the likely
351 variability that occurred in the past. The open and deep ocean represent the majority of the oceanic
352 water by volume, but many key biogeochemical processes impacting the ratios directly or indirectly,
353 take place in continental margins, including slope, shelf, and neritic areas, where e.g. large TA fluxes
354 and consumption occur, coupled to anoxia events, nutrient loads, freshwater mixing, and ice melting.
355 Previously reported results on seawater Mg:Ca and Sr:Ca ratios reconstruction should strictly
356 correspond to the water masses and the biogeographical region where the samples formed or the
357 processes took place (7, 22, 23). The further we go back in time, the less reliable measurements are,
358 and less data are available, thus it seems optimistic to extrapolate these data to the various past ocean
359 regions/areas and ecosystems as a whole. This becomes obvious when considering that the variability
360 in modern oceanic Mg:Ca and Sr:Ca ratios ranges more than 2 units, which is large compared to the
361 low variability needed for paleo-reconstructions, depending on the reconstructed ecosystem and habitat
362 of interest. It is reasonable to assume that a similar variability occurred throughout the past 600 million
363 years depending on the prevailing conditions and processes (Fig. 5), which could be one of the reasons
364 why different ratio reconstructions, based on different taxa, techniques, and environments, do not agree
365 on the end result/secular trend (see below).

367 **Mechanisms underlying modern ocean variability in Mg:Ca and Sr:Ca ratios**

369 It is of pivotal importance to understand at a global level what is causing the variability in the ratios,
370 what are the implications, and what can be learnt from a deeper understanding of the underlying
371 mechanisms to improve their use in marine science disciplines. It has been previously reported that
372 anomalies in Ca concentrations are due to removal from the upper ocean via calcification, enrichment
373 from carbonate dissolution during sinking, dissolution in surface layers in regions of low pH,
374 associated to terrestrial inputs, and groundwater Ca fluxes (also observed in this study; Fig. 3, 4). How
375 these critical processes drive the elements and ratios can be clearly seen in the cloud dispersion around
376 the IAPSO reference point along the TA gradient, considering all data points together (Fig. 3). TA is
377 considered pivotal in this study, since it represents the charge balance in seawater and the buffer
378 capacity to resist changes in pH_{total} . Thus, it has a strong relationship with salinity. Dissolution of

379 carbonates forms Ca^{2+} and CO_3^{2-} ; Ca^{+2} does not influence TA, but CO_3^{2-} increases TA by 2 units, and
380 thereby shows an indirect relationship between seawater Ca^{2+} concentrations and TA (Fig. 3a). For
381 example, in tropical areas of the Indian Ocean, Ca anomalies arise due to consumption by coral reefs
382 during biogenic calcification (25). This was also observed in our data from the West Indian Ocean,
383 with anomalies driving a higher seawater Mg:Ca ratio (Fig. 4a, b, blue dots). Additionally, the cycling
384 of Ca due to dissolution and precipitation of calcium carbonates modifies the TA in the surrounding
385 seawater within coral reef lagoons (26, 27), but also in the open ocean and coastal environments via the
386 carbonate/TA relation (Fig. 3a). The TA and DIC relation, in particular, with seawater Mg:Ca, was
387 magnified in continental margin upwelling areas, which in this dataset corresponds to the east Pacific in
388 the California Current (NOAA cruises) (Fig. 3, 4). In this particular case, seawater has a higher acidity
389 (higher DIC and CO_2 , lower pH_{total}), which in turn dissolves carbonates faster due to a shallower
390 saturation horizon. This results in overall higher seawater Mg:Ca and Sr:Ca ratios with respect to the
391 reference IAPSO standard, with a few exceptions. As a general rule, coastal sea samples in the Indian,
392 Pacific, and Atlantic Ocean, exhibited higher seawater Mg:Ca and Sr:Ca ratios than open ocean
393 regions, driven by a combination of biological and chemical processes (Fig. 4c).

394
395 Regions of riverine and glacial meltwater input influence TA concentrations, acting as competing
396 sources and sinks. Freshwater discharges act to dilute seawater carbonate and bicarbonate (the principal
397 components of seawater TA), lowering salinity, and thus reducing TA. However, these water sources
398 could contribute dissolved minerals that increase TA, and indirectly shift seawater Mg:Ca and Sr:Ca
399 ratios, as seen in this dataset, e.g. in the river discharge and glacial melting samples around the Atlantic
400 Ocean (Fig. 3). In polar regions, carbon cycling in sea ice brines leads to the abiotic precipitation of
401 carbonates in the ice, which can be released to the upper ocean during ice melt, shifting also seawater
402 Mg:Ca and Sr:Ca ratios. This, at the local/regional level, is an additional TA source when the
403 precipitated carbonate is also dissolved. TA is semi-conservative and can be used as a tracer for ocean
404 circulation and mixing as different water masses have different TA signatures as well as seawater
405 Mg:Ca and Sr:Ca ratios (assuming semi-conservative behavior in the open ocean). Deep and bottom
406 waters are typically TA-rich from remineralization and dissolution of carbonate/organic sinking
407 particles and sediment re-suspension. Ca^{2+} concentration in seawater is also modified via the
408 production and dissolution of biogenic carbonates from several calcareous organisms, e.g. foraminifera
409 tests, pteropod shells and coccoliths (28) that mainly inhabit open ocean water and upwelling regions.
410 This induces further variability in seawater Mg:Ca and Sr:Ca ratios in spatiotemporal terms (Fig. 3, 4).
411 The fundamental reasons for Mg and Sr anomalies are more complex. Their variability is linked to
412 profiles of phosphate (PO_4^{3-}) and nitrate (NO_3^-) that reflect biological consumption patterns (3), mostly
413 in the open ocean and upwelling regions (e.g. in meridional transects in the Atlantic and Pacific Ocean,
414 as well as the California Current), accounting for up to 5 % of the variation in the ratios (29). In
415 continental margins and coastal seas, the ratios are mainly governed by regional upwelling and mixing
416 of different water masses with riverine and groundwater inputs, which usually exhibit different
417 elemental concentrations than the surface/surrounding waters (30) (SI Appendix Table S1; Fig. 1, 3c).
418 Our results indicate greater variability (above 5%) for seawater Sr:Ca compared to previous work (8) (2
419 to 3 % change), which is attributed to the inclusion of more data encompassing a wider spatial scale.
420 Open ocean surface seawater Sr:Ca ratios are more variable than Mg:Ca ratios. This may be explained
421 by the abundance of acantharians and Sr use, in contrast to the relatively small amount of Mg that is
422 used by coccolithophores and foraminifera during biogenic calcification (31). Frequently, the
423 maximum density of acantharians in the oceans is found between 50 and 200 m depth (32). This
424 accounts for changes in seawater Sr composition in the upper ocean since acantharians utilize a
425 substantial fraction of Sr to produce their tests. Sinking tests of upper ocean organisms provide a
426 continuous vertical flux of Mg and Sr particulates out of the surface ocean, which dissolve while
427 sinking, enriching the pool of dissolved Mg and Sr in deeper waters. If these enriched deep waters are

428 upwelled, anomalies in the ratios occur (e.g. California Current; Fig. 3). Similarly, aeolian inputs
429 induce variations in dissolved mineral ion fluxes (33). Mg can be enriched in dust of African, Asian, or
430 North American origin, being deposited in all oceans, by between 0.5 and 2.3 gr/100gr (34). Also
431 abundant in dust are other metals, specifically iron, which can fertilize phytoplankton blooms and
432 enhance further biological uptake of Ca, Mg, and Sr, shifting the ratios. At large, the tradeoff between
433 input and consumption processes affects the final seawater Mg:Ca and Sr:Ca ratios. Overall, Ca, Mg,
434 and Sr are taken up during biological processes in the surface ocean and then dissolve as they sink
435 through the water column. Below 1000 m, ratio changes are a function of water mass circulation and
436 deep carbonate dissolution, which is driven by the saturation horizons.

437
438 Processes related to the removal and addition of seawater Ca, Mg, and Sr, as well as the relation to TA,
439 work at different spatiotemporal scales, including the ecosystem and habitat level (Fig. 3, 4). At large,
440 riverine discharge in continental shelves, hydrothermalism and MORs in the deep ocean, dominate
441 elemental (Ca, Mg, Sr) fluxes. In certain ecosystems such as coral reefs or calcifying planktonic
442 communities, organisms may significantly influence these fluxes and the ratios via calcification,
443 dissolution, presence of calcite/aragonite/Mg-calcite, and the relation with TA (via hydrothermalism or
444 neritic interactions, e.g. mangroves and seagrass meadows fluxes). The relation of TA with the
445 elements is particularly important because TA fluxes are indirectly balanced via Ca increase owing to
446 the CO_3^{2-} , and also Mg from rock weathering (35). An increased sink flux of Ca during the last 30
447 million years rather than changes in Mg and Sr is viewed as the force driving correlated increases of
448 seawater Mg:Ca and Sr:Ca (Fig. 3). Yet, this does not prevent local and regional processes to impact
449 the ratios on shorter time scales at the ecosystem and habitat level.

450 451 **Implications of modern ocean variability in Mg:Ca and Sr:Ca ratios**

452
453 While the importance of organisms carbonate Mg:Ca and Sr:Ca composition has been previously
454 noted, less considered are the effects of *in situ* modern seawater Mg:Ca and Sr:Ca ratios on the
455 calcification process and carbonate composition (35, 36). In coccoliths, a change of seawater Mg:Ca
456 values from 5.10 to 5.90 mol:mol, changes calcite Mg:Ca from 0.05 to 0.25 mmol:mol, which can
457 override paleo-thermometry reconstructions based on them, or ancient seawater proxies on the
458 assumption of constant seawater ratios (17). Similarly, changes in seawater Sr:Ca from 4.00 to 10.00
459 mmol:mol increases the calcite Sr:Ca from 1.3 to 3.5 mmol:mol, depending on the seawater ratio (36,
460 38), which challenges the application as paleo-productivity proxy (39, 40), because the modern
461 variability exceeds the reconstructed one. This demonstrates the necessity for routinely incorporating a
462 normalization of carbonate elemental ratios to seawater elemental ratios, which corresponds to the
463 partitioning coefficient (comparison of the solubilities of two solutes in a solution) for each element
464 (D_{Mg} and D_{Sr}) (3, 5). This is especially relevant for the comparison of carbonate samples from different
465 ocean regions, ecosystems, habitats, and taxa.

466
467 The response of carbonate Mg:Ca and Sr:Ca ratios of benthic organisms to changes in seawater Mg:Ca
468 and Sr:Ca ratios was recently compiled (3) (see Fig. 5) to investigate taxa-specific calcification during
469 geological times. In experimental work, a source of error can be introduced when an organism with a
470 fast generation/reproduction time is isolated from an estuary, from a neritic/subtidal setting, shelf or
471 oceanic environment, and is placed into experimental incubation media that use the locally available
472 seawater or a source that is not the organism's original habitat. Thus, the newly precipitated carbonate
473 structures may considerably differ from the previously formed carbonate that was precipitated under
474 the seawater source of differing elemental composition. This effect may significantly alter the bulk
475 carbonate Mg:Ca and Sr:Ca ratios. Organisms inhabit regions with seawater Mg:Ca and Sr:Ca ratios
476 that sometimes are different from those assumed in empirical work, and are used for extrapolation in

477 paleo reconstructions, or for e.g. experiments to test the effects of ocean acidification. Hence, when
478 other variables are modified (e.g. temperature or CO₂) results may also incorporate a response to an *a*
479 *priori* believed conservative property like seawater Mg:Ca and Sr:Ca ratios, confounding the meaning
480 of the response. For many organisms, changes within the observed range of modern seawater ratios
481 impact physiology, mineralogy, reproduction, skeleton stiffness, growth rate, and productivity (3),
482 which, in turn, can affect the skeletal carbonate ratios. Our dataset suggests that the application of
483 constant seawater elemental ratios needs to be carefully considered and could be a confounding factor
484 in experimental work, if the regional and ecosystem dimensions are not considered.
485

486 Another challenge is that modern interpretations of past seawater conditions rely on the fossil carbonate
487 record being related to a homogeneous seawater composition (23, 24, 41), but they do not account for
488 the environmental conditions and variability experienced by those organisms. Factors such as a life
489 history in varying seawater ratios, or organisms living in ancient coastal regions or estuaries with
490 seawater elemental ratios different from the assumed open ocean conditions, are two examples where
491 fossil signals could be potentially miss-interpreted. For instance, the projected variability of calcite
492 Mg:Ca and Sr:Ca ratios in many organisms over the range of modern ocean seawater ratios is between
493 1 and 2 units, which is equivalent to a temperature range greater than 5 °C for foraminifera (3) (Fig. 5).
494 There are numerous examples of the use of calcite Mg:Ca to reconstruct paleo-environmental
495 parameters. Foraminifera calcite Mg:Ca and Sr:Ca ratios have been calibrated vs temperature using
496 linear equations (42) and isotopic signatures (43), as well as molluscs aragonite Mg:Ca ratios vs
497 temperature, also using linear equations (44). Echinoderms have been used to reconstruct seawater
498 Mg:Ca ratios based on fossilized ossicles, using an exponential equation with respect to the skeleton
499 mol % MgCO₃ and the calcite Mg:Ca ratio (23). In a recent review (3), numerous benthic and
500 planktonic organisms' calcite Mg:Ca ratios were compared to seawater Mg:Ca to discuss the use of
501 their skeletons to reconstruct past seawater conditions, focusing on the fractionation coefficient and
502 temperature. Other techniques, use calcium carbonate veins (CCVs) fluids plotted against temperature
503 to reconstruct seawater Mg:Ca and Sr:Ca ratios. The seawater ratios from which the fluids originated
504 are determined from the fluid evolution trend. Finally, the CCVs age is determined from the isotopic
505 curves (7). In these cases, the re-constructed seawater does reflect regional and local conditions, and
506 extrapolations were always transferred to the global ocean. Elemental ratios from foraminifera
507 represent open ocean water column and seabed conditions, those from mollusks reflect continental
508 shelf and neritic areas, those from echinoderms (tropical) reflect continental shelf and neritic areas,
509 except if there is evidence, that they were deep-sea mollusks/echinoderms, CCVs represent open ocean,
510 MORs, and deep seabed water masses. In the case of the echinoderm's reconstruction, ossicles were
511 treated individually, and then a pooled number of tropical species were used to represent the modern
512 ocean giving a seawater Mg:Ca range. Our global seawater Mg:Ca range down to 4000 m varies from
513 4.80 to 5.60 mol:mol, which surprisingly agrees with the range in seawater Mg:Ca ratios determined
514 using tropical echinoderms ossicles, where it was concluded that modern seawater Mg:Ca ratios range
515 from 4.00 to 6.40 mol:mol (23). This is in total agreement with our measurements (Fig. 4, 5), and in
516 line with our suggestion that even if the averaged reconstructed seawater ratios are reliable, they must
517 include an error similar to that estimated from the modern ocean ratios, and can only act as an
518 approximation. In a recent study, model equations on foraminiferal calcite were adjusted to improve
519 seawater Mg:Ca reconstructions, and it was proposed that a seawater Mg:Ca error of 0.5 mol:mol could
520 be applied for the last 60 million years. This correction would mostly agree with other paleo-
521 reconstructions based on different organisms and techniques (24). Based on our dataset, we support this
522 error correction, and further propose that a seawater Mg:Ca confidence interval of between 1 and 1.5
523 mol:mol may be more appropriate to include most environmental and ecosystem-based variability. For
524 seawater Sr:Ca, this goes up to 1.9 mmol:mol (Fig. 5) to account for possible environmental variability.
525

526 The notion that different procedures to reconstruct seawater ratios resulted in secular variability for
527 different ecosystems seems logical when comparing the various methods and marine taxa, which
528 consequently reflect the inhabited environment (Fig. 5). Published studies and equations use
529 benthic/planktonic foraminifera, bivalves and belemnites, turritellid snails, CCVs, halite fluid
530 inclusions, and echinoderm ossicles, to reconstruct seawater ratios. There are also reliable linear
531 equations for echinoid spines and plates, worm tubes, crabs, Halimeda algae, coralline algae,
532 coccolithophores, and scleractinian corals (3). Considering the life histories, ecological and
533 geochemical differences associated with the taxa and the reconstruction techniques, we suggest that
534 there is nothing substantially erroneous with the way equations and proxies have been used, except in
535 the assumption of homogeneous seawater ratios in all ecosystems and habitats that may lead to
536 oversimplified estimations. If the reconstruction of secular changes requires assumptions of
537 homogenous global elemental distribution, it is necessary to identify the potential source of error
538 related to the environment/ecosystem/habitat being reconstructed. A separation of the ratios gives a
539 range that does not sustain the notion of constant ratios, except in the open ocean, and even there, not in
540 all areas. In the open ocean environment, paleothermometry and paleoproductivity proxies are robust
541 because seawater Mg:Ca and Sr:Ca are well constrained with depth, ranging from 4.80 to 5.30 mol:mol
542 and 7.70 to 8.70 mmol:mol (Fig. 4), respectively, with some exceptions. However, if a research study
543 requires low variability/constant ratios, which does not happen in the modern ocean and likely did not
544 happen in the ocean over geological times (Fig. 5), the results need to clearly indicate error ranges and
545 potential environmental variability associated with the organisms and method used for the
546 reconstruction. The narrowest variability we detected, even in the open and deep ocean, is seawater
547 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
548 ocean experiences sometimes major deviations from homogeneity. Changes in the ratios in the modern
549 ocean are similar to the reconstructed Neogene rise (20 million years), and above Quaternary changes
550 (2.5 million years), because they could be reflecting environmental variability. This suggests that
551 Neogene records and samples could also reflect to a certain extent local/regional conditions, being an
552 artefact of depositional environments, with variable seawater ratios, similar to the modern ocean. The
553 problem is not related to the marine archives themselves, but to the proxy being used and how it is
554 interpreted in relation to the reconstructed environment. For example, some of the most reliable
555 seawater ratio reconstruction records are derived from halite fluid inclusions, which are formed under
556 abnormal marine conditions. This begs the question whether they reflect global oceanic conditions, or
557 only those of the open ocean; we suggest they reflect the nearby environment from where they were
558 isolated. The question remains as to how spatial variability in seawater ratios compares to temporal
559 variability of the ratios within individual ecosystems and habitats. This research subject needs urgent
560 attention, in particular, in continental margins, where unknowns on how different taxa, ecosystems, and
561 environmental variability may play a role in proxy estimations.

562
563 The general assumption of conservative and constant seawater ratios in the fossil record and sediment
564 samples (45) comes into question, especially when considering that the variability of seawater Mg:Ca
565 and Sr:Ca ratios in the modern ocean is in the same range as the reconstructed rise of these ratios over
566 20 million years in the Neogene period. Consequently, it should be acknowledged that in geological
567 time periods, the oceanic Mg:Ca and Sr:Ca ratios also exhibited larger variability than commonly
568 presumed. We suggest that different seawater Mg:Ca and Sr:Ca reconstructions based on different taxa,
569 techniques, and abiotic processes, which have given rise to different results, do not necessarily
570 contradict each other, but show potential environmental paleo variability, with potential similar ranges
571 to those of the observations made in the modern ocean.

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575 **Materials and Methods**

576

577 Sampling surveys were conducted from 2009 until 2017 in as many global locations as possible
578 (Appendix 1; Fig. 1; SI Appendix Fig.S3, S4), sampling in 79 cruises, with emphasis on the euphotic
579 (0-300 m), mesopelagic (300-1000 m), and abyssal zones (>1000 m) including continental margins and
580 open ocean locations. For seawater sampling we used 15/50 ml sterile tubes, 50 ml sterile syringes,
581 0.20 μm sterile filters, plastic gloves, and *Parafilm*[®] (see Text S1). Most samples were recovered using
582 a Niskin-type bottle. Samples were filtered through a 0.22 μm sterile filter, and stored into 15/50 ml
583 polyethylene tubes with *Parafilm*[®] wrapped around the cap. Samples were stored in the fridge (4 to 8
584 $^{\circ}\text{C}$) and sent for analysis to the ICP-MS lab at Institute of Geosciences, Christian-Albrechts-Universität
585 zu Kiel, Germany, between 6 to 12 months after collection. After 1 year in storage, no signs of
586 seawater evaporation were observed (< 0.05% Mg/Ca and Sr/Ca ratios variability) (3). At the Institute
587 of Geosciences, Kiel University, Germany, all samples were analyzed in the same laboratory and
588 machine by the same person for Ca, Mg, Sr with simultaneous data acquisition using an inductively
589 coupled plasma – optical emission spectrometer (ICP-OES) SPECTRO Ciros[™] CCD SOP. Samples
590 were 50-fold diluted with 2% (v/v) freshly subboiled in HNO_3 and introduced with a GE Seaspray[™]
591 micro-nebulizer and thermostated Cinnabar[™] cyclonic spray chamber. Sample preparation was
592 performed under Class-100 clean bench conditions with ultrapure reagents (Elga Labwater). The
593 following emission lines were selected: Ca: 317.933 (II); Mg: 279.553nm (II); Sr: 407.771nm (II),
594 421.552nm (II), and measured simultaneously within the same preselected acquisition interval (“Phase
595 3”). A combined intensity calibration and drift-correction procedure using IAPSO standards (46, 47)
596 was applied for data processing (Appendix 4). Every batch of 6 samples was bracketed by an IAPSO
597 measurement for normalization to Mg:Ca = 5.140 mol:mol and Sr:Ca = 8.280 mmol:mol. A stepwise
598 linear drift correction was applied over a batch of 6 samples during all the analyses. Then, every second
599 batch of 6 samples, a one sample replicate measurement was done from the previous batch. The final
600 data are used as drift-corrected after applying the normalization factors for Mg:Ca and Sr:Ca ratios
601 following the stepwise drift-correction (see Appendix 4). Results were normalized to an external
602 standard (IAPSO, ORIL, U.K. using Mg:Ca = 5.140 mol:mol, Sr:Ca = 8.280 mmol:mol). This
603 approach minimizes variability, which re: IAPSO was 0.6 to 0.7% overall. Mean uncertainty from
604 duplicate measurements per sample on 33 randomly chosen samples was 0.1-0.2 and 0.1-0.4 %RSD
605 (1SD) for seawater Mg:Ca and Sr:Ca, respectively (see Appendix 4). This is well below 1% uncertainty
606 for the dataset, which provides confidence in the accuracy of the data.

607

608 The new measured dataset was complemented with a seawater Mg:Ca and Sr:Ca ratios literature survey
609 (Fig. 4d; SI Appendix 2). Publications and reports methods sections were screened for data quality and
610 analytical clarity to mine comparable data to our dataset based on standards used, and analytical
611 method/accuracy. We also put together a table on the historical use of seawater Mg:Ca and Sr:Ca ratios
612 in the last 100 years (SI Appendix Table S3). The final seawater Mg:Ca and Sr:Ca ratios database
613 (Appendix 3) was combined with seawater environmental metadata mined from GLODAPv2 (48, 49),
614 and used to analyze and classify seawater Mg:Ca and Sr:Ca ratios as a function of environmental
615 variables (Appendix 3). ArcGIS 10.0 (ESRI 2011) and the 3-D analytical tool “NEAR 3-D analysis”
616 were used to link environmental seawater conditions with the sample’s seawater ratios. When the
617 prediction was not sufficiently accurate, the closest value was manually selected. For comparison
618 purposes, the GEMS-GLORI database, despite being compiled from primary and secondary sources,
619 was used to provide a distribution map of seawater Mg:Ca ratios from river mouths/plumes around the
620 world (Appendix 6; SI Appendix Fig. S1), but it was not added to the statistical analyses or mechanistic
621 assessments. Lastly, various paleo proxies’ global databases were mined to provide distribution maps
622 of paleo reconstructions (SI Appendix Fig. S2), to identify where the majority of the paleo work has
623 been conducted around the world.

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The seawater Mg:Ca and Sr:Ca ratios were classified by Ocean, Longhurst Province, Ecosystem type, Latitude, Longitude, Depth (in 5 intervals) (Appendix 3), and then by all the metadata (chemistry). Ratios were mapped globally (Fig. 1; SI Appendix S1), vs depth and by ecosystem (Fig. 1, 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 distributions and the observations. A Generalized Linear Model (GLM) using forward stepwise selection was applied to the ratio's vs 5 depth intervals (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), SURFER (Golden Software, LLC.), and Corel Draw X3 (Corel Corp.). A full version of Materials and Methods can be found in Supplementary Information.

Data availability

Our published databases are publicly accessible for readers, and they 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).

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758

759 **Acknowledgments:** Thanks to the contributions by researchers, staff, and volunteers in all the
760 expeditions. One anonymous referee, and Bernhard Peucker-Ehenbrink, from WHOI, contributed
761 significantly to the final version of the manuscript. **Funding:** This study was developed under a grant
762 from the Federal Ministry of Education and Research (BMBF) to D.G.S. under contract No.
763 03F0722A, by the Kiel Cluster of Excellence “The Future Ocean” (D1067/87) to A.O. and M.L., and
764 by the “European project on Ocean Acidification” (European Community’s Seventh Framework
765 Programme FP7/2007-2013, grant agreement 211384) to A.O. and M.L. Additional funding was

766 provided from project DOSMARES CTM2010-21810-C03-02, by the UK Natural Environment
767 Research Council to the National Oceanography Centre. This is PMEL contribution number 5046.
768

769 **Author contributions:** All authors contributed to the interpretation of the results and provided input to
770 the paper. M.L., A.O. and S.B.A originally started the work. M.L., D.G.S, and J.C.M. concluded the
771 work and wrote the paper after all cruises and ICP-OES measurements were finished. K.B. and U.W.
772 measured samples and D.G.S. developed the method and processed the raw data. M.K., R.B., and
773 D.O.B.J. mined literature data and did Fig.s, with M.L. and D.G.S. The following authors collected
774 samples and coordinated work: M.L., D.G.S., M.N.M., A.D., D.I.R., D.G., R.A.F., M.L., S.B., A.P.,
775 M.G., L.B., J.C., J.B.R., C.P., S.O., K.R., L.M.J., A.K., R.W., O.G., L.M., J.B., C.A., N.D., S.Z.,
776 J.L.A., A.d.L., R.S.L., P.J., B.T., P.B.D.B., L.L., F.E.P., S.E.H., X. G. C., L.C.T. and J.S.H.

777 **Competing interests:** The authors declare no competing financial interests. **Data and materials**
778 **availability:** The data presented in this manuscript are available at the NOAA National Center for
779 Environmental Information (NCEI) under Accession Number 0171017 in
780 <http://accession.nodc.noaa.gov/0171017>.

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815 **Figure Legends**

816

817 **Fig. 1. Modern ocean global variability in seawater Mg:Ca and Sr:Ca ratios.** Averaged global
818 seawater Mg:Ca (a) and Sr:Ca (b) ratios from the upper 250 m, and separated in 5 depth intervals (0-5
819 m, 5-200 m, 200-1000 m, 1000-2500 m, and +2500 m), overlaid in 5° x 5° Latitude/Longitude quadrats
820 (see SI Appendix Fig. S4 for sampling effort). Extended seawater Mg:Ca ratios data from river mouths
821 can be found in SI Appendix Fig. S1. The final databases are deposited at the NOAA National Center
822 for Environmental Information (NCEI) under Accession Number 0171017 in
823 <http://accession.nodc.noaa.gov/0171017> (DOI:10.7289/V5571996).

824

825 **Fig. 2. Modern ocean seawater Mg:Ca and Sr:Ca ratios versus environmental parameters.** Data
826 horizontally classified for seawater Mg:Ca (a) and Sr:Ca (b) ratios as a function of environmental
827 variables (GLODAPv2; 41, 42) from the largest to the smallest dimension, and vertically in five depth
828 intervals of 0-5 m, 5-200 m, 100-1000 m, 1000-2500 m, and +2500 m. Data within the red lines
829 represent literature assumed knowledge of modern seawater ratios. Code for “Ocean” is: 1=Pacific,
830 2=Indian, 3=Atlantic, 4=Arctic, 5=Mediterranean, 6=Southern, 7=Red Sea, 8=China Sea, 9=Arabian
831 Sea, 10=Baltic Sea, 11=IAPSO. Code for “Longhurst Province” is in SI Appendix Table S1 and Vliz
832 (2009): http://www.marineplan.es/ES/fichas_kml/biogeog_prov.html. Code for “Ecosystem” is:
833 1=IAPSO (This study), 2=Coastal Sea, 3=Coastal Upwelling, 4=Open Ocean, 5=Open Ocean
834 Upwelling, 6=Shallow Hydrothermal Vent, 7=Coral Reef, 8=Deep Hydrothermal Vent, 9=Glacier
835 Seawater, 10=Estuary, 11=Mudflats, 12=Mangroves, 13=Seagrass. Extended analysis of seawater
836 Mg:Ca ratios data from river mouths to assess coastal waters can be found in SI Appendix Fig. S1.

837

838 **Fig. 3. Modern ocean seawater Ca, Mg and Sr, vs. Total Alkalinity (TA), Mg and Sr vs. Ca, and**
839 **Sr vs. Mg.** Cross plots indicating the relations of seawater ions with Total Alkalinity (TA) and
840 between each other. TA is used to identify biogeochemical processes that could be impacting
841 deviations from the ratios. In all figure panels, “IAPSO (This study)” seawater composition is used for
842 comparison. Normality test results, and Pearson correlation coefficients are included in the graphs.

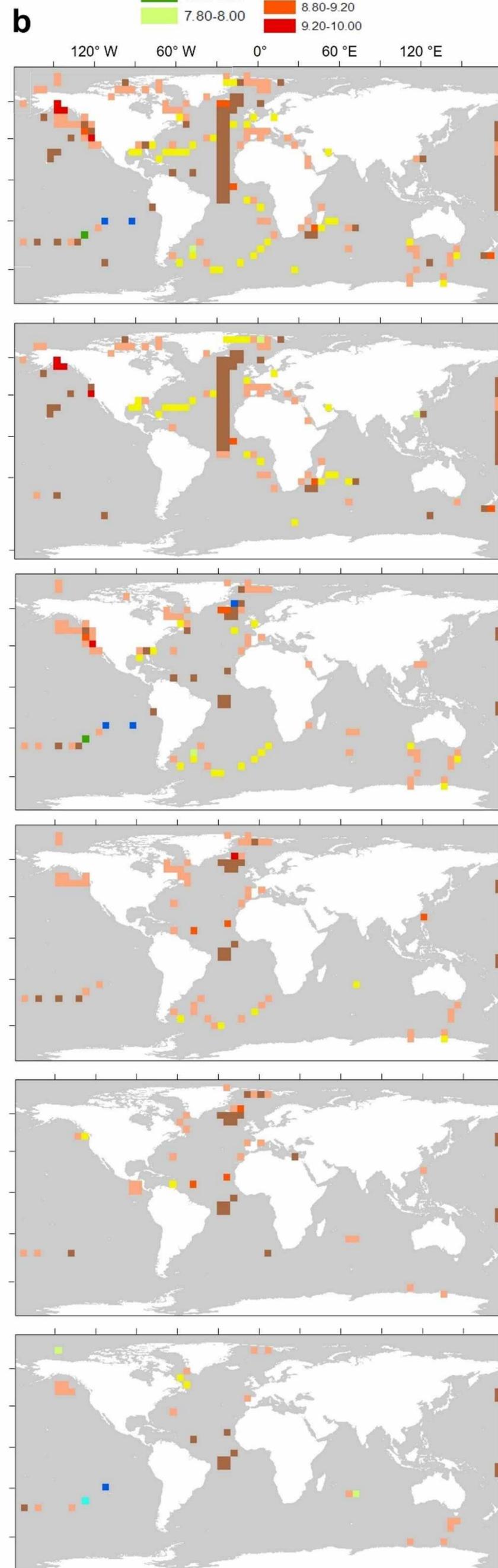
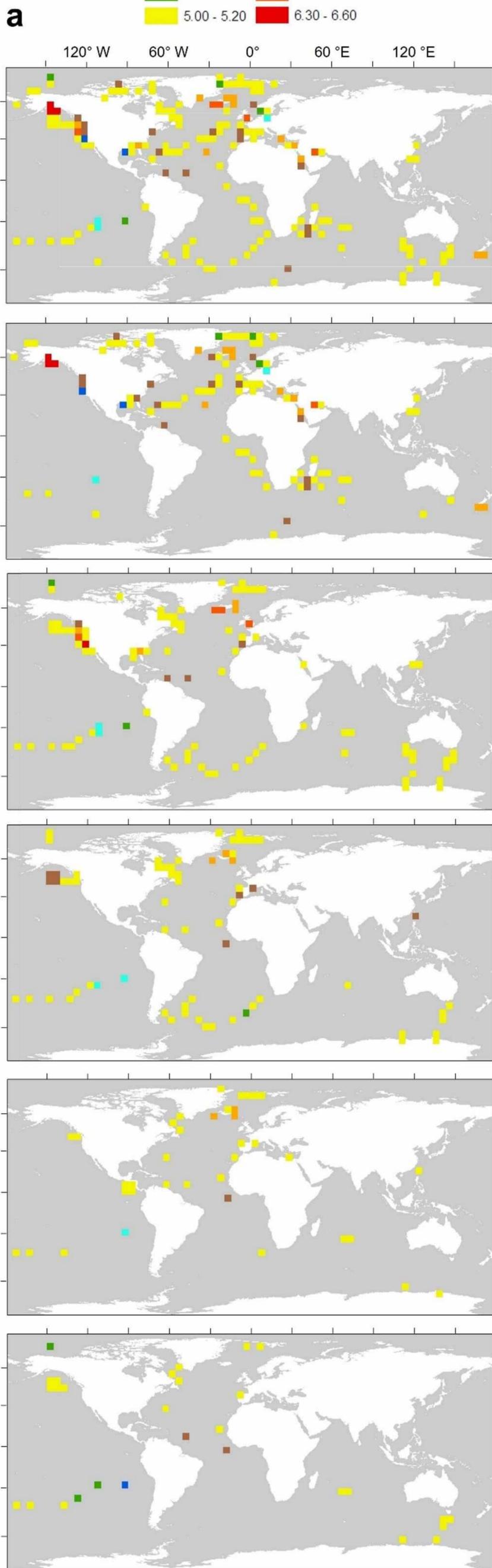
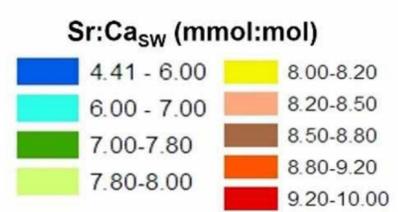
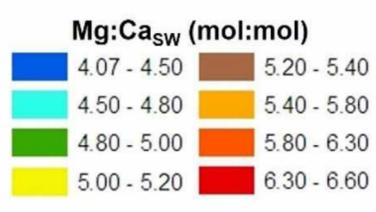
843

844 **Fig. 4. Modern ocean seawater Mg:Ca and Sr:Ca ratios vs. depth, and conceptual diagrams of**
845 **Sr:Ca vs. Mg:Ca to identify processes.** Data classified horizontally for seawater Mg:Ca (a) and Sr:Ca
846 (b) ratios per ecosystem, and vertically with depth. Seawater Mg:Ca ratios data from river mouths can
847 be found in SI Appendix Fig. S1. Data within the red lines represent literature assumed knowledge of
848 modern seawater ratios. (c) A selection of curated seawater Mg:Ca and Sr:Ca ratios vs depth, classified
849 as “Coastal Seas” and “Open Ocean” to distinguish variability at large, separating the two major
850 environments where marine science disciplines obtain samples/data. (d) Cross plots of averages and
851 standard deviations of modern seawater Mg:Ca vs. Sr:Ca ratios with arrows indicating the direction of
852 change for ocean processes. Also included individual data points cross plots comparing literature vs
853 this study data. In all figure panels, “IAPSO (This study)” seawater Mg:Ca and Sr:Ca ratios are used
854 for comparison.

855

856 **Fig. 5. Modern ocean seawater Mg:Ca and Sr:Ca ratios compared to reconstructions over**
857 **geological time intervals.** (a) Relation between seawater Mg:Ca and organism skeletal Mg:Ca,
858 indicating the effect of modern seawater Mg:Ca natural variability on marine calcification. (b) Upper
859 ocean integrated 250 m modern ocean values for seawater Mg:Ca and Sr:Ca in various ecosystems
860 showing that variability is similar to the reconstructed Neogene period (23.03 million years). (c)
861 Phanerozoic period (541 million years) values for seawater Mg:Ca and the last 200 million years of
862 seawater Mg:Ca and Sr:Ca ratios are presented for comparison with modern ocean variability.
863 Aragonite and calcite seas periods are included, and the geological periods: J-Jurassic, K-Cretaceous,

864 Pg-Paleogene, and Ng-Neogene. Data, boxed and within the red lines, represent literature assumed
865 knowledge of modern seawater ratios. In all figure panels, “IAPSO (This study)” seawater Mg:Ca and
866 Sr:Ca ratios are used for comparison. Graphs and data are taken from published papers (8, 12, 23)
867 under AAAS License Number 4192550299156, 4645271444588, and Creative Commons Attribution
868 4.0 International License (CC BY 4.0), respectively, granted to M. Lebrato. The raw data used in the
869 geological time reconstructions can be checked in the figure’s captions of the corresponding papers (8,
870 12, 23).



Integrated upper 250 m

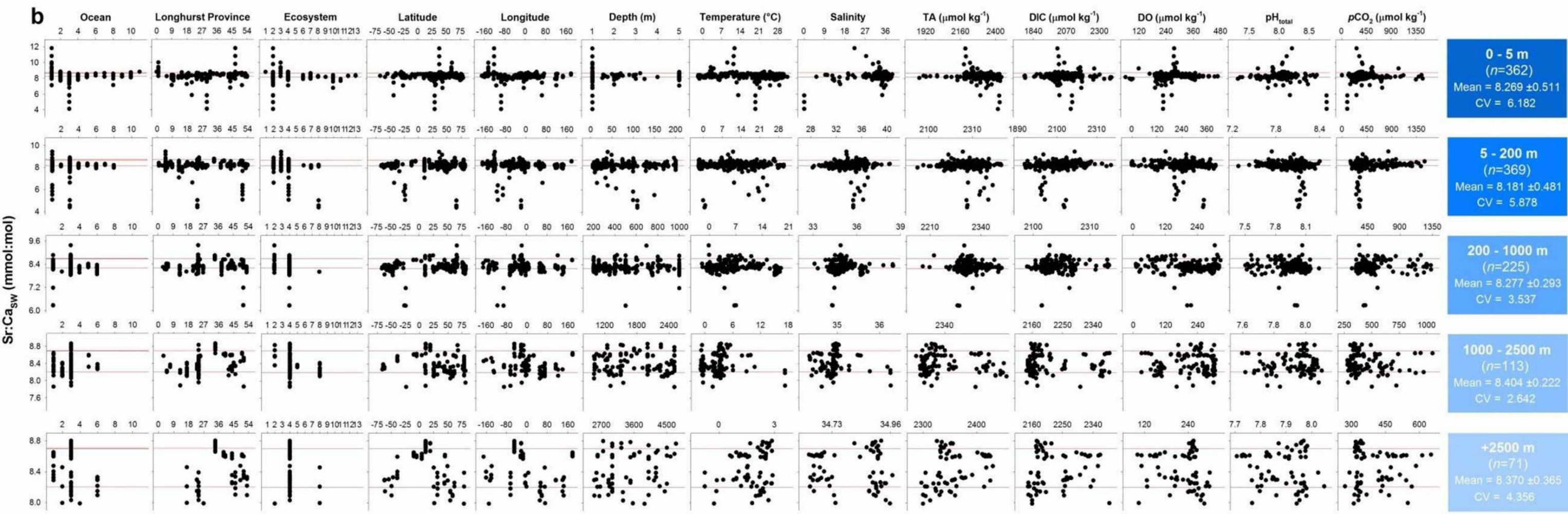
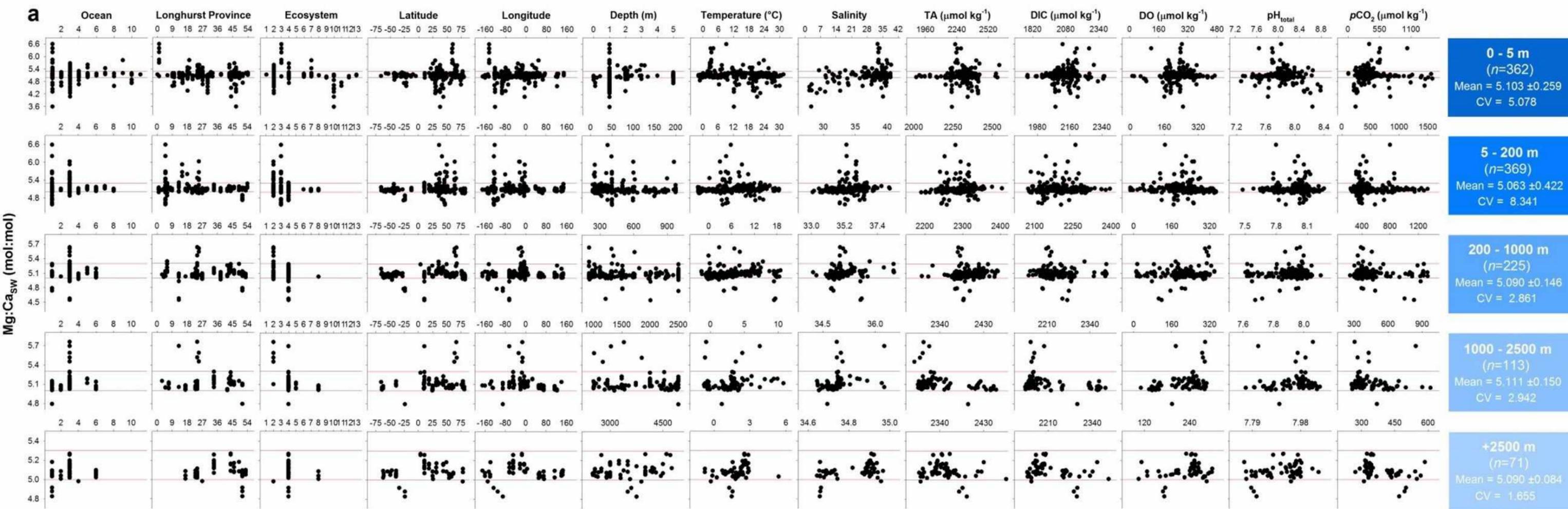
0 - 5 m

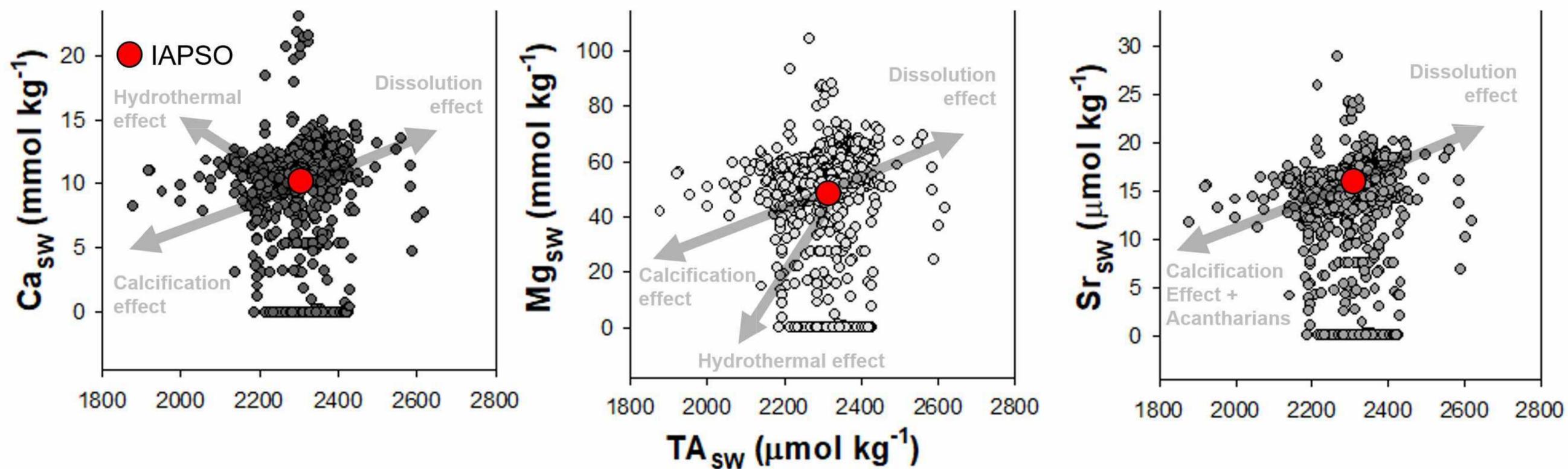
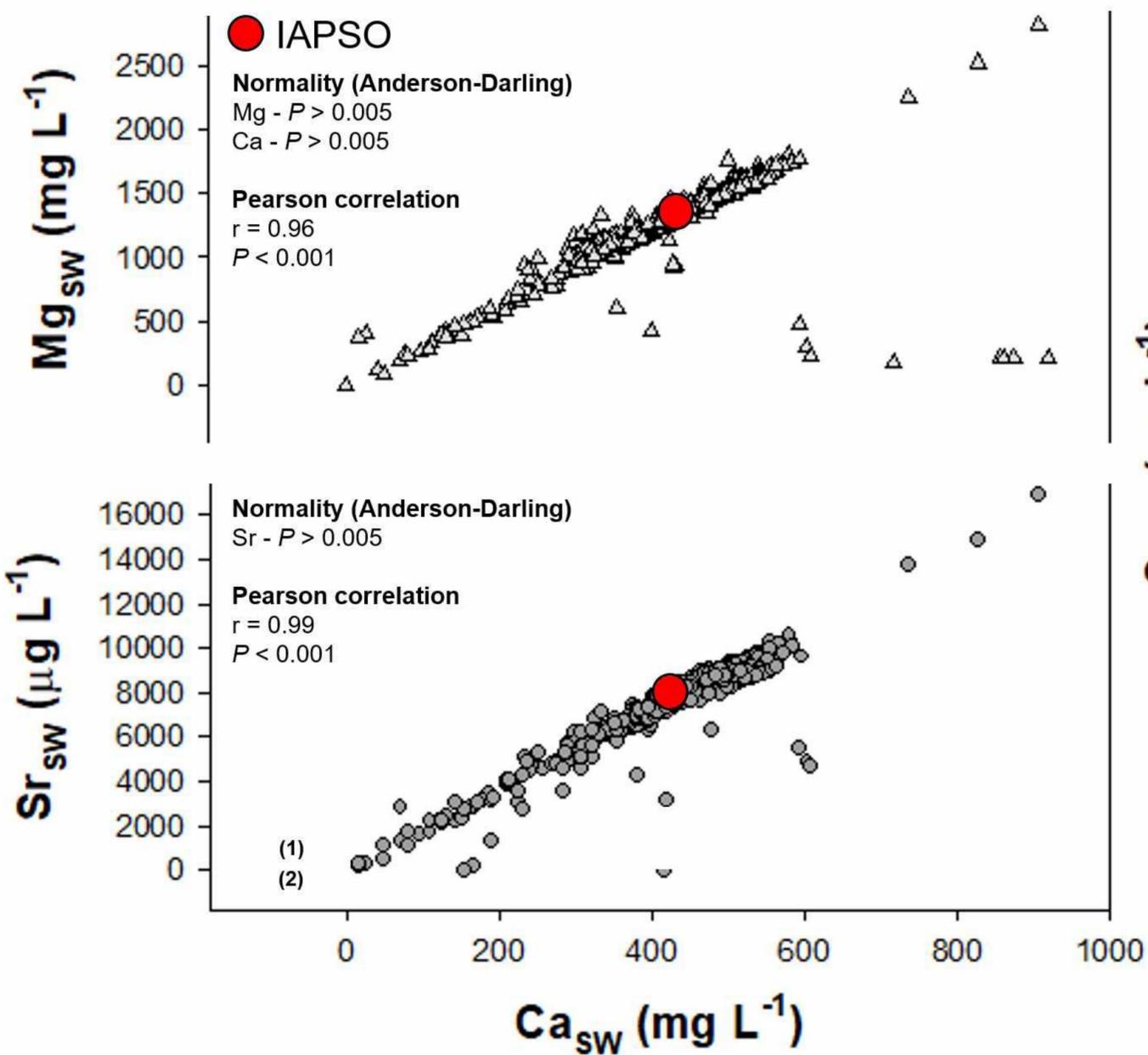
5 - 200 m

200 - 1000 m

1000 - 2500 m

+ 2500 m



a**b****c**