DEPENDENCE ON TEMPERATURE OF Ca/Mg RATIO OF SKELETAL STRUCTURES OF ORGANISMS AND DIRECT CHEMICAL PRECIPITATES OUT OF SEA WATER

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Relationship between Ca/Mg Ratio of Skeletal Structures of Organisms and Temperature

As shown by Chilingar (1953: 206) and Chave (1954), there is an inverse ("hyperbolic") relationship between the Ca/Mg ratio in the skeletons of organisms and the temperature of the water in which they live. Figures 2 through 11 show the relationship between the mean yearly temperature of sea water and the Ca/Mg ratio[1] of various groups of organisms, arranged in the order of increasing phylogenetic complexity. Sixty two per cent of the data plotted in these graphs are based on the analyses by Clark and Wheeler (1922) and 23 per cent on the results obtained by the writer. Although many analyses of organisms by Clark and Wheeler are not accompanied by temperature data, the exact description of location and depth enables one to determine the temperature from oceanographic literature. Additional data (15 per cent) were obtained from Chave (1954), who plotted $MgCO_3$ content of skeletons versus temperature of sea water. The "Ca/Mg ratio versus temperature" curves generally have a "hyperbolic" shape. The average Ca/Mg ratios of various groups of organisms, however, are different, and there is very little relationship between the average Ca/Mg ratio and the phylogenetic level (Figure 1).

Some scattering of the points in Figure 3 can be explained by the fact that samples of *Foraminifera* analyzed contained both benthonic and pelagic forms, whereas the temperature recorded is that of the bottom water.

Very high Ca/Mg ratios of the skeletons of madreporarian corals (Figure 5) are due to the fact that aragonitic organisms contain very small amounts of magnesium. Chave (1954) demonstrated that aragonitic organisms seldom contain over 1 per cent magnesium carbonate. The Ca/Mg ratio, therefore, largely depends on the mineralogic form of the carbonate. For example, in the case of gastropods and pelecypods

[1]Weight ratios. The Ca and Mg contents were determined by the writer by using wet chemical technique with double precipitation.

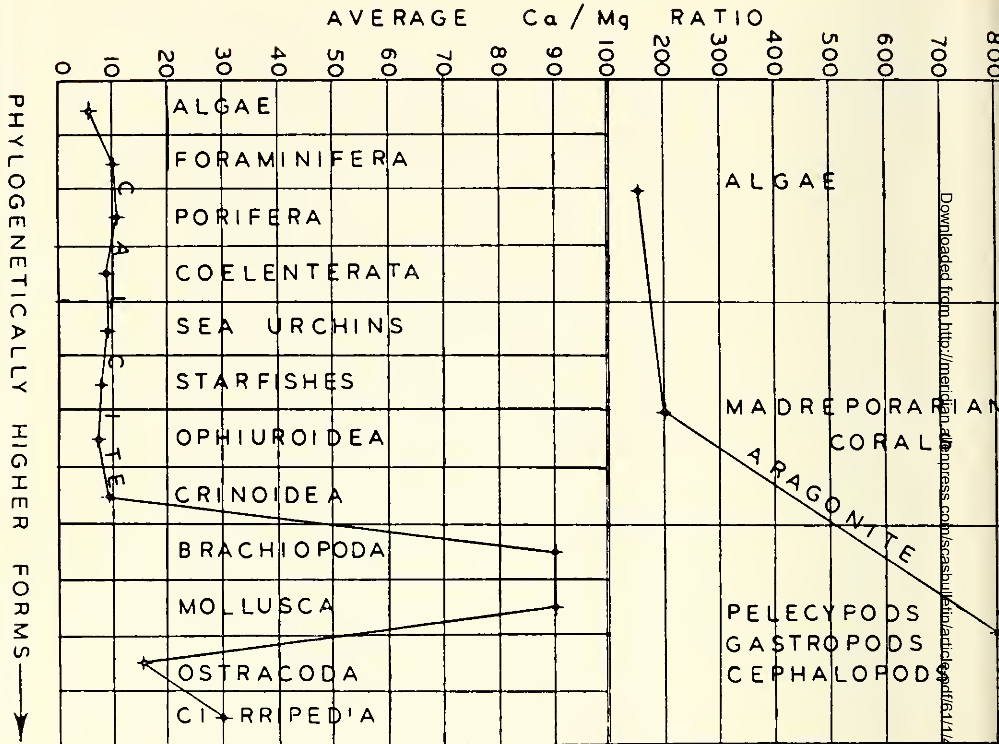

Figure 1. Relationship between Ca/Mg ratio and the phylogenetic level of organisms.

the presence of a few per cent of calcite causes a marked decrease in the Ca/Mg ratio.

The X-ray analysis conducted by the writer showed that madreporarian corals do not contain calcite, whereas the organisms plotted in Figures 2, 3, 4, 6, 7, 8, 9, 10, and 11 are devoid of aragonite.

Even small variations in temperature are reflected in the Ca/Mg ratios of organisms. For example, *Rhipidogorgia flabellum* Linné at 24.5° and 25° C. had Ca/Mg ratios of 9.04:1 and 8.3:1, respectively (Figure 4). The spines of *Tripneustes ventricosus* (Lamarck) have a Ca/Mg ratio of 14.3:1 at 24.5° C. and 12.1:1 at 26° C.

Effect of Temperature on Ca/Mg Ratios of Chemical Precipitates from Sea Water

Mixtures of $CaCO_3$ and $MgCO_3$ have been precipitated from 500 cc. samples of sea water on adding 300 cc. of saturated solutions of $Ca(HCO_3)_2$. Figure 12 shows inverse relationship between the temperature and Ca/Mg ratios of precipitates obtained at the end of 48 hours. The "hyperbolic" shape of "Ca/Mg ratio versus temperature" curve is possibly due to the rapid rate of precipitation of $CaCO_3$ at higher temperatures, which enables $CaCO_3$ to trap more $MgCO_3$.

In another set of experiments, 300 cc. of saturated solutions of $Ca(HCO_3)_2$ were added to 500 cc. samples of sea water with enough Na_2CO_3 to bring the solution to the verge of clouding. The higher magnesium content of the precipitates in these experiments (Figure 13) was possibly due to the precipitation of magnesium as $Mg(OH)_2$, because the solubility product of $Mg(OH)_2$ is exceeded at a pH of around 9.49.

Discussion

The similarity in shape of "Ca/Mg ratio versus temperature" curves of primitive invertebrates and direct chemical precipitates suggests that the Ca/Mg ratios of these organisms are either controlled to some extent by the conditions in the surrounding environment (namely, variation of the solubility products of $CaCO_3$, $MgCO_3$, $Mg(OH)_2$, etc. at different temperatures), or that the internal processes somewhat resemble the external processes. The former explanation becomes even more plausible when one remembers that primitive invertebrates do not have autonomous blood systems (open to outside environment) and their tissues are transfused by sea water.

Different organisms have different Ca/Mg ratios; hence, the chemical composition of protective and skeletal structures is not entirely controlled by the physical-chemical properties of the surrounding environment. Inasmuch as different organisms possibly attain different pH within their tissues, the Ca/Mg ratios of their skeletons is probably also related to this pH. The writer (1956a: 32) had previously shown that the Ca/Mg ratio of direct precipitates decreases with higher pH. Examination of Figures 12 and 13 also suggests that the "Ca/Mg versus temperature" curves of organisms, which could attain high pH ($\backsim\geqslant$ 9.49) within their tissues and precipitate magnesium as $Mg(OH)_2$, might approach a straight line.

It is also interesting to note that the writer (Chilingar, 1956b: 211) proved that the Ca/Mg ratios of *Strongylocentrotus purpuratus* (Stimp-

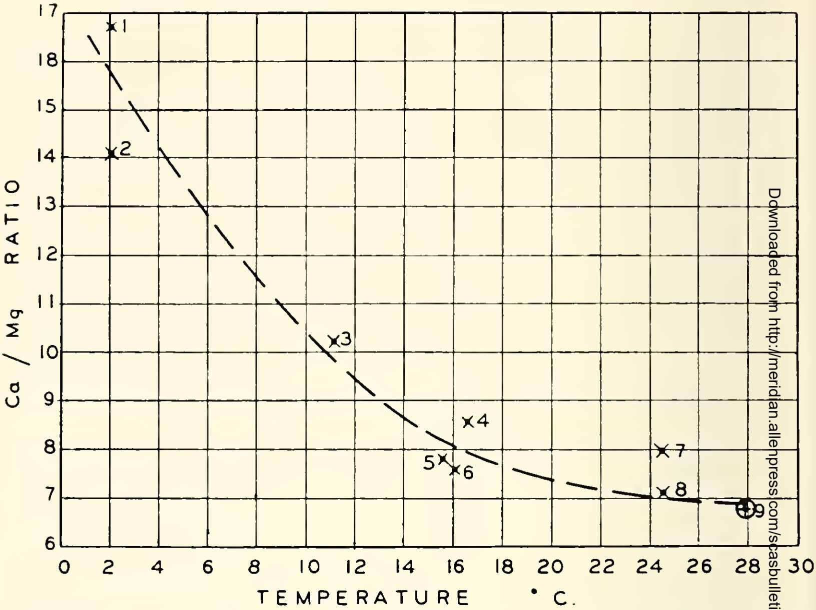

Figure 2. Relationship between the Ca/Mg ratio of *Lithothamnium* skeletons and temperature. Analyses by Chave (1954, p. 273): 1, 2—*Lithothamnium* sp., Alaska; 3—*Lithothamnium* sp., Maine; 4—*Lithothamnium* sp., California; 5, 6—*Lithothamnium* sp., Japan; 7-8—*Lithothamnium* sp., Bermuda. Analysis by Chilingar: 9—*Lithothamnium* sp., Guam.

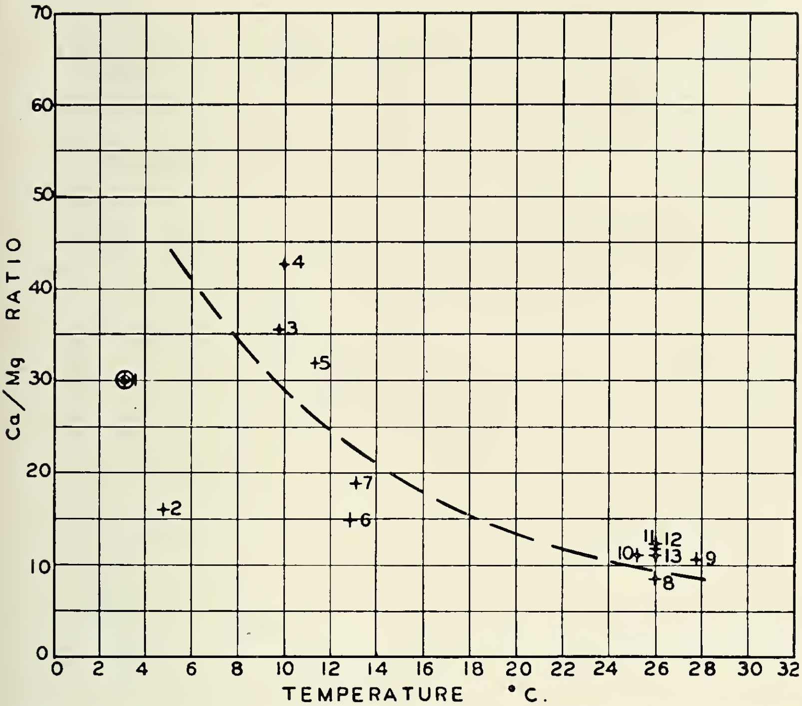

Figure 3. Relation between Ca/Mg ratio in skeletons of *Foraminifera* and temperature. Analysis by Clarke and Wheeler (1922, p. 2): 1—*Globorotalia menardii* d'Orbigny. Analyses by Chilingar: 2—*Foraminifera* sample No. 7, off San Diego, California, depth of 2560 feet (Bandy, 1953); 3—*Foraminifera* sample No. 4, off San Diego, California, depth of 380 feet (Bandy, 1953); 4—*Foraminifera* sample No. 1261, off San Diego, California, depth of 375 feet (Bandy, 1953); 5—*Foraminifera* sample No. 960, off San Diego, California, depth of 260 feet (Bandy, 1953); 6—*Foraminifera* sample No. 345, off San Diego, California, depth of 200 feet (Bandy, 1953); 7—*Foraminifera* sample off Louisiana, Gulf of Mexico, depth of 102 feet; 8—*Sorites* sp., South of Tortugas, Florida; 9—Sample of *Foraminifera* from Bikini; 10—*Miniacina alba* Linné, Bahamas; 11—*Quinqueloculina auberiana d'Orbigny*, south of Tortugas, Florida; 12—*Archaias adunca* Fichtel and Moll, Key West, Florida; 13—*Sorites marginalis* Lamarck, south of Tortugas, Florida, depth of 29.3 meters.

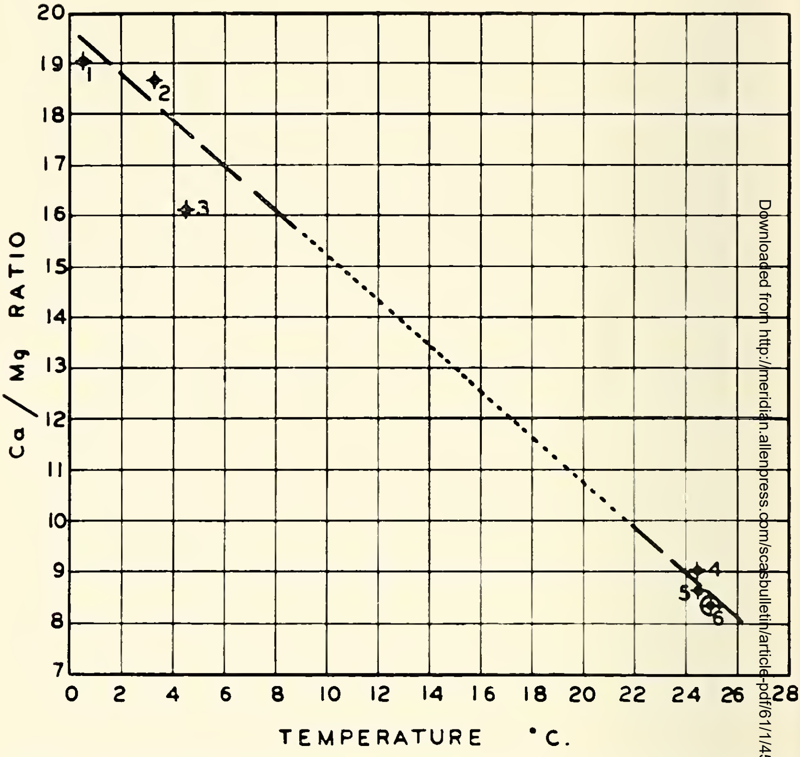

Figure 4. Relation between Ca/Mg ratio in skeletons of Alcyonarian corals and temperature. Analyses by Clarke and Wheeler (1922, p. 9): 1—*Alcyonium carneum* L. Agassiz, 2—*Lepidisis caryophyllia* Verrill, 3—*Pennatula aculeata* Dana, 4—*Rhipidogorgia flabellum* Linné. 5—*Gorgonia acerosa*. Pallas, Florida. Analysis by Chilingar: 6—*Rhipidogorgia flabellum* Linné. Bahamas.

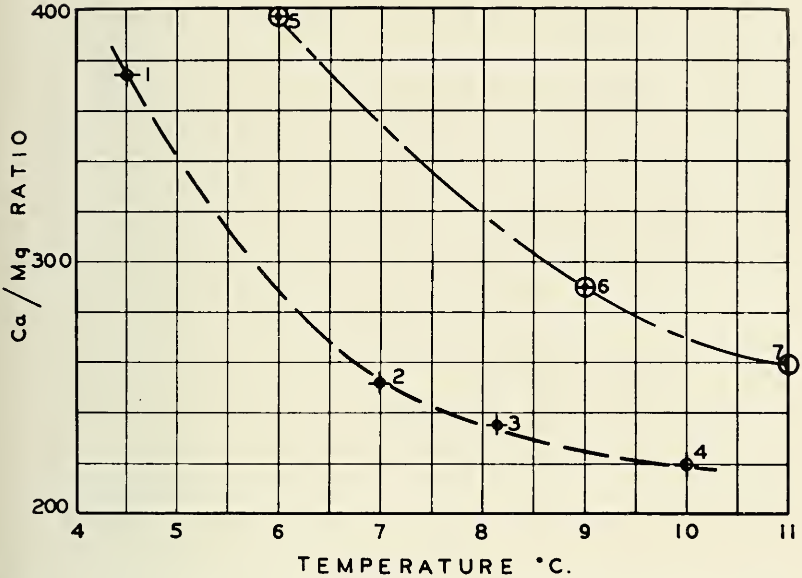

Figure 5. Relation between Ca/Mg ratio in skeletons of Madreporarian corals and temperature. Analyses by Clarke and Wheeler (1922, p. 6): 1—*Flabellum alabastrum* Moseley, 2—*Deltocyathus italicus* Michelotti, 3—*Desmophyllum ingens* Moseley, 4—*Dasmosmilia lymani* Pourtales. Analyses by Chilingar: 5—*Madrepora* sp., 6—*Madracis* sp., 7—*Dendrophyllia* sp.

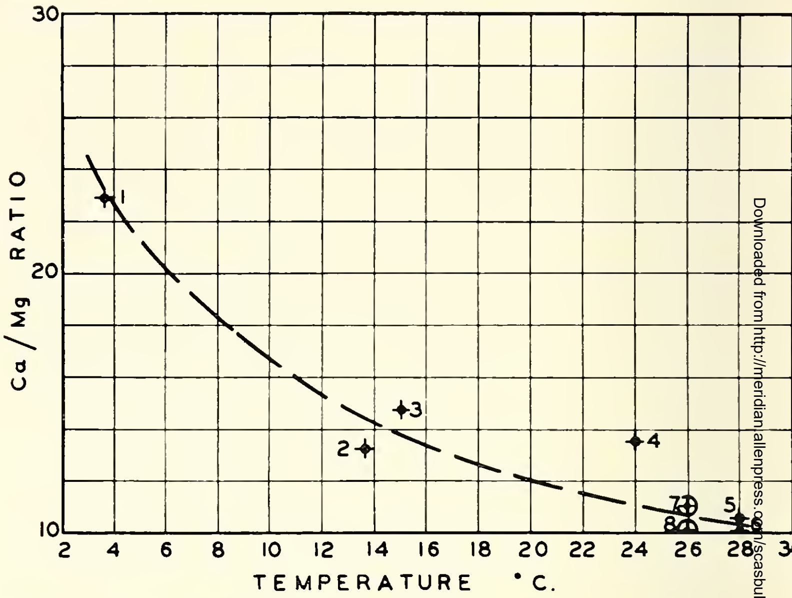

Figure 6. Relation between Ca/Mg ratio in skeletons of Sea Urchins and temperature. Analyses by Clarke and Wheeler (1922, p. 22): 1—*Echinus affinis* Mortensen, 2—*Strongylocentrotus fragilis* Jackson, 3—*Lytechinus anamesus* H. L. Clark, 4—*Tretocidaris affinis* Philippi, 5—*Echinometra lucunter* Linné, 6—*Mellita sexiesperforatus* Leske. Analyses by Chilingar: 7—*Eucidaris* sp., Bahamas, 8—*Echinometra lucunter* Linné, Bahamas.

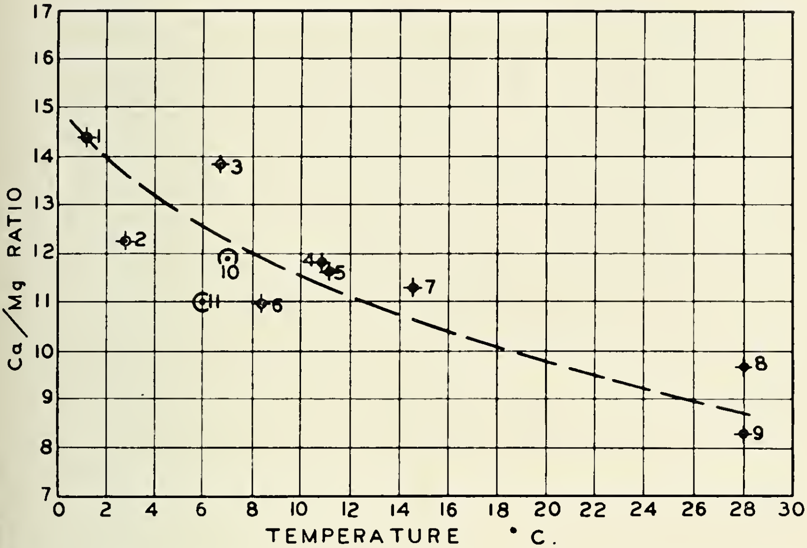

Figure 7. Relation between Ca/Mg ratio in skeletons of Star Fishes and temperature. Analyses by Clarke and Wheeler (1922, p. 26): 1—*Ctenodiscus crispatus* Retzius, 2—*Benthopecten spinosus* Verrill, 3—*Plutonaster agassizii* Verrill, 4—*Leptasterias compta* Stimpson, 5—*Odontaster hispidus* Verrill, 6—*Ctenodiscus procurator* Staden, 7—*Orthasterias tanneri* Verrill, 8—*Asterina minuta* Gray, 9—*Linckia guildingii* Gray. Analyses by Schmelck (1901): 10, 11—*Arcaster tenuispinus* (Düben and Koren).

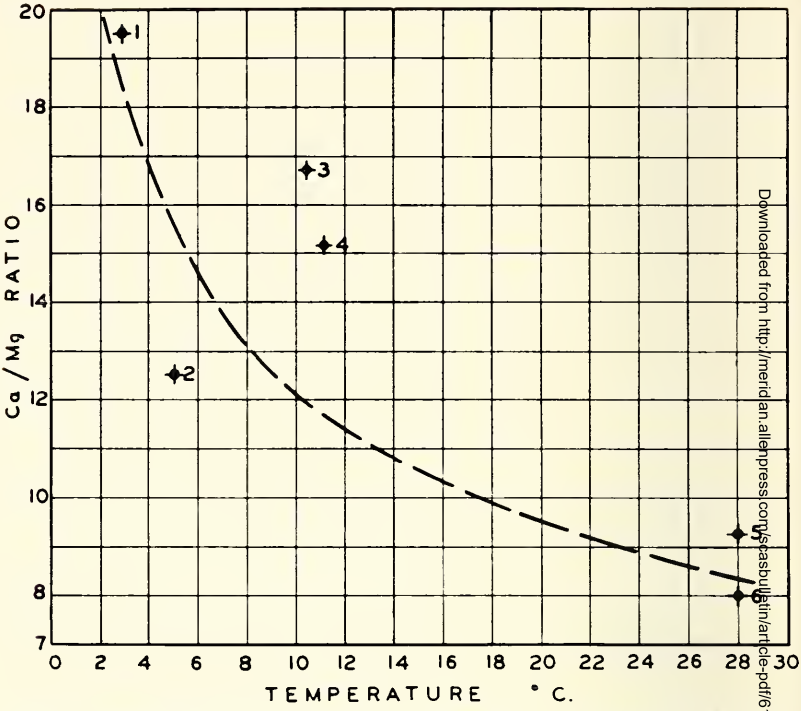

Figure 8. Relation between Ca/Mg ratio in skeletons of Ophiurans and temperature. Analyses by Clarke and Wheeler (1922. p. 29): 1—*Ophiomusium lymani* W. Thomson, 2—*Ophioglypha sarsii* Lütken, 3—*Ophiocamax fasciculata* Lyman, 4—*Ophioglypha lymani* (Ljungman), 5—*Ophiocoma pumila* Lütken, 6—*Ophiomyxa flaccida* Say.

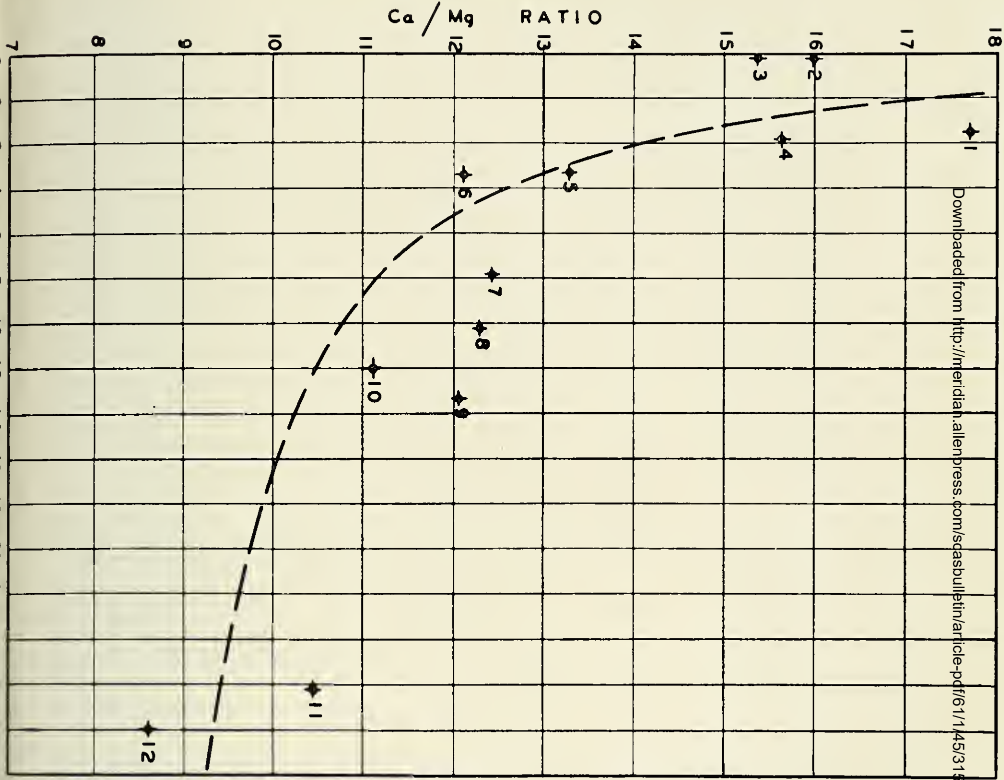

Figure 9. Relation between Ca/Mg ratio in Crinoid skeletons and temperature. Analyses by Clarke and Wheeler (1922, p. 17): 1—*Heliometra glacialis* (Leach) var. *maxima* (A. H. Clark), 2—*Promachocrinus kerguelensis* Carpenter, 3—*Anthometra adriani* Bell, 4—*Ptilocrinus pinnatus* Clark, 5—*Florometra asperrima* Clark, 6—*Pentametrocrinus japonicus* Carpenter, 7—*Hathrometra dentata* Say, 8—*Hypalocrinus naresianus* Carpenter, 9—*Metacrinus rotundus* Clark, 10—*Parametra granulata* Clark, 11—*Crinometra concinna* Clark, 12—*Tropiometra carinata* Lamarck.

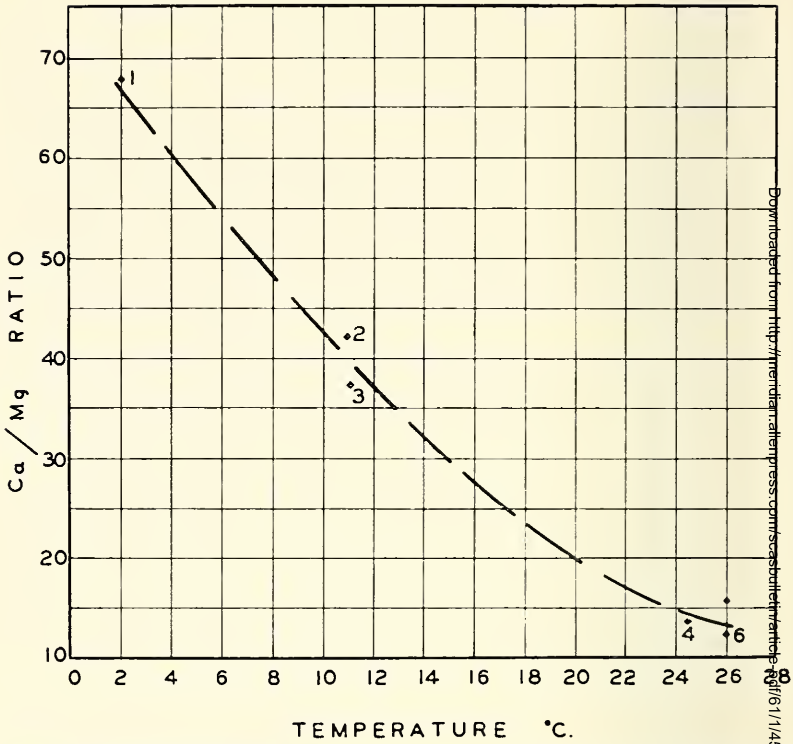

Figure 10. Relationship between temperature and Ca/Mg ratio in skeletons of Ostracods (analyses by Chave, 1954, p. 273).

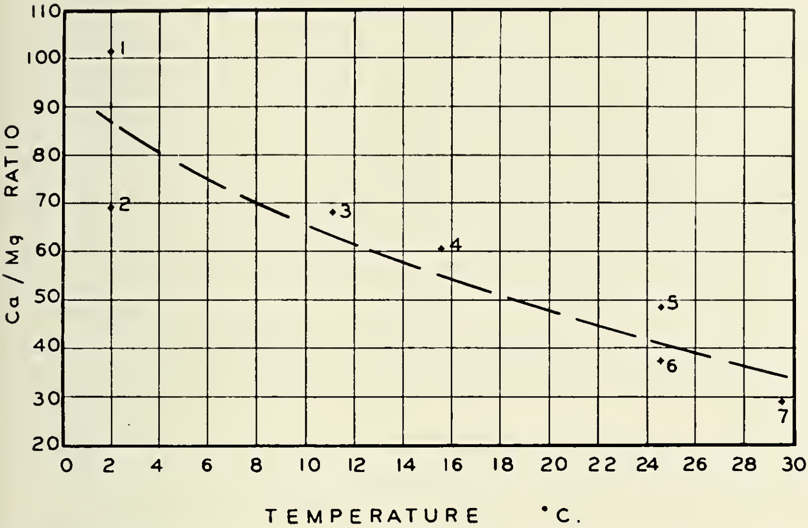

Figure 11. Relationship between Ca/Mg ratio in skeletons of Barnacles and temperature (analyses by Chave, 1954, p. 273).

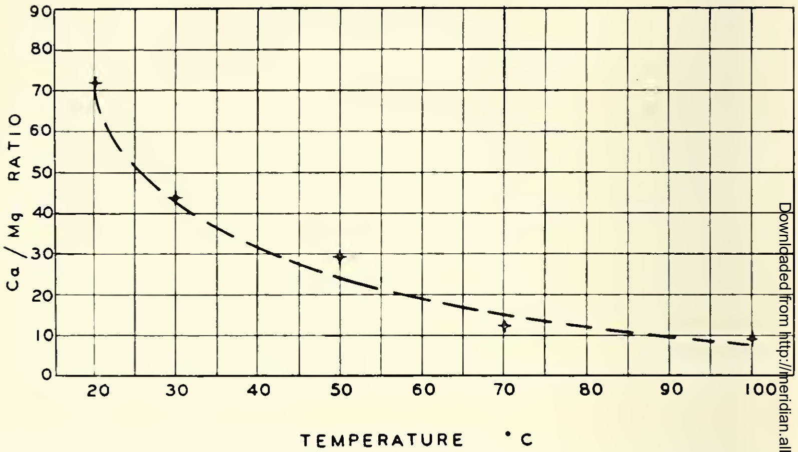

Figure 12. Relationship between temperature and Ca/Mg ratio of direct chemical precipitates from sea water on adding saturated solutions of $Ca(HCO_3)_2$.

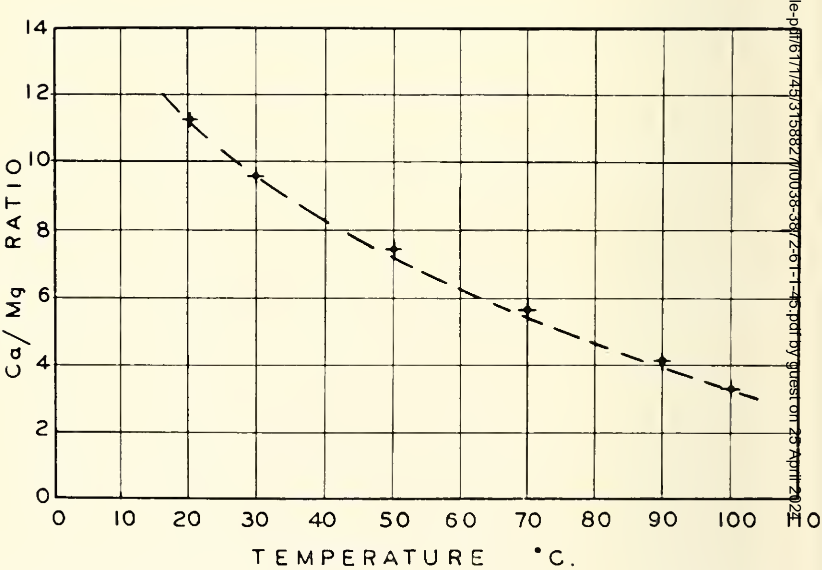

Figure 13. Relationship between temperature and Ca/Mg ratios of direct chemical precipitates from sea water on adding saturated solutions of $Ca(HCO_3)_2$ with Na_2CO_3.

son) and *Mytilus californianus* Conrad are proportional to the Ca/Mg ratio of sea water in the aquarium. This finding suggested that possibly other invertebrates also assimilate more magnesium in the environment having a higher concentration of magnesium.

Conclusions

The findings of the present study can be summarized as follows:

1. There is an inverse ("hyperbolic") relationship between the Ca/Mg ratio in the skeletons of organisms and the temperature of the water in which they live.

2. Different organisms have different Ca/Mg ratios and there is very little relationship between the Ca/Mg ratios and the phylogenetic level of organisms.

3. Inverse relationship exists between the Ca/Mg ratios of direct chemical precipitates out of sea water and the temperature.

4. The Ca/Mg ratios of direct chemical precipitates out of sea water are also controlled by the pH of the medium of deposition.

5. The similarity in shape of "Ca/Mg ratio versus temperature" curves of invertebrates and direct chemical precipitates suggests that the Ca/Mg ratios of these organisms are controlled to some extent by the effect of temperature on solubility products of $CaCO_3$, $MgCO_3$, $Mg(OH)_2$, etc. The differences in magnitude of Ca/Mg ratio in different organisms may be related to the growth mechanism and composition and pH of the body fluids.

The future line of research suggested by this work is to make a detailed study of the variation in the Ca/Mg ratios of skeletal and protective structures of organisms on varying the pH and chemical composition of the sea water.

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