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The Graduate School

Department of Geosciences

Strontium and Magnesium in Modern Carbonate Sediments and Ancient  
Carbonate Rocks

A Paper in

Geology

by

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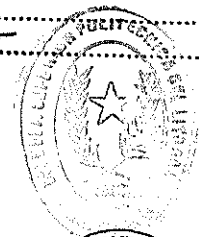
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STRONTIUM AND MAGNESIUM IN MODERN CARBONATE SEDIMENTS  
AND ANCIENT CARBONATE ROCKS

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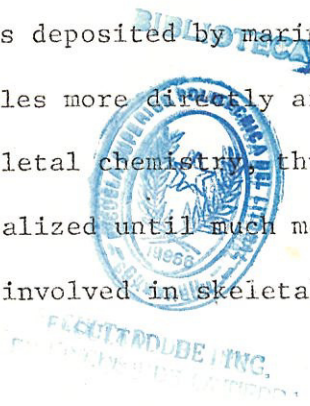


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ABSTRACT

In the last seventeen years, considerable effort has been expended in studying the distribution of Sr and Mg within modern carbonate sediments and its correlation to ancient carbonate rocks. It can be of both biologic and diagenetic interest. Mg is more readily accepted into the hexagonal calcite structure, while Sr is more readily accepted by the aragonite structure. Thus producing the following minerals in modern carbonate: (a) Low-magnesium calcite ( 4 mole %MgCO<sub>3</sub> = 1.15%Mg ) found in planktonic foraminifera and coccolith characteristic of deep-sea carbonates; (b) high-magnesium calcite ( generally more than 8 mole%MgCO<sub>3</sub> ) found in coralline algae, echinoderms; especially those of warm habitats; (c) aragonite ( 0.8-1.0 %Sr) found in oolites, pelletoids, lumps, and brown, green, red algae, etc., especially those of warm habitats; (d) dolomite ( 45.72%MgCO<sub>3</sub>= 13.18%Mg ) occurring in intertidal and supratidal zones within evaporitic areas. Aragonite and high-magnesium calcite are unstable forms of CaCO<sub>3</sub> but predominates in shallow-water carbonate sediments. Low-magnesium calcite is the stable form of CaCO<sub>3</sub> dominating in deep-water carbonate sediments. Temperature, salinity, water depth, sea water composition, and/or other such parameters may in part determine the levels of Mg and Sr concentration in carbonates deposited by marine invertebrates, but it would appear that these variables more directly affect physiological processes which in turn control skeletal chemistry, thus paleoenvironmental conditions are not going to be realized until much more is learned about the complex physiological processes involved in skeletal calcification.

The decrease in Sr content of carbonate rocks with increasing age results from conversion of aragonite to calcite during diagenesis by solution-precipitation.



precipitation reaction that is greatly accelerated by movement of relatively fresh waters through intergranular voids in the carbonate sediment. Also there is taken account of that the partition coefficient for aragonite (1.02) is higher than the coefficient for calcite (0.14) and decrease with temperature. It explains that the Sr concentration in ancient carbonate rocks is from 350 to 500 ppm, while in Recent sediments is about 10000 ppm. This progressive change is noted in the modern carbonate sediments in South Florida (71% Aragonite, 19% High-magnesium calcite and 11% Low-magnesium calcite) while in the Pleistocene sediments (21% Aragonite, 2% High-magnesium calcite). Variations in the Sr content is used for facies analyses. Also Sr is a reliable indicator of salinity and temperature; its concentration increases both with salinity and temperature. The Sr concentration is lower in clay and calcareous clays of marine deposits than in fresh-water sediments, while Mg is a good indicator of temperature.

The increase in Mg content of carbonate rocks with increasing age, suggests a trend of dolomitization in early Paleozoic and Precambrian or formation of dolomite by depositional and diagenetic environments reigning in those periods. In Recent dolomites a molar ratio  $aMg^{2+}/aCa^{2+}$  above 8.4 is required for efficient dolomitization. The process begins with evaporation of sea water causing precipitation of gypsum which raises the Mg/Ca ratio of the water, thus, the heavy brine originated migrates to the lowest possible topographic depressions, and seeps slowly through the underlying sediments resulting in a progressive dolomitization.

The Sr/Ca (0.009 mol percent) and Mg/Ca (5.2 mol per cent) in oceans has been reasonably constant for at least the past 600 million years.

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## INTRODUCTION

The literature on the distribution of Sr and Mg in carbonate minerals and rocks is voluminous but largely descriptive ( Bathurst, 1971; Turekian, 1964; Muller and Friedman, 1968 ). It is known that aragonite and magnesian calcites are the dominant minerals of Recent marine carbonate skeletons and sediments forming in shelf environments, whereas calcite predominates in deep-water marine carbonate sediments rich in the skeletons of planktonic organisms such as foraminifera. Sr is incorporated to aragonite and Mg to magnesian calcite. Thus the emphasis of this paper will be correlate modern carbonate sediments with ancient carbonate rocks in order to explain the diagenesis of carbonates, analysis of facies, reconstruction of environments. It also is important include the study of the carbonate particles within a sediment and relationship between Sr and Mg content and phylogeny of calcareous skeletons.

Sr content may be reported as ( ppm, %, Sr/Ca or Ca/Sr mol percent)

Mg content may be reported as ( %, mole %MgCO<sub>3</sub> , Mg/Ca or Ca/Mg mol percent )



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## Geochemical characteristics of Strontium and Magnesium

Most marine carbonates contain two minor cations (  $Mg^{++}$  ,  $Sr^{++}$  ), one major cation (  $Ca^{++}$  ) and a number of prominent trace cations (  $Fe^{++}$  ,  $Mn^{++}$  ,  $Ni^{++}$  ,  $Na^+$  ,  $K^+$  and others ) .

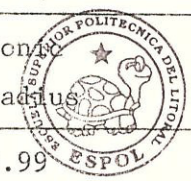
Mg, Sr and Ca and other cations that are usually incorporated in carbonates are listed in Table 1.

Table 1. Ranks and abundances in the earth's crust, atomic weights, charges and radii ionic of common elements contained within carbonates. Data from Mason ( 1958, 1966 ).

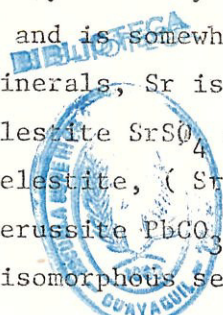
Element	Rank	Earth's crust weight percentage	Atomic weight	Ionic charge	Ionic radius
Ca	5	3.63	40.08	+2	0.99
Mg	8	2.09	24.32	+2	0.60
Fe	4	5.00	55.85	+2	0.74
Mn	12	0.095	54.94	+2	0.80
Zn	24	0.007	65.38	+2	0.74
Sr	15	0.045	87.63	+2	1.12
Pb	36	0.0013	207.21	+2	1.20
Ba	16	0.04	137.36	+2	1.34

At present only about 25 strontium minerals are known. In most of them, Sr is bound to oxygen ( or OH, H<sub>2</sub>O ) exclusively and its valency is always two, The ionic radius of  $Sr^{2+}$  is between those of  $Ca^{2+}$  and  $Ba^{2+}$  and is somewhat smaller than the  $Pb^{2+}$  radius. Therefore, in a number of minerals, Sr is replaced by these atoms and also replaces them; for example, celestite  $SrSO_4$  is isotypic with barite  $BaSO_4$ , anglesite  $PbSO_4$  and baryto-celestite, ( Sr, Ba ) $SO_4$  Strontianite  $SrCO_3$  is isotypic with witherite  $BaCO_3$ , cerussite  $PbCO_3$ , and aragonite  $CaCO_3$  ( but not with calcite which forms an isomorphous series with carbonates of smaller cations ).

Magnesium is the eight most abundant element in the earth's crust, making up about 2% of its mass. It is widely distributed, principally as the silicate minerals such as asbestos (  $CaMg_3Si_4O_{12}$  ) and the carbonate, oxide, and chloride.



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Magnesite (  $MgCO_3$  ) and dolomite (  $MgCO_3 \cdot CaCO_3$  ) are the principal sources of magnesium in addition to seawater and deep salt wells.

The magnesium ion is found in very large amounts in sea water, the percentage being about 0.13 per cent of the sea water, which corresponds to about 3.69 per cent of the total salts. ( Table 2. )

Table 2. Mg, Sr, Ca, ( Cl, Na, K ) ions in sea water. Data from Mason ( 1966 ).

ION	Cl=19 parts/1,000 ( or g/Kg )	Percent
Cl	18.980	55.05
Ca	0.400	1.16
Mg	1.272	3.69
Sr	0.008	0.03
Na	10.556	30.61
K	0.380	1.10



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Most of the compounds of magnesium which crystallize from sea water during evaporation are hydrated chlorides and sulphates, either alone or jointly with potassium and, more rarely, calcium. The magnesium is usually present as the hexahydrate ion, with six water molecules grouped around each metal ion at the six corners of an octahedron. The magnesium ion in crystallized salts is therefore often associated with six water molecules, as in bischofite and carnallite.

The magnesium minerals from sea water evaporates crystallize relatively late compared with the bulk of the anhydrite and rock salt. The reason for this lies partly in the preponderance of sodium over magnesium and potassium in sea water, and partly in the great solubility of most of the magnesium compounds involved compared with the low solubility of calcium sulphate.

Regarding to Strontium, by being excluded from ultrabasic and basic rocks, it works upward in the lithosphere during fractional crystallization because of its large ionic radius. It is found abundantly along with potassium in volcanics rocks, alkali rocks, and pegmatites, as shown by Noll ( 1934 ).

From these and other igneous rocks and from sediments strontium, along with calcium, is removed in weathering and passes down the rivers partly in solution and partly in the crystalline particles of silt. The crystalline fraction is immediately deposited in marine argillaceous sediments, and the soluble fraction tends to increase the strontium concentration in the sea.

However, the incorporation of strontium into the carbonate and phosphatic skeletons of organisms removes strontium from the sea, together with calcium, in about the same Sr/Ca ratio as in the materials coming down the rivers.

The strontium-bearing calcareous and argillaceous deposits are elevated in the course of orogenesis and are subsequently eroded, so that the strontium and calcium return again to the sea.

With respect to magnesium weathering cycle, for example, products of weathering of magnesian olivine has been recognized as serpentine. Talc is most probably the product of weathering of orthorhombic pyroxens, chlorite is the ordinary product of weathering of magnesian mica and probably of aluminous pyroxens.

Quantitatively more important than the formation of hydrous magnesian silicates, however, is the production of the magnesium ion as a solute in aqueous solutions, certainly in most cases as bicarbonate solutions. In most cases of weathering the magnesium ion enters the cycle of sedimentation, in other cases it is precipitated on the spot as magnesite,  $MgCO_3$ , or as dolomite, especially in the weathering of olivine and olivine rocks. Considerable masses of olivine rocks can be converted in this way into magnesite, most of the silica being removed in solution.

Finally Mg, Sr, and Ca concentrations in certain types of rocks are tabulated in Table 3

Table 3. Abundance of (Mg, Sr, Ca) in rocks. Data from Turekian and Wedepohl (1961)

Element	Granite		Basalts	Shales	Sand-stones	Carbonate rocks
	High Ca	Low Ca				
Mg (wt%)	0.94	0.16	4.60	1.50	0.70	4.70
Ca (wt%)	2.53	0.51	7.60	2.21	3.91	30.23
Sr (ppm)	440	100	465	300	20	610



### Location of Sr and Mg in structure of carbonate minerals.

Carbonate minerals include those minerals composed of  $\text{CO}_3^{2-}$  and one or more cations. The principal cations that are usually incorporated in carbonates were tabulated in Table 1.

Most carbonate minerals are either rhombohedral or orthorhombic in crystal habit. Rhombohedral carbonate minerals have six-fold coordination ( 2 cations for every oxygen ), while orthorhombic minerals have nine-fold coordination ( 3 cations for every oxygen ). Fig 1.

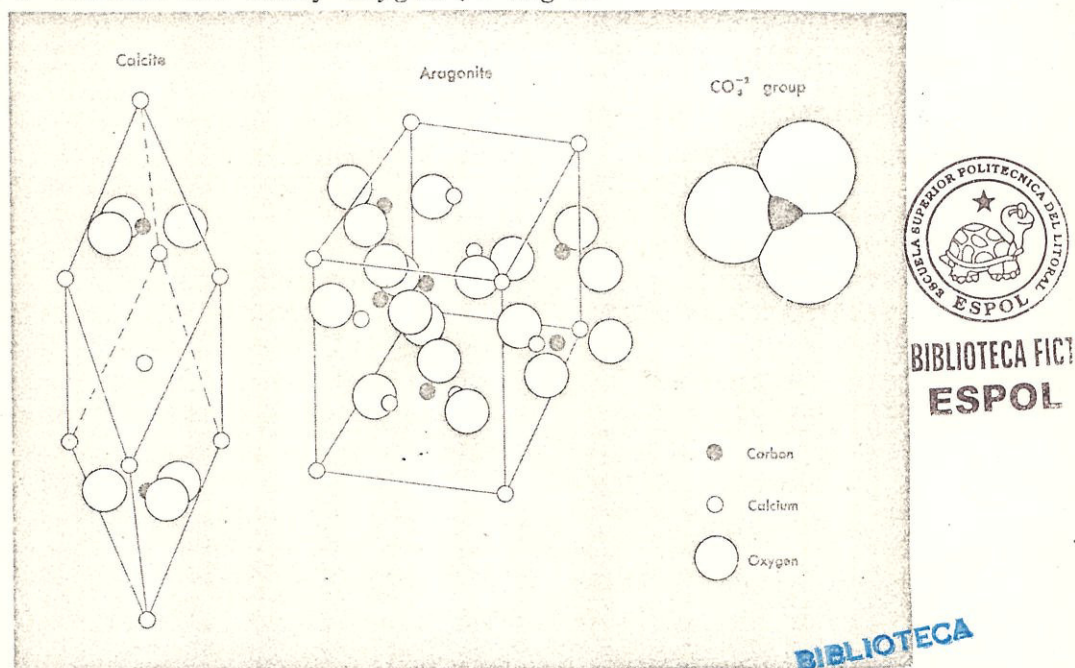
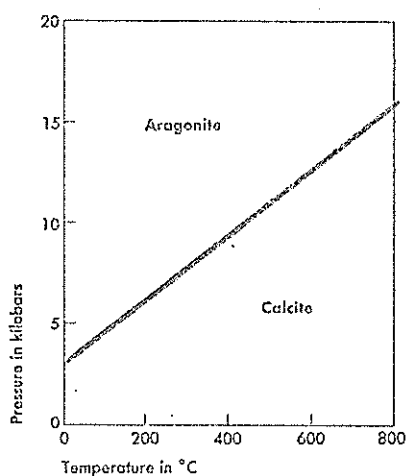


Fig. 1 Diagrammatic arrangements of atoms in crystal structures of calcite and aragonite.

Smaller cations, such as Mg, (Fe, Mn, Zn) are energetically favored in six-fold coordination, while larger cations, such as Sr, (Pb, Ba) are favored in the larger orthorhombic structure. Calcium occupies a unique position in that its ionic radius (  $0.99 \text{ \AA}$  ) is intermediate between the small and large cations, and as such can form either rhombohedral ( calcite ) or orthorhombic ( aragonite ) carbonates. Aragonite is the high pressure polymorph of calcium carbonate ( Jamieson, 1953; Clark , 1957 ), and at present earth-surface conditions is metastable. Fig. 2. Aragonite, which has a more compact, ordered atomic arrangement than calcite ( that is, it has a lower entropy and a smaller volume ), is stable on the high-pressure, low-temperature side of the P-T curve of positive slope relating the 2 polymorphs.



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Fig.2 Equilibrium curve for  $\text{CaCO}_3$  . .

Other common calcite-type rhombohedral carbonates include Magnesite ( $\text{MgCO}_3$ ), siderite ( $\text{FeCO}_3$ ), rhodochrosite ( $\text{MnCO}_3$ ) and smithsonite ( $\text{ZnCO}_3$ ). Aragonite-type orthorhombic carbonates include strontianite ( $\text{SrCO}_3$ ), witherite ( $\text{BaCO}_3$ ) and cerussite ( $\text{PbCO}_3$ ).

Carbonate minerals are seldom pure; rather they tend to contain other cations within their lattices. Aragonite-type minerals show preferential substitution with larger cations, while calcite-type minerals prefer smaller cations. For example, calcite rarely contains more than 2000 to 3000 ppm Sr, but aragonite can contain up to 3.3% (Hutton, 1936).

The amount of substitution of larger cations into aragonite structures, however, seldom exceeds a few percent at earth-surface conditions. In contrast, complete Mg-Fe and Fe-Mn transitions can occur in the calcite group (Deer et al., 1962; Goldsmith, 1959). The crystal structure of calcite itself, however, is such that complete solid-solution substitution by other cations is not common at normal earth-surface temperatures and pressures (Graf, 1960). Although thermodynamic calculations suggest that similarly small amounts of Mg should substitute with calcium at earth-surface conditions (Goldsmith, 1959), calcites with more than 20 mole %  $\text{MgCO}_3$  are common in modern oceanic sediments. The great availability of Mg in oceanic waters accounts for this difference. Those calcites

containing more than 1 % Mg ( 4 mole %  $\text{MgCO}_3$  ) are called high magnesium (or magnesian) calcites ( Chave, 1952 ).

In the mineral dolomite,  $\text{CaMg}(\text{CO}_3)_2$ , the great disparity between the sizes of calcium and magnesium ions leads to cation ordering, that is,  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  occupy alternate cation levels in the structure in a perfectly regular manner. Dolomite, then, is an intermediate compound, and its existence does not imply simple solid solution between  $\text{CaCO}_3$  and  $\text{MgCO}_3$ , at least below very high temperatures. The isobaric temperature-composition diagram is presented in Fig. 3. At elevated temperatures, calcite in equilibrium with dolomite becomes more magnesian; concomitantly the coexisting dolomite becomes slightly more calcic. At temperatures in excess of  $1,075^\circ \text{C}$ , the crest of the solvus, complete solid solution exists.

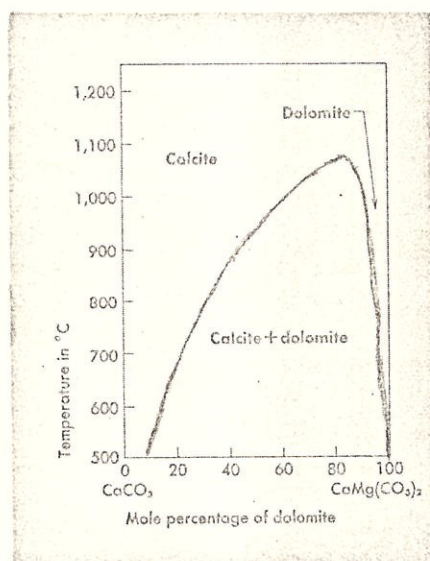


Fig. 3 Isobaric temperature-composition phase relations for the system  $\text{CaCO}_3$ - $\text{CaMg}(\text{CO}_3)_2$ , at one atmosphere total pressure.

Both iron and manganese can substitute for the magnesium to form ankerite  $\text{Ca}(\text{Mg, Fe, Mn})(\text{CO}_3)_2$ .

The lattice spacings of pure dolomite are considerably smaller than those of calcite ( for example,  $2.84 \text{ \AA}$  versus  $3.04 \text{ \AA}$  in the 211 plane ), because magnesium ions have smaller ionic radii than calcium ions.

At present earth-surface temperatures calcite ( including magnesian calcite), aragonite and dolomite are the common carbonate minerals.

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## Incorporation of Sr and Mg into different carbonate components of unconsolidated sediments

The carbonate particles within a sediment can be differentiated into organic and inorganic components. Illing (1954) classified grains as skeletal and non-skeletal. Non-skeletal components are defined as grains which do not appear to have been precipitated as skeletal tests.

**Lithoclasts.**— Carbonate lithoclasts are defined as fragments of limestone (Folk, 1959). Also lithoclast is used to imply a rock fragment derived from outside the basin of carbonate deposition by erosion and transport. Mineralogy commonly depends upon the age and source of the rock. Late Quaternary lithoclasts in continental shelf sediments off the eastern United States are composed mostly of aragonite and magnesian calcite, but most older lithoclasts, such as those derived from Miocene outcrops, are calcitic (Milliman, 1972).

**Pelletoids.**— Pelletoids are round, oblong or cylindrical (rod-like) carbonate grains that have a disoriented or cryptocrystalline granular texture. Pelletoids range in length from 0.2 to 2 mm with diameters from 0.1 to 0.4 mm. Most pelletoids are fecal in origin, but others may be altered or recrystallized ooids.

The composition of unrecrystallized pelletoids is directly related to the composition of their constituent fine-grained sediments, generally aragonite and magnesian calcite. The chemical composition of pelletoids is similar to that of the other non-skeletal fragments (Table 4).

Fecal pellets can be recognized by an internal texture of unoriented silt and clay-size grains, bound together by an organic and carbonate matrix. Fragments of larger grains also may be incorporated into the pellet. Organic matter tends to be higher in unrecrystallized pellets than in other non-skeletal grains, about 5% (Table 4). Recrystallized pellets contain less organic matter and are composed almost entirely of aragonite.

**Ooids.**— An ooid is defined as a "... grain which displays one or more regular lamellae formed as successive coatings around a nucleus..." and in which "... the constituent crystals of the lamellae must show a systematic crystallographic orientation with respect to the grain surface" (Newell et al., 1960). An oolite refers to a sediment composed of ooids. Individual

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laminae generally range from 3 to 15 microns in thickness; some ooids contain as many as 175 to 200 lamellae. Component crystals average from 1 to 4 microns in length. Ooids contain perforating blue-green and green algae, together with lesser amounts of fungi and bacteria.

Modern ooids are dominantly aragonite. A nucleus with a different composition may affect the ooid's total mineralogy, depending upon the size of the nucleus. Organic carbon in ooids is less abundant than in other non-skeletal fragments, but tends to be higher than the 0.13% reported by Newell et al., (1960) ( Table. 4 ). Strontium values are higher than in any other marine carbonate, averaging close to 1%. Magnesium is very low, often less than 0.1%.

Ooids in Laguna Madre ( Texas ) contain both magnesian calcite and aragonite. The magnesian calcite is restricted to the radially oriented crystal layers and the aragonite to the tangentially oriented and micritic crystals ( Frishman and Behrens, 1969 ). The magnesian calcite contains 13 to 15 mole %  $MgCO_3$ , while the aragonite contains about 1.1% Sr. The reason for the variable composition and crystal structure in the Laguna Madre ooids is not known.

Aggregates and cryptocrystalline lumps.- The term "aggregate" describes two or more fragments joined together by a cryptocrystalline matrix which constitutes considerably less than half the grain. The matrix consists of disoriented aragonite needles, usually less than 10 microns long, or aragonitic discs, about 5 to 10 microns in diameter.

Cryptocrystalline grains ( lumps ) have been defined by Purdy (1963) as grains that have been altered, filled and encrusted (inorganically) to the point where their original source can not be recognized. In non-skeletal sediments, cryptocrystalline lumps often are composed of altered aggregates, while in skeletal-sediments, *Halimeda* and foraminifera ( especially peneropliids and miliolids ) are major sources of cryptocrystalline lumps.

Aggregates have similar compositions to other non skeletal fragments. Magnesian calcite ( usually less than 10% of the total carbonate ) may be unrecrystallized detritus or may represent an prior stage of cementation ( Winland and Matthews, 1969 ). When calculated on a 100% aragonite basis

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the concentrations of Sr, Mg and various trace elements are similar to those found in ooids and pelletoids, Because of the difficulty in separating them from other grains, no analyses have been made on cryptocrystalline lumps, but sediments abundant in these lumps have compositions similar to other non-skeletal fragments (Milliman, 1967). Table 4.

Table 4. Composition of modern marine non-skeletal carbonate grains. Data from Newell et al. (1960), Kahle (1965), Milliman (1967) and Kinsman (1969)

Carbonate component	Org. matter %	Mineral	Ca %	Mg %	Sr %	NA %	Fe ppm	Mn ppm
<b>Pelletoids</b>								
Great Bahama Bank(87%oolite)	4.7	87% Arag.		0.41	0.80	0.23	1290	80
Great Bahama Bank ( recrxl)	2.3	96% Arag		0.19	1.00	0.23	274	10
<b>Oolite</b>								
Great Bahama Bank	1.9	99% Arag.	38.2	0.08	0.99	0.24	300	3
Great Inagua Island, Bahamas Bimini Lagoon	2.5	88% Arag.		0.32	0.94	0.44	350	7
Bahamas(87% oolite)		97% Arag	37.8	0.69	0.96		14	5
Mersian Gulf Suez, Red Sea	0.34	99% Arag. Arag.	37.8	0.12 0.05	0.97			
<b>Aggregates</b>								
Great Bahama Bank		95-96% Arag.		0.40	0.92	0.32		
Serrana Bank	2.6	88% Arag.		0.63	0.97	0.39	285	47

Skeletal components.- The most commonly occurring skeletal composition and by far the most important in terms of sediment deposition is calcium carbonate. Non-skeletal components were defined before like grains which do not appear to have been precipitated like skeletal tests, however, they could have once been skeletal or have an inorganic origin; it only signifies that in their present state no skeletal origin can be ascertained.

Most trace elements are substantially more diffuse in shells than in the soft parts of the organism. For instance, only calcium, strontium and perhaps magnesium are present in higher concentrations in mollusk shells than in corresponding soft parts;

Many different units have been used in reporting the concentrations of Sr and Mg in skeletal material such as parts per million, weight percent of the element, weight percent of the oxide of the element, weight percent of the carbonate of the element, mol percent of the element carbonate, mol ratio of the element to Ca and concentration factors relative to the medium from which the skeleton formed.

$$\text{concentration factor} = \frac{\text{Conc. element in carbonate/Conc. Ca in carbonate}}{\text{Conc. element in seawater/Conc. Ca in seawater}}$$

Values of less than 1 indicate a selective exclusion of the element from the skeleton. Many of the data for Sr have been published in terms of Sr/Ca atom ratios whereas Mg data are commonly used in mol percent  $\text{MgCO}_3$ .

The concentration factors of the major ( Mg, Sr ) and trace elements ( Mn, Fe, Zn, Pb, Ba ) within calcite and aragonite phases of the various organic carbonate components are shown in Tables 5 and 6. From these data can be deduced that the concentration values for strontium and barium, are near unity in one or both mineral phases; that is, partitioning of these elements relative to calcium appears to be minor. Other elements tend to be concentrated relative to calcium ( manganese, iron and lead ) and magnesium is notably excluded.

Elemental composition depends strongly upon the mineralogy of the skeleton. Cations with large ionic radii, such as strontium and to a lesser extent barium and lead, tend to be more concentrated in aragonite than in calcite. Elements with small ionic radii such as magnesium, manganese and iron prefer calcite. The relation between ionic radius and mineralogy seems logical in view of the lattice structures of aragonite and calcite.

Table 5. Concentration factors of Mg, Sr and related cations within various calcitic carbonates. Data from Milliman ( 1974 ).

	Mg*	Sr	Ca	Fe	Zn	Mn	Pb	Ba
Coccoliths	0.8	0.2	3-5		0.3	130		6
Red algae	20-70	0.3	1-5	15-300		6-120		0.01
Benthonic Foraminifera	0.5-40	0.2	3-5	0.5-5		1-25		1-7
Planktonic Foraminifera	0.1	0.1	3	7-10		5		
Porifera	20	0.3		10		5		0.7
Coelenterata	30	0.2	2	16-30	5-7	2-3	300	
Bryozoa	15	0.3		450	2-3			
Brachiopoda	2	0.2						
Mollusca: Pelecypoda	2	0.2	0.4	12-26	0.9	15-110	30-600	0.3
Cephalopoda	9	0.5						0.9
Annelida: Serpulidae	10-40	0.3	1-2	23-47		11-32	70-330	1
Arthropoda: Cirripedia	2-3	0.3	1	15		30-100	100	1
Decapoda	20	0.5	0.6	2-10		10-20	30	0.2
Echinoder- mata	10-40	0.3	7	2-27	1-2	4-17		0.4

\* Only Mg concentration factor is  $\times 10^{-3}$ .



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Table 6. Concentration factors of Mg, Sr and related cations within various aragonitic carbonates. Including ooids and aggregates. Data from Milkiman ( 1974 ).

	Mg*	Sr	Fe	Zn	Mn	Pb	Ba
Ooids	0.4	1.3	10-30		0.4		0.6
Aggregates	4	1.2	30		4		
Red algae	6	1	20		5		
Brown algae	3	1					
Green algae	0.6	1	16-360	3	4-8		
Coelenterata	1-2	1	1-17	0.4-7	1-7	20-330	0.3-3
Bryozoa	1	1	100				0.7
Mollusca:							
Amphineura	0.8	0.8					0.4
Scaphopoda	0.4	0.2					0.3
Cephalopoda	0.4	0.4	3		2	4200	
Pelecypoda	0.2	0.2-0.4	8-34	0.3-16	5-10	30	0.3
Gastropoda	0.5	0.2-0.3	1-26	0.06-5	2-30	100	0.4
Pteropoda	1	0.1				6700	
Annelida:							
Serpulidae	1	1	27-92		18-28		
Arthropoda:							
Cirripedia	0.6	1					

\* Only Mg concentration factor is  $\times 10^{-3}$ .

Strontium in marine carbonate components.- This review of Sr and Mg content in marine carbonate components will be used later relating to diagenesis, facies analysis, paleoenvironmental reconstruction, Sr/Ca and Ca/Mg ratios.

Strontium values are 3 to 5 times higher in most aragonites than in calcites (Figs. 4-5). Values are greatest in non-skeletal oolite and aggregates (0.9-1.1%) and somewhat lower in green algae, coral, bryozons, cirripeds and ascidian spicules (0.7-0.9). Only the mollusks (except amphineura 0.6-0.78%) are able to discriminate effectively against strontium; their shells generally contain between 0.2 and 0.3% Sr. With the exception of cephalopods (argonauta 0.35%) and cirripeds (0.3-0.4%), strontium content in calcites mostly are less than 0.3%. (Fig. 5).

Sr and Mg are the two elements most easily related to physiological processes. Lowestam (1963, 1964) demonstrated that more phylogenetically advanced organisms contain less strontium. Referring to mollusks one can see a slight decrease in strontium with increasing physiologic complexity (Fig. 4); mollusks appear to be totally unique in their ability to selectively discriminate against strontium. Within calcitic organisms, one can note a slight tendency towards increased strontium content with greater complexity (Fig 5).

Magnesium in marine carbonate components.- Magnesium values within aragonites are uniformly low, never more than 0.5% Mg and generally less than 0.25% Magnesium concentrations in calcite can be either high (more than 4 mole %  $MgCO_3 = 1\%Mg$ ) or low, but seldom in between. Coccoliths, planktonic foraminifera, brachiopods and calcitic mollusks and arthropods (except decapods) generally contain less than 1 mole %  $MgCO_3$ . In contrast, red algae, many benthonic foraminifera, sponges, octocorales, bryozons, decapods and echinoderms contain more than 8 mole%  $MgCO_3$  (High-magnesian calcites). The only organisms that contain intermediate amounts of magnesium are the cephalopods (argonauta) and some benthonic foraminifera.

Chave (1954) showed a trend of decreasing magnesium content within magnesian calcites in more complex organisms. No such tendency is seen within the low magnesian calcites, but a slight trend of decreasing magnesium is noted in the aragonites (Fig. 4).

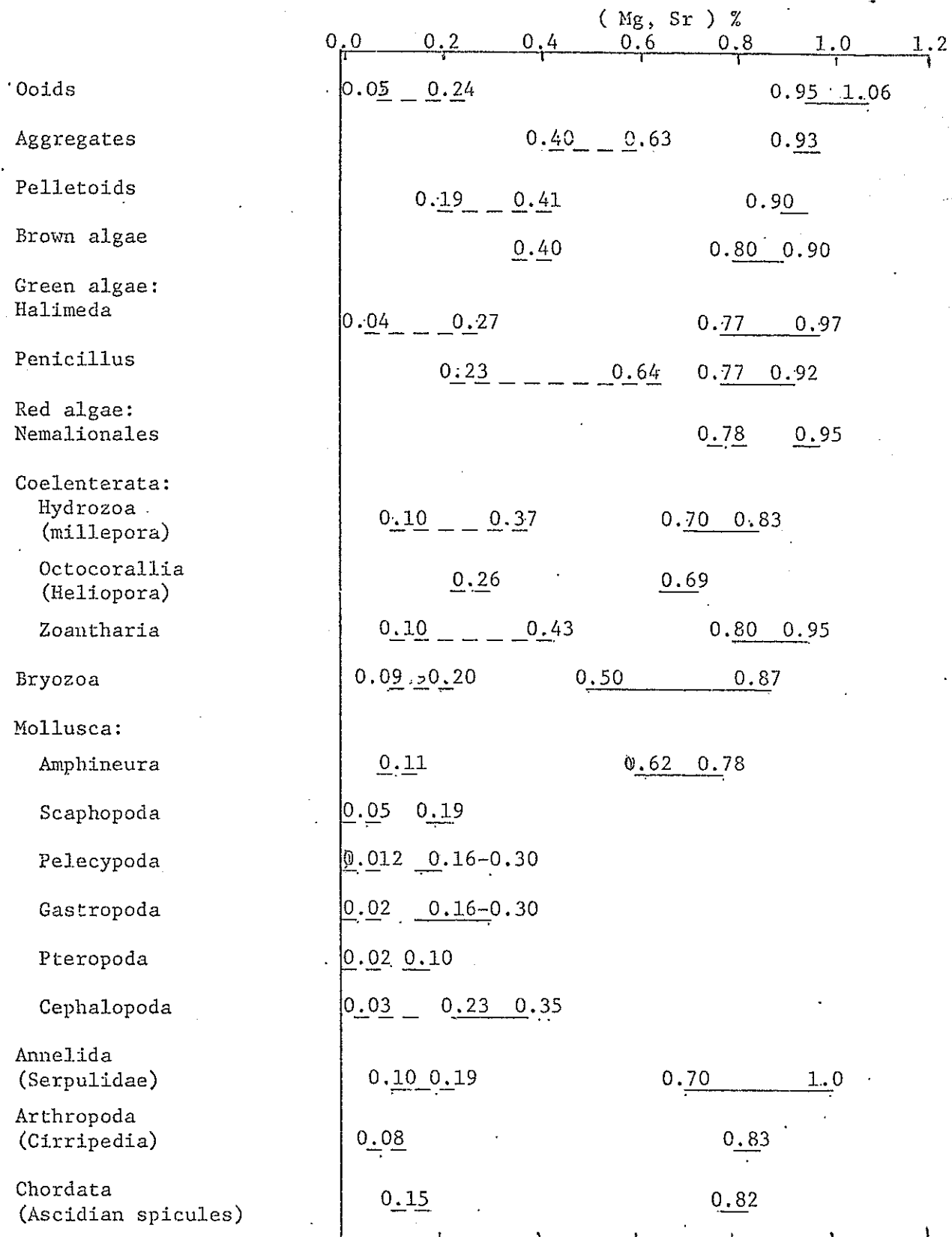
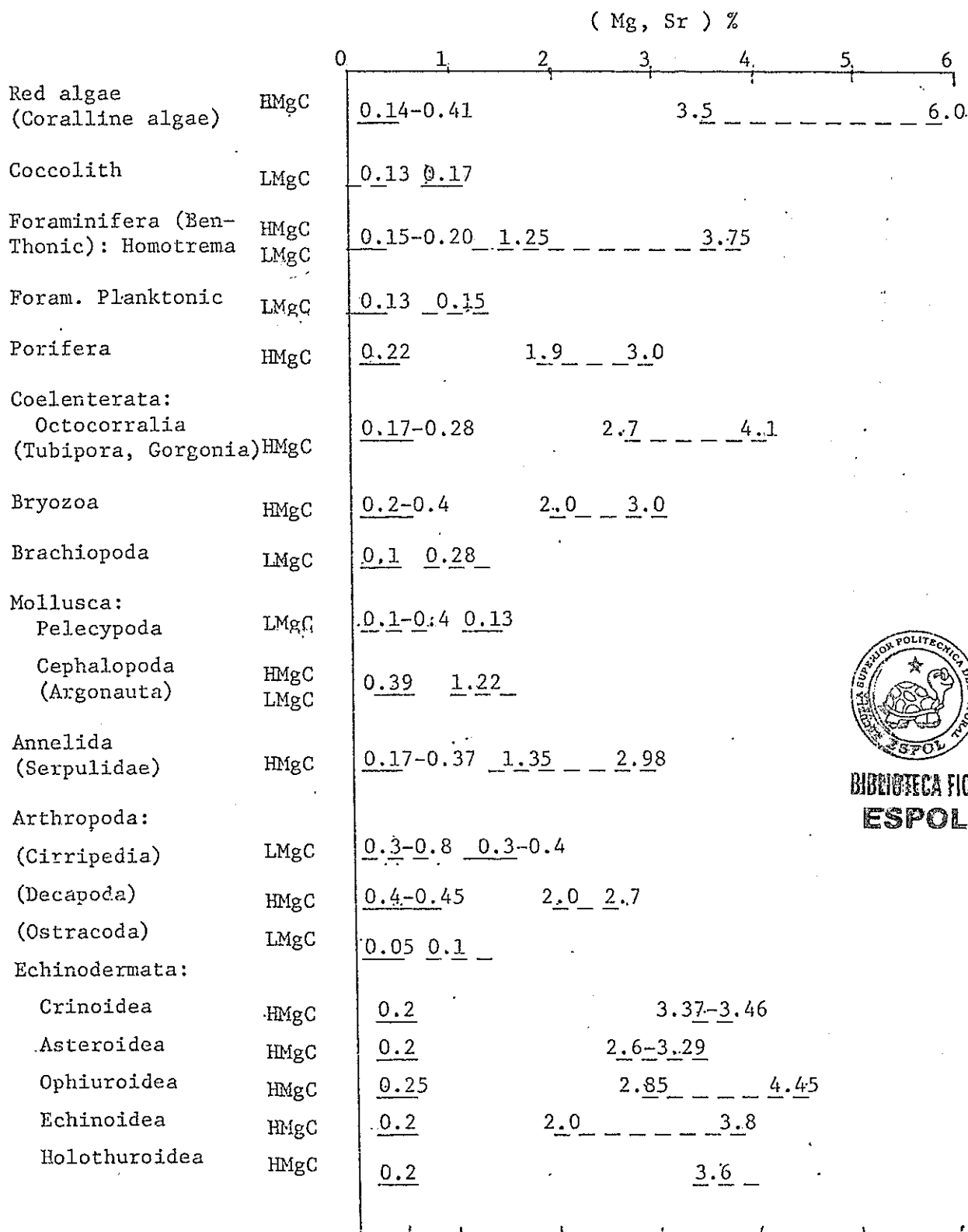


Fig. 4. Mg (---) and Sr (—) contents in aragonitic carbonate components. Data from Vinogradov (1953), Chave (1954), Thompson and Chow (1955) and Milliman (1974).



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Fig. 5. Mg (---) and Sr (—) contents in magnesian calcite (+1%Mg) and calcite-carbonate components. Data from Vinogradov(1953), Chave (1954), Thompson and Chow (1955) and Milliman (1974).



## Sr and Mg in carbonate rocks

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Most of the Sr introduced into carbonate sediments is substituted for Ca in calcite and, more especially, aragonite. Smaller amounts precipitate as  $\text{SrSO}_4$  in environments of evaporite deposition. Smaller percentages of celestite occur in the chemical precipitate of dolomite and magnesian calcite being formed today in certain shallow lakes of South-Australia. Odum (1951) confirmed by x-ray diffraction the presence of celestite reported, on the basis of optical and chemical tests, in the skeletons of some Acantharian radiolaria. As Odum pointed out, however, the skeletons are quantitatively insignificant as sources of Sr. Not only pure celestite, but also solid solutions of  $\text{SrSO}_4$  with  $\text{BaSO}_4$  occur in sedimentary rocks.

The distribution of most of the celestite found in carbonate rocks, like that of barite, suggests secondary redistribution. It occurs as nodular masses, coatings on cavern walls, in geodes, and as replacing bodies containing masses of unaltered or slightly altered limestone. Cavities with smooth faces are left when the celestite crystals are removed. The crystals are not vug fillings, but are believed to have formed when the rest of the rock had not yet solidified.

Kulp, Turekian, and Boyd (1952) analyzed 153 carbonate rocks spectrographically and obtained an over-all average of  $\text{Sr}/\text{Ca} = 0.71 \times 10^{-3}$ . The Sr content of fossils was found to vary greatly, but they generally contained twice as much Sr as the surrounding carbonate matrix, a result attributed both to the probable presence of some inorganic, low-Sr carbonate in the matrix and to more rapid Sr loss from the finer grained matrix because of more rapid aragonite-to-calcite transformation of fossil fragments. Goldberg (1957) stated that  $\text{CaCO}_3$  inorganically precipitated from sea water is aragonite with a

Sr/Ca ratio greater than that of sea water ( $8.9 \times 10^{-3}$ ). According to Goldberg recrystallization of fossils, the great majority of which originally have a Sr/Ca ratio less than that of sea water, should lead to lowered Sr/Ca values only if it takes place in nonmarine waters of reduced Sr/Ca ratios.

The progressively lower Sr contents of calcites from the basin, forereef, and backreef areas of the Steinplatte reef complex of Austria, 380 to 1570, 150 to 420, and 60 to 150 ppm Sr, respectively, were attributed by Sternberg et al. (1959) to more through recrystallization away from the basin.

Kulp, Turekian, and Boyd (1952) detected no trend of Sr/Ca values with geologic age in analyses of 63 North American carbonate rocks ranging in age from Precambrian to Tertiary, because variable amounts of recrystallization apparently had taken place in rocks of the same age. However, the analyses of carbonate rocks from the Russian platform (Vinogradov et al., 1952) (Fig. 6) showed a definite decrease in Ca/Sr ratios from the Permian to <sup>the</sup> Tertiary which would suggest that Sr lost from fossils during recrystallization is in general not retained locally as celestite, and that the number of samples taken (some 3600) was sufficient for obtaining a statistically valid increase in the amount of recrystallization with geologic time.

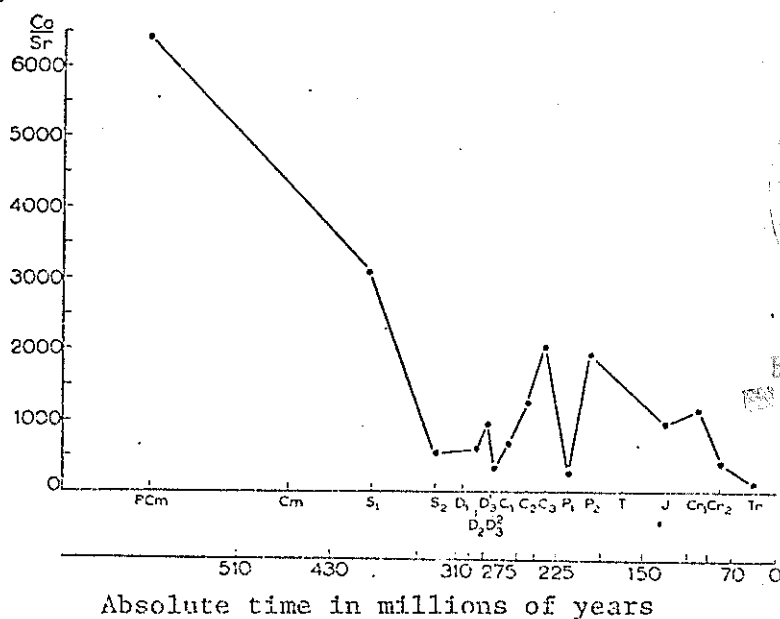
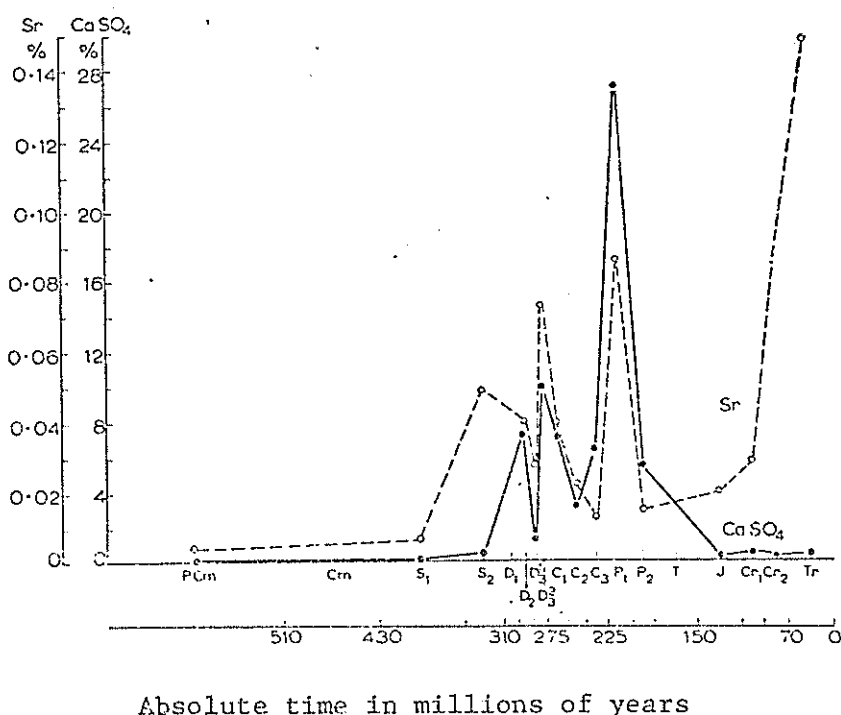


Fig. 6- Variation of Ca/Sr of carbonate rocks of Russian platform with time.

Examination of the plots of the percentage of  $\text{CaSO}_4$  and that of Sr ( Fig. 7 ) show that the high-post Permian values are unrelated to chemically precipitated celestite associated with anhydrite ( and evaporite dolomite ), as appears to be the case with the early Permian and some of the Devonian Sr maxima. The latter maxima coincide with several of the pre-Mesozoic points for samples in figure 6 that fall below the apparent general trend line and illustrate the inability of a simple Ca/Sr ratio to depict a situation in which Sr is being contributed in two different forms, one quite independent of the carbonate crystal structure, and in which Ca is present both as calcite and anhydrite. The additional criticism may be made that the value of Ca should be increased by an amount corresponding in mol percent to the Mg present in dolomite. For both evaporite dolomite and replacive dolomite the important quantity to be measured is the amount of carbonate material formed concurrently with the original Sr deposition. The use of a  $(\text{Ca}+\text{Mg})/\text{Sr}$  ratio would have improved the quality of the fit of the points in figure 6 to a straight line.



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Fig. 7- Variation of  $\text{CaSO}_4$  and Sr contents (in %) of carbonate rocks of Russian platform with time. ( Vinogradov et al., 1952 ).

Dolomites apparently may contain either less or more Sr than limestones, depending upon whether celestite is present. Kulp, Turekian, and Boyd (1952), found a fair positive correlation between the percentage of Sr and that of Mg in Indiana limestones.

Recent dolomite formation can be observed only in the sediments of tropical waters, where the salinity is locally high ( for example, in lagoons, and episodically flooded supratidal regions in South Australia, Florida, the Persian Gulf, and so on, Skinner (1963) and Wells (1962) and others. These dolomites were proven to be of recent origin by  $C^{14}$  dating techniques. Dolomite is probably always a reaction product of  $CaCO_3$  and Mg-rich, highly saline brines and is formed during the early stages of diagenesis. In certain older stratigraphic horizons, such as the Kupferschiefer, this type of dolomite formation has also been recognized from the regional pattern of dolomite and calcite distribution relative to the distance from the shore line. Conditions favorable for the early diagenetic formation of dolomite are probably realized too seldom to account for the great abundance of the mineral. Other processes such as late diagenesis, epigenetic reactions, and metasomatism are probably responsible for the formation or most of the dolomite deposits.

The increase of the Mg content of limestones with geologic age, as observed, for instance, by Goldschmidt (1954) is probably due to the fact that older rocks were more likely to come into contact with Mg-rich solutions than younger ones. The alternative possibility that the Mg/Ca ratio of the sea water has decreased conspicuously during the Earth's history can not be excluded, but it is less probable. The dependence of the Mg content on the age of the rocks has been observed even in relatively young rocks. Wedepohl's a-

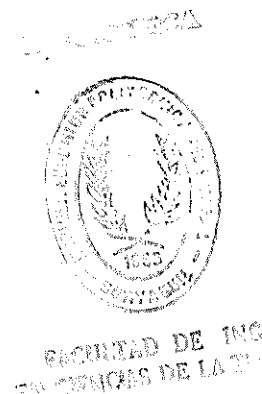
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analyses determined a mean MgO content of 1.3 percent in 32 samples of Devonian limestones, 0.9 percent MgO in 45 samples from the Jurassic, and 0.5 percent MgO in 16 samples from the Cretaceous.

Degens (1965) reported on a detailed study of fossiliferous and unfossiliferous beds in Mesozoic and Tertiary limestones and concluded that (1) the Ca/Mg ratio decreases as salinity increases, and (2) fossils occur only in formations where the Ca/Mg ratio is greater than 50. The absence of fossils is believed to reflect hypersaline conditions.

In his studies of Recent carbonates, Cloud (1962) found that the magnesium-content of the calcite fraction is either high (11-19mol%) or low (0.5 mol %)  $MgCO_3$ . The low-Mg calcite is particularly abundant in near-shore localities and in bottom core samples that reached bed rock. The abundance of High-Mg calcite increases offshore, and Cloud stated that it is probably all skeletal. The conditions prevailing in highly saline lagoons are prerequisite also for the sedimentary formation of magnesite ( Alderman and Skinner, 1957; Graf et al., 1961 ). Magnesite is frequently encountered in clays in clays interbedded in the salina deposits of Zechstein age.



Behavior of Mg and Sr in diagenetic processes involving carbonate sediments and rocks

A definition most applicable to the present study is which states: diagenesis includes all physicochemical, biochemical and physical processes modifying sediments between deposition and lithification at low temperatures and pressures characteristic of surface and near-surface environments. Hence diagenesis in its broad sense includes mineralogical, textural, fabric, and geochemical changes at low temperature and pressure. The last one includes removal of magnesium and strontium, and change in the stable isotope composition in carbonate minerals. The numerous diagenetic processes include: (1) recrystallization; (2) genesis of non-carbonate components; (3) solution and leaching; (4) adsorption-diffusion-absorption; and (5) precipitation of carbonate cement and nodules.

Recrystallization.- One problem that requires the full attention of researchers is the enigma of expulsion versus uptake of elements in relation to recrystallization, for example, are they a cause or an effect of secondary changes. For instance, Siegel (1960) concluded that Sr has to be leached out of the calcium carbonate before inversion can take place of aragonite to calcite, whereas others maintain that recrystallization leads to the expulsion of trace elements. It seems possible that, depending on the circumstances and the types of elements concerned, either one or the other, or both, explanations may be true. On the other hand, during recrystallization there is a possibility of Mg uptake from the connate fluids.

Taft (1962) found that a high concentration of Mg in sea water or interstitial fluids prevents transformation of aragonite and high-Mg calcite to the more stable low-Mg and Mg-deficient calcites. On the other hand, Stehli and

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Hower (1961) mentioned that although it is known that high-Mg calcite is the least stable among the carbonates present in the Recent sediments investigated by them, the ultimate disposition of the Mg released is still far from clear. Recrystallization rates are controlled by the concentration of particular cations, for example, recrystallization in solutions containing  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  ions, and in distilled water occurs at different rates. Consequently, one of the principal factors controlling recrystallization is clearly the degree of saturation and rate of migration of the sea water and interstitial fluids.

There seems little doubt that recrystallization causes migration of elements but the processes are complex. For example, contents of Mg, Sr, Fe, Mn, and Cl in an oolitic limestone are comparable to those of an average limestone. The distribution of these elements, however, is particularly significant. Mg, Sr, Fe, and Mn are concentrated in the calcitic matrix, whereas ooliths are enriched in Cl. The higher contents of elements in the matrix might explain by assuming that recrystallization of the ooliths expelled these elements. The Cl is thought to be present in inclusions in the ooliths. Kulp et al. (1952) found a definite relationship between recrystallized and unaffected fossil specimens: the former always had lower Sr/Ca ratios. These investigators suggested that the release of Sr during recrystallization may have given rise to the celestite ( $\text{SrSO}_4$ ) that has been encountered in the same sediments. There is also evidence that cone-in-cone structures may have been formed by recrystallization of a marl and that this process was accompanied by a loss of both Sr and Mg ions.

Genesis of non-carbonate components.- Odum (1957 a) mentioned that percolating waters are enriched and carbonate sediments are depleted in Sr content. Celestite ( $\text{SrSO}_4$ ) forms when the Sr-rich fluids come in contact with sulfate

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either in solution or as a mineral. Inasmuch as the solubility product of  $\text{SrCO}_3$  in sea water ( $5 \times 10^{-7}$ ) is smaller than that of  $\text{SrSO}_4$  ( $10^{-5}$ ), strontianite will tend to replace celestite and celestite, in turn, will replace gypsum. That this has occurred is indicated by studies of crystal pseudomorphs. Odum also pointed out that a number of investigators suggested that the associated dolomite deposits contains the Sr that was released by inversion of aragonite and/or by the dolomitization of the limestone. On the other hand, the possibility must be considered that the aragonite precipitation and/or dolomite genesis took place in a saline environment and that the celestite was formed directly from the sea water.

**Solution and leaching.**— Conversion of high-Mg calcite and high-Sr aragonite to calcite and aragonite devoid ( or having only a trace ) of Mg and Sr, respectively, has been explained as the result of "leaching", for example.

In a number of cases contradictory information is given on whether an element can be removed from a crystal that is in contact with a fluid, or whether complete solution and recrystallization are required to remove it from the crystal lattice. Zeller and Wray (1956) stated that Sr can not be selectively removed without complete solution or recrystallization of the carbonate. On the other hand, Siegel (1960) mentioned that Sr can be leached from the carbonate lattice prior to recrystallization. In the case of magnesium, under suitable conditions (pH, etc.) it would go into solution and, therefore, would be selectively extracted from the carbonate rock.

Chave ( 1954 ) mentioned that the removal of Mg by circulating waters can be observed in the Pleistocene formations of Southern Florida. The extensively leached oolitic limestone studied by him now has only 0.37%  $\text{MgCO}_3$ , although it contains 15% of echinoids, Foraminifera and Bryozoa that originally were probably rich in Mg content. Here again, however, solution and reprecipita -

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tion could be involved.

Lithification of calcium carbonate sediments.- Conversion of the calcium carbonate sediments into limestone rock involves a large number of reactions and processes, which may leave original depositional textures essentially unaltered, on the one hand, or which may so completely rearrange the constituents that original depositional textures are completely obscured or obliterated, on the other. The subject of lithification, which is only part of the broader topic of diagenesis, has been much studied, both from the point of view of the chemical reactions involved ( Taft, 1966 ) and of changes in porosity and permeability ( Harbaugh, 1966 ).

The following discussion traces some of these changes in a sequence that proceeds from the stage of imperceptible alteration of original features of the sediment to the stage of complete obliteration of original features. the subject is conveniently, even if somewhat arbitrarily, subdivided into two parts :

: (1) changes of individual grains, and (2) changes within the sediment mass.

(1)- Changes of individual grains: Many of the changes that influence the individual grains in calcium carbonate sediments do not strictly involve lithification of these grains to form limestone rock; but because these grain changes almost invariably take place during this transformation, they are properly included in this general summary. Two kinds of changes occur: (A) changes in mineralogy of the grains without external modification of the texture; and (B) addition of external concentric coatings to the grains.

(A)- Changes in grain mineralogy.- Recent nearshore marine calcium carbonate sediments contain the minerals aragonite, high-magnesian calcite, and low-magnesian calcite. In ancient limestones, however, of these minerals, only low-magnesian calcite is at all common; the other two occur but rarely (Cha-

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ve, 1954, 1962; Stehli and Hower, 1961; Friedman, 1964, 1969). An order of increasing stability among these minerals is: high-magnesian calcite, aragonite, low-magnesian calcite (Friedman, 1964).

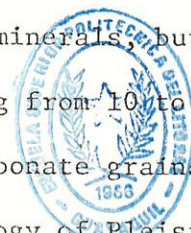
The loss of magnesium from reef sands in the Bahamas may consist of removal of magnesium from high-magnesian calcite to yield low-magnesian calcite, or a solution and deposition reaction on a micro scale, in which high-magnesian calcite is removed and low-magnesian calcite deposited without textural changes in the grains involved (Friedman, 1964). Coralline algae, for example, which secrete particles of high-magnesian calcite, commonly persist in limestones with original texture preserved; but after diagenesis, in limestones, these grains consist of low-magnesian calcite.

The changes in grain mineralogy, as shown by Friedman (1964), are well illustrated by comparing Recent reef sediments and skeletal, and oolitic sands from Bermuda, the Bahamas, Red Sea, and other areas, with nearby Pleistocene limestones that consist of the lithified equivalents of these sediments.

Recent reef sediments consist of aragonite in greater abundance than high-magnesian calcite (Fig. 8), indicating a preponderance of coral material. With only one exception, low-magnesian calcite is absent in the Bermuda samples studied by Friedman (1964).

The Recent skeletal sands from Bermuda contain these same minerals, but also include a variable amount of low-magnesian calcite, ranging from 10 to 15%, the variation being due to the presence of terrigenous carbonate grains from Pleistocene limestones on the island (Fig. 8). The mineralogy of Pleistocene limestones formed by lithification of skeletal sands varies according to whether their post-depositional history involved complete subaerial exposure or partial subaerial exposure and partial exposure to sea water (Fig. 9).

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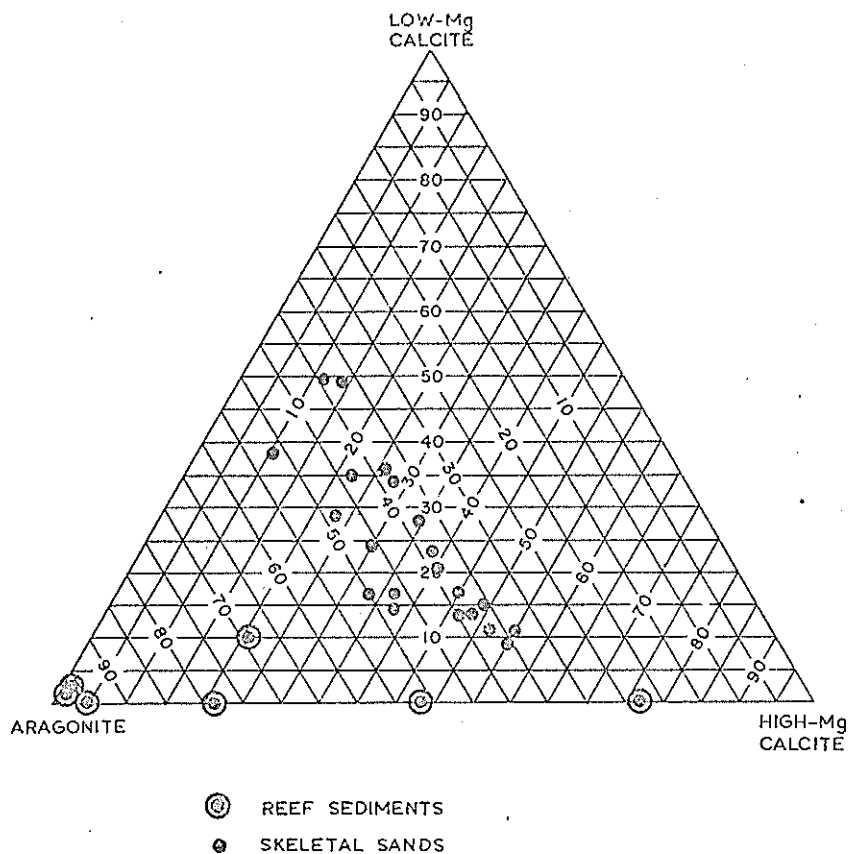


Fig. 8.- Mineralogy of Recent Carbonate Sediments from Bermuda. (Friedman, 1964)

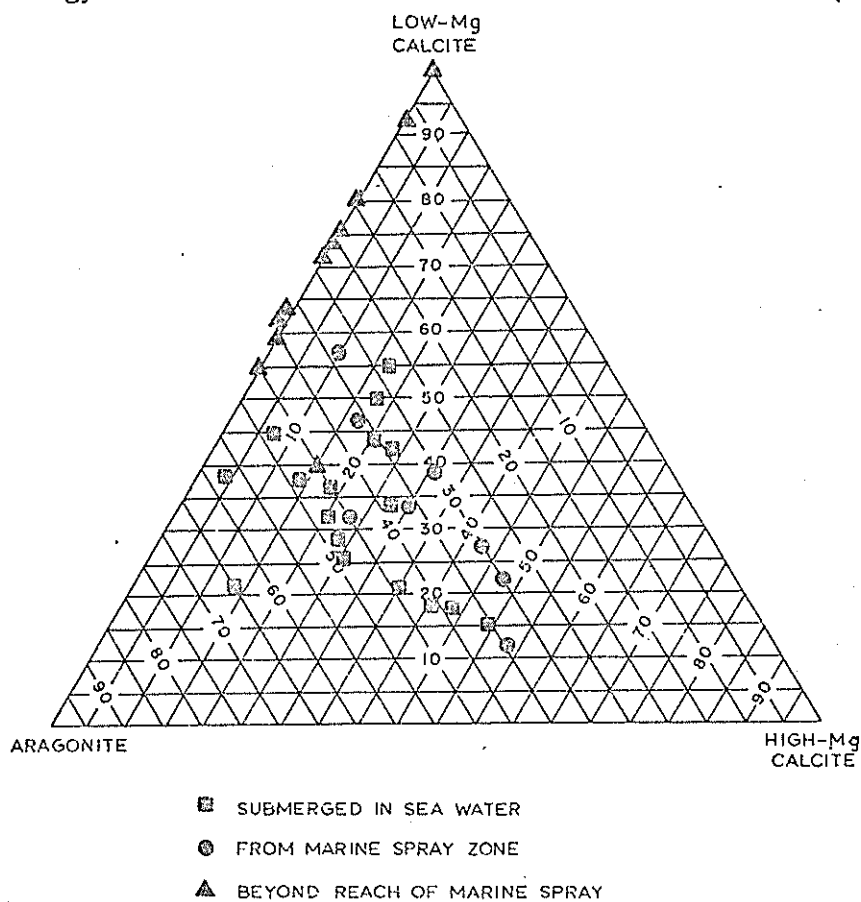


Fig. 9.- Mineralogy of Pleistocene skeletal sands from Bermuda. Note that Pleistocene carbonate sands submerged in sea water or exposed to marine spray contain high-magnesian calcite and that those beyond the reach of the sea water are, with one exception, devoid of magnesium. The absence of magnesium is due to removal by fresh-water leaching at a post-depositional stage of subaerial exposure.

Paramorphic replacement of aragonite by low-magnesian calcite commonly occurs where the aragonite exists in the form of structureless lime mud, crypto-crystalline grains, or ooids (Friedman, 1964). Presumably this replacement of aragonite by low-magnesian calcite occurs with an intervening solution-deposition stage on a micro-scale. The result is a complete change of mineralogy of the grains but a retention of their original depositional texture. Thus, for example, ooids and aggregate grains of non-skeletal sand-size particles, which are deposited originally as aragonite in Recent calcium carbonate sediments (Illing, 1954; Newell et al., 1960), almost always consist of low-magnesian calcite in limestone (Friedman, 1964). This paramorphic replacement contrasts markedly with the large-scale dissolution of aragonite skeletal debris and subsequent deposition of low-magnesian calcite in the empty space formerly occupied by the shells.

(B) Additions of concentric coatings to grains.- Grains of calcium carbonate and other minerals, such as quartz or feldspar, found in environments of Recent calcium carbonate sedimentation, commonly show external concentric coatings of calcium carbonate. These occur as envelopes of unoriented crypto-crystalline aragonite crystals (lime mud or micrite according different authors), these envelopes are commonly responsible for the preservation of original shapes of aragonite grains, for they are typically more resistant to dissolution than an aragonite skeletal particle. Thus, they preserve the shape of the coated particle, even if the aragonite of this particle has been removed by dissolution.

Also occur as layers of clear, oriented needle-like aragonite crystals with concentric or radial structure, or as various combinations of the cited ones.

(2) Changes within the sediment mass.- Changes within the sediment mass involve selective dissolution, which increases pore space; precipitation of mi-



neral cement in pore spaces, which decreases pore space; and recrystallization, the effect of which on pore space is not established. Precipitation of mineral cement between grains or mineral infilling of molds generally does not disturb the texture, but selective dissolution and recrystallization tend to destroy original textures.

Formation of sedimentary dolomite.- The apparent correlation of dolomite formation in recent sediments with high salinity and its lack of formation from ordinary sea water has not yet been explained on a comprehensive theoretical basis. Deffeyes et al. (1965) suggest that a high molar ratio  $Mg^{2+}/Ca^{2+}$ , which commonly occurs in supersaline waters as a result of evaporative concentration of  $Mg^{2+}$  accompanied by precipitation of  $Ca^{2+}$  as gypsum, promotes dolomite formation.

Von der Borch (1965) points out that a better correlation is found between elevated pH and dolomite formation, with dolomite occurring in lakes where the maximum pH, during the annual cycle of variation, reaches values as high as 10 and a  $Mg^{2+}/Ca^{2+}$  ratio possibly between 6 and 10.

Adams and Rhodes (1960) suggested a mechanism ( evaporative reflux ) by which dolomite is formed in carbonate rocks : Evaporation of sea water results in precipitation of gypsum which raises the Mg/Ca ratio of the water, thus, the heavy brine originated migrates to the lowest possible topographic depressions, and seeps slowly through the underlying sediments resulting in a progressive dolomitization.



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## Use of Sr and Mg in facies analysis and paleoenvironmental reconstruction

Recent carbonates differ distinctly from fossil limestones in their absolute Sr content as well as in the relative strontium contents representing each of the different facies areas. Absolute strontium contents in recent carbonates average about several 1000 ppm, and thus they are about ten times higher than those of fossil limestones. The relative strontium content of recent carbonates is as follows: reefs have maximum values, also in lagoonal limestones the values are high; but in the correlated basin sediments they are low. This behaviour corresponds to the distribution of aragonite and calcite in these sediments.

In fossil limestones, consisting only of calcite, the distribution is completely reversed: in reef complexes the strontium content is low, while in correlated basin sediments it is high (Chester, 1965). Sternberg et al. (1959) reported values of 60-150 ppm, 150-420 ppm, and 380-1570 ppm  $\text{SrCO}_3$  for the back reef, fore reef and basin sediments, respectively. Their investigations indicated that carbonates which have undergone recrystallization have low Sr contents due to depletion. This interpretation is supported by the high Sr values of unrecrystallized reef samples. The relatively high Sr content and the well preserved organisms in the basin sediments indicated that diagenetic to epigenetic depletion due to recrystallization has been less intense here.

Magnesium variations in ancient carbonates have not been reported by Flugel (1962) while strontium distribution change, as stated above. On the other hand, Siegel (1961) found that in Recent carbonate sediments the Mg concentration decreases as the Sr content increases and reaches a maximum where Sr

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content is at a minimum. The iso-strontium/calcium atom ratio lines plotted by Siegel showed that Sr/Ca atom ratio of the sediments increase with distance offshore from the Pleistocene reef and as the living reef is approached. The maximum value for Sr content is reached about one nautical mile on the leeward side of the living reef and decreases at the reef and seaward from it. As the reef organisms consist mainly of aragonite with a high Sr content, these results suggested that most of the reef-debris is deposited about one mile on the leeward side of the reef. Chilingar (1960) found that the Ca/Mg ratio of carbonate sediments from Great Bahama Bank and the Persian Gulf increases with depth and distance from shore. In some instances, the low Ca/Mg ratios of near shore, shallow-water calcareous sediments can be attributed to the abundance of magnesium-bearing coralline algae in the near-shore waters.

According to Odum (1957), the Sr/Ca ratios of marine carbonate sediments are higher than those of the calcareous deposits of open fresh-water basins. Because of the size and diversity of the ocean, however, a wide range in Sr/Ca values can be expected. Odum concluded that the Sr/Ca ratio varies partly with depth because of differential sedimentary accumulation of the calcareous deposits; this has been borne out by the works of Turekian, Lowenstam. In some localities, the Sr/Ca ratio may be controlled largely by the variation in content of insoluble components. In areas where there is no chemical precipitation of carbonate sediment, the Sr/Ca ratio is determined by the taxonomic composition of the calcareous skeletons. In marine, as well as in lake sediments, as the Ca concentration diminishes, the Sr/Ca ratio approaches the value characteristic of the acid insolubles; and when the Ca content increases, the Sr/Ca ratio approaches that of the carbonates present.

Kubler (1962) found that both fresh-water and marine limestones contain the same amount of Sr and concluded that the Sr content may be independent of sa-

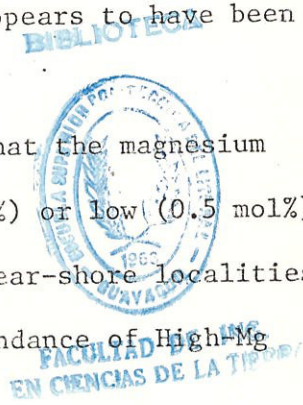
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linity. On the other hand, Degens (1959) showed that recent fresh-water limestones have a lower content of Sr than marine carbonate sediments; this is caused presumably by the lower amounts of Sr in fresh water. With an increase in age of limestones, however, the difference in Sr/Ca ratio between the fresh-water and marine sediments appears to diminish; and the Sr contents of Paleozoic carbonates, independent of facies, do not deviate much from the average value of 500 ppm. Hence, fresh-water limestones must have gained and marine limestones loss Sr during the geologic history as a result of diagenesis-epigenesis.

Jan Veizer (1974) showed that the distribution of Sr in Mesozoic carbonate rocks of the Central Western Carpathians is facially controlled, being the distribution of the strontium bimodal with high Sr concentrations in hypersaline, dark coloured and deep sea rock types and low Sr concentrations in littoral, neritic and shallow bathyal limestones of organogenic and organodetrital types. Their data indicated also a higher Sr content for early diagenetic dolomites than for the late diagenetic ones.

Kubler (1962) concluded that the Sr content is a useful parameter in environmental interpretations. In general, Kubler found in his studies that the maximum content of Sr occurs in sediments containing aragonite; and that light-colored carbonates are poor in Sr in both Mg-calcite and dolomite in contrast to the darker carbonate rocks. During diagenesis the Sr appears to have been mobilized in some cases to form celestite.

In his studies of Recent carbonates, Cloud (1962) found that the magnesium content of the calcite fraction is either high (11-19 mol%) or low (0.5 mol%) Mg CO<sub>3</sub>. The low-Mg calcite is particularly abundant in near-shore localities and in bottom core samples that reached bed rock. The abundance of High-Mg



calcite increases offshore, and Cloud stated that it is probably all skeletal. Kubler (1962) described regional facies changes of two cycles of sedimentary units rich in carbonate sediments of lacustrine (fresh-water), brackish, and marine environments. In addition to numerous differences not considered here, each cycle exhibits a different carbonate phase. Calcite is the dominant mineral in the whole profile. In the fresh-water limestone of cycle one, the Mg present occurs as detrital dolomite. In cycle two, however, the Mg is present in the calcite lattice to form Mg-calcite of various compositional ranges. The interbedded carbonates associated with coal deposits contain the maximum amount of Mg-rich calcite having the highest Mg content. In general, there are often two types of Mg-rich calcite: one with a  $MgCO_3$  content of about 20%, and an other with as high as 40%  $MgCO_3$ .

Skinner(1963) reported the formation of Mg-rich carbonate sediments on the saline Coorong lagoon which is an elongated finger of the ocean and is connected to the sea at the northern extremity. He also described a string of isolated, shallow, saline lakes which are isolated remnants of the Coorong lagoon. The amount of Mg being precipitated from the saline water in the form of carbonates appears to increase southward, away from the mouth of the Coorong lagoon, and reaches a maximum in the isolated lakes. Inasmuch as the lakes became isolated from the Coorong lagoon by marine regression, it is possible to assign relative ages to the lakes or group of lakes. This age in turn seems to delimit the type of sediment and carbonate petrology. A high Mg/Ca ratio of these carbonates is associated with increasing age.

The Ca/Mg and Ca/Sr ratios also are useful parameters in environmental interpretations.

The Ca/Mg may be usable for judging the original salinity, if suitable possi -

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bilities for absorption by the sediment were prevalent. The Ca/Mg ratio only plays a role in the case of organic material, which is notable for a high propensity for adsorption (peat). However, it must be mentioned that the Ca/Mg ratio is apparently dependent on age (Vinogradov, 1957).

The Ca/Sr ratio is a valid index of salinity. According to Krejci-Graf (1962) it is higher in clays and calcareous clays of marine deposits than in fresh-water sediments. On the other hand Turekian (1964) established only a decrease in the Ca/Sr ratio with time and Odum confirmed a fall in Sr content in beds from the Ordovician to the Late Carboniferous. The effect of aging on the Sr/Ca ratio was thought by Krejci-Graf to be a local effect due to differing sediment source.

The Ca/Mg ratio should be established for the calcite component of the sediment and should not be merely the gross ratio in the mixture, because the  $Mg^{2+}$  is selectively adsorbed by illite clays, and so the gross ratio may only reflect the total illite content or perhaps the degree of diagenesis. Within the calcite fraction, it has been established that  $Mg^{2+}$  is selectively favored by certain taxonomic groups of organisms and tends to be positively temperature dependent within any such group (Chave, 1954; Chilingar, 1962). Depending on the water temperature at any particular season of the year, the ratio may reflect the growth period. Different parts of the shell may thus have different ratios (Lowenstam, 1954, 1961).

Inasmuch as shallow, near-shore waters are systematically warmer as a rule than deep off-shore waters, the gross Ca/Mg ratio of a mixed detrital carbonate sediment reflects temperature-depth-distance from shore relationships (Chilingar, 1960) Fig. 12. Owing to the ecologic distribution of certain biotas, which may be of the high or low Mg-secreting taxa; however, there

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are anomalous concentrations which should not be misinterpreted in terms of temperature, etc. (Chave, 1954; Cloud, 1962). Fig. 13

Identical  $MgCO_3$  content in a reef complex may thus indicate a common faunal make-up or a similar environmental temperature.

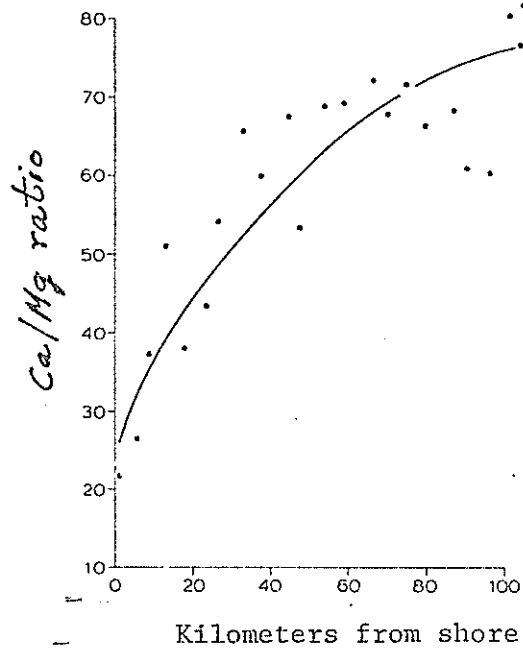


Fig. 12. Variation in Ca/Mg ratios of Great Bahama Bank sediments versus distance from shore. ( Data from Chilingar, 1960 ).

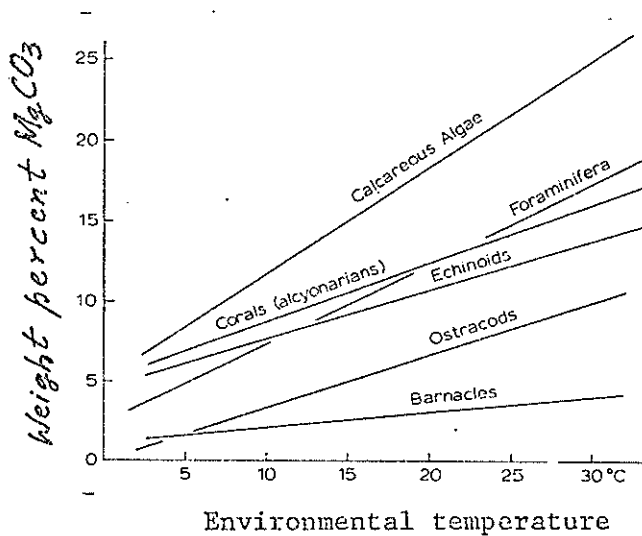


Fig. 13. Response of selected members of certain taxonomic groups to thermal range; note increasing Mg content with rise in temperature.

Kudymov (1962) has shown that by the spectral logging curves for calcium and magnesium, the carbonate part of the section can be distinguished from the terrigenous part. In certain cases the terrigenous strata contain carbonate material. Kudymov also concluded that the magnitude of the differential density of the calcium and magnesium lines reveals the degree of dolomitization of limestones. Therefore it is possible to establish the existence or absence of paragenetic relationships between the elements in various stratigraphic levels, formations, beds and deposits. The use of Ca/Mg ratios in locating dolomitized carbonate oil reservoirs proved to be of value in some areas.

The Ca/Sr ratio is essentially an attribute of the aragonitic carbonates, for calcite usually carries very little Sr. This ratio is thus a useful relationship only with respect to warm environments, which are favorable to aragonitic organisms and the inorganic precipitation of aragonite. Further restricting its usefulness is the metastable character of aragonite. According to Krinsley (1960), nevertheless,  $\text{Sr}^{2+}$  tends to be more stable than  $\text{Mg}^{2+}$  with time. The Ca/Sr ratio of sea water seems to be constant, regardless of temperature or salinity. On the average, marine aragonites carry 0.1 - 1.0 % Sr, marine calcites about 0.01 % Sr, and fresh-water calcites about 0.001 % Sr. In the modern marine environment, as with the Ca/Mg ratio, the Ca/Sr ratio partly reflects temperature-depth-distance from shore (Siegel, 1961); again it partly indicates local ecologic concentrations of the aragonite-secreting taxa (green-alga *Halimeda*).

Finally the following values of Sr/Ca atom-ratio in Recent sediments appears to be a reliable indicator of the salinity and the temperature of the environment. It increases both with salinity and temperature.

Deep-water carbonates oozes : 2.38- 2.61; Aragonite sediments of shallow-water tropical regions: 4.0-10.8 and more; lagoonal dolomites: 11.4 Sr/Cax1000.

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Unfortunately, this interdependence can not be applied to ancient sediments, because Sr disappears already during diagenesis. Nevertheless, higher contents of Sr in limestones point to their origin at a higher temperature and possibly also to a higher salinity. The content of Sr can also be indicative of inorganic or biological origin. The organic fraction, i. e. in the tests of pelecypods, brachiopods contains more Sr than the inorganic parts of limestones.

	Sr/Ca atom-ratio x 1000
Average content in shells of Recen sediments	4.64
Average content in total Recent carbonate sediments	2.68.

Changes in Ca/Sr and Ca/Mg in oceans over geologic time and their significance as far as carbonates are concerned.

It is very important to know the salinity and alkalinity of typical sea water at Precambrian-Cambrian boundary. Simple calculations of present-day productivity rates, and extrapolation back for half a billion years or more, will simply not suffice, when there is little concept of the former dimensions of the planet, its volume of ocean water and its atmospheric composition.

A number of geochemical indicators can, however, be used to appraise the situation. The Sr/Ca ratio in sea water has remained essentially constant during the last  $200-250 \times 10^6$  years (Lowenstam, 1961), and interprets his data to mean essential constancy of the magnesium concentration and Mg/Ca ratio during the last  $200 \times 10^6$  years. This interpretation of the magnesium data depends, in part, on the role assigned to diagenetic changes in the material studied, and is not as well substantiated as that referring to the Sr/Ca ratio. The constancy of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in limestones of Paleozoic age and younger (Gast, 1955; Hedge, 1963) is the strongest argument for suspecting that the Sr/Ca ratio of the oceans has been constant during the Phanerozoic. It implies a significant supply of strontium from limestones during diagenesis and weathering. If the mean Sr/Ca ratio of streams draining limestones of various age at any given time was constant and the removal ratio was equal to that supplied, the constancy of the Sr/Ca ratio of sea water would follow.

The absence of much preserved limestone in the Precambrian and the observed low  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios for some of those preserved indicates that one can be less certain about the Precambrian seas.

The present-day rate of accumulation of calcium carbonate in the deep sea is a

adequate to account for the supply of calcium to the sea by streams. Hence because of the preferential loss of strontium during the diagenesis of limestones, the net Sr/Ca ratio supply to the oceans must decrease with time if no recycling occurs. This will result in an exponential decrease with time in the Sr/Ca ratio in sea water if the Sr/Ca ratio of supply and removal are the same and no massive resolution of the deep-sea carbonates occurs.

In summary, there are ways in which the sea can change in its strontium concentration. There are no unequivocal ways, however, of testing the extent of this change from the fossil record. The Sr/Ca ratio appears to have remained constant for all practical purposes during the Phanerozoic. As a corollary the high strontium concentrations of some fossil shells may be interpreted as diagenetic addition of strontium.

Vinogradov (1956) showed that the Ca/Sr ratio in the carbonate rocks of the Russian platform rises as one goes back into the Precambrian ( see Fig. 6, p. 17 ), while in the carbonate rocks of North America the rise in the Ca/Sr is not very pronounced. ( Fig. 14 ). There seem to be two possible interpretations about the curves of the figs. 6 and 14: (a) that there has been a steady decrease of recrystallization and leaching ( and Sr loss ) with time; (b) that there has been a steady rise in temperature of shallow seas across North America and Russian platforms through time, this favouring increased aragonite ( and Sr ) concentrations. Possibly both were operative.

In contrast the Ca/Mg ratio in the ancient carbonate rocks show a systematic drop prior to the Cretaceous. ( Daly, 1907; Vinogradov, 1956; Chilingar, 1956 ). A possible reason for the decrease in Ca/Mg ratio since the Cretaceous is the fact that pelagic calcareous foraminifera and coccoliths started to extract great quantities of calcium out of the sea water and deposit it in the oceans

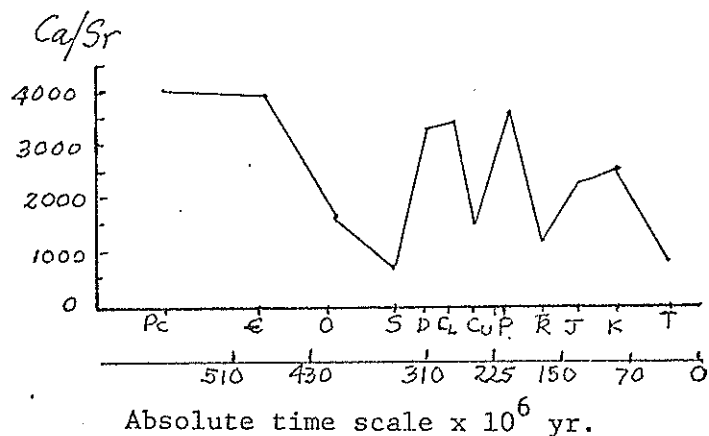


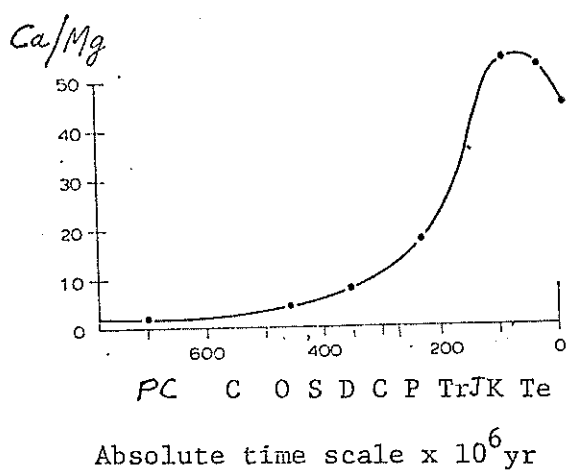
Fig. 14. Variation with time of the Ca/Sr ratio in the carbonate rocks of North America. ( Based on data from Kulp et al., 1952 ).

during and after Cretaceous. This calcium is thus withdrawn from the cycle and never returned to the lands. If this removal of calcium to the deep seas should continue, the Ca/Mg ratio of sediments might drop down to the value of Precambrian time (4:1).

In other words carbonate rocks become more dolomitic and enriched in magnesium with increasing rock age. Figs 15 and 16 illustrates the Ca/Mg ratio in carbonates through time according to Chilingar (1956) and Vinogradov (1956).

Comparison of the Ca/Mg curve for the carbonate rocks of the Russian platform with the analogous curve based on Chilingar data for the North American rocks reveals parallelism in the chemical evolution of these rocks. (Fig. 17).

This suggests that the diminution of the Mg content in carbonate rocks with time was a regular and general process for the entire earth. Both curves ( Figs 15-16) show a relatively slow increase in the Ca/Mg ratio during the Paleozoic and a sharp increase at the beginning of the Mesozoic, indicating a radical change in the conditions of formation of carbonates in post-Paleozoic marine basins. Recent carbonate rocks are nearly pure calcium carbonate with Ca/Mg ratio about 45 whereas Cambrian carbonates approach dolomite in composition. The scarce analysis of Precambrian carbonates give a Ca/Mg ratio from



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Fig. 15. Changes in average Ca/Mg ratio of North America- carbonate rocks through time. ( Based on data from Chilingar, 1956 ).

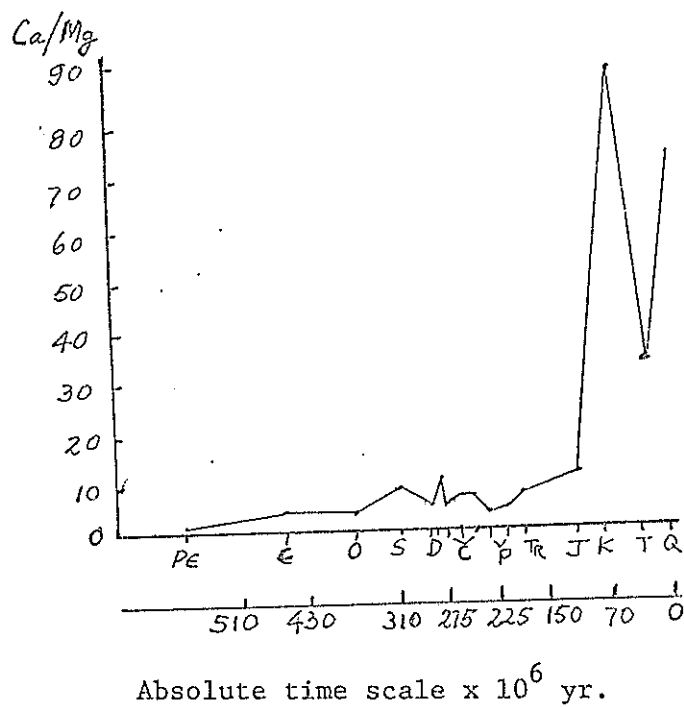


Fig. 16. Changes in average Ca/Mg ratio of Russian- carbonate rocks through time. ( Vinogradov, 1956 ).

2 to 4, suggesting that the the trend shown in Fig. 17 extends into the Pre - cambrian.

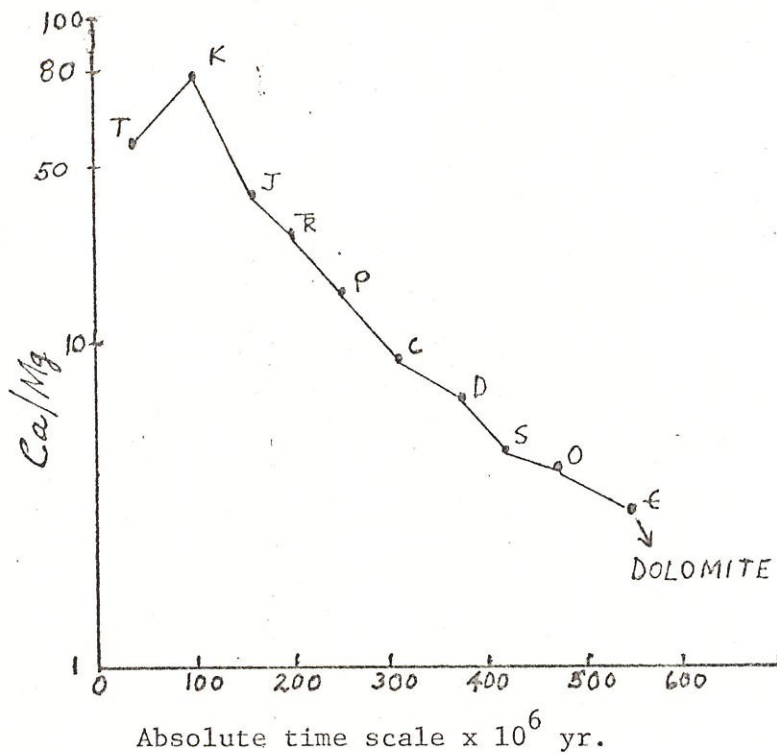
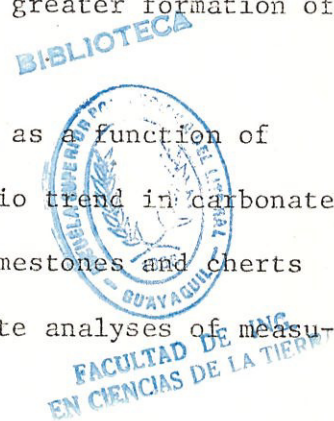


Fig. 17. Period averages of the Ca/Mg ratio of North-America and Russian Carbonate rocks plotted against age. (Data from Chilingar, Vinogradov, 1956)

Fairbridge (1964) has discussed the four explanations which have been proposed for the observed overall trend: (1) increasing probability of older rocks being dolomitized, (2) widespread growth of magnesium-rich algal limestones in early Paleozoic and Precambrian, (3) higher Paleozoic water temperatures, (4) higher  $P_{CO_2}$  in the Paleozoic and Precambrian resulting in greater formation of primary dolomites.

The oxygen isotopic composition of Phanerozoic limestones as a function of their ages provides a clue to the origin of the Ca/Mg ratio trend in carbonate rocks. Fig. 18 shows a plot of  $\delta^{18}O$  values of average limestones and cherts for various Periods. The limestone data represent composite analyses of measur-



rements made by Degens (1962) and Keith and Weber (1964). The chert analyses were carried out by Degens on samples intimately associated with the limestones analyzed.

There is a drop-trend with age in  $\delta^{18}\text{O}$  values for both limestones and cherts. In addition, with increasing age the  $\delta^{18}\text{O}$  values for both rock types approach the  $\delta^{18}\text{O}$  values of their respective fresh water analogues. Although the deficiency of  $\delta^{18}\text{O}$  in progressively older limestones could in part reflect higher sea water temperatures in ancient oceans or a progressive increase in the  $\text{O}^{18}/\text{O}^{16}$  ratio of sea water from the Cambrian to the present, it is much more likely that the observed trends are the result of partial equilibration of the limestones and cherts with isotopically lighter continental surface and sub-surface waters ( Degens, 1962; Keith and Weber, 1964 ). The older the rock the greater the probability that it was bathed in meteoric waters.

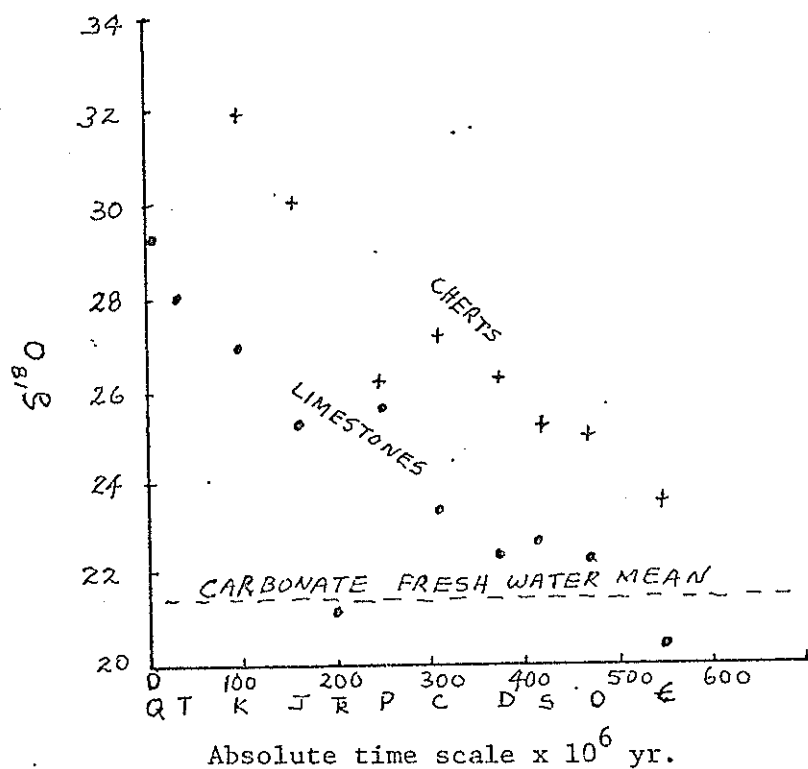


Fig. 18. Period averages of oxygen isotopic composition of carbonate rocks and cherts plotted against age. (Based on data from Degens, 1962).

There is a moderately good relationship between the  $\delta^{18}\text{O}$  values of limestones, their Ca/Mg ratio and geological age. Fig. 19 illustrates the average  $\delta^{18}\text{O}$  values of Phanerozoic limestones plotted against their respective Ca/Mg ratios expressed in percent differences from dolomite.

$$\delta \text{Ca/Mg} = \frac{\text{Ca/Mg (geological period)} - \text{Ca/Mg (dolomite)}}{\text{Ca/Mg (dolomite)}} \times 100$$

Younger limestones have a relatively high Ca/Mg ratio and are isotopically heavy, whereas older limestones have a low Ca/Mg ratio nearly equivalent to that of dolomite, and are isotopically light. The progressive overall trend (Fig. 19) with increasing age for the Ca/Mg and  $\delta^{18}\text{O}$  values of limestones suggests that the individual Ca/Mg and  $\delta^{18}\text{O}$  trends (Figs. 17 and 18) have similar causes. Consequently, despite the fact that dolomite can form in a variety of ways and that the data for both the Ca/Mg ratios of carbonates and the  $\delta^{18}\text{O}$  values of limestones do not necessarily pertain to rocks having the same mode of formation, it is likely that the progressive decrease of the Ca/Mg ratio of limestone represents an increased opportunity for the older rocks to be dolomitized by continental, isotopically-light, meteoric waters.

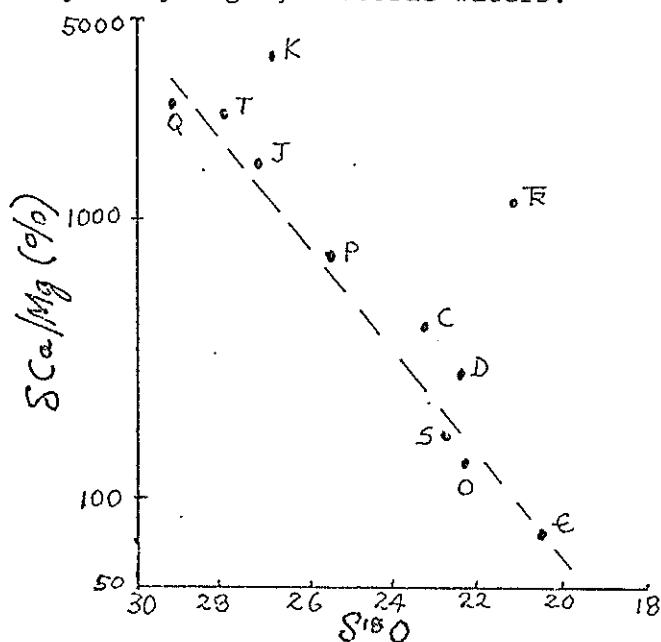


Fig. 19. Relationship Ca/Mg -- geological period --  $\delta^{18}\text{O}$ . ( Based on data from Vinogradov, 1956; Chilingar, 1956; Degens, 1962 ).



It appears that long-term diagenetic processes are quantitatively more important in affecting the composition of the total mass of carbonate rocks than are penecontemporaneous and early diagenetic dolomitization. It is possible that the magnesium derived from shales during their stabilization was transferred to contemporaneous limestones by subsurface water movement and this led to their dolomitization.

The chemical, mineralogical and oxygen isotopic changes in carbonate rocks with increasing age reflect long-term diagenetic process. Most of the available data are for Phanerozoic carbonate; however, the Ca/Mg trend extends into the Precambrian.

It is difficult at present to determine whether or not the oceans are chemically stable. The fossil and evaporite rock record for the past 600 million years is consistent with little change having occurred in sea water composition. Indeed, the oxygen isotopic content and the Sr/Ca, and Mg/Ca ratios of fossil brachiopods in Mississippian age rocks (Lowenstam, 1961) suggest that sea water of that time was like that of today. It is unlikely that drastic changes in sea water composition could have occurred during the Phanerozoic because it would have been difficult for a variety of marine organisms to have flourished and survived from Cambrian times until today. Consequently, it is likely that the composition of sea water has been reasonably constant for at least the past 600 million years:



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## Summary and concise synthesis of current knowledge

The amount of  $Mg^{2+}$  or  $Sr^{2+}$  substituted for  $Ca^{2+}$  in a carbonate skeleton is a function of phylogeny, shell mineralogy, water temperature, water composition, and the type of organic tissue. As far as geochemistry is concerned, it is becoming increasingly clear that our earlier expectations for utilizing the chemical composition of invertebrate shells as an important source of information about paleoenvironmental conditions are not going to be realized until much more is learned about the complex physiological processes involved in skeletal calcification.

Modern ooids are dominantly aragonite and Sr values are higher than in any other marine carbonate, averaging close to 1% and Mg is very low, often less than 0.1%.

When calcite or aragonite grows by inorganic processes under equilibrium conditions, the amount of Sr or Mg ion substitution is determined by the properties of the crystal surface in contact with the water, the composition of the water, pressure and temperature. Therefore, in dealing with such minerals, it is often possible to determine much about the environment of formation from analysis of Sr and Mg composition.

The partition coefficients for strontium in aragonite and calcite have been determined by Kinsman (1969), and has shown that early formed crystals, do not react with the solution and that only surface equilibrium is maintained between the precipitates and the solution. That is, strontium in aragonite is zoned in a manner similar to the frequent zonation of calcium concentration in plagioclase feldspars, so that changes of the molar ratio  $Sr^{2+}/Ca^{2+}$  in the solution will be reflected in a zoning of the crystal.

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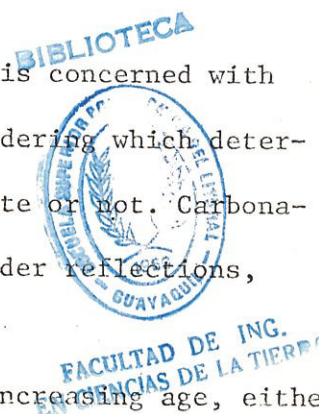
A decrease in strontium content of limestones with increasing age is due from conversion of aragonite to calcite during diagenesis. The conversion from aragonite to calcite is generally a solution-precipitation reaction that is greatly accelerated by movement of relatively fresh waters through intergranular voids in the carbonate sediment. Therefore, it is to be anticipated that most changes will occur very early in the history of the sediment, before deep burial.

The content of strontium in the diagenetic calcite must be low because the partition coefficient for coprecipitation of strontium with calcite at 25°C is only 0.14 and decreases to 0.08 at 100°C. For aragonite the analogous values are 1.1 and 0.8. The capacity of calcite to accommodate strontium in its crystal structure is thus about 10% that of aragonite so that calcitic limestone should contain no more than about 1000 ppm strontium, compared to nearly 10000 ppm in aragonitic limestone.

In recent sediments, the content of strontium in carbonate sediments increases both with salinity and temperature. Content of Sr can also be indicative of inorganic or biological origin. The organic fraction contains more strontium than the inorganic parts of limestones. Could settle the question, as the increased percentage of strontium indicates the presence of biological detritus.

Much of the research into the nature of Recent dolomites is concerned with the degree of ordering in the lattice, since it is the ordering which determines, whether the calcium-magnesium carbonate is a dolomite or not. Carbonates with composition  $\text{Ca}_{50}\text{Mg}_{50}$  are known which, lacking order reflections, are not dolomites despite their chemical composition.

A increase in magnesium content of carbonate rocks with increasing age, either



may in part reflect the increased opportunity with time for a carbonate rock to become dolomitized or reflect a greater prevalence of the depositional and diagenetic environments conducive to the formation of dolomite in the Paleozoic and Precambrian as contrasted to later times.

In a marine-like water the activity ratio  $aMg^{2+}/aCa^{2+}$  must be above 8.4 for efficient dolomitization, this high value is due the precipitation of gypsum, i. e. Coorong (South Australia ).

The constancy of the ratios Sr/Ca and Mg/Ca throughout the oceans is well-known, but variations in these ratios occur in nearshore areas by introduction of river effluents as well as in areas of high biologic activity and chemical precipitation.



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Problems remaining to be solved

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Many analyses have been made of carbonate rocks to determine the types and amounts of Mg and Sr they contain but these data are difficult to evaluate in terms of the diagenesis of the rock. Nearly all the analyses are of bulk samples and, therefore, there is no certain way to determine the proportion of Mg and Sr content that results from inclusions in the carbonate rock rather than from inclusion in the calcite structure. Of course, most of the magnesium in ancient limestones probably exists in dolomite rather than in metastable high magnesium calcites. For example, the magnesium content of an ancient limestone can vary by an order of magnitude because of dolomite amounts that are not easily detectable by normal X-ray diffraction analysis. Strontium content is from 350 up to 500 ppm and is probably present within the crystal structure of calcium carbonate minerals because celestite and strontianite are rare in limestones.

The interdependence of Sr content with salinity and temperature in recent sediments is reliable, but unfortunately, this interdependence can not be applied to ancient carbonate rocks, because Sr disappears already during diagenesis.

In many modern dolomites, and in some ancient ones, the dolomite is not ordered and has a composition close to  $\text{Ca}_{56}\text{Mg}_{44}$ , the larger calcium ions cause a widening of the lattice spacings of certain planes in the dolomite crystal structure and thus a shift in the position of certain X-ray diffraction peaks.

Available data are inadequate to distinguish a carbonate rock become dolomitized through time or by depositional and diagenetic environments dominating in ancient times.

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No known dolomitization is taking place today in normal sea water.

No known arguments exists for recognizing a primary dolomite in ancient carbonate rocks. But it is true also that some dolomite in Recent sediments and much dolomite in ancient carbonate rocks that lack visible evidence of a secondary or replacement origin.

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Recommendations for further research

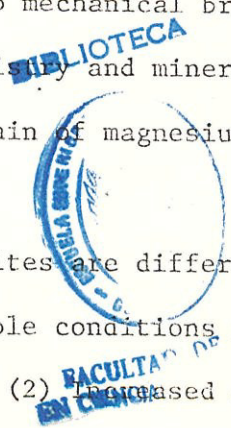
In order to understand the Mg and Sr composition of natural calcite or aragonite, we must first ascertain whether the mineral was the product of biochemical processes within the tissue of organisms and was thus determined by the metabolic processes of the organism or whether the Mg and Sr content was determined by physical-chemical processes taking place in a solution without direct biochemical influence.

Organic processes undoubtedly predominate in providing the raw materials from which the bulk of Phanerozoic ( post- Precambrian ) limestones have formed. The course of their subsequent diagenesis has largely depended on physical processes, i. e. The content of Sr can be indicative of inorganic or biological. The organic fraction contains more Sr than the inorganic parts of limestones. Many direct and indirect inter-relationship undoubtedly occur and will be the subject of much research in future years.

Degree of recrystallization of metastable carbonates to stable form is probably a function of the magnesium concentration in interstitial waters.

There is not relationship between mineral and chemical composition, and sediment grain size in modern carbonate sediments and it depends on local conditions of biogenic productivity and susceptibility to mechanical breakdown that play a more important role in controlling chemistry and mineralogy of fine-grained carbonate particles than do loss or gain of magnesium after burial of these sediments.

The occurrences, composition and genesis of Recent dolomites are different, from these parameters can be deduced that the most suitable conditions for the deposition of dolomite are : (1) Increased pH value, (2) Increased al -



kaline reserve, (3) Increased partial pressure of  $\text{CO}_2$ , (4) Presence of a major amount of organism with Mg- calcite in tests, (5) Predominant sedimentation of fine-grained material, (6) Probably also an absence of a larger amount of organic matter, (7) Excess of Mg ions due to gypsum precipitation.



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