

## OXYGEN ISOTOPE COMPOSITION AND Sr/Ca RATIO: GEOCHEMICAL EVIDENCES FOR THE ORIGIN OF DOLOMITE IN MESSINIAN DIATOMACEOUS SEQUENCES FROM CENTRAL SICILY

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**ABSTRACT.** — Mineralogy of the carbonate component, oxygen isotope composition of dolomites and Sr/Ca atom ratios have been determined in 53 samples from six diatomaceous sequences outcropping in central Sicily.

The results allow to distinguish dolomites from at least three different genetic environments: *a*) dolomite formed by influxes of meteoric waters in marine basins ( $\delta^{18}\text{O}$  values more negative than those of the coexisting  $\text{CaCO}_3$ : up to  $\sim -2\text{‰}$ ; 1000 Sr/Ca atomic ratio averaged 2.07); *b*) dolomite formed by replacement of the existing  $\text{CaCO}_3$  (calcite or aragonite) in normal marine or moderately restricted basins ( $\delta^{18}\text{O}$  values, from +1.3 to +4.4 ‰, substantially analogous to those of the coexisting  $\text{CaCO}_3$ ; 1000 Sr/Ca has an average of 1.76, but the ratio can exceed the value of 10 in the presence of aragonite); *c*) dolomite primarily precipitated from marine waters extremely evaporated (high positive values of  $\delta^{18}\text{O}$ : up to  $\sim +9\text{‰}$ ; low content of strontium: 1000 Sr/Ca < 1).

**RIASSUNTO.** — La mineralogia della frazione carbonatica, la composizione isotopica dell'ossigeno nelle dolomiti e i rapporti atomici Sr/Ca sono stati determinati in campioni di sei sequenze diatomiche affioranti nella Sicilia centrale.

In base ai risultati ottenuti sono stati riconosciuti tre differenti tipi di dolomite corrispondenti ad altrettanti ambienti genetici: *a*) dolomite originata per diluizione di acque marine per infussi di acque meteoriche (valori di  $\delta^{18}\text{O}$  più negativi rispetto a quelli del  $\text{CaCO}_3$  coesistente: fino a circa  $-2\text{‰}$ ; valore medio dei rapporti atomici 1000 Sr/Ca = 2); *b*) dolomite originata per sostituzione da un precursore carbonatico (calcite o aragonite) in ambiente marino normale o moderatamente ristretto (valori di  $\delta^{18}\text{O}$  da +1,3 a +4,4 ‰, sostanzialmente simili a quelli del  $\text{CaCO}_3$  coesistente; valore medio dei rapporti atomici 1000 Sr/Ca = 1,76 ma, in presenza di aragonite, il rapporto può superare il valore di 10); *c*) dolomite di precipitazione primaria in acque marine fortemente concentrate per evaporazione (valori molto positivi di  $\delta^{18}\text{O}$ : fino a circa +9 ‰; bassi contenuti di stronzio: 1000 Sr/Ca < 1).

### Introduction

The diatomaceous sequences, underlying the Messinian evaporites of the Mediterranean area, comprise dolomites irregularly alternating with marly and carbonate levels. These materials commonly contain dolomite as the only carbonate phase or associated with calcite and/or aragonite. Isotopic, chemical, mineralogical, and textural data, obtained from Sicilian sequences (Tripoli Formation), point out widely variable environments of deposition (McKENZIE et al., 1979-1980; BELLANCA et al., 1982a, 1982b, 1982-83). So, levels attributed to normal marine or moderately restricted basins are intercalated with levels showing evidences of a deposition in marine waters extremely concentrated by evaporation; also, isotopic data relative to the carbonate component of some samples are indicative of periodical influxes of meteoric waters (BELLANCA et al., 1982a).

The behaviour of strontium and the oxygen isotope composition of dolomites are studied, in the present work, together with the mineralogy of the carbonate fraction of samples from diatomaceous sequences in central Sicily. In addition to verify to what extent the variations of Sr are depending on the depositional environment, the Authors look for possible answers to the fascinating problem of the dolomite formation.

### Materials and methods

The locations of the Sutera (UB877546), Gaspa Torre (VB304635), Poggio Muto (UB811269), Cozzo Disi (UB835525), Vil-

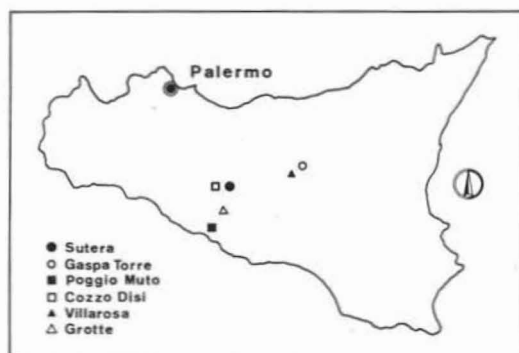


Fig. 1. — An outline map of Sicily showing the locations of the studied sections.

larosa (VB246612), and Grotte (UB838402) sections are reported in fig. 1. Details on lithology and stratigraphy, further mineralogical data and textural features, concerning these sections, are reported in the works of BELLANCA et al. (1982 a, 1982-83) in which are also to be found some isotopic data mentioned in the present work. Only samples containing dolomite were studied among those collected in the above-cited sections.

The oxygen isotope composition of the dolomite was determined according to well-known procedures suggested by MCCREA (1950). When both  $\text{CaCO}_3$  and dolomite were present, the procedures used were those suggested by EPSTEIN et al. (1964) and by BECKER and CLAYTON (1972). The analytical results are expressed in  $\delta\text{‰}$  units and are reported against the PDB-1 standard.

The Sr and Ca concentrations were determined by AA-spectrophotometry from solutions obtained by treating the samples with diluted HCl. An excess of La was added to the sample and standard solutions according to indications in the ANONIMO'S manual (1968).

## Results and discussion

In addition to the oxygen isotopic ratios in dolomites, Sr and Ca concentrations and the relative proportions of carbonate minerals are shown in table 1.

The formation of dolomite in the studied sequences is attributed to different environmental conditions which also affected the distribution of Sr. So, we can distinguish the following groups:

a) *Diatomites of Villarosa, Gaspa Torre*

and *Cozzo Disi*: the dolomite, in subordinate amounts compared to calcite, shows  $\delta^{18}\text{O}$  values more negative than those of the calcite (calcite: from +1.21 to +2.50 ‰; dolomite: from -1.79 to +1.17 ‰). The process of dolomitization may have occurred under conditions substantially different from those acting during the precipitation of  $\text{CaCO}_3$ . In particular, dilution of pore-waters by periodical inflows of meteoric water, probably, promoted the formation of dolomite.

These samples ( $n = 7$ ) have an average content of Sr = 472 ppm ( $\sigma = \pm 182$ ) and 1000 Sr/Ca averaged 2.07 ( $\sigma = \pm 0.32$ ).

b) *Diatomites of Sutera and Poggio Muto*: the dolomite, subordinate to calcite, shows  $\delta^{18}\text{O}$  values slightly more positive than those of the calcite (calcite: from +0.01 to +2.64 ‰; dolomite: from +1.27 to +4.36 ‰). In these samples the formation

TABLE 1  
*Isotopic data, mineralogy of the carbonate fraction, and concentrations of Sr and Ca in the studied samples*

Sample	Lithology	Mineralogy of the carbonate fraction		$\delta^{18}\text{O}$ ‰ dolomite	Sr ppm	Ca ppm	1000 Sr/Ca atom ratio	
		Calcite	Aragonite Dolomite					
S1	diatomite	90	10	+2.53	414	12.09	1.57	
S2	"	88	12	+2.80	8	2.04	0.80	
S3	"	92	8	+2.92	414	10.58	1.79	
S4	"	96	4		567	13.95	1.82	
S5	dolomitic marl	91	100	+7.54	217	14.55	0.68	
S6	diatomite	91	9	+2.86	462	11.44	1.85	
S7	"	90	10	+2.42	460	13.84	1.55	
S8	"	91	9	+2.21	477	11.06	1.87	
S9	"	92	8	+1.27	646	12.42	2.20	
S10	"	92	8	+1.57	414	10.82	1.75	
S11	dolomitic marl	79	100	+6.67	100	10.02	0.46	
S12	diatomite	92	21	+2.48	710	7.02	4.42	
S13	"	82	18	+2.65	408	8.74	1.91	
S14	"	94	6	+2.54	540	9.74	1.85	
S15	"	92	8	+4.36	594	17.84	1.55	
S17	"	89	31	+2.95	413	10.77	1.75	
S18	calcareous-dolomitic marl	78	74	+6.82	583	18.44	1.37	
S19	"	80	20	+3.80	647	11.89	1.90	
S20	dolomitized diatomite	100	100	+6.77	71	5.66	0.58	
S21	"	100	100	+7.76	130	9.49	0.63	
S22	"	100	100	+7.17	121	10.13	0.55	
S23	"	100	100	+6.17	189	8.71	0.99	
S24	calcareous dolostone	23	77	+7.12	248	25.26	0.45	
S25	dolomitized diatomite	100	100	+6.27	176	8.46	0.93	
S26	calcareous dolostone	36	64	+7.19	269	27.13	0.45	
S27	dolomitic marl	100	100	+8.89	195	13.36	0.63	
S28	"	100	100	+6.13	229	10.84	1.04	
S29	"	100	100	+8.16	410	22.59	0.83	
S30	dolomite	100	100	+7.05	158	13.14	0.55	
S31	dolomitic marl	5	87	0	+3.51	4646	23.50	9.04
S32	diatomite marl	1	100	+7.08	228	16.50	0.56	
S33	dolomitic limestone	57	48	+4.72	733	26.86	1.28	
S36	aragonitic marl	2	95	3	+1.98	7871	25.91	10.02
S37	"	3	94	3	+2.29	7557	22.42	10.66
S38	"	32	52	16	+2.31	2654	27.67	1.72
S39	calcareous-dolomitic marl	17	83	+6.63	364	11.91	1.40	
PM	diatomite	88	12	+3.80	207	6.99	1.25	
PM	"	89	11	+2.57	346	10.29	1.66	
PM1	dolomitized diatomite	100	100	+7.88	125	2.91	1.48	
PM2	"	100	100	+8.53	100	4.47	1.02	
GR	dolostone	100	100	+7.57	102	22.46	0.91	
GR	"	100	100	+7.84	291	18.23	0.70	
GT24	dolomitized diatomite	100	100	+7.37	368	18.36	0.91	
GT25	"	100	100	+7.68	244	16.83	0.86	
GT31	diatomite	95	5	-1.79	270	4.71	2.62	
GT34	"	90	10	+0.30	346	7.09	2.00	
GT35	"	95	5	+1.17	717	16.40	2.13	
GT36	"	91	9	+0.43	954	13.40	1.92	
GT37	"	91	9	-0.32	334	7.13	2.14	
CD	"	95	5	+0.50	689	17.30	1.82	
CD	"	95	5	+0.50	689	17.30	1.82	
CD1	"	22	78	+4.18	436	10.00	1.99	
CD	"	89	11	-0.25	396	10.76	1.64	

S = Sutera; PM = Poggio Muto; GR = Grotte; GT = Gaspa Torre; CD = Cozzo Disi; V = Villarosa.

of dolomite occurred at expense of the existing calcite in waters substantially similar or slightly more evaporated than those in which the calcite precipitated (normal marine or moderately evaporated waters).

The mean content of Sr is 449 ppm ( $\sigma = \pm 106$ ;  $n = 15$ ); 1000 Sr/Ca averaged 1.76 ( $\sigma = \pm 0.22$ ).

c) *Dolomitized diatomites of Sutera, Poggio Muto and Gaspa Torre*: the dolomite, of micritic texture, covers, more or less extensively, the felt of diatoms and impregnates the sediment preserving, however, the original textures. The dolomite, which is the only carbonate phase present in the samples, shows very positive values of  $\delta^{18}\text{O}$  (from +6.17 to +8.53 ‰). Textural features and isotopic data suggest a formation of these dolomites by precipitation in interstitial spaces of the diatomaceous sediment from highly evaporated waters.

Mean value of Sr = 169 ppm ( $\sigma = \pm 90$ ;  $n = 9$ ); 1000 Sr/Ca averaged 0.86 ( $\sigma = \pm 0.29$ ).

d) *Carbonate and marly levels of Sutera and Grotte* intercalated with the diatomites or overlying these to mark the passage towards the Basal Limestone or the Gypses. Under observation in thin section these dolomites appear anhedral and very fine-grained. The highly positive  $\delta^{18}\text{O}$  values (up to +8.89 ‰) are indicative of restricted environments characterized by extremely concentrated waters. We suggest the hypothesis of a primary precipitation of the dolomite or, at the most, the formation of this at a very early diagenetic stage. In some samples the dolomite is associated with variable quantities of calcite which always shows very negative values of  $\delta^{13}\text{C}$  (up to -38.40 ‰). The formation of the calcitic phase is attributed to calcitization of pre-existing gypsum, after the formation of dolomite. Such a genetic mechanism is suggested by the isotopic data but also by textural evidences such as: monoclinic or prismatic moulds of formerly present gypsum crystals and presence of pyrite produced from reduced sulphur.

In samples with entirely dolomitic carbonate component Sr averaged 256 ppm ( $\sigma = \pm 126$ ;  $n = 9$ ); mean value of the 1000 Sr/Ca ratios: 0.72 ( $\sigma = \pm 0.20$ ).

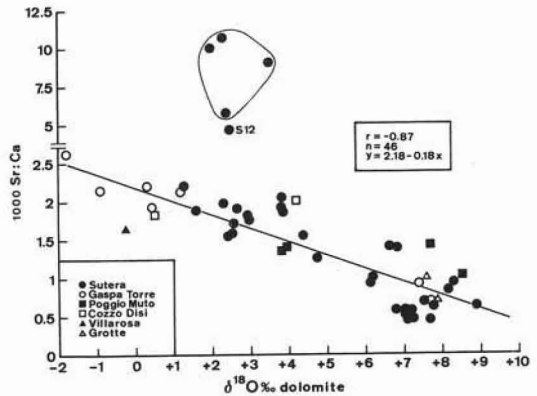


Fig. 2. — Relation between the  $\delta^{18}\text{O}$  of dolomites and 1000 Sr/Ca atom ratios in the studied samples. The representative points of prevalently aragonitic samples are located within the delimited area.

e) *Prevalently aragonitic marly samples of Sutera*: the dolomite and the coexisting aragonite show similar values of  $\delta^{18}\text{O}$  ( $\approx +2.50$  ‰). The formation of dolomite may have occurred at the expense of aragonite from normal marine or partially evaporated waters.

According to literature data (BAUSCH, 1968; BATHURST, 1971), these samples show the highest concentrations of Sr. In particular, the values of about 8000 ppm, relative to the two samples containing  $\sim 90$  % of aragonite, result similar to those predicted by KINSMAN (1969) for aragonite inorganically precipitated in marine waters.

From the above reported data one can observe, excluding the aragonitic samples, that the highest Sr/Ca ratios are those of the diatomites showing evidences of meteoric water influxes in the sedimentation basin (group a). The ratios are, instead, slightly lower in the diatomites deposited in normal marine to moderately restricted environments (b). Finally, the lowest values of the ratios are registered in the dolomitized diatomites (c) and in the carbonate and marly levels (d), interbedded in the preevaporitic sequences, which show evidences of a deposition in extremely concentrated waters.

A binary diagram (fig. 2), in which Sr/Ca ratios and dolomite  $\delta^{18}\text{O}$  values are plotted against, shows an inverse correlation between the two parameters ( $r = -0.87$ ; significant for  $p = 0.001$ ; aragonitic samples are excluded). On the other hand, BELLANCA et al.

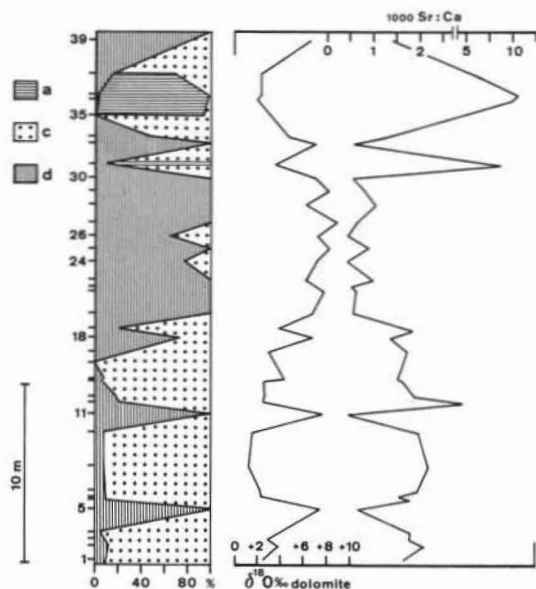


Fig. 3. — Profiles illustrating the variations of the percentages and  $\delta^{18}\text{O}$  of dolomites and the 1000 Sr/Ca atom ratios through the Sutera stratigraphic sequence; *a* = aragonite, *c* = calcite, *d* = dolomite.

(1982 b) report a similar correlation ( $r = -0.71$ ) between Sr/Ca ratios of diatomites and  $\delta^{18}\text{O}$  values relative to the calcitic component of the same samples. Then, we deduce that, in the pre-evaporitic sequences, the evolution towards restricted environmental conditions involves enrichment in  $^{18}\text{O}$  and, contemporaneously, depletion in the Sr/Ca ratio of the carbonate phases. The Sr/Ca ratio reflects that of the original solutions which, under evaporitic conditions, is determined by solubility products of gypsum, anhydrite, celestite, carbonate phases and by partition coefficients of Sr between solutions and minerals (HOLSER, 1979).

The significance of the  $\delta^{18}\text{O}$  values and of the Sr/Ca ratios, as markers of a typical environmental evolution, is also proved in the case of a vertical sampling. In fact, the profiles reported in the fig. 3 (stratigraphic sequence of Sutera) show a positive correlation between percentages and  $\delta^{18}\text{O}$  of dolomite while inverse correlations exist between these two parameters and the Sr/Ca ratios. In this sequence, levels deposited in highly concentrated marine waters ( $\delta^{18}\text{O} > +6\text{‰}$ ) show dominant presence of dolomite and Sr/Ca ratios  $< 1$ . The dolomite de-

creases, instead, in favour of calcite or aragonite in levels, deposited in normal marine or moderately restricted conditions, which show Sr/Ca ratios greater than 1.

The exact mechanism of the dolomite formation is a still open problem. According to a widely diffused opinion, the dolomite does not precipitate primarily in marine waters but forms by replacement of pre-existing calcite or aragonite (LIPPMANN, 1973; VON ENGELHARDT, 1977). FRIEDMAN and SANDERS (1967), in defining the dolomite as an « evaporitic mineral », are sceptical about its direct precipitation and define « primary dolomite » that originated by penecontemporary replacement of Ca-carbonate-rich sediments. FOLK and LAND (1975) suggest that dolomite can readily form, in « schizoline » environments, by periodical dilution of brines with meteoric waters. Recently, PISCIOTTO and MAHONEY (1982) have reported dolomite primarily precipitated in deep sea organic carbon-rich sediments.

In some cases the dolomite of the studied pre-evaporitic sequences precipitated, according to FOLK and LAND (cited work), from marine waters diluted by inflows of meteoric waters.

Dolomite clearly originated by pre-existing calcite occurs in some other diatomaceous levels.

Finally, we have dolomites, showing extremely positive values of  $\delta^{18}\text{O}$ , formed in restricted conditions from highly evaporated waters. The textural features (anhedral and very fine-grained dolomite) could indicate, according to WEBER (1964) and FONTES et al. (1972), a primary precipitation of these dolomites or at the most, according to VEIZER and DEMOVIC (1974), an origin by replacement of not or only partially lithified muds (early diagenesis). A dolomite showing similar  $\delta^{18}\text{O}$  values, found in the sediments of an hypersaline lake (Solar Lake), is interpreted as a replacement product of a pre-existing aragonite (AHARON et al., 1977). MCKENZIE et al. (1979-1980) attributed to the same process the formation of dolomite in the two diatomaceous sections of Falconara (Agrigento) and Monte Capodarso (Caltanissetta).

We have found evidences of a transformation aragonite  $\rightarrow$  dolomite only in the

aragonitic marls. In these samples the two coexisting phases show analogous isotopic compositions. As the  $\delta^{18}\text{O}$  values of this dolomite ( $\approx +2.5\%$ ) are very different from the averaged value ( $+7\%$ ) for the dolomites not associated with aragonite, it is possible that the formation of these last dolomites is to refer to an other mechanism.

Elaborating experimental data on the repartition coefficients of Sr between aragonite and dolomite (VEIZER and DEMOVIC, cited work), we obtain that a dolomite, derived from an aragonite with concentration of Sr similar to those measured in the Sutera samples ( $\text{Sr} = \sim 8000$  ppm), should contain almost 500 ppm of Sr. Also, BUTLER (1973) report the value of 660 ppm for a dolomite derived from aragonite under evaporitic conditions. These values are both higher com-

pared to the mean value of strontium in samples with entirely dolomitic carbonate component. Finally, the Sr/Ca ratios of these samples ( $\text{Sr}/\text{Ca} < 1$ ) are lesser than those reported by VEIZER and DEMOVIC (cited work) for dolomites formed in an early diagenetic stage.

In conclusion, the oxygen isotopic composition and the Sr concentrations, relative to those dolomites which do not keep memory of an aragonitic precursor, are consistent with the interpretation that the dolomite formed as a primary chemical precipitate.

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## REFERENCES

- AHARON P., KOLODNY Y. and SASS E. (1977) - *Recent hot brine dolomitization in the «Solar Lake», Gulf of Elat, isotopic, chemical and mineralogical study.* Jour. Geology, 85, 27-48.
- ANONIMO (1968) - *Analytical methods for atomic absorption spectrophotometry.* Perkin Elmer Corp., Norwalk Conn..
- BATHURST R.G.C. (1968) - *Carbonate sediments and their diagenesis.* Elsevier, 620 pp..
- BAUSCH W.M. (1968) - *Outlines of distribution of strontium in marine limestones.* In Recent Developments in Carbonate Sedimentology in Central Europe (eds. G. Müller and G.M. Friedman), Springer-Verlag, pp. 106-115.
- BECKER R.H. and CLAYTON R.N. (1972) - *Carbon isotopic evidence for the origin of a banded iron-formation in Western Australia.* Geochim. Cosmochim. Acta, 36, 577-596.
- BELLANCA A., CALDERONE S. and NERI R. (1982 a) - *Isotopic, mineralogical and textural study of diatomaceous sediments of the Lower Messinian (Tripoli Formation) from central Sicily.* Miner. Petrogr. Acta, 26, 1-14.
- BELLANCA A., DECIMA A. and NERI R. (1982 b) - *Indagini composizionali su diatomiti messiniane (Tripoli) della Sicilia centrale.* Miner. Petrogr. Acta, 26, 49-59.
- BELLANCA A., CALDERONE S. and NERI R. (1982-83) - *Evidenze geochimiche e mineralogiche di episodi evaporitici nella sequenza diatomitica (Messiniano «pre-evaporitico») di Sutera (Sicilia centrale).* In questo volume.
- BUTLER G.P. (1973) - *Strontium geochemistry of modern and ancient calcium sulphate minerals.* In The Persian Gulf (ed. B.H. Purser), Springer-Verlag, pp. 423-452.
- ENGELHARDT Von W. (1977) - *The origin of sediments and sedimentary rocks.* In Sedimentary Petrology, Part III, Schweizerbart, pp. 359.
- EPSTEIN S., GRAF D.L. and DEGENS E.T. (1964) - *Oxygen isotope studies on the origin of dolomites.* In Isotopic and Cosmic Chemistry (eds. H. Craig, S.L. Miller and G.T. Wasserburg), North-Holland Publ. Comp., pp. 169-190.
- FOLK R.L. and LAND L.S. (1975) - *Mg/Ca ratio and salinity: two controls over crystallization of dolomite.* Amer. Ass. Petroleum Geol. Bull., 59, 60-68.
- FONTES J.-CH., LETOLLE R., NESTEROFF W.D. and RYAN W.B.F. (1972) - *Oxygen, carbon, sulfur and hydrogen stable isotopes in carbonate and sulfate mineral phase of Neogene evaporites, sediments, and in interstitial water.* DSDP Initial Reports, 13, 788-796.
- FRIEDMAN G.M. and SANDERS J.E. (1967) - *Origin and occurrence of dolostones.* In Developments in Sedimentology: Carbonate Rocks (eds. G.V. Chilingar, H.J. Bissel and R.W. Fairbridge), Elsevier Publ. Comp., pp. 267-348.
- HOLSER W.T. (1979) - *Trace elements and isotopes in evaporites.* In Marine Minerals (ed. R.G. Burns), Miner. Soc. Amer. Short Course Notes, pp. 295-346.
- KELTS K. and MCKENZIE J.A. (1982) - *Diagenetic dolomite formation in Quaternary anoxic diatomaceous muds of Deep Sea Drilling Project Leg 64, Gulf of California.* DSDP Initial Reports, 64, 553-569.

- KINSMAN D.J.J. (1969) - *Interpretation of Sr<sup>+</sup> concentrations in carbonate minerals and rocks.* Jour. Sed. Petrology, 39, 486-508.
- LIPPMANN F. (1973) - *Sedimentary Carbonate Minerals.* Springer-Verlag, pp. 228.
- MCCREA J.M. (1950) - *On the isotopic chemistry of carbonates and a paleotemperature scale.* Jour. Chem. Phys., 18, 849-857.
- MCKENZIE J.A., JENKYN H.C. and BENNET G.G. (1979-1980) - *Stable isotope study of the cyclic diatomite-claystones from the Tripoli Formation, Sicily: a prelude to the Messinian salinity crisis.* Paleogeogr. Paleoclim. Paleoecol., 29, 125-141.
- PISCIOTTO K.A. and MAHONEY J.J. (1981) - *Isotopic survey of diagenetic carbonates, Deep Sea Drilling Project Leg 63.* DSDP Initial Reports, 63, 595-609.
- VEIZER J. and DEMOVIC R. (1974) - *Strontium as a tool in facies analysis.* Jour. Sed. Petrology, 44, 93-115.
- WEBER J.N. (1964) - *Trace element composition of dolostones and dolomites and its bearing on the dolomite problem.* Geochim. Cosmochim. Acta, 28, 1817-1868.