

Trace elements in Cenozoic Algal Limestones of the Venetian Region: Mn^{2+} - Sr^{2+} negative correlation

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ABSTRACT — Cenozoic rhodolites from Veneto region are studied from the geochemical viewpoint, taking into consideration the Mg^{2+} , Sr^{2+} , Fe^{2+} and Mn^{2+} contents. The Cenozoic rhodolites presently consist of low-Mg calcite (LMC); they have lower Sr^{2+} and Mg^{2+} contents and higher Mn^{2+} and Fe^{2+} contents with respect to the modern nodules. This situation support the hypothesis that the Cenozoic rhodolites analysed were originally composed of high-Mg calcite (HMC), which altered into LMC during meteoric diagenesis. The chemical behaviour and in particular the negative correlation between Sr and Mn, are consistent with the model of meteoric diagenesis recently proposed by Pingitore (1978) and Brand & Veizer (1980).

RIASSUNTO — [Elementi in traccia in calcari algali cenozoici del Veneto: correlazione negativa fra Mn^{2+} e Sr^{2+}] — Vengono studiati calcari algali cenozoici del Veneto da un punto di vista geochimico, mediante l'analisi dei seguenti elementi in traccia: Mg^{2+} , Sr^{2+} , Fe^{2+} e Mn^{2+} . Questo set di elementi è stato scelto perché offre la possibilità di dedurre le caratteristiche chimiche dell'ambiente di deposizione dei noduli algali, la mineralogia delle fasi carbonatiche primarie e di valutarne il grado di diagenesi meteorica (Friedman, 1969; Brand & Veizer, 1980).

I campioni studiati contengono essenzialmente *Melobesiae* e si possono classificare come biocalcareni e biocalciruditi. I noduli algali sono qui indicati col termine di rodoliti (Bosellini e Ginsburg, 1971). I dati analitici da noi ottenuti sono stati confrontati con le medie riportate nella letteratura per le *Melobesiae* attuali (Milliman, 1974).

I rodoliti cenozoici sono composti di calcite a basso contenuto di Mg (LMC), mentre quelli attuali sono costituiti di calcite ricca di Mg (HMC). Inoltre rispetto agli attuali, i noduli algali cenozoici presentano un impoverimento in Sr^{2+} e Mg^{2+} ed un arricchimento in Mn^{2+} e Fe^{2+} .

La variazione nel tenore in Sr e Mn ci permette di formulare l'ipotesi che anche i rodoliti analizzati fossero originariamente composti di HMC, trasformata in LMC per diagenesi meteorica.

D'altra parte la relazione tra i contenuti in Fe e Mn trovati, potrebbe indicare un ambiente di deposizione lagunare, dove il tenore in Mn sarebbe stato elevato già dall'origine. Tuttavia non è possibile accettare a priori questa interpretazione senza ulteriori conferme chimiche e biologiche. Preferiamo quindi per ora attribuire l'elevato contenuto in Mn dei nostri campioni all'arricchimento diagenetico. Secondo questa ipotesi inoltre la correlazione negativa tra Sr e Mn, generalmente osservata nei campioni cenozoici, ben si accorda col modello diagenetico proposto da Pingitore (1978) e, qualora si considerino insieme con le variazioni chimiche, le conseguenti modificazioni tessiturali, è anche in armonia col modello di diagenesi meteorica, recentemente presentato da Brand e Veizer (1980).

INTRODUCTION

Trace elements geochemistry in carbonate sediments is a valid source of information on the water chemistry of depositional environments, and provides us with a means of determining the original mineral phase, and an evaluation of the degree of meteoric diagenesis of the resulting carbonate rocks (Friedman, 1969; Brand & Veizer, 1980).

In this paper, the authors report Mg, Sr, Mn and Fe data on Cenozoic algal limestones from the Venetian region.

This report aims at being the first contribution of systematic research on the *Melobesiae* Limestones

(« Calcarei Nulliporici ») of the Venetian region, from the petrographic, mineralogical and geochemical viewpoints. The aim is that of completing, with sedimentological and diagenetic information, knowledge on these deposits, which have until now mainly been studied from the paleontological and stratigraphic viewpoints (Beckman, Bolli, Kleboth & Proto Decima, 1982).

MATERIAL ANALYSED

The samples studied come from some Lower Miocene outcrops of the Eastern Veneto area (Val Calda, Rolle, Miane, Campea and Saccol), where the sequence shows quite uniform characteristics. The total thick-

ness is 25-20 m: a better estimation is not possible due to the detritic cover.

The complete sequence is as follows:

At the base are layers between 50 cm and 1 m thick of biocalcarenites and biocalcirudites, pale brown in colour, well cemented, and containing progressively increasing quantities of rhodophyceal debris, with secondary skeletal fragments of benthic macro- and micro-foraminifers, of Bryozoa, Echinids and Anellid tubes. At the top the algal nodules gradually become more complete and larger, so that the top is composed of layers 1-3 m thick, formed of real rhodolites (1) which are whitish, about 10 cm in diameter, more or less compacted, and embedded in a grey, almost exclusively terrigenous matrix, of mainly coarse sandstone.

ANALYTICAL DATA

Mg, Mn and Fe were determined with an AAS, preparing the solutions according to the method of Veizer *et al.* (1978). Sr was determined by means of X-ray fluorescence. The insoluble residue (IR) was estimated gravimetrically. Ca was calculated by means

of the equation $[100-(I.R.-MgCO_3)] \cdot 0,4$ (Veizer *et al.*, 1978).

Both algal nodules separated from the host-rock (CV₈, CV₉, CV₁₁, ROA, ROB, ROC, ROD, MC₁₃, MC₁₄ and MC₁₅) and total rock, i.e. host-rock and rhodolites together, were analysed. However, since isolated rhodolites also contained matrix and variable quantities of terrigenous material, all analytical data were later recalculated on the total carbonate (insoluble residue-free) basis. The values thus obtained, both in the isolated nodules and in the whole samples, show a very heterogeneous distribution, which is in any case independent of the insoluble residue (2). For this reason, it was not thought appropriate to keep the two sample groups distinct.

Table 1 shows the values obtained.

(1) Rhodolites: from the class name of the algae nodules and detached branched growth with a nodule form composed principally of coralline algae (Bosellini & Ginsburg, 1971).

(2) Various authors (Bencini & Turi, 1974) have shown that the I.R. does not influence the determinations of Mn, since this element is essentially associated with the carbonate fraction.

Table 1

Samples	I.R.%	Ca%	Mg ppm	Fe ppm	Sr ppm	Mn ppm	MgCO ₃ mol.%
CV ₁	30.09	27.17	5698	16850	721	110	2.33
CV ₂	24.66	29.43	5080	11639	845	64	2.07
CV ₃	29.82	27.22	6093	12339	750	84	2.48
CV ₄	21.26	30.65	6063	12289	664	68	2.48
CV ₅	37.33	23.36	12298	9367	698	120	5.03
CV ₆	38.21	22.91	13022	8058	546	146	5.30
CV ₇	17.30	31.97	7898	16042	700	89	3.25
CV ₈	5.31	37.14	5319	3015	698	71	2.17
CV ₉	23.23	28.92	12946	15864	709	91	5.23
CV ₁₁	3.04	38.11	4853	1913	762	54	1.98
CV ₁₂	27.74	28.90	8679	20569	1000	134	3.53
ROA	36.82	24.05	8802	5093	675	46	3.59
ROB	4.30	37.69	4224	4386	499	116	1.72
ROC	25.48	28.22	11472	7020	761	62	4.67
ROD	10.68	35.09	4561	5878	902	37	1.86
MC ₁₃	30.51	26.62	22885	17264	912	115	9.27
MC ₁₄	6.97	36.13	7797	4144	1052	61	3.18
MC ₁₅	3.01	38.26	3862	4306	1071	61	1.56
	I.R.%	Ca%	Mg ppm	Fe ppm	Sr ppm	Mn ppm	MgCO ₃ mol.%
N=18	20.70	30.65	8414	9776	775	84	3.42
m-M	3.01/ 38.21	22.91/ 38.26	3862/ 22885	1913/ 20569	499/ 1071	37/ 146	1.56/ 9.27
σ	10.8	5.09	4563	5584	154	30	1.80

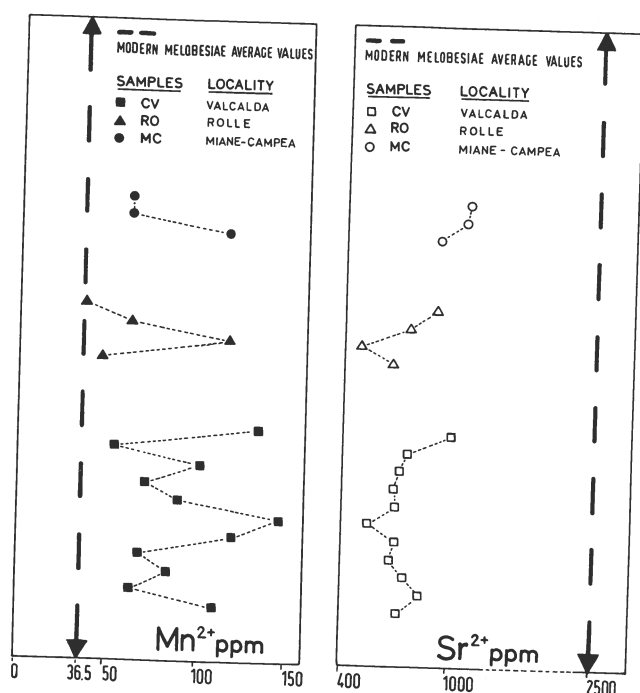
COMMENTS

— Mg

The samples analysed were composed of calcite with low Mg contents (3.42 moles % of MgCO_3), while the corresponding modern algal forms from Bermuda (Bosellini & Ginsburg, 1971) and various other localities (Milliman, 1974) are composed of about 18 moles % MgCO_3 .

— Sr

Sr occurs in varying quantities from 499 ppm to 1071 ppm. These values are significantly lower than the average values of modern Melobesia (2500 ppm; Milliman, 1974) (Text-fig. 1).



Text-fig. 1 - Mn^{2+} and Sr^{2+} contents of Cenozoic rhodolites with respect to modern Melobesia.

— Mn

Mn contents range from 37 to 146 ppm; the corresponding modern forms contain 36.5 ppm on average (Milliman, 1974).

The average value of the analysed samples is 84 ppm; thus, Mn values are generally double with respect to recent algal nodules (Text-fig. 1).

— Fe

Fe ranges between 3015 and 20569 ppm, while the corresponding modern forms contain an average of 182 ppm. Fe is therefore significantly more abundant than in the limestones analysed by Veizer, Lemieux, Jones, Giblin & Savell (1978).

DISCUSSION

Sr, Mg, Mn and Fe replace Ca in the CaCO_3 lattice due to different mechanisms: diadochy, adsorption by unsatisfied charges, and also by lattice anomalies. These different possibilities may be related on one hand to the original carbonate phase (and thus to the depositional environment of the sediment), on the other, to the diagenetic mechanism and conditions.

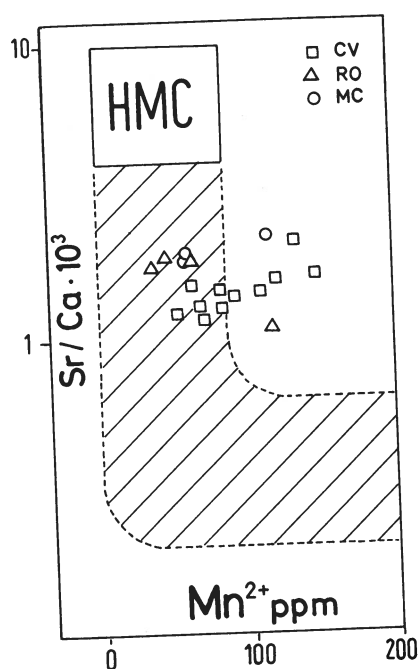
In effect, the original mineral phases and their later diagenetic stabilization are controlled by the following factors: partition coefficient (K), water/rock ratio, chemistry of the interstitial water, slow dissolution - reprecipitation diffusion, and fast flow transport into the pore water. It has been shown that, during meteoric diagenesis, changes in these factors may alter the original mineral phase (A - LMC; HMC - LMC) (3), bringing about a decrease in Sr and Mg and an increase in Mn and Fe (Pingitore, 1978; Brand & Veizer, 1980).

The composition of the Cenozoic rhodolites analysed, which turns out to be more depleted in Sr and Mg and richer in Mn and Fe with respect to modern Melobesia (Text-fig. 1), may be explained by diagenetic alterations similar to those indicated by the above authors. It may therefore be admitted that the Cenozoic rhodolites were originally composed of HMC and contained larger Sr and Mg contents and smaller Mn and Fe ones. The current values were reached by ion transfer through the « Messenger film », as suggested by Brand & Veizer (1980), in a partially open diagenetic system. These conditions are confirmed by the fact that the decrease in Sr is not so great as it could have been in a definitely open system (see, for example, the oolitic limestones, Scudeler Baccelle, 1980, and the Mississippian Burlington Limestones, Brand & Veizer, 1980). The textural features observed in thin section also support this hypothesis, owing to the occurrence of pseudosparite. Moreover, as may be seen in Text-fig. 2, most of the data points fall in the HMC transformation field in a partially open system, while others (CV₁, CV₅, CV₆, CV₉, CV₁₂, ROB and MC₁₃) are shifted towards a more open system.

In this partially open system, the Sr « auto-depletion » (its partition coefficient being less than 1) and the Mn « auto-enrichment » (whose coefficient is greater than 1) were possible, according to the process proposed by Pingitore (1978).

However, the concomitant possibility of « allo-enrichment » due to the terrigenous fraction, supply-

(3) A = aragonite, LMC = Low-Mg calcite, HMC = high-Mg calcite.



Text-fig. 2 - The data points in the dashed area fit the Brand & Veizer model (1980); the others, which are shifted towards higher Mn^{2+} contents, fall in the field of open systems.

ing the diagenetic solutions with a large ion contribution, cannot be excluded for Mn. Moreover, the deposition water may have been Mn-rich, corresponding to a lagoonal environment, as shown by the Fe/Mn ratio (Friedman 1968) (Text-fig. 3).

However, these last explanations seem unlikely: on one hand, the IR values of our samples do not correlate with the Mn contents and, on the other, the water chemistry needs to be further confirmed by tests on sodium and potassium contents and by biological associations. Also, reducing conditions, as shown by the occurrence of glauconite, mean greater

availability of Mn^{2+} (replacing for Ca in calcite; Benicini & Turi, 1974).

As regards Fe contents, the very high contents encountered cannot be explained by a simple enrichment parallel to the Mn trend, but, at least according to current knowledge, it may be referred to the contribution of the terrigenous fraction. Further details are necessary before this problem can be solved.

CONCLUSIONS

A) The Mg, Sr, Mn and Fe(?) contents in the samples analysed turn out to be associated essentially with the carbonate fraction, and are independent of the IR variations.

B) The mineral phase (LMC), the composition of minor elements, and the textural characteristics of the rhodolites analysed suggest that their original mineralogy was HMC.

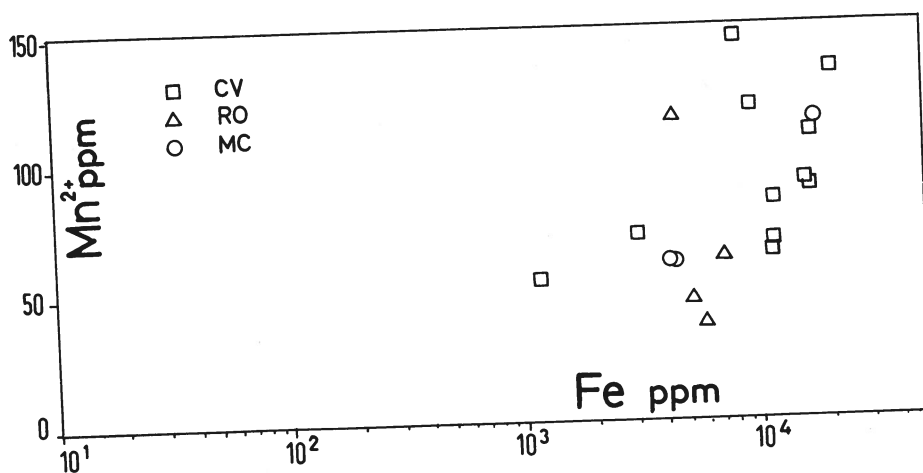
Alteration from HMC to LMC involved a depletion in Sr and Mg contents, and an increase in Mn and Fe (p.p.) during meteoric diagenesis in a partially open system, according to the models proposed by Pingitore (1978) and Brand & Veizer (1980).

C) Further chemical and biological confirmation is necessary in order to verify the chemistry of the depositional environment.

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Text-fig. 3 - Mn^{2+} versus Fe^{2+} contents in the Cenozoic rhodolites.

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