

Differential diagenesis of sedimentary components and the implication for strontium isotope analysis of carbonate rocks

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Received 20 April 1998; accepted 7 July 1999

Abstract

Geochemical analyses of various components (foraminifera, coccoliths and siliciclastic fractions) of limestone and marl samples from the marine Trubi Formation (Early Pliocene) of southern Italy revealed subtle diagenetic contamination. The coccolith fraction is altered from its original value both in its trace element (Sr/Ca, Mg/Ca, Fe/Ca, Mn/Ca, Na/Ca all were higher) and isotopic ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$) composition. Coccolith $^{87}\text{Sr}/^{86}\text{Sr}$ values (limestones 0.709010; marls 0.708951) are lower than those of coeval Early Pliocene seawater (0.709025–60 [Farrell, J.W., Clemens, S.C., Gromet, L.P., 1995. Improved chronostratigraphic reference curve of Late Neogene seawater $^{87}\text{Sr}/^{86}\text{Sr}$. *Geology* 23, 403–406]) and similar to the $^{87}\text{Sr}/^{86}\text{Sr}$ values of Messinian evaporites (0.70887 to 0.70896 [Müller, D.W., Mueller, P.A., 1991. Origin and age of the Mediterranean Messinian evaporites: implications from Sr isotopes. *Earth Planet. Sci. Lett.* 107, 1–12]). Foraminiferal calcite is unaltered and retains its elemental and isotopic composition, with $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.709052) within the range for Early Pliocene seawater. However, unaltered $^{87}\text{Sr}/^{86}\text{Sr}$ values were obtained only when the foraminifera were cleaned in acid to remove all contaminating coccoliths. Simple hand-picking and ultrasonic cleaning in water is inadequate to remove adhering coccoliths and may result in erroneous $^{87}\text{Sr}/^{86}\text{Sr}$ values being quoted. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Foraminifera; Sr isotopes; Trace elements; Stable isotopes; Diagenesis

1. Introduction

Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) have traditionally been used as a chronostratigraphic tool (e.g., Burke et al., 1982; Faure, 1982; Farrell et al., 1995; Patterson et

al., 1995) and also as a proxy for chemical weathering rates over geologic time (e.g., Capo and De-Paolo, 1990; Palmer and Edmond, 1992; Richter et al., 1992). However, diagenesis can alter $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from their original values and a firm understanding of the alteration processes is required if high precision studies are to be conducted effectively. Here, we present new evidence from the

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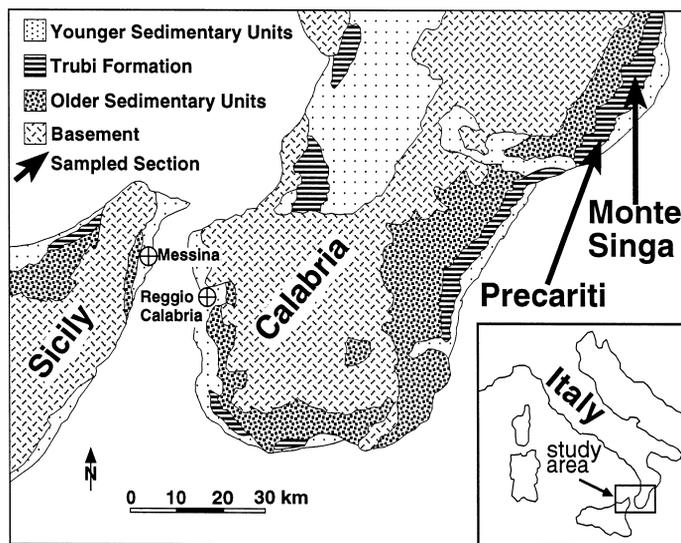


Fig. 1. Geological map of southern Italy showing the location of the Monte Singa and Precariti sections.

Trubi Formation of southern Italy of subtle diagenetic alteration selectively affecting the Sr isotopic composition of certain textural components of sedimentary carbonate rocks (Fig. 1).

2. Methods

2.1. Sample preparation

The Trubi Formation is a marine sedimentary unit that is characteristically composed of alternating limestone and marl layers. The two sections that were analyzed (Precariti and Monte Singa; Fig. 1) were temporally equivalent (Early Pliocene) and were, respectively, 7 and 20 m thick representing 217 and 260 ka of deposition (Hilgen, 1987; Hilgen and Langereis, 1989; Langereis and Hilgen, 1991; Fig. 2).

Samples were disaggregated by soaking in distilled water for 24 h. Individual foraminiferal tests (*Globigerinoides obliquus*) from the Precariti section were hand-picked for geochemical analysis (3–5 mg) washed in distilled water (ultrasound), and then dissolved in 2.5 N HCl. The Monte Singa foraminifera in contrast were crushed and washed in a dilute HCl

solution (0.01 N) to dissolve any carbonate contaminants and to etch the outer surface of the foraminiferal tests. This was followed by an ultrasound wash in distilled water. Monte Singa samples were then dissolved in concentrated acetic acid (80%) to minimize the dissolution of any siliciclastic contaminants and the solution was drawn off before all the carbonate was consumed. The sample solutions were then centrifuged to remove any residue and then dried down and reacidified with 2.5 N HCl.

Coccoliths (3–15 μm) from the Monte Singa section were concentrated by repeated gravity settling to remove the coarser and finer fractions. The concentration of coccoliths (approximately 70–80%) was then checked using both light microscopy and SEM. The coccoliths were washed several times in distilled water and then selectively dissolved using concentrated acetic acid (80%) to minimize any potential contaminating effect of the clay minerals.

The silt/clay fraction was collected by sieving and the siliciclastic component was isolated by dissolving the carbonate fraction in a concentrated weak acid (acetic 80%). The siliciclastic residue was repeatedly rinsed in distilled water and dissolved using a combination of concentrated HF and strong nitric (12 N) acids which was gently heated at 125°C for 24 h.

Precariti Section

Coordinates: UTM 33 627418
4250661

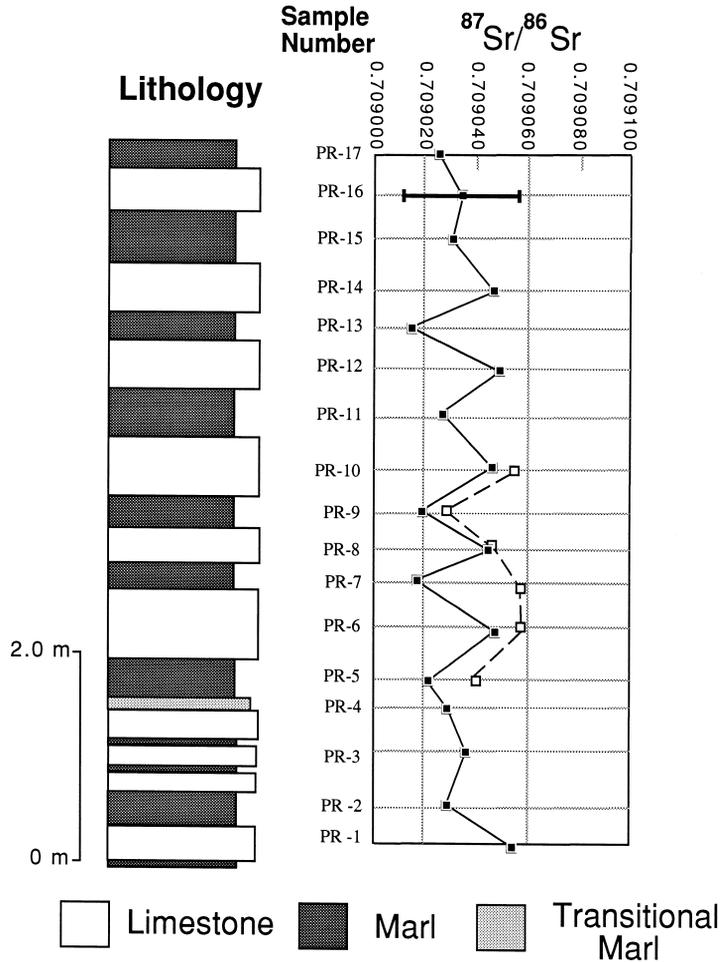


Fig. 2. Stratigraphic section from the Precariti location showing the cyclical relationship of the $^{87}\text{Sr}/^{86}\text{Sr}$ values with lithology. The solid line represents the $^{87}\text{Sr}/^{86}\text{Sr}$ results using the HCl digestion method and no preleaching; the dashed line represents results using the acetic acid digestion method and preleaching. The error bar represents two standard deviations (s.d.).

2.2. Geochemical methods

Sr and Ca were separated from the sample solutions using ion-exchange columns of BioRad AG50 X-8 resin with 2.5 N HCl as the eluting agent. The separation of Sr from Ca was achieved using a second column that used Teflon powder coated with bis(2-ethylhexyl) phosphoric acid (HDEHP), with 0.01 N HCl as the eluting agent. The isotopic composition of the Sr was measured on a Finnigan-MAT

261 multicollector mass spectrometer operated in static mode (100 integrations over 27 min). Replicate analysis of NBS 987 standard over the analysis period had a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710248 ± 20 (2 s.d.) and our laboratory blanks were < 400 pg. All $^{87}\text{Sr}/^{86}\text{Sr}$ values reported here had within-run statistics that were at or below $\pm 1.5 \times 10^{-5}$ (2 s.d.).

Elemental analyses (Sr, Na, Ca, Mn, Mg, Fe) of the bulk foraminiferal and coccolith samples were conducted by ICP-AES (inductively coupled

plasma–atomic emission spectrometry) analysis at ARECO (Nepean, Ontario, Canada).

Oxygen and carbon isotopic compositions of the coccoliths and foraminifera (three to six specimens of *G. obliquus*) were determined at the Ottawa-Carleton Geoscience Centre Stable Isotope Facility at the University of Ottawa. Sample material was baked at 400°C under vacuum to remove any organic compounds and then dissolved with H₃PO₄ and analyzed with a VG (SIRA-12) mass spectrometer.

3. Initial results

3.1. Precariti section

Seventeen marl and limestone samples from the Precariti stratigraphic section of the Trubi Formation

were analyzed (Fig. 2; Table 1). ⁸⁷Sr/⁸⁶Sr values from planktic foraminifera (*G. obliquus*) extracted from this section oscillate in harmony with the marl and limestone lithologies (Fig. 2). The values from the carbonate-rich limestones yielded a mean value of 0.709044 ± 14 (2 s.d.) corresponding to 4.79 Ma (Howarth and McArthur, 1997). This value is very close to the open-ocean ⁸⁷Sr/⁸⁶Sr value for the age range of the section (4.3–4.5 Ma; 0.709051–53; Howarth and McArthur, 1997) and was independently determined based on: (i) the chronostratigraphic boundaries of the *G. margaritae* biozone (4.64–4.13 Ma; Langereis and Hilgen, 1991), (ii) the stratigraphic correlation with the nearby paleomagnetically dated Monte Singa section 1 (Hilgen, 1987), and (iii) the average sedimentation rate of 21.7 ka per couplet (Hilgen and Langereis, 1989; Fig. 2).

Table 1

Foraminiferal strontium isotope data for the Precariti section (PR samples) and the Monte Singa section (MS samples)

Sample	Precariti Foraminifera				Sample	Monte Singa Foraminifera				Bulk rock	
	HCl		Acetic			Acetic		Acetic		Limestone	Marls
	⁸⁷ Sr/ ⁸⁶ Sr		⁸⁷ Sr/ ⁸⁶ Sr			⁸⁷ Sr/ ⁸⁶ Sr		⁸⁷ Sr/ ⁸⁶ Sr			
Limestone	Marls	Limestone	Marls	Limestone	Marls	Limestone	Marls	Limestone	Marls		
PR1	0.709054	–	–	–	MS1	0.709033	–	–	–	–	
PR2	–	0.709028	–	–	MS2	–	0.709033	–	–	0.708933	
PR3	0.709035	–	–	–	MS3	0.709044	–	–	0.708996	–	
PR4	–	0.709029	–	–	MS4	–	0.709068	–	–	–	
PR5	–	0.709020	–	0.709038	MS5	0.709053	–	–	–	–	
PR6	0.709047	–	0.709058	–	MS6	–	0.709043	–	–	–	
PR7	–	0.709017	–	0.709057	MS7	0.709057	–	–	0.708996	–	
PR8	0.709044	–	0.709047	–	MS8	–	0.709063	–	–	0.708970	
PR9	–	0.709018	–	0.709029	MS9	0.709060	–	–	–	–	
PR10	0.709046	–	0.709057	–	MS10	–	0.709055	–	–	–	
PR11	–	0.709026	–	–	MS11	0.709071	–	–	–	–	
PR12	0.709049	–	–	–	MS12	–	0.709072	–	–	–	
PR13	–	0.709014	–	–	MS13	0.709056	–	–	–	–	
PR14	0.709046	–	–	–	MS14	–	0.709061	–	–	–	
PR15	–	0.709030	–	–	MS15	0.709045	–	–	–	–	
PR16	0.709034	–	–	–	MS16	–	0.709048	–	–	–	
PR17	–	0.709025	–	–	MS17	0.709046	–	–	–	–	
–	–	–	–	–	MS18	–	0.709046	–	–	–	
–	–	–	–	–	MS19	0.709045	–	–	–	–	
–	–	–	–	–	MS20	–	0.709047	–	–	–	
–	–	–	–	–	MS21	0.709053	–	–	–	–	
–	–	–	–	–	MS22	–	0.709035	–	–	–	
–	–	–	–	–	MS23	0.709064	–	–	–	–	
–	–	–	–	–	MS24	–	0.709057	–	–	–	
Mean (2 s.d.)	0.709044 ± 14	0.709023 ± 12	0.709054 ± 12	0.709041 ± 29	Mean (2 s.d.)	0.709052 ± 21	0.709052 ± 25	0.708996	0.708952 ± 52		

The foraminifera from the carbonate-poor marls have consistently lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with a mean of 0.709023 ± 12 (2 s.d.) (Fig. 2; Table 1). Although the magnitude of the oscillations (average shift of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is 2.1×10^{-5}) fall within the uncertainty associated with strontium isotopic measurements ($\pm 2 \times 10^{-5}$), the regularity of the signal and

the consistent agreement between rock type and $^{87}\text{Sr}/^{86}\text{Sr}$ values suggested that the oscillations were real.

3.2. Monte Singa section

In order to test the validity of the oscillations seen in the Precariti section, foraminifera samples ex-

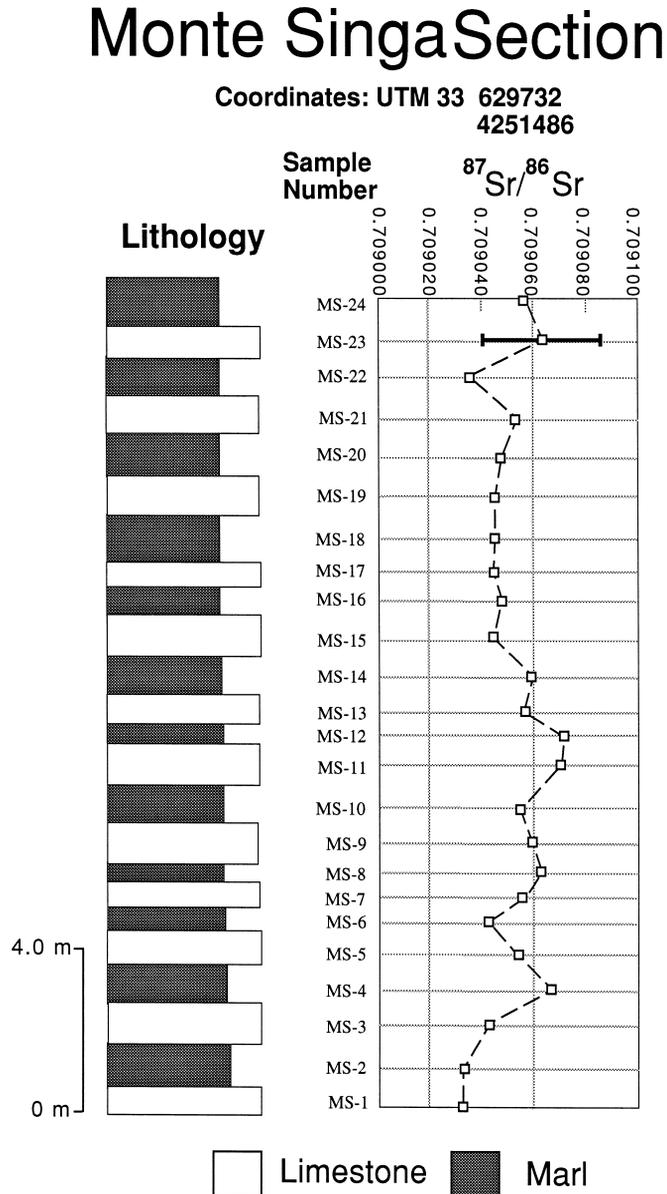


Fig. 3. Stratigraphic section from the Monte Singa location showing no relationship of the $^{87}\text{Sr}/^{86}\text{Sr}$ values with lithology. The error bar represents 2 s.d.

tracted from 24 alternating marl and limestone layers of the Monte Singa section were cleaned more rigorously (see Section 3.1). The results did not exhibit the rhythmic $^{87}\text{Sr}/^{86}\text{Sr}$ oscillations previously found in the Precariti section (Fig. 3; Table 1). $^{87}\text{Sr}/^{86}\text{Sr}$ values of both the marls and the limestones in the Monte Singa section had identical means of 0.709052, slightly higher than the mean values for the marls and limestones from the Precariti section at 0.709023 and 0.709044 (Table 1). Six replicate samples from the Precariti section using the more rigorous cleaning procedure did not reproduce the results obtained in the initial analyses. The replicate samples had higher means than the initial Precariti results and were closer to the mean values of the Monte Singa section (Fig. 2; Table 1).

4. Isolation of contaminants

The data presented above point to the existence of a contaminating phase affecting the results of the $^{87}\text{Sr}/^{86}\text{Sr}$ analyses of the less rigorously cleaned samples (see Section 2.1). To identify the contaminating phase, the major components of four samples from the Monte Singa section were isolated and their isotopic (O, C, Sr) and the trace element compositions (Mg, Sr, Fe, Mn, Na) were determined. These constituents were the coccoliths, the siliciclastic components of the $< 53\ \mu\text{m}$ grain size fraction, and the $> 53\ \mu\text{m}$ size foraminifera tests. The use of trace elements and isotopic analyses has been shown to be an important technique in the assessment of diagenetic alteration (e.g., Carpenter et al., 1991; Veizer et al., 1992; Denison et al., 1994).

4.1. Foraminiferal geochemistry of the Monte Singa samples

The tests of the foraminifera from the four samples (MS2, 3, 7, 8) from the Monte Singa section retained their original Pliocene $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition and retained much of their original trace element composition (Fig. 4; Table 2).

The Mg/Ca ratios in the planktic foraminiferal calcite of the four samples have values (Table 2) that are within the range of Mg/Ca levels found in Recent and sub-Recent planktic foraminifera (i.e.,

2.5 to 7×10^{-3} ; Savin and Douglas, 1973; Bender et al., 1975; Lorens et al., 1977; Graham et al., 1982; Delaney et al., 1985; Rosenthal and Boyle, 1993; Puechmaille, 1994; Nürnberg et al., 1996). Deviations from Mg/Ca ratios of modern planktic foraminifera, can be indicative of diagenetic alteration (Brand and Veizer, 1980; Marshall, 1992); therefore, it appears that the Mg/Ca ratios of foraminiferal calcite from the Monte Singa section have remained unaltered.

The Sr/Ca levels of the foraminifera from the four Monte Singa samples are closely clustered ranging from 1.4 to 1.5×10^{-3} (Fig. 4; Table 2). These values were obtained from a collection of planktic foraminiferal species and are within the reported ranges of recent and older planktic foraminifera (last 80 Ma), which typically range from 1.1 to 1.8×10^{-3} (Odum, 1957; Turekian, 1957; Wangersky and Joensuu, 1964; Bender et al., 1975; Lorens et al., 1977; Graham et al., 1982; Delaney et al., 1985; Müller, 1993; Puechmaille, 1994). Lower levels of Sr/Ca within biogenic carbonates can indicate alteration as abiotic recrystallization tends to discriminate against the reincorporation of strontium (Matter et al., 1975; Veizer, 1983; Richter and DePaolo, 1987; McArthur, 1994). Thus, the close clustering of the Sr/Ca values and the general agreement with modern and older planktic foraminiferal values indicate that the strontium concentration of the foraminifera from the Monte Singa section has remained substantially unchanged.

The planktic foraminifera have also preserved their $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios. The mean $^{87}\text{Sr}/^{86}\text{Sr}$ value of the 24 analyses from the lower Monte Singa section (the base of our section is less than 10 m above the Miocene/Pliocene boundary) is 0.709052 which gives an age of 4.3 Ma (5.2–2.4 Ma (2 s.d.)) using the data of Howarth and McArthur (1997) (Table 2). This age, based on the planktic foraminifera that were cleaned in HCl and dissolved in acetic acid, is consistent with the biostratigraphic (base of the Zanclean biozone) and magnetostratigraphic determinations previously carried out on the section and the Trubi in general (Gudjonsson, 1987; Zijdeveld et al., 1991; and see Hilgen and Langereis, 1993 for a full discussion).

The Na/Ca ratios of the foraminifera ranged from 3.0 to 3.7×10^{-3} (Fig. 4; Table 2) which is

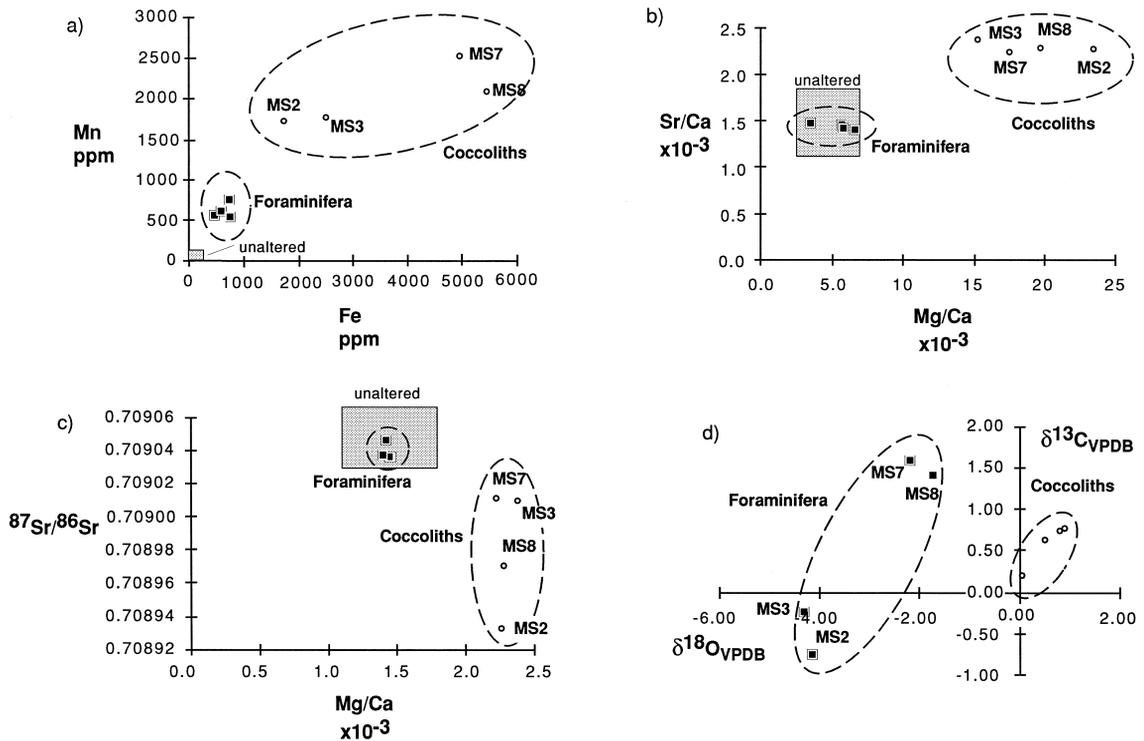


Fig. 4. (a–d) Bivariate plots of the trace element and isotopic compositions of the foraminifera and coccoliths (and associated oxyhydroxides) from the four samples (MS2,3,7,8) from the Monte Singa section.

slightly lower than the reported value of 4.0 to 7.0×10^{-3} for Recent and sub-Recent planktic foraminifera (Bender et al., 1975; Lorens et al., 1977; Graham et al., 1982; Delaney et al., 1985; Puechmaile, 1994). The incorporation of Na into calcite is not as well understood as other trace elements (Graham et al., 1982). The lower Na/Ca ratios may be indicative of slight diagenetic alteration of the foraminiferal tests or environmental parameters that affected the uptake of Na by the planktic foraminifera (Land and Hoops, 1973; Kitano et al., 1975; White, 1978; Graham et al., 1982).

The mean Mn/Ca and Fe/Ca values of the planktic foraminifera tests from the Monte Singa section were very high (means: 1.2×10^{-3} and 1.3×10^{-3} , respectively; Fig. 4; Table 2) compared to those found in modern and sub-recent planktic foraminifera (Wangersky and Joensuu, 1964). Elevated levels of Mn and Fe within biogenic calcite have been linked with diagenetic alteration (Brand and Veizer, 1980; Denison et al., 1994). Levels of

Mn higher than 75 ppm and Fe levels higher than 300 ppm can be indicative of diagenetically altered calcite. The concentrations of Mn and Fe in the foraminiferal calcite within the four samples from the Monte Singa section had respective ranges of 544–767 ppm and 522–717 ppm (Table 2). These high values are attributed to the presence of oxyhydroxide coatings on the foraminiferal calcite (McArthur, 1994; Wu and Hillaire-Marcel, 1995) as numerous SEM–EDS analyses of cross-sections of foraminiferal calcite found undetectable levels of Mn and very low levels of Fe.

The $\delta^{18}\text{O}_{\text{‰}}$ and $\delta^{13}\text{C}_{\text{‰}}$ (PDB) levels of the foraminiferal calcite from the Monte Singa section are reported in Fig. 4 and Table 2. The values from MS7 and MS8 match closely the stable isotope values reported from the Monte Singa section by Gudjonsson (1987) ($\delta^{18}\text{O}_{\text{‰}}$ (PDB) -0.39 to -2.39 and $\delta^{13}\text{C}_{\text{‰}}$ (PDB) 0.27 to 1.64) and from other sections of the Trubi Formation (De Visser et al., 1989; Müller, 1993). However, the other two sam-

Table 2

Trace element concentrations in ppt (mg/g) and ppm ($\mu\text{g/g}$), ratios of trace elements relative to Ca, $^{18}\text{O}\%$ and $\delta^{13}\text{C}\%$ values (PDB) and $^{87}\text{Sr}/^{86}\text{Sr}$ values for the sediment components of the Monte Singa section

	Samples	Lithology	Ca (ppt)	Mg/Ca ($\times 10^{-3}$)	Mg (ppm)	Sr/Ca ($\times 10^{-3}$)	Sr (ppm)	Fe/Ca ($\times 10^{-3}$)	Fe (ppm)	Na/Ca ($\times 10^{-3}$)	Na (ppm)	Mn/Ca ($\times 10^{-3}$)	Mn (ppm)	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	$^{87}\text{Sr}/^{86}\text{Sr}$
Foraminifera	MS2	M	365	3.5	779	1.5	1169	1.4	717	3.7	779	1.5	767	-4.12	-0.75	0.709036
	MS3	L	376	5.7	1304	1.5	1193	1.0	522	3.0	652	1.1	587	-4.30	-0.24	0.709036
	MS7	L	374	5.8	1319	1.4	1160	1.3	699	3.1	659	1.1	544	-2.16	1.58	0.709046
	MS8	M	352	6.7	1429	1.4	1079	1.3	629	3.5	714	1.1	544	-1.73	1.39	0.709037
Coccoliths	MS2	M	339	23.5	4821	2.3	1677	3.7	1752	2.2	429	3.7	1720	0.07	0.17	0.708933
	MS3	L	398	15.3	3689	2.4	2066	4.6	2533	1.6	369	3.2	1770	0.94	0.77	0.709009
	MS7	L	386	17.4	4087	2.2	1882	9.2	4972	1.7	372	4.8	2545	0.84	0.73	0.709011
	MS8	M	381	19.6	4534	2.3	1904	10.3	5441	2.1	453	4.0	2101	0.52	0.6	0.708970
Siliciclastic	MS2	M	6	2841.4	10,419	6.0	80	4784.7	40,310	1010.3	3504	27.3	227	-	-	0.716167
	MS3	L	5	2234.1	6878	5.3	59	6019.4	42,576	1203.5	3504	30.7	214	-	-	0.716912
	MS7	L	5	2599.6	8362	5.1	59	5319.4	39,314	1066.6	3245	31.2	227	-	-	0.716506
	MS8	M	7	1859.8	7972	3.7	58	3736.0	36,794	859.8	3486	26.6	258	-	-	0.716305

ples MS2 and MS3 have lower $\delta^{18}\text{O}\text{‰}$ and $\delta^{13}\text{C}\text{‰}$ (PDB) levels, suggesting that these samples may be slightly altered.

4.2. Coccolith geochemistry

The siliciclastic component of the samples has very high $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.716167–0.716912; Table 2). This implies that the low $^{87}\text{Sr}/^{86}\text{Sr}$ values found in the foraminifera extracted from the marly layers of the Precariti stratigraphic section (Fig. 2) cannot be the result of fine-grained siliciclastic particles contained in the foraminifera tests after an inadequate cleaning procedure. Other major constituents of both limestone and marl layers of the Trubi Formation are the coccoliths, representing between 43 and 54% of the bulk rock volume (Table 3). SEM examination of the coccoliths reveals variable degrees of preservation, ranging from dissolved, through well preserved to overgrown. Trace element geochemistry of the coccolith fraction points to a considerable diagenetic alteration (Fig. 4; Table 2) as discussed below.

The Fe/Ca and Mn/Ca levels are significantly higher in the coccoliths (means: 7.0×10^{-3} and 4.0×10^{-3} , respectively) than in the planktic foraminifera (Fig. 4; Table 2). No preleaching was

done on the coccolith samples before dissolution for ICP–AES analysis. The solution had a considerable amount of suspended Fe oxides that settled out of suspension with centrifuging. The amount of oxyhydroxides that is actually part of the coccolith crystal structure is difficult to determine (McArthur, 1994), however, like the foraminifera the high levels of Fe and Mn are probably due to coatings on the coccoliths.

Coccolithophores, like planktic foraminifera, discriminate against the incorporation of Mg into their calcite crystal lattice. Therefore, coccoliths are composed of low-Mg calcite with Sr and Mg concentrations that are very similar to those of planktic foraminifera (Milliman, 1974; Matter et al., 1975; Veizer, 1983). This is not the case for samples from Monte Singa in which coccoliths have Sr/Ca ratios that are approximately 30% larger than those of the planktic foraminifera (Fig. 4; Table 2). The concentration of Mg in the coccoliths (4000–5000 ppm; Fig. 4; Table 2) is much higher than the highest values (2000 ppm) reported from the pelagic sediments of the Shatsky rise in the NW Pacific by Matter et al. (1975), and is also much higher than the values reported by Elderfield et al. (1982) from Ontong Java Plateau (maximum Mg/Ca value of 4.4×10^{-3}). These high values suggest some form of diagenetic alteration of the coccolith calcite. However, recrystallization tends to decrease Sr/Ca and Mg/Ca ratios and our results indicate the opposite (Veizer, 1983). Some of this Mg and Sr may be in the form of oxyhydroxides coatings, although Wu and Hillaire-Marcel (1995) found in their study that Sr/Ca values were not affected by oxyhydroxide coatings.

The Na/Ca levels in the coccoliths are lower than the values in the planktic foraminifera (Fig. 4; Table 2). Assuming that the normal level of Na for the coccoliths is within the range for planktic foraminifera, the lower values could indicate abiogenic overgrowth formation that contains less Na than biogenic precipitates.

Since coccolith calcite is precipitated in isotopic equilibrium with seawater, its $\delta^{18}\text{O}\text{‰}$ and $\delta^{13}\text{C}\text{‰}$ (PDB) values should be in close agreement with those of associated planktic foraminifera (McIntyre, 1967; Douglas and Savin, 1975; Margolis et al., 1975; Anderson and Steinmetz, 1981). However,

Table 3
Table showing the compositional characters of the marl and limestone samples (MS2,3,7,8) and the concentration of strontium of the four fractions relative to the bulk rock

Sample	MS2	MS3	MS7	MS8
Lithology	M	L	L	M
<i>Rock composition</i>				
Foraminifera (%)	2	7	8	4
Coccoliths (%)	43	54	54	50
Siliciclastic (%)	55	39	38	46
<i>Carbonate composition</i>				
Coccoliths (%)	95	87	85	92
Foraminifera (%)	5	13	15	8
<i>Rock Sr concentration</i>				
Foraminifera Sr (ppt)	0.02	0.08	0.09	0.04
Coccoliths Sr (ppt)	0.72	1.12	1.02	0.95
Siliciclastic Sr (ppt)	0.04	0.02	0.02	0.03

$\delta^{18}\text{O}\text{‰}$ and $\delta^{13}\text{C}\text{‰}$ (PDB) values from the coccolith fraction from our samples are all positive, in contrast with the predominantly negative values obtained for the planktic foraminifera (Fig. 4; Table 2). Such contrast suggests that the coccoliths were diagenetically altered.

The $^{87}\text{Sr}/^{86}\text{Sr}$ values from the coccolith fraction also clearly indicates alteration. The coccolith fraction has significantly lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the foraminifera and the siliciclastic component (Fig. 4; Table 2). The difference between foraminiferal and coccolith $^{87}\text{Sr}/^{86}\text{Sr}$ values in the marls ranges between 6.7×10^{-5} and 10.3×10^{-5} and it is greater than in the limestone samples ($2.7\text{--}3.5 \times 10^{-5}$). The difference between the coccolith and foraminiferal ratios is significant in the marls but within the error limits in the limestones. Previous nanoplankton biostratigraphic studies of the Trubi Formation indicate only minor reworking of older specimens (that may have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) thus ruling out reworking as a significant source of contamination (Rio et al., 1984). The lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the coccoliths compared to the foraminifera indicate alteration of the former with strontium not derived from the dissolution of carbonate sediment from within the section.

The ratios from the coccolith fraction are very similar to the ratios from the Lower Messinian evaporites (0.70887 to 0.70896; normalized to NBS 987 = 0.710248) and slightly higher than the upper evaporites (0.70853 to 0.70887; Müller and Mueller, 1991). We hypothesize that the low $^{87}\text{Sr}/^{86}\text{Sr}$ values of the coccoliths are probably due to diagenetic alteration from interstitial waters geochemically imprinted by the Messinian evaporites. Evaporites are absent in the immediate vicinity of the studied sections but they are common in nearby locations (e.g., 8 km to the west of the Precariti section). A similar model of diagenetic alteration of the original $^{87}\text{Sr}/^{86}\text{Sr}$ Sr signal in Paleogene carbonate samples to less radiogenic values by the influx of brines derived from older evaporite deposits was proposed by Denison et al. (1993).

The reason for the variation in $^{87}\text{Sr}/^{86}\text{Sr}$ values in the coccoliths between the marls and the limestones in the Monte Singa section is not clear from our analyses. The concentration of Sr in the coccoliths does not differ significantly between marls and limestones (Table 2), however, the $^{87}\text{Sr}/^{86}\text{Sr}$ values from the marls indicate that they were altered to a higher degree than in the limestones. The increased siliciclastic content in the marls and their associated

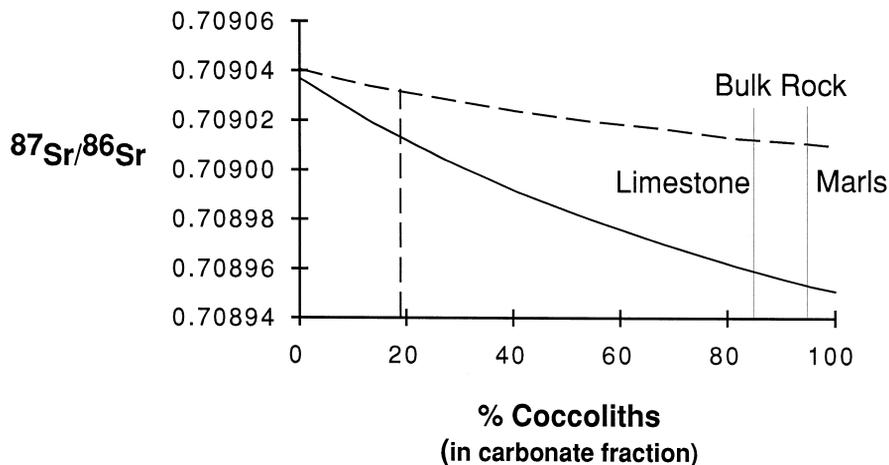


Fig. 5. Two-component mixing equation with foraminiferal and coccolith fractions as two end-members. Dashed line is the mixing curve for limestones and the solid line is the mixing curve for the marls. Vertical dashed line represents the percent contamination of the foraminiferal calcite that is needed to obtain the 2×10^{-5} difference in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios found in the Precariti section. Range of marl and limestone bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ values are also indicated.

lower permeabilities may have caused preferential retention of the brine waters and corresponding diagenesis of the coccolith fraction.

4.3. Discussion

The contrast in $^{87}\text{Sr}/^{86}\text{Sr}$ values and Sr concentration amongst the various components of the marl and limestone samples demonstrates the potential contaminating effect of the coccolith fraction (Fig. 4; Tables 1–3). By considering $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the coccolith fraction we can account for the lower $^{87}\text{Sr}/^{86}\text{Sr}$ values in the marls that were originally found in the Precariti section (Fig. 2). Using a two-component mixing equation with the mean coccolith and foraminifera $^{87}\text{Sr}/^{86}\text{Sr}$ values in the marls and the limestones (from the Monte Singa section) and their respective concentrations as the two end-members, we can account for the original cyclical signal in the Precariti section (Fig. 5; Table 1). Assuming a constant contamination level in both lithologies, the required 2×10^{-5} change in the $^{87}\text{Sr}/^{86}\text{Sr}$ values of the foraminifera can be reached with an 18% coccolith fraction contamination in both the limestone and the marls (Fig. 5). The greater contamination effect in the marls is apparently due to the lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the coccoliths found in the marls. Infillings of coccoliths within the foraminiferal tests were abundant when thin sections were examined with an SEM. It would not require a significant amount of infills to cause the 18% contamination for the 2×10^{-5} change in the $^{87}\text{Sr}/^{86}\text{Sr}$ signal and there is no reason to believe that the degree of infilling would change between alternating marl and limestone beds. Careful cleaning by crushing and preleaching eliminates the potential contamination, and this procedure was followed in the Monte Singa samples.

The bulk rock $^{87}\text{Sr}/^{86}\text{Sr}$ values both in the limestones and the marls are dominated by the Sr concentration from the coccoliths (1.02–1.12 ppt and 0.72–0.95, respectively; Table 3). Considering the abundance of coccoliths within both marls (94% of carbonate fraction) and the limestones (86%) the lower ratios in the bulk rock samples are due to the lower $^{87}\text{Sr}/^{86}\text{Sr}$ values of the coccolith fraction (Fig. 5; Table 1). These results have very important implications for the use of bulk rock samples for Sr isotope

stratigraphy and emphasize the need for careful selection of individual unaltered components.

5. Conclusions

Marl/limestone samples of the Trubi Formation were thought to have been subjected to minimal diagenesis because of their poor induration, but have in fact undergone subtle alteration of the coccolith fraction which was recognized through detailed trace element and isotopic analyses. These results indicate that great care must be taken in the selection and preparation of samples for $^{87}\text{Sr}/^{86}\text{Sr}$ determinations even when diagenesis is thought to be minimal.

The contamination that resulted from the presence of altered coccoliths within the tests of planktic foraminifera in the $^{87}\text{Sr}/^{86}\text{Sr}$ determinations was not exceptionally great, with the difference in the mean ratios being just outside analytical uncertainty at 2×10^{-5} . However, with the inevitable increases in analytical precision and with the development of higher resolution $^{87}\text{Sr}/^{86}\text{Sr}$ curves, recognition of subtle diagenesis will become more and more important (McArthur, 1994). We therefore recommend for any strontium isotopic analysis: (1) selection of the less diagenetically altered constituent(s) which should be appropriately cleaned and selectively analyzed; and (2) bulk rock analysis should be avoided because they can provide misleading results.

Acknowledgements

This research was supported by NSERC (R.T.P.), NATO (R.T.P. and W.C.), CNR (W.C.), MURST (W.C.) and research funds provided by J.B. Critical comments by J.M. McArthur and an anonymous reviewer led to improvement in the manuscript.

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