# Isotopic and geochemical features of rocks from Punta delle Pietre Nere, Gargano Peninsula, southern Italy

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ABSTRACT. — The locality called Punta delle Pietre Nere is a relatively small geological system, where Upper Triassic black limestones and gypsum outcrops occur together with Paleocene melasyenite and melagabbro and Upper Pleistocene biocalcarenites. In the present work, sedimentary lithologies were investigated for major and selected minor (Sr and Mn) elements and for stable isotope compositions ($\delta^{13}C$, $\delta^{18}O$, $\delta^{34}S$ and $^{87}Sr/^{86}Sr$).

The results suggest that the intrusion of the igneous bodies did not substantially alter the chemical and isotopic compositions of limestone and gypsum. Sr and Mn distributions in limestones reflect post-depositional recrystallization of sediments with the intervention of seawater; the $\delta^{18}O$ values yield an isotopic temperature of about 40°C and indicate pervasive water-rock interaction. The $\delta^{13}C$ values indicate variable contributions of bicarbonate in pore water due to oxidation of organic matter, this reaction probably being associated with bacterial reduction of sulfate ions. The $\delta^{34}S$ signature of pyrite from limestones appears to be biogenic far from the contact with melasyenite and magmatic close to the contact. The $\delta^{13}C$ and $\delta^{18}O$ values of biocalcarenites are normal marine.

The $^{87}Sr/^{86}Sr$ ratio in limestones matches their Upper Triassic age. The $^{87}Sr/^{86}Sr$ and $\delta^{34}S$ of gypsum are in good agreement with its age.

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RIASSUNTO. — La Punta delle Pietre Nere rappresenta un sistema geologico arealmente molto limitato (0.8 km²), nel quale coesistono calcari e gessi (Trias Superiore), melasieniti e melagabbri (Paleocene) e biocalcareniti (Pleistocene Superiore). Nel presente lavoro, le litologie sedimentarie sono state analizzate per gli elementi maggiori ed alcuni elementi minori (Sr e Mn) e per la composizione isotopica del C, O, S and Sr ($\delta^{13}C$, $\delta^{18}O$, $\delta^{34}S$ and $^{87}Sr/^{86}Sr$).

Dai risultati ottenuti, l'intrusione ignea non ha fondamentalmente modificato la composizione chimica ed isotopica sia dei calcari che dei gessi. Le distribuzioni di Sr e Mn nei calcari sono compatibili con una ricristallizzazione diagenetica in presenza di acqua di mare; i valori di $\delta^{18}O$ sono compatibili con una temperatura di ricristallizzazione di circa 40°C e con alti rapporti acqua-roccia. I valori di $\delta^{13}C$ nei calcari suggeriscono contributi variabili di bicarbonato da ossidazione di materia organica, e verosimilmente connessi a processi batterici solfato-riducenti. I calcari sono disseminati di pirite, la cui composizione isotopica $\delta^{34}S$ si accorda con un'origine biogenica dello zolfo lontano dal contatto con la melasienite e con un'origine magmatica a contatto con il corpo igneo. I valori di $\delta^{13}C$ e $\delta^{18}O$ delle biocalcareniti sono tipici di normali condizioni deposizionali marine.

Il rapporto $^{87}Sr/^{86}Sr$ nei calcari è in linea con l'età triassico-superiore della roccia. Analogamente i gessi presentano rapporti $^{87}Sr/^{86}Sr$ e valori $\delta^{34}S$ compatibili con la loro età.

## INTRODUCTION

This paper deals with Triassic limestone and gypsum outcrops, occurring together with Paleocene magmatic rocks at Punta delle Pietre Nere in the Gargano promontory on the Adriatic Sea (Puglia province, southern Italy). Biocalcarenites of possible Pleistocene age are also investigated.

The aims of the work are: (1) to verify carbon, oxygen and strontium isotopic variations in carbonates and gypsum due to interaction with fluids during emplacement of the igneous bodies, (2) to provide new sulfur isotopic data on gypsum, thus implementing the only datum available (Bigazzi *et al.*, 1996), and (3) to confirm the Upper Triassic age of gypsum by means of an appropriate database of $\delta^{34}S$ values.

## GEOLOGICAL OUTLINE

Punta delle Pietre Nere is a small area of about 0.8 km$^2$ composed of a number of lithotypes, which include (fig. 1):

1) Two igneous bodies (De Fino *et al.*, 1981) separated by the Acquarotta canal, consisting of an alkali melasyenite dike and a group of small outcrops mainly represented by alkali melagabbros and subordinate ultramafites and porphyritic facies. K/Ar datings on dark mica provide ages of 58-59 Ma for melasyenite and 62 Ma for melagabbro (Bigazzi *et al.*, 1996).

2) Stratified black limestones with intercalated marls, dated to the Carnian-Norian (Posenato *et al.*, 1994, and references therein). They are somewhat recrystallized, with grain size increasing towards the contact with the melasyenite (Posenato *et al.*, 1994), where thermo-metamorphic effects are observed (Bigazzi *et al.*, 1996). As a consequence, the limestone-melasyenite contact is not tectonic,

as claimed by Amendolagine *et al.* (1964). Abundant pyrite occurs in the limestones, with clusterings of millimetric crystals close to the contact with the melasyenite. Fossil malacofauna is widespread through the limestone outcrop, and basically consists of well-preserved benthic molluscs (Di Stefano, 1895, and references therein), typical of hypohaline water and generally pyritized. Faunal distribution and composition, together with the high organic matter content of limestones, indicate shallow-water conditions for the depositional basin (Ricchetti *et al.*, 1994).

3) Gypsum outcrops along the banks of the D'Acquarotta canal as white to grey chaotic masses, containing layers and lenses of marls and fragments of magmatic rock and black limestone. They are attributed to the Burano Anhydrite Formation of Upper Triassic age (Bigazzi *et al.*, 1996, and references therein), which has been recognized beneath the Gargano promontory by deep drilling (Foresta Umbra 1 well) east of the Pietre Nere point (Martinis and Pieri, 1964). The log stratigraphy of this well shows calcareous dolomite and dolomite from 0 to 3015 m depth, dolomite and breccia of calcareous dolomite from 3015 to 3290 m, and massive anhydrite from 3290 to 5071 m. As reported by Bigazzi *et al.* (1996), dolomite is encountered below the anhydrite layer when the well was deepened.

4) Yellowish *Cladocora caespitosa*-bearing biocalcarenites (Viola and Di Stefano, 1893), bordering the sea to the east of the D'Acquarotta canal and outcropping from the sea and the beach. They are tentatively referred to the Upper Pleistocene (Tyrrhenian; Boni *et al.*, 1969).

According to Bigazzi *et al.* (1996), limestone and evaporite at Punta delle Pietre Nere were squeezed and pushed upwards to the surface by a tectonic event, possibly during Late Pliocene-Early Pleistocene times, after which gypsification of anhydrite took place at a very shallow depth. The squeezing process also
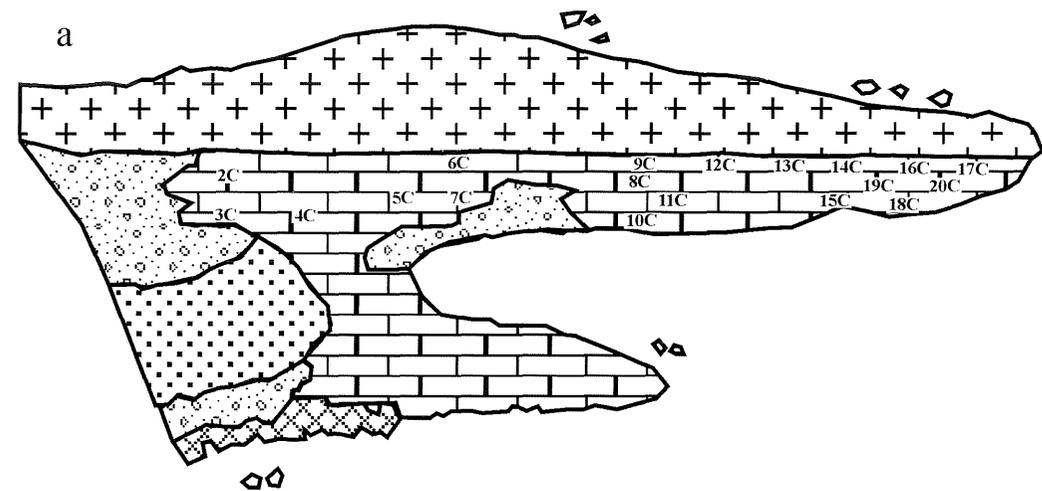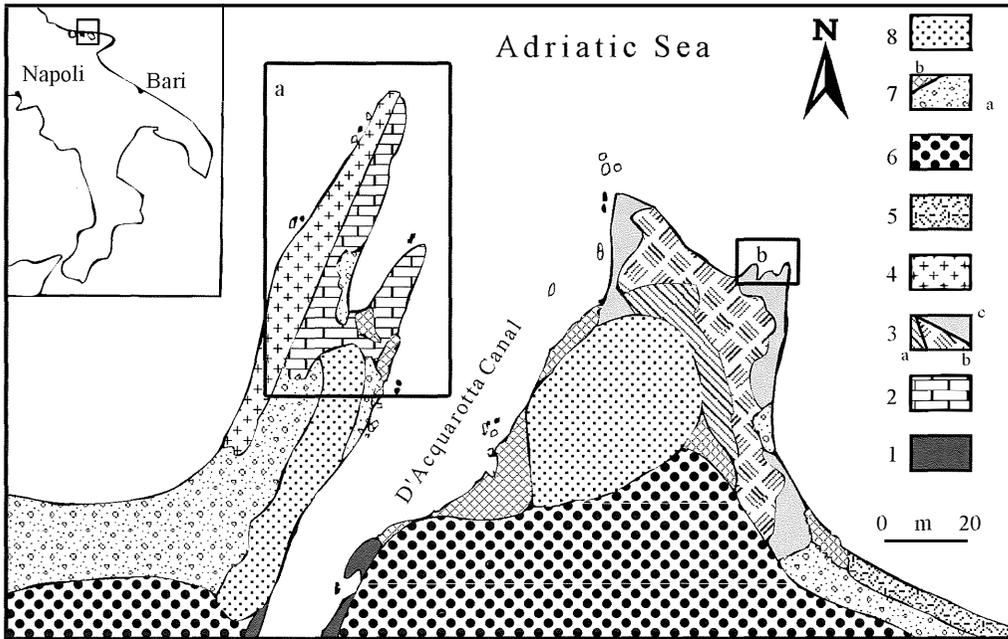
Fig. 1 – Schematic geological map of Punta delle Pietre Nere (modified from De Fino *et al.*, 1981). Enlarged sketch (inset a) shows positions of black limestone samples (C) relative to contact with melasyenite. Biocalcarenite samples are from area shown in inset (b). Gypsum samples were collected on both sides of D'Acquarotta canal between lock and bridge. 1: gypsum (Upper Triassic); 2: black limestones (Upper Triassic); 3: melagabbroid body (Lower Paleocene), a: alkali ultramafites, b: alkali melagabbros, c: porphyritic types; 4: alkali melasyenitic body (Upper Paleocene); 5: biocalcarenites (Upper Pleistocene); 6: marine deposits and dunes (Upper Pleistocene); 7: modern beach deposits (a) and pebbles of various rock types (b); 8: rubble.

involved igneous rocks emplaced at depth during the Paleocene. This evolutionary model conflicts with that of Cotecchia and Canitano (1954), Amendolagine *et al.* (1964) and Martinis and Pieri (1964), who proposed that gypsum rose from depth, diapyrically dragging magmatic rocks and black limestone. Surface evidence for fossil hydrothermal systems is totally lacking in the area.

Again according to Bigazzi *et al.* (1996), melasyenite and melagabbro underwent «…a relatively long period of almost stationary temperature…» not higher than 120°C, followed by «…a fast cooling phase in Late Pliocene-Early Pleistocene times».

## ANALYTICAL PROCEDURES

Chemical and isotopic analyses of black limestones were performed on selected sample chips with no visible vein material. Salt deposits from biocalcarenites were removed by repeated washings with deionized water in an ultrasonic bath. X-ray diffractometry revealed calcite ± dolomite in the carbonate fraction and quartz with subordinate albite, mica and pyrite in the non-carbonate fraction of black limestones. This main mineralogy was also shown by biocalcarenites, with the exception of pyrite. The percentages of calcite and dolomite were estimated by gasometry, applying the method of Leone *et al.* (1988). Four mostly calcitic limestones were treated with 5% acetic acid at room temperature and pyrite separated from the residue by hand picking.

Major and trace (Sr and Mn) element concentrations were measured by X-ray fluorescence spectrometry. The LOI was determined by heating aliquots of samples at 950°C to constant weight.

Carbon and oxygen isotopic analyses were carried out on the $CO_2$ extracted from calcite with 100% $H_3PO_4$ at 25°C (McCrea, 1950) by means of a GEO 20-20/Europa Scientific mass spectrometer. Limestone and biocalcarenite samples were reacted for 30', thus minimizing the amount of $CO_2$ from decomposition of dolomite (e.g. Cortecci *et al.*, 1975). Carbon and oxygen isotopic abundances are reported as $\delta^{13}C$ and $\delta^{18}O$ per mil values relative to PDB and V-SMOW standards, respectively. Analytical precision (duplicate preparation and measurement) was better than ± 0.1‰.

The sulfur isotopic composition of gypsum and pyrite was measured on the $SO_2$ obtained from the samples, using a VG MICROMASS mod. 903 mass spectrometer. Briefly, gypsum was dissolved in deionised water and the sulfate precipitated as $BaSO_4$, which was thermally decomposed to yield $SO_2$, basically by means of the method of Yanagisawa and Sakai (1983). Pyrite was combusted to $SO_2$ with molecular oxygen at 1100°C, after purification from carbonate by treatment with diluted HCl. The sulfur isotopic composition is given in the $\delta^{34}S$ notation in per mil, relative to the CDT standard. Analytical precision was within ± 0.2‰.

The $^{87}Sr/^{86}Sr$ ratio was measured in the calcitic fraction of four limestone and two gypsum specimens. Carbonates were leached with 0.25N HCl at room temperature, thus excluding the dolomitic fraction in the rock. Sr was extracted from the leachate using cation exchange resin, then eluted and analysed mass-spectrometrically. Gypsum was mixed with $Na_2CO_3$ and then treated with water at 70°C for 6 h to obtain $CaCO_3$. After dissolution with HCl and evaporation to dryness, the resulting $CaCl_2$ was dissolved in HCl and Sr in solution separated by cation exchange chromatography using Dowex 50W-X8 cation exchange resin, then eluted and analysed. Analytical precision was between 0.00002 and 0.00005. The measured ratios were normalized to a $^{86}Sr/^{88}Sr$ ratio of 0.1194 in natural strontium. Repeated analyses of the NBS 987 $SrCO_3$ standard yielded a mean value of 0.71024 ± 0.00002.

## RESULTS AND DISCUSSION

The results of chemical and isotopic measurements are listed in Tables 1 and 2.

TABLE 1

*Chemical composition (% by weight) of limestones (C) and biocalcarenites (B) from Punta delle Pietre Nere.*

| Sample | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | LOI | Sr (ppm) | Mn (ppm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2C | 14.41 | 0.26 | 4.60 | 2.05 | 6.68 | 39.34 | 0.92 | 0.82 | 0.02 | 30.9 | 366 | 319 |
| 3C | 10.31 | 0.16 | 1.60 | 2.53 | 6.63 | 41.29 | 0.53 | 0.15 | 0.00 | 36.8 | 390 | 344 |
| 5C | 17.85 | 0.37 | 7.15 | 2.70 | 3.82 | 37.03 | 0.82 | 1.12 | 0.04 | 29.1 | 348 | 318 |
| 6C | 20.21 | 0.43 | 8.08 | 1.97 | 2.87 | 34.74 | 0.88 | 1.17 | 0.05 | 29.6 | 390 | 281 |
| 7C | 11.76 | 0.23 | 2.70 | 2.30 | 4.37 | 42.30 | 0.88 | 0.35 | 0.01 | 35.1 | 376 | 325 |
| 8C | 15.52 | 0.32 | 5.01 | 1.77 | 4.12 | 40.73 | 1.31 | 0.79 | 0.03 | 30.4 | 329 | 284 |
| 9C | 15.66 | 0.29 | 5.20 | 3.44 | 6.93 | 39.33 | 0.86 | 1.47 | 0.02 | 26.8 | 497 | 354 |
| 10C | 17.75 | 0.24 | 5.07 | 2.70 | 4.03 | 36.09 | 1.00 | 1.20 | 0.02 | 31.9 | 496 | 287 |
| 11C | 14.15 | 0.32 | 4.38 | 2.48 | 3.82 | 39.90 | 0.81 | 0.62 | 0.02 | 33.5 | 439 | 296 |
| 12C | 15.02 | 0.28 | 4.35 | 2.55 | 6.51 | 38.41 | 1.13 | 0.83 | 0.02 | 30.9 | 444 | 284 |
| 13C | 14.60 | 0.29 | 5.10 | 1.99 | 3.68 | 39.99 | 1.00 | 0.92 | 0.03 | 32.4 | 318 | 322 |
| 14C | 14.15 | 0.29 | 5.04 | 2.52 | 3.65 | 41.76 | 0.99 | 0.87 | 0.03 | 30.7 | 352 | 232 |
| 15C | 15.11 | 0.33 | 5.34 | 2.44 | 4.29 | 37.73 | 0.82 | 0.80 | 0.04 | 33.1 | 444 | 318 |
| 16C | 19.77 | 0.43 | 7.94 | 1.61 | 3.20 | 35.24 | 0.95 | 1.44 | 0.02 | 29.4 | 319 | 301 |
| 17C | 15.36 | 0.28 | 5.21 | 1.65 | 6.67 | 37.66 | 1.02 | 0.73 | 0.02 | 31.4 | 343 | 276 |
| 18C | 13.83 | 0.30 | 4.12 | 2.47 | 4.01 | 39.57 | 0.88 | 0.60 | 0.02 | 34.2 | 413 | 294 |
| 19C | 13.30 | 0.27 | 3.85 | 1.72 | 3.38 | 41.78 | 0.73 | 0.54 | 0.03 | 34.4 | 362 | 307 |
| 20C | 17.58 | 0.33 | 4.49 | 2.80 | 3.89 | 37.51 | 0.90 | 3.06 | 0.04 | 29.4 | 306 | 299 |
| 1B | 11.46 | 0.15 | 3.28 | 2.72 | 4.58 | 39.44 | 0.45 | 0.78 | 0.04 | 37.1 | 1313 | 1973 |
| 2B | 13.00 | 0.19 | 3.54 | 2.81 | 4.65 | 38.34 | 0.50 | 1.22 | 0.05 | 35.7 | 810 | 4232 |
| 3B | 15.69 | 0.19 | 4.12 | 2.51 | 4.50 | 37.26 | 1.00 | 0.54 | 0.59 | 33.6 | 1233 | 2941 |
| 4B | 10.61 | 0.19 | 2.75 | 2.15 | 4.54 | 41.01 | 0.37 | 0.17 | 0.41 | 37.8 | 1582 | 1154 |

## BLACK LIMESTONES AND BIOCALCARENITES

### Major and minor chemistry

The carbonate fraction in the limestones ($n = 19$) varies between 53 to 80%, calcite and dolomite being estimated in the ranges of 44 to 65% and 1 to 26% of whole rock, respectively. The carbonate fraction in the biocalcarenites ($n = 4$) is comparable to that of limestones (66 to 81%), as well as the percentages of whole rock of calcite (58 to 75%) and dolomite (8 to 13%). The non-carbonate fraction ranges between 20 and 39%, thus testifying a notable detrital portion in both limestones and biocalcarenites. This may indicate a nearshore depositional environment for the carbonates.

The major element composition of the limestones is strongly influenced by the detrital portion. Positive correlations exist between $Al_2O_3$ and $SiO_2$, $TiO_2$, $K_2O$ and $Na_2O$ (fig. 2), supporting their association with the siliciclastic fraction. Quartz, plagioclase and micas were found as the main constituents of the detrital fraction, although $Fe_2O_3$ does not correlate with $Al_2O_3$ (fig. 3), as expected. Iron probably underwent diagenetic mobilization from the detrital fraction in reducing conditions promoted by organic matter, and was partially fixed as $FeS_2$ by biogenic $H_2S$. Some iron (and sulfur) may have been supplied by the magmatic bodies during their emplacement at depth. The bacterial reduction of sulfate may have been enhanced more in black limestones than in biocalcarenites due to the greater amount of organic matter in the precursor sediments of the former.

TABLE 2

*Isotopic composition of limestone, biocalcarenite, gypsum and pyrite samples from Punta delle Pietre Nere.*

| Sample | $\delta^{13}C$ (‰) *vs* PDB | $\delta^{18}O$ (‰) *vs* V-SMOW | $\delta^{34}S$ (‰) *vs* CDT | $^{87}Sr/^{86}Sr$ |
|---|---|---|---|---|
| *Limestone* | | | | |
| 2C | -1.33 | +24.77 | | |
| 3C | -0.45 | +24.78 | | |
| 5C | -0.35 | +24.96 | | |
| 6C | -0.44 | +24.65 | | |
| 7C | -0.65 | +24.79 | | 0.70766 |
| 8C | -1.14 | +24.17 | | |
| 9C | -1.15 | +24.03 | | |
| 10C | -0.71 | +24.82 | | 0.70769 |
| 11C | -0.66 | +24.99 | | |
| 12C | -1.58 | +24.79 | | |
| 13C | -1.08 | +24.20 | | |
| 14C | -2.06 | +24.29 | | |
| 15C | -9.21 | +24.03 | | 0.70761 |
| 16C | -1.42 | +25.07 | | |
| 17C | -1.68 | +24.37 | | |
| 18C | -0.66 | +25.07 | | |
| 19C | -0.51 | +24.91 | | |
| 20C | -1.48 | +24.99 | | 0.70767 |
| *Biocalcarenite* | | | | |
| 1B | +1.52 | +31.51 | | |
| 2B | +1.68 | +31.43 | | |
| 3B | +1.40 | +31.18 | | |
| 4B | +1.69 | +31.35 | | |
| *Gypsum* | | | | |
| 6G | | | +15.7 | |
| 8G | | | +16.0 | |
| 10G | | | +15.0 | |
| 11G | | | +15.0 | 0.70779 |
| 12G | | | +14.6 | 0.70761 |
| 14G | | | +14.6 | |
| 16G | | | +15.6 | |
| 18G | | | +16.1 | |
| *Pyrite*[1] | | | | |
| 5C[2] | | | +15.1 | |
| 13C[3] | | | -1.2 | |
| 14C[3] | | | +0.6 | |
| 17C[3] | | | -1.6 | |

[1] Symbols of samples refer to limestones from which pyrite was separated.
[2] Microcrystalline.
[3] Pentagonododecahedric (*p*), cubic (*c*) and octahedric (*o*) crystals, with abundance order: *p* >> *c* > *o* in samples 13C and 17C, and *c* > *p* >> *o* in sample 14C.

Concentrations of Sr in black limestones vary between 306 and 497 ppm. Assuming no Sr in the non-carbonate fraction and substitution of Sr into Ca sites in the carbonate fraction, calculated concentrations in calcite range from 503 to 877 ppm (mean 623 ± 115 ppm). The effect of the non-carbonate fraction on these calculated values for calcite is probably small. For example, sample 17C has a non-carbonate content of 39% (and 2% dolomite) and a calculated calcite Sr content of 523 ppm. Sample 3C has a non-carbonate content of 20% (and 7% dolomite) and its calculated calcite Sr content is 488 ppm, which is in good agreement with that of sample 17C. Assuming a Sr content of 523 ppm for calcite 17C, the Sr concentration in the non-carbonate fraction is found to be about 15 ppm, which is a very reasonable value for siliciclastic sediments. Therefore, it may be concluded that the Sr concentration of calcite in the black limestones of Pietre Nere is greater than about 500 ppm. The Sr concentration in the dolomitic fraction is about one-half that of calcite (e.g., Land, 1980) or lower (Vahrenkamp and Swart, 1990). Biocalcarenites are richer in Sr (810 to 1582 ppm) with respect to limestone, with calculated concentrations in the calcitic fraction of 1303 to 2284 ppm Sr. These values are within the range displayed by most molluscs (e.g., Morse and MacKenzie, 1990, and references therein), in keeping with the malacofauna preserved in the rocks and the general dicrimination of molluscs against Sr. Conversely, the Sr content in limestones is much lower than predicted for seawater calcite (about 1400 ppm; Land, 1980) and may account for the diagenetic «purification» of the original $CaCO_3$ from Sr, possibly controlled by a distribution coefficient ($D^{Sr}_{cal}$) of about 0.6 as reported by Katz *et al.* (1972) for the slow crystallization of calcite from aragonite at 40 to 98°C. In this case, recrystallization may have occurred from seawater, in open system conditions.

Concentrations of Mn in limestones show a narrow range of values from 232 to 354 ppm, with a mean of 302 ± 28 ppm. These values are
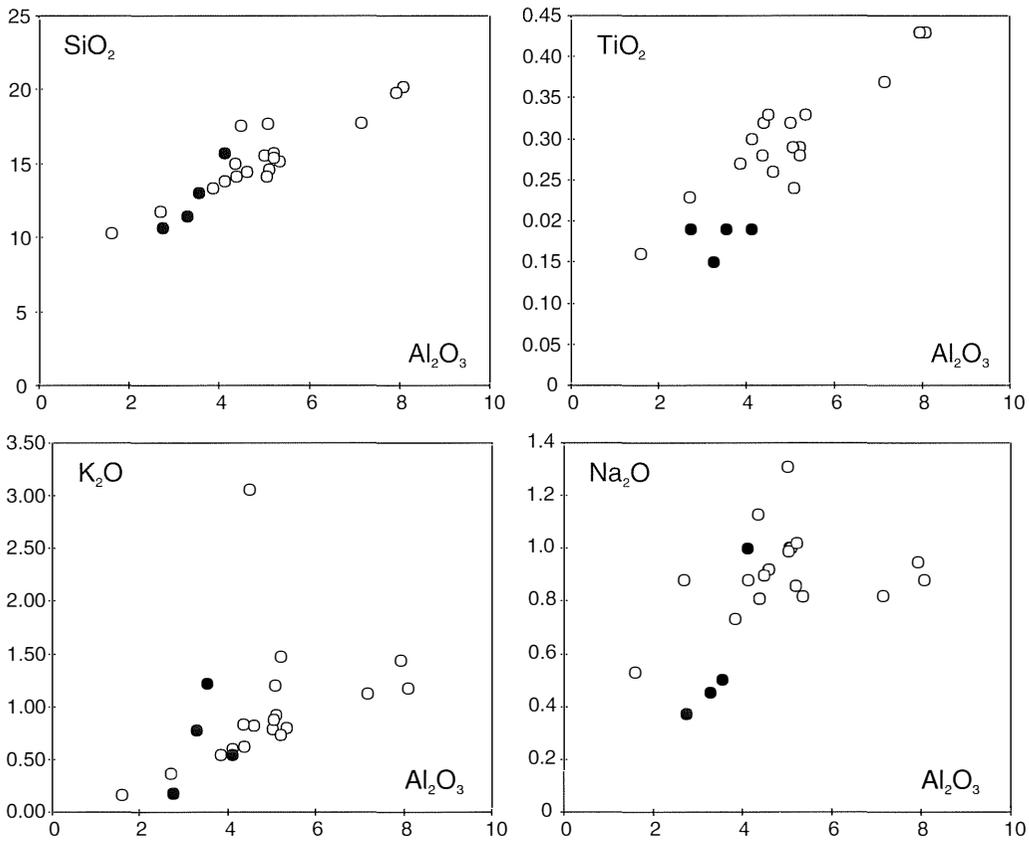
Fig. 2 – Correlations between major elements and $Al_2O_3$ in limestones (open circle) and biocalcarenites (filled circles). Data as weight % of oxide.
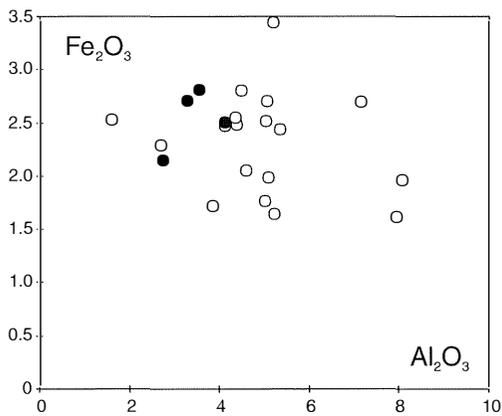


Fig. 3 – $Fe_2O_3$ *vs* $Al_2O_3$ plot for limestones (open circles) and biocalcarenites (filled circles). Data as weight % of oxide.
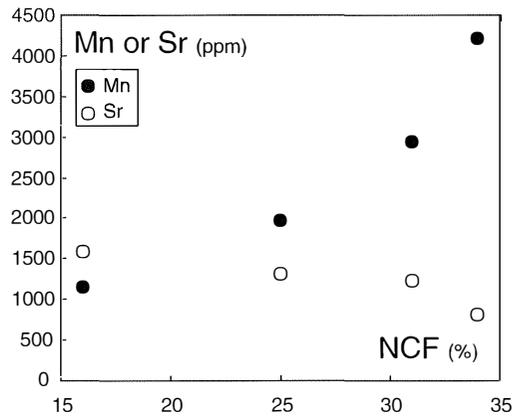
Fig. 4 – Relationships of Mn and Sr with NCF (non-carbonate fraction) in biocalcarenites.

much lower than those of 1154 to 4232 ppm measured in the biocalcarenites. The chemical uniformity in limestones corresponds to a fairly narrow range of the non-carbonate fraction from about 24 to 39% (mean 29.6%). In biocalcarenites, Mn correlates positively with the non-carbonate fraction (NCF), whereas Sr is nearly constant or follows a slightly negative trend (fig. 4). No clear cut correlation is observed between Mn and NFC in either limestone. The Mn/Fe weight ratio in limestones varies between 0.013 and 0.022, i.e. within the range displayed by a number of worldwide carbonate rocks and sediments (e.g., Wedepohl, 1978). The Mn/Fe ratio in biocalcarenites is much higher, with values of 0.08 to 0.22, comparable with those found for both limestones and clayey sediments (e.g., Wedepohl, 1978). In the Mn vs Fe plot (fig. 5), the data points on biocalcarenites roughly define a positive trend, indicating that Mn is basically related to the non-carbonatic fraction of rocks and that the original sediments did not undergo appreciable redistribution of Mn after deposition. The presence of some pyrite (undetected by XRD) cannot be excluded in these rocks, because Mn is basically associated with clay minerals (averaging 700 to 2600 ppm Mn; Deer et al, 1962) and possibly with iron oxides.

Limestones behave differently from biocalcarenites. They show a quite flat distribution in the Mn vs Fe plot (fig. 5), possibly due to substantial removal of Mn from the siliciclastic fraction under reducing conditions, and diagenetic redistribution in the carbonate fraction by substitution for Ca (fig. 6), coupled with the presence of variable amounts of pyrite in the rocks. Therefore, the Mn content in the carbonate fraction of limestones can be calculated at approximately 346 to 545 ppm. These Mn concentration values may be higher than in the original carbonate sediment, if aragonitic ($\pm$ 20 ppm Mn; e.g., Thompson, 1972) rather than calcitic composition ($\pm$ 340 ppm Mn; e.g., Bencini and Turi, 1974) is assumed for the latter.

### Carbon and oxygen isotopes

The calcite $\delta^{13}C$ composition in limestones ranges between $-9.2$ and $-0.3‰$, with all but one of samples between $-2.1$ and $-0.3‰$ (mean $-1 \pm 0.5‰$). The latter values are slightly lower
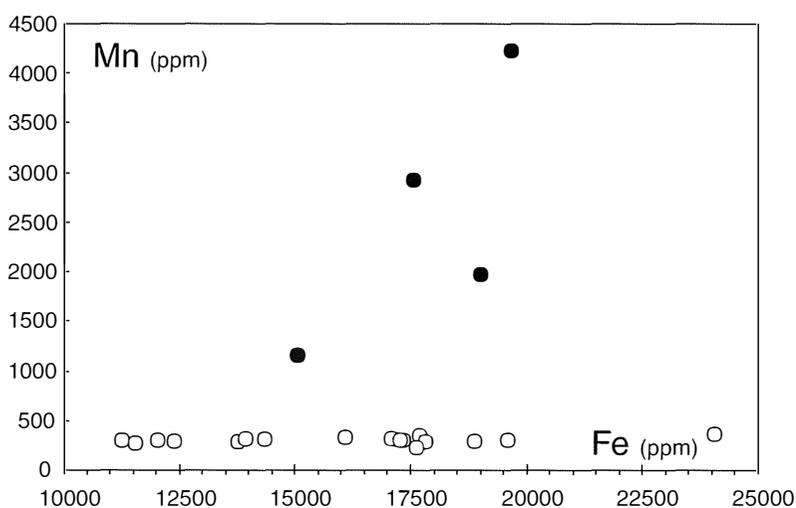


Fig. 5 – Mn *vs* Fe plot for limestones (open circles) and biocalcarenites (filled circles).
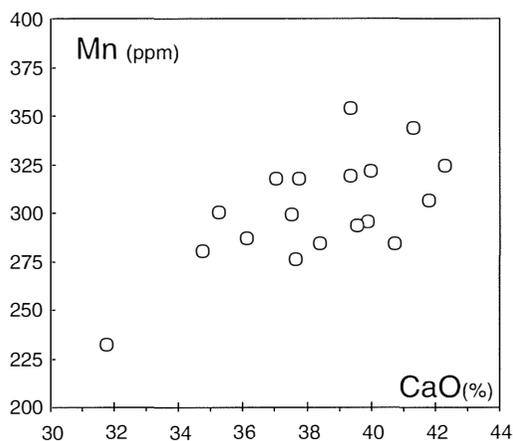
Fig. 6 – Mn distribution in limestones as a function of the CaO content in the rocks .

than expected for both recent marine (e.g., Land, 1989) and Upper Triassic carbonates (e.g., Veizer *et al.*, 1999), suggesting the contribution of some ^{13}C-depleted carbon due to oxidation of organic matter ($\delta^{13}C \approx -14$ to $-25‰$; Deines, 1980). This source of carbon was probably important, especially for calcite with the lowest $\delta^{13}C$ of $-9.2‰$ (sample 15C). Pyrite in this limestone and in others may be biogenic, due to bacterial reduction of sulfate, and this reaction involves the concomitant oxidation of organic matter. The calcite $\delta^{13}C$ composition of biocalcarenites is quite uniform, with positive values of $+1.4$ to $+1.7‰$, i.e., normal marine (fig. 7). The $\delta^{18}O$ composition of these samples is also marine (fig. 7), with measured values of $+31.2$ to $+31.5‰$, corresponding to equilibrium crystallization of calcite from seawater with $\delta^{18}O$ of about $+1.5‰$ at 20°C (Arthur *et al.*, 1983), or a slightly higher to about $+2‰$ (Kim and O'Neil, 1997). These $\delta^{18}O$ values are consistent with present-day ones in Eastern Mediterranean seawater (Cortecci, unpublished data).

The $\delta^{18}O$ of calcite from limestones is quite uniform through the outcrop, with values close to a mean of $+24.6 \pm 0.5‰$. This isotopic signature is definitely lower than that of

primary marine calcite (e.g., Land, 1989; Veizer *et al.*, 1999), testifying that the original sediment underwent considerable isotopic exchange with diagenetic water. Due to the areal uniformity of the $\delta^{18}O$ values, carbonate recrystallization during diagenesis was probably extensive, presumably involving a high water-rock ratio and open system interaction. Diagenesis may have involved Triassic seawater ($\delta^{18}O \approx -1‰$, there being no ice around in those times; see Hudson, 1977, and Veizer *et al.*, 1999) at a temperature of 40 $\pm$ 2°C, as calculated from the calcite-water oxygen isotope fractionation factors of O'Neil *et al.* (1969) or Kim and O'Neil (1997). Lower temperature estimates of 13 to 29°C are obtained by assuming the intervention of meteoric water with $\delta^{18}O$ of $-3.5$ to $-6‰$, as expected for rains in temperate to tropical coastal areas (Land, 1989). The emplacement of the igneous bodies probably released some magmatic water, which may have interacted with the Triassic lithotypes. The related isotopic effects on the latter were probably small, basically due to the low to very low fluid/rock ratio involved. Lastly, diagenetic
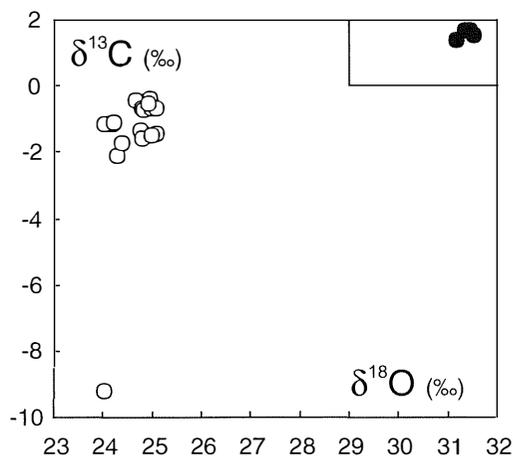


Fig. 7 – $\delta^{13}C$ *vs* $\delta^{18}O$ plot for limestones (open circles) and biocalcarenites (filled circles), compared with boxed isotopic field of «normal» seawater $CaCO_3$ (e.g., Land, 1989).

equilibration for oxygen isotopes does not necessarily imply equilibration for carbon isotopes, due to the large difference in the water-rock ratios required for equilibrating the two isotopic systems (e.g. Banner and Hanson, 1990) and the low carbon isotope exchange rate between $CaCO_3$ and $HCO_3^-$ compared with the oxygen isotope exchange rate between $CaCO_3^-$ and $H_2O$ (Land, 1989). This explains the more uniform $\delta^{18}O$ values in limestones with respect to the $\delta^{13}C$ values.

### Sulfur isotopes

The $\delta^{34}S$ values of the eight gypsum specimens fall between +14.6 and +16.1‰ (mean +15.3 ± 0.6‰), and are nearly equal to the value of +14.4‰ reported by Bigazzi et al. (1996) for a gypsum sample from the same outcrop of Punta delle Pietre Nere. All these data are in good agreement with those available for the Burano Anhydrite Formation in Italy (+14.2 to +17.4‰, mean +15.2 ± 1.2‰, $n = 14$; Cortecci et al., 1981; Bigazzi et al., 1996; Dinelli et al., 1999). These features indicate that recrystallization processes did not affect the original $\delta^{34}S$ signature of the evaporite, thus excluding the involvement of fluids rich in sulfur with distinct isotopic composition, like magmatic fluids during the Paleocene ($\delta^{34}S = 0 ± 5‰$; Ohmoto and Goldhaber, 1997).

Macrocrystalline pyrite (millimetric cubic to octahedral crystals; see Bigazzi et al., 1996) and microcrystalline pyrite from four limestone samples reveal quite different $\delta^{34}S$ values of $-1.6$ to $+0.6‰$ and $+15.1‰$, respectively. The highest value is equal to that of gypsum and refers to a pyrite specimen relatively far away from the contact with the melasyenite. A biogenic origin may be concluded for this pyrite, due to bacterial reduction of Triassic marine sulfate during burial in a partially closed packet of sediment (e.g., Ohmoto and Goldhaber, 1997).

Pyrite with low $\delta^{34}S$ around 0‰ derives from limestone handspecimens at the contact with the melasyenite, and may be magmatic. Alternatively, their isotopic composition may be explained by a biogenic origin from rapid

reduction of Triassic seawater sulfate in sediments open to aqueous sulfate, with a sulfate-sulfide kinetic isotope effect of about 15‰ (Ohmoto and Goldhaber, 1997). This effect may have been associated with a near-shore depositional environment (Ohmoto and Rye, 1979).

### Strontium isotopes

The $^{87}Sr/^{86}Sr$ ratios of 0.70761 to 0.70769 in calcite from limestones are in keeping with the value reported by Burke et al. (1982) for Upper Triassic marine strontium ($^{87}Sr/^{86}Sr = 0.7076-07077$). These values are consistent with the mean ones reported by Faure et al. (1978) for Tethys Sea strontium during the Upper Triassic of Val Camonica in the Lombardy Alps, northern Italy (0.70776 to 0.70791). The $^{87}Sr/^{86}Sr$ ratios in the gypsum samples match also the Upper Triassic value, and are consistent with that reported for a gypsum specimen from the Burano Formation of Tuscany ($^{87}Sr/^{86}Sr = 0.70789$ and $\delta^{34}S = +14.6‰$; Dinelli et al., 1999).

Strontium isotope values support the hypothesis that Upper Triassic seawater was the parental and diagenetic fluid for both carbonate and sulfate, and once again indicate that the emplacement of the igneous bodies during the Paleocene and subsequent tectonic events did not influence the isotopic and chemical composition of Sr in the sedimentary lithologies.

### CONCLUSIONS

The Triassic sedimentary lithologies represented at Punta delle Pietre Nere by black limestone and gypsum outcrops did not undergo modifications of chemical and/or isotopic composition during the emplacement of the Paleocene igneous bodies, nor afterwards during a number of tectonic events which ended in Plio-Pleistocene times.

Sr and Mn in the limestones were redistributed during diagenesis, probably by

fluids essentially composed of seawater. According to the $\delta^{18}O$ signature, seawater-rock interactions may have occurrred at about 40°C and in high water-rock ratio conditions. The $\delta^{13}C$ signature suggests that organic bicarbonate ions due to bacterial reduction of interstitial sulfate entered the diagenetic fluids, thus lowering the original isotopic composition considerably.

The $^{87}Sr/^{86}Sr$ ratio of limestones is in keeping with their Upper Triassic age. The $^{87}Sr/^{86}Sr$ ratio and $\delta^{34}S$ of gypsum also agree with the Upper Triassic age of sulfate, and are nearly identical with those of the Burano Anhydrite Formation of Italy. The $\delta^{34}S$ values of pyrite separate from limestones at the contact with melasyenite suggest a magmatic origin of this mineral. The $\delta^{34}S$ signature of pyrite looks biogenic far from the contact.

Biocalcarenites are much richer in Sr and Mn with respect to local limestones, and Mn shows a good positive correlation with Fe, suggesting that the original sediments did not suffer appreciable redistribution of Sr and Mn after deposition. The $\delta^{13}C$ and $\delta^{18}O$ values are normal marine.

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