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THE APUANE ALPS METAMORPHIC COMPLEX, NORTHERN TUSCANY: CHEMICAL AND ISOTOPIC FEATURES OF GREZZONI AND MARMI DOLOMITICI

Abstract - The carbonate Grezzoni and Marmi Dolomitici formations of the Nucleo Metamofico Apuano (Apuane Alps Metamorphic Core) were investigated for major and selected minor elements, and carbon, oxygen and strontium isotope compositions of calcite and dolomite. The interposed Brecce di Seravezza horizon was also analysed.

The chemical and isotopic results on Grezzoni and Marmi Dolomitici match well with those of the age-equivalent Mesozoic sedimentary formations of the Tuscan Nappe, this similarity excluding significant effects due to interaction with fluids during the Alpine-Apenninic regional metamorphism in Oligocene-Miocene times. This interpretation also applies to the Brecce di Seravezza.

The «dry» character of the metamorphism experienced by the rocks in question should testify that the protoliths were lithified and diagenetically stabilized when the Apuane Alps orogeny began, about 180 Ma after the original sediments were deposited. The Grezzoni formation may have acted as a barrier towards metamorphic fluids possibly circulating into the basement.

Key words - Apuane Alps, Grezzoni, Marmi Dolomitici, Brecce di Seravezza, chemical composition, isotopic composition, metamorphic effects.

Riassunto - *Il complesso metamorfico delle Alpi Apuane, Toscana settentrionale: caratteristiche chimiche ed isotopiche dei Grezzoni e dei Marmi Dolomitici.* È stato condotto uno studio geochimico ed isotopico delle formazioni carbonatiche dei Grezzoni e Marmi Dolomitici (Nucleo Metamorfico Apuano), interessate durante l'Oligocene-Miocene dall'orogenesi Apenninica. Sono state studiate anche le Brecce di Seravezza interposte fra le due formazioni. Il lavoro analitico ha riguardato la composizione chimica degli elementi maggiori e di alcuni minori, e la composizione isotopica del carbonio, ossigeno e stronzio di calciti e dolomiti.

I risultati ottenuti si accordano con le caratteristiche geochimiche dei possibili protoliti (Falda Toscana), escludendo per le rocce studiate effetti metamorfici significativi. Il metamorfismo è stato di tipo «anidro», ed ha interessato protoliti ormai litificati e diageneticamente stabilizzati, dopo circa 180 Ma dalla deposizione dei sedimenti originari.

La formazione dei Grezzoni potrebbe aver costituito una barriera nei confronti dei fluidi metamorfici circolanti nel basamento dell'edificio apuano.

Parole chiave - Alpi Apuane, Grezzoni, Marmi Dolomitici, Brecce di Seravezza, composizione chimica, composizione isotopica, effetti metamorfici.

INTRODUCTION

The Apuane Alps are worldwide known especially for the Carrara statuary marble, that was used by Michelangelo to sculpture his famous Mosé. The marble, dated to Hettangian, consists of almost pure calcite (>96%; e.g. Herz and Dean, 1986), fairly homogeneous, equigranular and fine to medium grained. This marble formation was extensively studied from a geological and archeological point of view, including isotope geochemistry (e.g. Cortecci and Orlandi, 1975; Herz and Dean, 1986; Cortecci et al., 1992 and 1994).

The $\delta^{13}C$ and $\delta^{18}O$ values of Carrara Marble are indistinguishable from those of the possible protolith, the latter being represented by the age-equivalent Calcare Massiccio (massive limestone) of the unmetamorphosed Tuscan Nappe sequence (Carmignani et al., 1978). The preservation of the original isotopic signature was interpreted by Cortecci and Lupi (1994) as due to metamorphic recrystallization under low to very low water to rock ratio in a basically closed system. On the other hand, the dehydration of schists in the terrigenous Paleozoic basement was probably a major source of water during the regional metamorphism (Cortecci et al., 1992), but an uprising plumbing system may have been precluded by the hydraulic barrier represented by the dolomitic Grezzoni formation that plugs the basement (Cortecci and Lupi, 1994; Cortecci et al., 1994). In order to verify this hydrologic-metamorphic model, a geochemical study was undertaken on the Grezzoni formation and the Marmi Dolomitici (dolomitic marbles) formation, the latter being in places interposed between the Grezzoni and the Hettangian Carrara Marble. The Brecce di Seravezza, that is a breccia found in places along the Grezzoni-Marmi Dolomitici contact, were also investigated. The geochemical tools used involve carbon, oxygen and strontium isotope abundances in calcite and dolomite, along with major and minor chemistry of rocks.

GEOLOGICAL OUTLINE

The Apuane Alps massif is a large tectonic window of northern Apennines (Trevisan, 1970), close to the Tyrrhenian coast in northern Tuscany. Main tectono-stratigraphic units are the unmetamorphosed Tuscan Nappe and Ligurids complex, and the metamorphic autochtho-

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nous series (Carmignani et al., 1978; Ciarapica and Passeri, 1978 and 1982; Coli, 1990). The metamorphic autochthon (Nucleo Metamorfico Apuano; NMA) consists of a Paleozoic-Triassic basement made up mainly of phyllites, quartzites and felsic metavolcanics and their volcanoclastic products. This basal unit is overlain, locally with interpositions of Triassic silicoclastic-carbonatic terrains, by the dolomitic formation of Grezzoni (Norian and possibly Rhaetian), followed by the Marmi Dolomitici (Rhaetian to Hettangian?), the Carrara Marble (Hettangian) and other Jurassic to Oligocene formations both carbonatic and terrigenous.

According to Carmignani and Kligfield (1990), the NMA was affected by a compressional phase at about 27 Ma and by an extentional phase around 12 Ma, during the Alpine-Apennine orogeny. The metamorphic grade of NMA was in the greenschist facies, with estimated peak temperature of 380-500°C and pressure of 3-4 Kbars (Di Pisa et al., 1985 and references therein).

The sedimentary environment of the Grezzoni formation is interpreted as a hyperhaline carbonate platform, passing to a shallow coastal basin westwards (Ciarapica and Passeri, 1978 and 1982; Coli and Fazzuoli, 1992). The Calcare Cavernoso (a pock-marked dolomitic limestone of hyperhaline to shallow water origin; Norian) and the Calcare a *Rhaetavicula contorta* (a platform carbonatic marly rock highly terrigenous; Rhaetian to lower Hettangian?) of the Tuscan Nappe may have been the protoliths of the Grezzoni metamorphites. Pock-marks of

Calcare Cavernoso were filled of gypsum, then dissolved by circulating water.

The Marmi Dolomitici formation consists of metalimestones with centimetric to metric dolomite layers and locally of nearly pure dolomite beds. The sedimentary environment of this formation should have been a sub-intertidal to supratidal carbonate platform (Coli and Fazzuoli, 1992). These sediments should be equivalent to those of the Calcare Massiccio formation (Hettangian to Sinemurian?) of the Tuscan Nappe (Nardi, 1966).

The Brecce di Seravezza horizon is constituted by calcite and dolomite fragments, within a cement of lateritic composition, this testifying that the breccia formed in subaerial conditions (Giglia and Trevisan, 1967). The breccia is older than the Apennine metamorphism, which also affected the breccia cement.

SAMPLING AND ANALYTICAL PRECEDURES

The sampling points are shown in the tectonic map of Fig. 1, and localized within the reconstructed stratigraphies of Fig. 2. Samples are from major outcrops of Grezzoni and Marmi Dolomitici through the NMA.

Mineralogical and geochemical analyses were performed on selected sample chips with no visible vein material. As from X-ray diffractometry, main mineralogy is dolomite ± calcite in the Grezzoni and calcite and dolomite in the Marmi Dolomitici, and a common subordinate silicate fraction made up of quartz, albite, muscovite and kaolinite. In the Brecce di Seravezza, main mineralogy is the same, but some samples show a largely prevailing non-carbonate mineral fraction. The percentages of calcite and dolomite in the rock specimens were estimated by a gasometric method (Leone et al., 1988).

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

The carbon and oxygen isotopic analyses were carried out mass-spectrometrically on CO_2 extracted from calcite or dolomite with 100% H_3PO_4 at 25°C (McCrea, 1950). Calcitic samples were reacted overnight, whereas dolomitized samples were reacted for 30' to avoid significant contamination of the calcite-CO_2 by the dolomite-CO_2. Dolomite was reacted for at least 72 h, after removal of calcite by treatment of the sample with 5% acetic acid for 30' at room temperature. A number of rocks with comparable calcite and dolomite proportions was submitted to the fractional extraction method (e.g. Cortecci et al., 1985). The carbon and oxygen isotopic abundances are reported in the $\delta^{13}C$ and $\delta^{18}O$ notations, in per mil, relative to PDB standard and V-SMOW standard, respectively. The precision of measurements was better than ±0.1‰. The $^{87}Sr/^{86}Sr$ ratio was measured in several calcite and dolomites, including coexisting mineral phases. Calcite was leached in 40% acetic acid at room temperature, thus excluding the dolomitic fraction. Dolomite was leached in warm 2.5N HCl, after removal of calcite by acetic acid treatment. Sr was extracted from the leachates by cation exchange chromatography, then eluted and analysed. The precision of measurements was between ± 0.00002 and ± 0.00005. The measured ratios were normalized to a
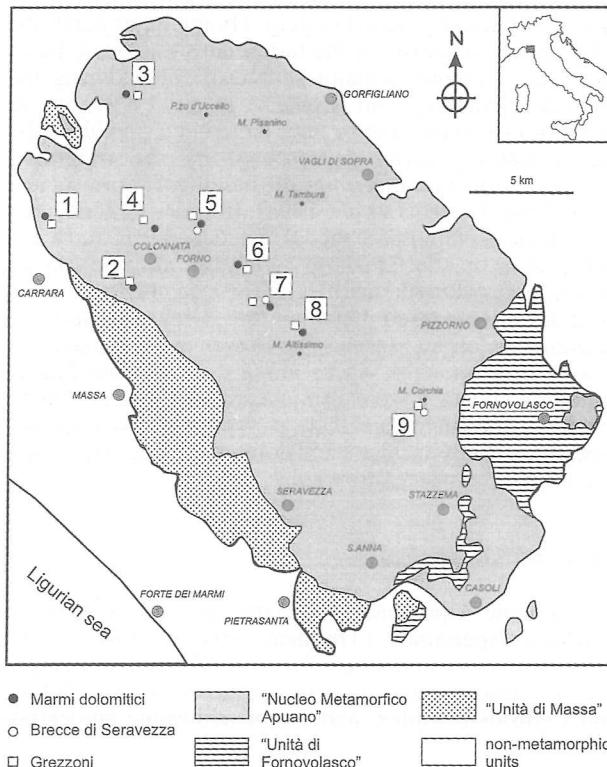

Fig. 1 - Simplified structural map of Apuane Alps (after Ciarapica and Passeri, 1982), with location of sampling points.
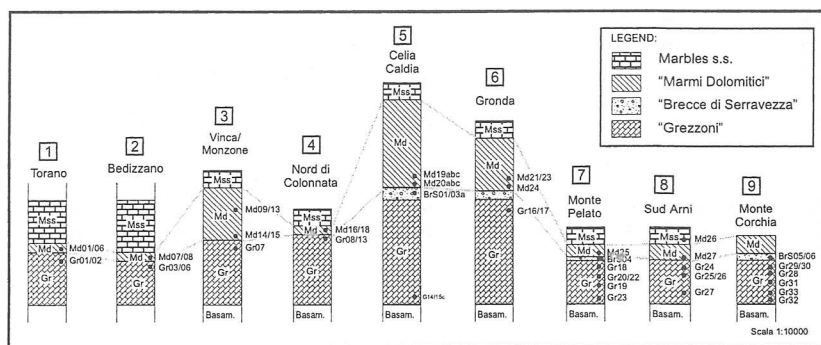
Fig. 2 - Reconstructed stratigraphies at the Grezzoni, Marmi Dolomitici and Brecce di Seravezza sampling sites (see Fig. 1 for numbering). Sampled formations are specified by symbols. The appoximate positions of samples within the stratigraphic column are shown by filled circles. Marbles *s.s.* include the Carrara marble.

^{86}Sr/^{88}Sr ratio of 0.1194 in natural strontium, and to NBS 987 SrCO$_3$ standard for which a mean ^{86}Sr/^{88}Sr ratio of 0.710200 ± 0.000012 was obtained.

RESULTS AND DISCUSSION

The chemical and isotopic results for Grezzoni, Marmi Dolomiti and Breccie di Seravezza are reported in Tabs. 1 to 3, respectively. Chemical and isotopic data of Grezzoni and Marmi Dolomitici are compared in Table 4 with those of relevant sedimentary and metamorphic carbonate formations of northern Tuscany.

Grezzoni formation

As far as the major chemistry is concerned, [CaO + MgO + CO$_2$] ranges between 73.0 to 99.6%, with only one sample (Gr11) with 47.8%. Both Ca and Mg can be basically attributed to the carbonate fraction, due to the very good agreement between measured and calculated CO$_2$ percentages in the samples. The only significant exceptions are represented by the notably siliciclastic samples Gr9 and Gr11. In the first case, the percentage of calculated CO$_2$ is by 9.7% lower than the measured one, thus suggesting the evolution of additional gas from the rock, possibly H$_2$S from HCl decomposition of pyrite during the gasometric analysis. In the second case, the percentage of calculated CO$_2$ is by 6.5% higher than measured, likely due to the presence of Mg/Ca silicates. Other elements, like Al, Fe, K, Ti and P can be attributed to the non-carbonate fraction, whereas Na may be partly related to calcite and dolomite.

Sr concentration in whole rock samples varies between 41.9 and 990.3 ppm, that is from 43 to 1000 ppm in the carbonate fraction, if no Sr is assumed in the siliciclastic fraction. The Sr contents measured in the possible protoliths are 178 ppm in a Calcare Cavernoso calcitic specimen (Cortecci and Lupi, 1994), and 27 to 190 ppm (mean 115 ppm; n = 7) and 179 to 1273 ppm (mean 483 ppm; n = 10) in mostly dolomitic or calcitic specimens of Calcare a *Rhaetavicula contorta,* respectively (Manetti and Turi, 1973; Cortecci and Lupi, 1994). The Sr contents in the carbonate fraction of most (dolomitic) Grezzoni specimens (43 to 187 ppm; mean 93.9 ± 36 ppm) are comparable with those of the Calcare a *Rhaetavicula contorta*. High values of 415 to 1000 ppm are randomly distributed

in the studied outcrops, and refer to nearly pure dolomite (93 to 100%) and calcite (91 and 99%) specimens. In the most terrigenous sample (Gr11, 53% siliciclastic minerals, 21% dolomite and 26% calcite), the Sr concentration in the carbonate fraction is calculated close to 90 ppm, that is consistent with that of most essentially carbonate samples. These features support a genetic link of Grezzoni especially with the Calcare a *Rhaetavicula contorta* formation and a preservation of the diagenetic effects during the metamorphism of the protolith.

Therefore, the Sr features in the Grezzoni are in the following discussed in terms of diagenetic effects, also assuming that effectively the metamorphic effects should have been minor or very minor, as in general suggested by the findings on rocks which underwent regional metamorphism (e.g. Sighinolfi, 1978 and references therein). This assumption is supported by the δ^{18}O values, which will be discussed later on. According to Vahrenkamp and Swart (1990), the Sr data set of most dolomite samples may be explained with combined diagenetic effects related to dolomitization of the precursor carbonate by fluids with a by weight Sr^{2+}/Ca^{2+} ratio less than 0.02 (seawater) and to different deviation degrees of the mineral from stoichiometry. The dolomitizing fluid would have been seawater, possibly lowered in its Sr^{2+}/Ca^{2+} ratio by dissolution of calcite/aragonite and perhaps gypsum/anhydrite in the original supratidal-intertidal sediments. Dolomites with high Sr content may have formed rapidly, this involving a higher distribution coefficient D$_{Sr}$^{dolomite}. Such a supposed positive relationship between D$_{Sr}$^{dolomite} and crystalization rate is supported by the positive relationship observed during calcite crystallization (Dickson, 1985). The higher Sr contents in calcitic specimens compared to nearby dolomitic specimens match with the greater distribution coefficient of Sr for calcite than for dolomite (e.g. Land, 1980). The dishomogeneous distribution of Sr within the formation may account for variable proportion of aragonite to calcite in the original sediments, as well as for areally variable water to rock ratios during the diagenesis.

The Mn in whole rock samples varies between 28.3 and 668.6 ppm. This range of values includes pure dolomites, which also show the lowest and the highest contents. This feature suggests that Mn is almost completely hosted in the carbonate fraction, and the silicate fraction acts as diluent (see also Bencini and Turi, 1974, and Wedepohl, 1978). All but one Mn content values recalculated in the carbonate fraction are in the range 28 to 304 ppm, with a

Tab. 1 - Chemical and isotopic data for rock samples from the Grezzoni formation.

Sample	Carbonate mineralogy*	CO_2 wt%	CaO wt%	MgO wt%	SiO_2 wt%	Al_2O_3 wt%	TiO_2 wt%	Fe_2O_3 wt%	Na_2O wt%	K_2O wt%	Sr ppm	Mn ppm	Rb ppm	$\delta^{13}C_{cal}$ ‰	$\delta^{13}C_{dol}$ ‰	$\delta^{18}O_{cal}$ ‰	$\delta^{18}O_{dol}$ ‰	$^{87}Sr/^{86}Sr_{cal}$	$^{87}Sr/^{86}Sr_{dol}$
Gr01	d(100)	46.9	29.6	22.1	0.64	0.26	0.01	0.23	0.16	0.06	43	107			2.9		29.5		0.708392
Gr02	d(99)	46.8	29.5	22.0	0.88	0.39	0.01	0.15	0.11	0.09	60	62			2.9		29.3		0.708638
Gr03	d(100)	47.1	29.9	22.4	0.25	0.10		0.08	0.16	0.04	83	64			2.4		29.2		
Gr03b	d(90) c(4)	44.1	30.3	21.6	3.49	0.08	0.01	0.16	0.11	0.04	119	85			1.8		29.8		0.708196
Gr04	d(93)	43.3	26.7	20.3	5.47	2.60	0.09	0.64	0.38	0.46	70	53	13		2.9		30.2		
Gr05	d(100)	46.3	29.7	22.2	1.27	0.18	0.01	0.13	0.16	0.06	79	56			2.6		30.2		
Gr06	d(100)	46.8	29.9	22.4	0.56	0.10	0.01	0.09	0.15	0.04	71	29			2.9		30		
Gr07	d(96)	44.6	26.8	20.4	5.05	2.05	0.06	0.58	0.07	0.39	97	189	14		1.8		29.2		
Gr08	d(75) c(16)	42.8	29.8	17.7	6.16	1.89	0.05	0.52	0.26	0.48	154	49	13		1.8		30		
Gr09	d(63) c(14)	36.2	23.0	13.8	16.32	6.73	0.19	1.44	0.17	1.47	143	171	50		1.9		30.1		
Gr10	d(9) c(91)	44.0	52.8	2.5	0.24	0.08		0.13	0.17	0.04	428	77		1.7		24.7			
Gr11	d(21) c(26)	21.5	18.7	7.6	30.71	12.41	0.49	2.89	0.29	2.74	42	143	96		3.3		29.5	0.708138	
Gr12	d(75)	35.8	21.7	16.5	13.96	6.55	0.19	1.36	0.37	1.43	85	201	52		2.6		30.1		
Gr13	d(86) c(7)	44.1	28.4	19.6	4.09	1.80	0.05	1.01	0.15	0.35	116	135	12		2.6		30.6		0.708901
Gr14	d(100)	47.0	30.0	21.9	0.51	0.25	0.01	0.1	0.11	0.07	57	63			1.7		27.9		
Gr15a	d(92) c(5)	45.9	28.5	20.7	2.73	1.28	0.04	0.31	0.24	0.25	62	78	6		1.9		27.8		0.709007
Gr15b	d(89)	41.3	25.6	18.7	8.24	3.73	0.11	1.11	0.67	0.53	80	65	24		2.3		29.6		
Gr15c	d(98)	46.1	29.9	21.5	1.27	0.6	0.02	0.31	0.15	0.12	79	54	4		2.3		30.7		0.708262
Gr16	d(96) c(2)	46.7	30.2	22.2	0.25	0.12	0.01	0.15	0.04	0.03	86	105			2.2		32.2		
Gr17	d(97) c(2)	46.9	30.4	22.1	0.25	0.10		0.15	0.04	0.02	94	116			2.3		32.5		
Gr18	d(86) c(10)	45.1	30.9	18.9	2.75	1.49	0.05	0.49	0.08	0.21	113	90	13		0.9		31.5		
Gr19	d(100)	47.1	29.3	22.6	0.63	0.11		0.14	0.05	0.02	62	40			3.1		31.3		
Gr20	d(100)	46.5	29.2	22.3	1.01	0.53	0.02	0.125	0.05	0.08	54	55			1.7		32		
Gr21	d(100)	47.1	29.7	22.6	0.22	0.08	0.01	0.16	0.04	0.02	69	39			3.4		31.4		
Gr22	d(100)	47.0	29.8	22.7	0.14	0.06	0.01	0.13	0.05	0.02	52	32			3.2		32.2		
Gr23	d(100)	47.2	29.5	22.7	0.35	0.05		0.17	0.04	0.02	69	71			3.7		29.5		
Gr24	d(75) c(20)	44.6	30.7	19.4	2.36	1.30	0.04	0.60	0.11	0.22	125	143	9	1.6	2	26.5	30.5		
Gr25	c(99)	43.4	54.6	0.4	0.90	0.22	0.01	0.28	0.07	0.06	750	67	4	1.3		23.7			
Gr26	d(79) c(19)	45.4	31.9	19.4	1.84	0.81	0.02	0.36	0.08	0.14	155	58	7	0.9	-0.2	30.5	29.3		
Gr27	d(100)	47.0	29.5	22.6	0.43	0.15	0.01	0.17	0.08	0.02	63	36			2.7		30.2		
Gr28	d(93) c(6)	46.2	29.9	21.4	1.23	0.67	0.02	0.26	0.05	0.13	990	67	7		1.7		32.9		
Gr29	d(78) c(18)	44.4	30.6	19.1	3.00	1.68	0.07	0.48	0.09	0.33	398	156	16	-0.2	0.2	28	31.5		
Gr30	d(65) c(29)	43.1	32.7	16.5	3.83	2.24	0.09	0.54	0.08	0.46	141	157	22	-0.5	0.2	28.4	30.2		
Gr31	d(100)	46.7	29.9	22.4	0.37	0.21	0.01	0.23	0.03	0.04	95	101			2.6		32.6		
Gr32	d(100)	46.2	29.4	21.6	1.06	0.35	0.01	1.19	0.07	0.08	108	669			0.1		26.5		
Gr33	d(100)	46.9	29.1	22.6	0.69	0.30	0.01	0.21	0.04	0.06	74	207			2.4		28.6		

* c: calcite; d: dolomite; ( ): wt % of the mineral

mean of 106 ± 73 ppm. This mean figure is consistent with that of 92 ± 50 ppm found by Bencini and Turi (1974) in the carbonate fraction of the *Rhaetavicula contorta* limestone in the Lima valley not far from Apuane Alps in northern Tuscany. Such a consistency points to a preservation of the Mn diagenetic distribution in the Grezzoni during metamorphism. The high of 669 ppm Mn, as well as the observed Mn variability through the formation, may be interpreted in terms of variable aragonite to calcite ratios in the original sediments from shallow water deposition, with aragonite largely depleted in Mn with respect to calcite (e.g. Deer *et al.*, 1962). Diagenetic dolomitization did not modify appreciably the original Mn content distribution of sediments.

The $\delta^{13}C$ values of dolomite and calcite vary from –0.2 to +3.7‰ (mean +2.2 ± 0.9‰; n = 34) and from –0.5 to +1.7‰ (mean +0.8 ± 0.9‰; n = 6), respectively (Fig. 3). They are consistent with the range of values of -1.9 to +4.0‰ obtained for calcites and dolomites from the presumed protolith(s) (Cortecci *et al.*, 1985; Cortecci and Lupi, 1994), which is in turn nearly identical to that found for both Triassic and modern carbonate sediments (-2 to +4‰; Gross, 1964; Veizer and Hoefs, 1976; McKenzie, 1981; Land, 1989).

The $\delta^{18}O$ of dolomite and calcite ranges between +26.5 and +32.9‰ (mean +29.9 ± 1.6‰) and between +23.7 and +30.5‰ (mean +27.0 ± 2.5‰), respectively. Values on calcite higher than +24.7‰ refer to rocks with a largely predominant dolomitic composition and may be in excess due to contamination by dolomite-CO_2 during the selective acid decomposition procedure of samples.

All but one $\delta^{18}O$ values of dolomite are considerably higher than the few ones available for the non-metamorphic Triassic terrains of the Tuscan Nappe (+26.6 to +27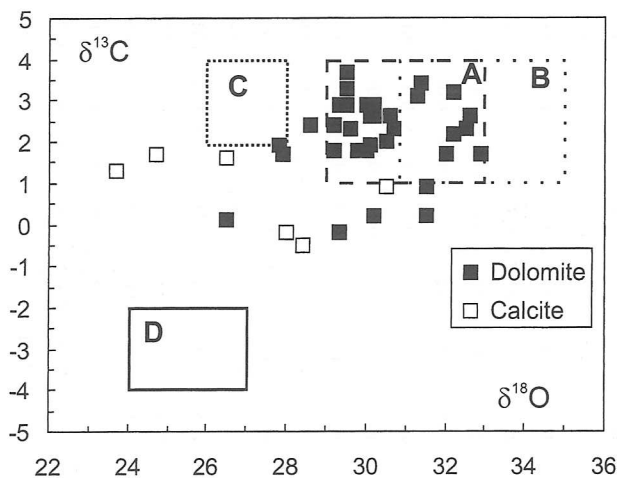.6‰; Cortecci and Lupi, 1994). All these are consistent with those found for Holocene (Land, 1980; Mckenzie, 1981) and pre-Holocene (Land, 1980 and references therein) dolomites, including most Triassic analogues (+26 to +33‰; Veizer and Hoefs, 1976). Calcite $\delta^{18}O$ values are consistent with those observed for Triassic analogues from the Tuscan Nappe (+25.7 to +26.3‰; Cortecci *et al.*, 1985; Cortecci and Lupi, 1994), as well as with the range shown by worldwide Triassic limestones (+23 to +29‰, with most values from +26 to +29‰; Veizer and Hoefs, 1976). On the whole, the $\delta^{18}O$ values would seem to exclude significant isotopic effects on Grezzoni due to metamorphism.

Marmi Dolomitici

The [CaO + MgO + CO_2] percentages in all but two marbles are in the range 94 to 99%. Low percentages of 63% and 82% are shown by the most impure samples in terms of each other major element. In both the latter two samples, however, the amounts of measured and calculated CO_2 are identical. Therefore, Ca and Mg in the Marmi Dolomitici formation can be attributed basically to the carbonate fraction, whereas the other major elements are hosted by the siliciclastic fraction.

In nearly pure calcite (≥ 99%), the Sr content varies between 47 to 1181 ppm. Lower contents of 48 to 604 ppm Sr are shown by calcite-dolomite mixtures, with values of 48 to 125 ppm (mean 87 ppm; n = 10) in rocks with 67 to 95% dolomite. All these values for calcite and dolomite are within the overall range measured in analogues from the Calcare Massiccio in the Apuane Alps (Cortecci and Lupi, 1994) and northern Apennines (Manetti and Turi, 1973; Cortecci and Lupi, 1994), that is 0 to 2173 ppm Sr (mean 465 ppm; n = 34) for calcitic rocks and 70 to 195 ppm Sr (mean 137 ppm; n = 7) for dolomitic rocks. They are also consistent with those observed in the Grezzoni both for dolomitic and calcitic rock specimens. Also similar are the concentrations and distributions of Sr in the Calcare Massiccio and Calcare a *Rhaetavicula contorta*, in keeping with a common origin from epicontinental platform sedimentation, followed by comparable diagenetic effects. With respect to the overlying Carrara Marble (111 to 248 ppm Sr, mean 164 ± 40 ppm, n = 11; Herz and Dean, 1986), the Marmi Dolomitici appear to be much more dishomogeneous, possibly due to the transitional platform environment in which their precursor sediments formed. This interpretation is supported by the Sr/Ca trend through the formation (Fig. 4), that possibly depicts the evolution from aragonite sediments rich in Sr (shallower water) to calcite sediments poor in Sr (deeper water), moving upwads through the formation (see also Crisci *et al.*, 1975).

The Mn in whole rock specimens varies between 0 and 258 ppm. Recalculated Mn contents in the carbonate fraction are in the range 0 to 298 ppm, with most values between 0 and 88 ppm (mean 30 ppm; n = 30). High values of 125 to 298 ppm (n = 3) refer to rocks with 84 to 95% dolomite. In general, Mn appears to correlate positively with the dolomitic fraction (Fig. 5), this feature suggesting that dolomitization occurred from fluids enriched in Mn with respect to seawater and/or Mn parti-

Fig. 3 - $\delta^{13}C$ vs $\delta^{18}O$ of calcite and dolomite from the Grezzoni, compared to the isotopic fields of primary calcite (A) and dolomite (B), and presumed protoliths Calcare a *Rhaetavicula contorta* (C) and Calcare Cavernoso (D). Data on primary carbonates are from Land (1989). Data on Calcare a *Rhaetavicula contorta* are from Kalk (1990) and Cortecci and Lupi (1994); those on Calcare Cavernoso are from Cortecci *et al.* (1985) and Cortecci and Lupi (1994).

Tab. 2 – Chemical and isotopic data for rock samples from the Marmi Dolomitici formation.

Sample	Carbonate mineralogy*	CO_2 wt%	CaO wt%	MgO wt%	SiO_2 wt%	Al_2O_3 wt%	TiO_2 wt%	Fe_2O_3 wt%	Na_2O wt%	K_2O wt%	Sr ppm	Mn ppm	Rb ppm	$\delta^{13}C_{cal}$ ‰	$\delta^{13}C_{dol}$ ‰	$\delta^{18}O_{cal}$ ‰	$\delta^{18}O_{dol}$ ‰	$^{87}Sr/^{86}Sr_{cal}$	$^{87}Sr/^{86}Sr_{dol}$
Md01	c(99)	43.5	55.0	0.6	0.24	0.09	0.01	0.05	0.16	0.06	1011	8		2.4		27.9			
Md02	c(33) d(49)	37.9	32.3	11.5	9.02	4.67	0.19	1.09	0.31	0.19	425	53	44	0.2		27.4			
Md03	c(66) d(32)	44.3	47.4	6.5	0.92	0.38	0.02	0.13	0.26	0.15	418	19		2.2	2.8	28.3	29.9		
Md04	c(100)	44.0	54.9	1.0	0.29	0.13	0.01	0.06	0.17	0.07	823	12		1.6		28		0.707651	
Md05	c(100)	44.0	55.1	0.7	0.22	0.09	0.01	0.06	0.17	0.05	604	7		3.1	3.2	28.8	29.4	0.707675	
Md06a	c(79) d(18)	43.3	50.5	4.0	0.75	0.31	0.01	0.12	0.18	0.11	331	8	5	2.7		28.6			
Md06b	c(64) d(35)	44.8	45.7	7.9	0.72	0.28	0.02	0.10	0.26	0.14	273	11		2.6		28.7			
Md07c	c(70) d(30)	41.5	45.5	7.9	0.26	0.10		0.07	0.16	0.06	181	78		2.4		27.9		0.707755	
Md07d	c(14) d(85)	46.7	31.9	20.4	0.38	0.16	0.01	0.18	0.14	0.06	125	258			3.1		28		0.708191
Md08	c(89) d(5)	41.5	49.6	2.5	3.23	1.52	0.06	0.54	0.18	0.39	365	53	14	2.2	2.2	29			
Md09	c(67) d(33)	45.2	47.0	7.4	0.16	0.06	0.01	0.16	0.07	0.02	103	37	4	1.6	2.2	27.1	31.5		
Md10	c(95) d(5)	44.1	54.6	1.3	0.11	0.04		0.16	0.07	0.02	152	14	5	1.6		27.1			
Md11	c(97) d(3)	44.1	54.8	1.0	0.08	0.03		0.16	0.08	0.02	156	14	5	1.8		27.6			
Md12	c(33) d(67)	46.5	38.1	15.1	0.28	0.12	0.01	0.15	0.07	0.03	97	39		1.7	2.2	28.5	31.9		
Md13	c(83) d(17)	44.6	49.5	5.6	0.14	0.06	0.01	0.16	0.08	0.02	109	19		1.8	2.5	29.8	31.7		
Md14	c(82) d(18)	44.6	48.2	6.6	0.43	0.11	0.01	0.18	0.08	0.04	88	46	5	2.1	1.9	26.9	29.1		
Md15	c(5) d(95)	47.5	31.9	10.3	0.45	0.19	0.01	0.15	0.07	0.05	83	125			2.6		31.3		
Md16	c(100) d(8)	44.0	55.3	0.9	0.19	0.06	0.01	0.06	0.16	0.06	514	7		2.3		28.4			
Md17	c(91)	43.8	53.5	2.1	0.31	0.09	0.01	0.07	0.14	0.06	294	4	5	2.2		29.2			
Md18	c(29) d(68)	45.2	37.6	15.3	0.62	0.28	0.01	0.17	0.16	0.10	104	52		1.7	2.4	28.5	29.1		
Md19a	c(17) d(79)	45.2	32.7	18.9	1.77	0.78	0.03	0.25	0.15	0.11	88	74			2.7		29.9		
Md19b	c(20) d(44)	29.8	20.4	12.6	20.07	10.12	0.47	1.97	0.29	2.25	83	191	83	2	3	29.3	29.4		
Md19c	c(24) d(76)	46.8	32.7	19.5	0.63	0.26	0.01	0.09	0.15	0.07	86	83			2.7		30.3		
Md20a	c(12) d(87)	46.8	31.6	19.9	0.81	0.32	0.02	0.11	0.24	0.12	48	73			2.5		26.2		0.708404
Md20b	c(15) d(84)	46.7	32.8	20.1	0.16	0.09	0.01	0.04	0.15	0.05	72	87			2.6		29.2		
Md20c	c(15) d(84)	46.7	32.6	19.7	0.78	0.34	0.02	0.08	0.15	0.08	77	148			2.6		29.8		
Md21	c(78) d(22)	44.8	49.2	5.7	0.23	0.11	0.01	0.18	0.07	0.03	96	17	4	2.2	2.8	29	31.1		
Md21b	c(91) d(9)	44.3	54.0	1.8	0.20	0.09	0.01	0.17	0.08	0.03	117	10	5	1.7		28.2			
Md22s	c(97) d(3)	44.1	54.4	1.3	0.13	0.05		0.16	0.08	0.02	112	9	4	1.7		27.3			
Md23	c(99)	43.5	54.2	0.9	0.76	0.42	0.02	0.27	0.09	0.09	121	8	7	1.2		27.2			
Md24	c(100)	44.0	55.9	0.2	0.08	0.03	0.01	0.16	0.08	0.02	287			-3.9		26.3			
Md25	c(98)	43.1	53.3	1.0	1.39	0.95	0.04	0.21	0.08	0.18	174	22	6	-0.6		27.6			
Md26	c(99)	43.5	55.4	0.4	0.14	0.07	0.01	0.16	0.07	0.02	47	6		-1.6		26.9			
Md27	c(100)	44.0	55.4	0.5	0.26	0.08	0.01	0.18	0.08	0.03	1181	19		1.2		25.2			

*: c: calcite; d: dolomite; ( ): wt % of the mineral

Tab. 3 - Chemical and isotopic data for rock samples from the Brecce di Seravezza.

Sample	Carbonate mineralogy*	CO_2 wt%	CaO wt%	MgO wt%	SiO_2 wt%	Al_2O_3 wt%	TiO_2 wt%	Fe_2O_3 wt%	Na_2O wt%	K_2O wt%	Sr ppm	Mn ppm	Rb ppm	$\delta^{13}C_{cal}$ ‰	$\delta^{18}O_{cal}$ ‰
BrS01	c(0) d(0)	0	32.6	0.9	18.0	14.1	0.92	6.0	0.47	1.56	114	138	79		
BrS02	c(0) d(0)	0	3.4	1.3	44.1	30.5	1.87	10.1	0.46	1.49	77	233	76		
BrS03	c(0) d(0)	0	1.7	1.9	44.3	28.1	1.91	14.8	0.50	1.81	29	253	82		
BrS03a	c(0) d(0)	0	0.2	1.0	47.4	31.8	1.96	10.6	0.337	1.85	40	212	107		
BrS04	c(99) d(0)	43.5	53.4	0.8	1.4	0.8	0.02	0.4	0.08	0.16	47	11	8	-4.1	26.7
BS05	c(100)	44	54.7	0.8	0.5	0.2	0.01	0.3	0.08	0.05	97	175	4	1.6	32.6
BrS06	c(97)	42.6	53.9	0.7	1.2	0.4	0.03	0.4	0.12	0.13	86	172	6	2.2	33.1

* c: calcite; d: dolomite; ( ): wt % of the mineral

tioning preferred Mg sites rather than Ca sites during recrystallization of sediments (e.g. Wildeman, 1969).
On average, the Mn content in the Marmi Dolomitici is nearly identical to that in the Carrara Marble (17 to 60 ppm, mean 30 ppm, n = 11; Herz and Dean, 1986). Marmi Dolomitici and Grezzoni are consistent in term of Mn ranges, but their average contents are distinct. The higher Mn content in the Grezzoni may testify a higher calcitic character of the original sediments, corresponding to a meanly deeper depositional environment. On the other hand, there is consistency with the Calcare Massiccio (whole range in the carbonate fraction of 21 to 185 ppm Mn, mean 59 ppm, n = 33; Bencini and Turi, 1974), which displays Mn in most samples (n = 29) between 21 and 93 ppm and a mean of 48 ppm. The low Mn content in both formations is in line with a parental link, as well as with an essentially aragonitic composition of the original sediments. Therefore, it appears to be likely that the Marmi Dolomitici basically preserved the Mn diagenetic features of the protolith, and then the dishomogeneous distribution of the element may be interpreted once again in terms of aragonite vs calcite proportion in the original sediments and areally variable water to rock ratios during diagenesis. The $\delta^{13}C$ values of calcite and dolomite vary between

-3.9 and $+2.4‰$ (mean $+1.5 \pm 0.7‰$; n = 27) and between $+2.2$ and $+3.1‰$ (mean $+2.5 \pm 0.7‰$; n = 11), respectively (Fig. 6). The negative values of -3.9 to $-0.6‰$ refer to calcites close to the contact with the Brecce di Seravezza (Md24 and Md25 samples) and the Carrara Marble (Md26 sample). The slight ^{13}C-enrichment of dolomite relative to calcite should reflect the partitioning of carbon isotopes during secondary dolomitization. In the dolomite-calcite pairs Md03 and Md09 the observed carbon isotope fractionation ($\Delta^{13}C_{dol-cal} = 1000 \ln\alpha_{dol-cal} \approx \delta^{13}C_{dol} - \delta^{13}C_{cal}$) of $0.6‰$ (Table 2) corresponds to an isotopic temperature of 380°C (Sheppard and Schwarcz, 1970). However, it may also represent a diagenetic isotopic fractionation between syngenetic dolomite and calcite (McKenzie, 1981).
The positive $\delta^{13}C$ values ($+0.2$ to $+3.1‰$; mean $+1.9 \pm 0.6‰$) are both in line with a «normal» marine origin of the carbon and consistent with those of calcite ($+2.3$ to $+3.2‰$) and dolomite ($+3.5$ to $+4.5‰$) in the Calcare Massiccio (Cortecci and Lupi, 1994), as well as in the Carrara Marble ($+1.6$ to $+2.5‰$; Herz and Dean, 1986). These features exclude appreciable isotopic effects on Marmi Dolomitici during metamorphism. Instead, the negative $\delta^{13}C$ values, together with the stratigraphic posi-
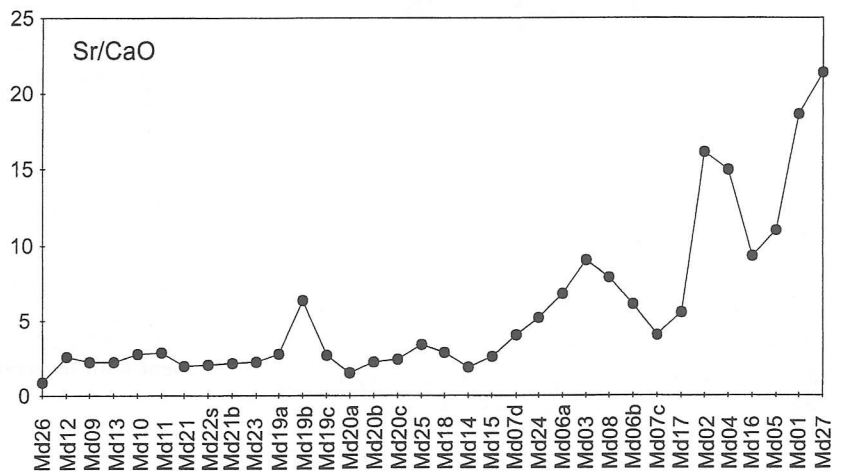

Fig. 4 - Trend of the Sr/Ca ratio through the Marmi Dolomitici from the top (close to the Carrara Marble) to the bottom (close to the Brecce di Seravezza or the Grezzoni) of the formation. The Sr content refers to the carbonate fraction of samples.
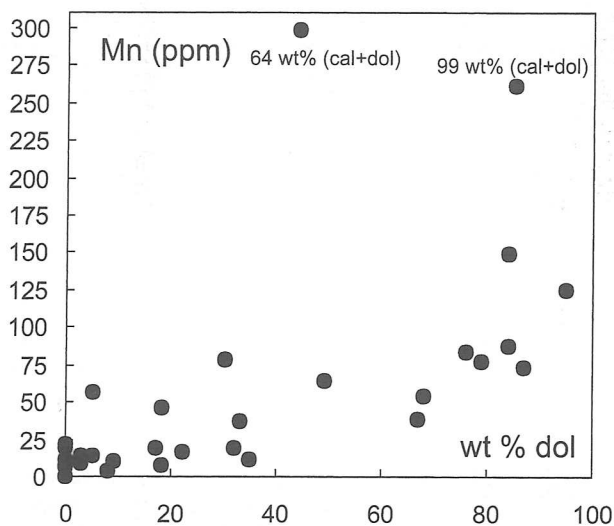
Fig. 5 - Recalculated Mn contents in the carbonate fraction versus dolomite percentages in the Marmi Dolomitici.

tion of samples, may be interpreted as due to recrystallization of calcite from metamorphic fluids depleted in ^{13}C. This isotopically light source of carbon exists in the basement of the Apuane complex in the form of carbonaceous matter (Dallan Nardi and Nardi, 1974) and carbonate lenses (e.g. *Orthoceras* dolomite: $\delta^{13}C = -4.7‰$; Cortecci et al., 1994), as well as locally in the underlying Brecce di Seravezza (see later on). Alternatively, we may imagine a complete closure of the Marmi Dolomitici to the metamorphic fluids, and explain the isotopic depletion as due to local meteoric recrystallization/replacement of carbonate by vadose/phreatic water (e.g. Allan and Metthews, 1977) during emersion of the platform.

The $\delta^{18}O$ values of calcites cluster between +26.9 and

Fig. 6 - $\delta^{3}C$ vs $\delta^{18}O$ of calcite and dolomite from the Marmi Dolomitici, compared to the isotopic fields of primary calcite (A) and dolomite (B), and presumed protolith Calcare Massiccio (C). Data on primary carbonates are from Land (1989). Data on Calcare Massiccio are from Kalk (1990) and Cortecci and Lupi (1994).
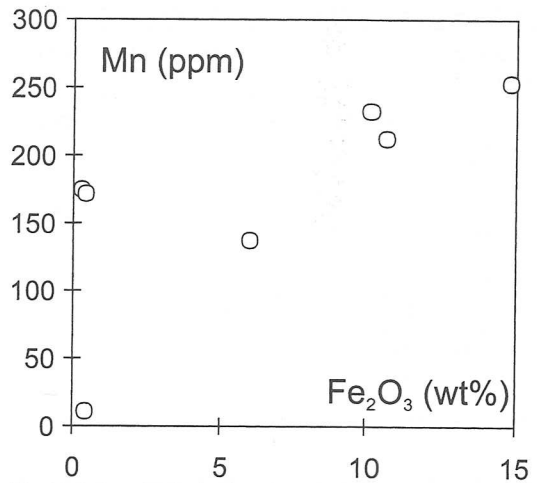
Fig. 7 - Mn vs Fe_2O_3 in the Brecce di Seravezza.

+29.8‰ (mean +28.2 ± 0.8‰; n = 24), and those of dolomites range between +26.3 and +31.9‰ (mean +29.6 ± 1.5‰). Dolomite-calcite $\Delta^{18}O$ fractionations are 1.6‰ (Md03 pair) and 4.4‰ (Md09 pair). According to Sheppard and Schwarcz (1970), they provide quite unconsistent isotopic temperatures of 201 and 33°C; or absurd negative thermometric estimates according to Zheng (1999). Moreover, the $\delta^{18}O$ signature of Marmi Dolomitici matches well with that of Calcare Massiccio (+27 to +31‰; Cortecci and Lupi, 1994) and Carrara Marble (+27 to +30‰; Herz and Dean, 1986). In addition, the $\delta^{18}O$ values of +26.3 to +27.6‰ of calcites Md24 - 26 fall within the range shown by the Calcare Massiccio, so that their interpretation in terms of metamorphic or meteoric effects appears to be problematic. Therefore, it may be concluded that dolomite and calcite of Marmi Dolomitici are in isotopic disequilibrium, and the isotopic signature of the carbonate protolith was basically preserved during metamorphism.

Brecce di Seravezza

The few specimens studied consist of siliciclastic (high Rb content) and carbonate rocks (low Rb content), and major chemistry is consequent. Carbonate samples are almost pure calcite, with variable Sr and Mn contents, which are not too dissimilar from those of the non-carbonate samples. In the latter, Mn correlates positively with Fe_2O_3 (Fig. 7), thus suggesting that adsorption of Mn on ferric iron oxides occurred during sedimentation. As expected, both Sr and Mn concentrations in the carbonate breccias are consistent with those measured in the underlying Grezzoni.

Isotopically, BrS04 sample is considerably depleted in both ^{13}C and ^{18}O with respect to BrS05 and BrS06 samples, the latter showing typical marine values. In agreement with the genetic history of the breccia, the isotopic depletion has likely to be related to localized recrystallization of older carbonate from shallow meteoric water (e.g. Allan and Matthews, 1977) during the emersion of the precursor.
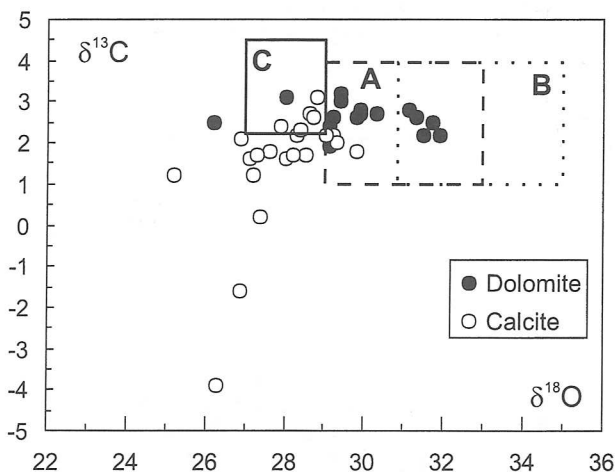
Table 4 - Chemical and isotopic comparison of Grezzoni and Marmi Dolomitici with relevant sedimentary and metamorphic formations of northern Tuscany. *Data from the present work are in italics.* Reference data are from Cortecci and Lupi (1994) (1), Manetti and Turi (1973) (2), Bencini and Turi (1974) (3), Herz and Dean (1986) (4) and Cortecci et al. (1985) (5).

Formation	Sr (ppm) mean	Sr (ppm) range	Mn (ppm) mean	Mn (ppm) range	$\delta^{13}C$ (‰) mean	$\delta^{13}C$ (‰) range	$\delta^{18}O$ (‰) mean	$\delta^{18}O$ (‰) range	$^{87}Sr/^{86}Sr$	Source
Grezzoni (1)										
Whole rock										
Dolomite	*94 ± 36*	*42 - 990*	*106 ± 73*	*28 - 669*	*+2.2 ± 0.9*	*-0.2 - +3.7*	*+29.9 ± 1.6*	*+26.5 - +32.9*	*0.708566 ± 0.00035*	
Calcite		*43 - 187*		*28 - 304*	*+0.8 ± 0.9*	*-0.5 - +1.7*	*+27.0 ± 2.5*	*+23.7 - +30.5*	*0.708138 ± 0.000015*	
C.C.(wr).	169									(1), (5)
C.R.C. (wr)		27 - 1273				-4.0 - -2.0		+24.0 - +26.1		(1), (2)
C.R.C. (dol)	115	27 - 190				+2.7 - +4.0		+26.6 - +27.6	0.70819 ± 0.00005	(1), (2)
C.R.C (cal)	483	179 - 1273				+2.1 - +3.1		+25.7 - +26.3	0.70812	(1), (2)
C.R.C. (caf)			92 ± 50							(3)
Marmi Dolomitici (1)										
Whole rock	*465*	*47 - 1181*		*0 - 258*						
Calcite		*47 - 1181*			*+1.5 ± 0.7*	*-3.9 - +2.4*	*+28.2 ± 0.8*	*+26.9 - +29.8*	*0.707694 ± 0.000054*	
Calcite + dolomite		*48 - 604*								
Dolomite	*87*	*48 - 125*			*+2.5 ± 0.7*	*+2.2 - +3.1*	*+29.6 ± 1.5*	*+26.3 - +31.9*	*0.708297 ± 0.000106*	
C.M. (wr)		0 - 2173								(1), (2)
C.M. (cal)		0 - 2173				+2.3 - +3.2		+27.0 - +28.9	0.70821 ± 0.00023	(1), (2)
C.M. (dol)	137	70 - 195				+3.5 - +4.5		+28.0 - +29.4	0.70855 ± 0.00062	(1), (2)
C.M. (caf)			59	21 - 185						(3)
CA.MA.	164 ± 40	111 - 214	30	17 - 60		+1.6 - +2.5		+27.3 - +30.6	0.70791 ± 0.00010	(4)

(1) Abbreviations: C.C. = Calcare Cavernoso; C.R.C. = Calcare a *Rhaetavicula contorta*; C.M. = Calcare Massiccio; CA.MA. = Carrara marble; wr = whole rock; cal = calcite; dol = dolomite; caf = carbonate fraction.
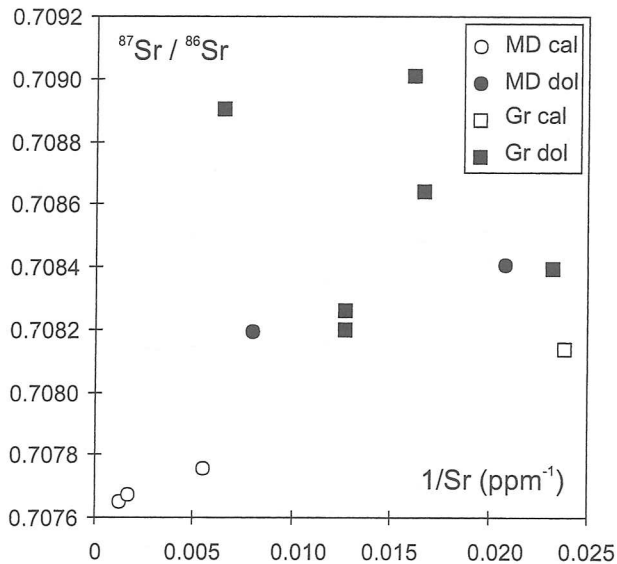
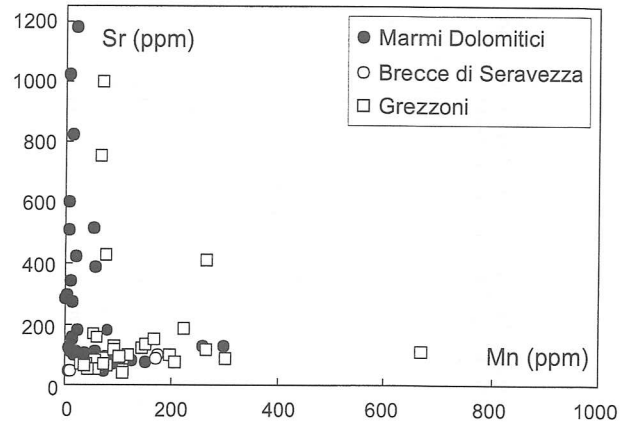Fig. 8 - $^{87}Sr/^{86}Sr$ vs 1/Sr in Grezzoni and Marmi Dolomitici handspecimens.

Fig. 9 - Relation between Sr and Mn in the carbonate fraction of studied Grezzoni, Marmi Dolomitici and Brecce di Seravezza. Seemingly, most data points display a nearly hyperbolic distribution.

$^{87}Sr/^{86}Sr$ ratios in Grezzoni and Marmi Dolomitici

In the Grezzoni, the $^{87}Sr/^{86}Sr$ ratio of calcite (0.708138 ± 0.000015) matches well with that of the Upper Norian seawater Sr (0.70815 ± 0.00025), as proposed by Faure et al. (1978). The $^{87}Sr/^{86}Sr$ ratios in dolomites are much higher, with a mean value of 0.708566 ± 0.00035. Possibly, the dolomitization involved terrestrial fluids rich in radiogenic Sr, that is fluids with a meteoric component. With respect to the Calcare a *Rhaetavicola contorta* (Cortecci and Lupi, 1994), the agreement is good for calcite (0.708125), but not for dolomite (0.70819).

The $^{87}Sr/^{86}Sr$ ratio in the Marmi Dolomitici is quite different for calcite (mean 0.707694 ± 0.000054) and dolomite (mean 0.708297 ± 0.000106). The calcite ratio is within the range suggested by Faure *et al.* (1978) for Rhaetian to Hettangian seawater Sr (0.70791 ± 0.00015 to 0.70762 ± 0.00021). In dolomite, the observed enrichment in radiogenic Sr can be ascribed to a late diagenetic origin of the mineral from the replacement of already stabilized calcite by fluids rich in ^{87}Sr leached from terrigenous sediments. In the Calcare Massiccio, mean $^{87}Sr/^{86}Sr$ ratios are 0.70821 ± 0.00023 in calcite and 0.70855 ± 0.00062 in dolomite (Cortecci and Lupi, 1994), compared to a mean of 0.70791 ± 0.00010 in the Carrara Marble (Herz and Dean, 1986). Whereas Calcare Massiccio and Carrara Marble are comparable, Marmi Dolomitici are distinct. Possibly, they incorporated some ^{87}Sr during early diagenesis from primary sediment. This radiogenic Sr was leached fom siliciclasts (variable both in the $^{87}Sr/^{86}Sr$ ratio and the Sr content) and mixed with marine ^{87}Sr (Fig. 8).

Sr vs Mn relationship in Grezzoni and Marmi Dolomitici

The relation between Sr and Mn in the carbonate fraction of studied rocks is nearly hyperbolic (Fig. 9), as expected from recrystallization in diagenetic open systems where Sr-rich sediments are washed out by water enriched in Mn with respect to seawater by leaching of non-carbonate minerals under reducing conditions. Several factors are playing, which include the water to rock ratio (i.e. the number of recrystallizations; see Land, 1980) and the concentration values of elements in the original carbonate and in the fluid.

CONCLUSIONS

Main conclusions that can be drawn are:
1. The chemical and isotopic signatures of Grezzoni and Marmi Dolomitici formations match those of their age-equivalent sedimentary protoliths from the Tuscan Nappe. The diagenetic features were basically preserved during the regional metamorphism experienced by the rocks, due to the absence of circulating fluids. Metamorphism was «dry», as previously concluded also for the Carrara Marble formation overlying the Marmi Dolomitici. Possibly, fluids from the basement were dammed by the thick and impervious Grezzoni formation, that is an about 180 Ma old protolith, which should have been diagenetically stabilized and lithified when metamorphism began in Oligocene times.
2. The metamorphic effects on the Brecce di Seravezza were also of minor importance, and observed depletions in ^{13}C and ^{18}O with respect to marine-diagenetic contents may be attributed to recrystallization in vadose environment prior to metamorphism.
3. Dolomite from both formations is on average a slightly enriched in ^{13}C and ^{18}O with respect to calcite. However, carbon and oxygen isotope fractionations between dolomite-calcite pairs provide unconsistent or absurd thermometric estimates, thus denoting isotopic disequilibrium and supporting a secondary origin of dolomite.
4. Dolomite is systematically enriched in ^{87}Sr relative to calcite, the $^{87}Sr/^{86}Sr$ ratio of the latter closely approacing

that of parental seawater. Dolomitization was promoted by fluids enriched in heavier Sr remobilized from terrigenous sediments, and probably replaced already stabilized calcite during late diagenesis.

5. Sr and Mn in the carbonates show a hyperbolic relationship, as expected from repeated diagenetic recrystallization of the precursor sediment from fluids with a lower Sr to Mn ratio than seawater. These fluids may have been seawater chemically modified by interaction with terrigenous sediments or binary mixtures of seawater and terrestrial water.

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