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Geochemical evidence for fluid-rock interaction along high angle faults in the Alpi Apuane, NW Tuscany, Italy

GIANNI CORTECCI^{1*}, ENRICO DINELLI¹, GIANCARLO MOLLI^{2,3} and GIUSEPPE OTTRIA³

¹ Dipartimento di Scienze della Terra e Geologico-Ambientali, P.za Porta S. Donato 1, University of Bologna, I-40126 Bologna, Italy

² Dipartimento di Scienze della Terra, Via S. Maria 53, University of Pisa, I-56126 Pisa, Italy

³ Istituto di Geoscienze e Georisorse-Centro di Studio della Geologia Strutturale e Dinamica dell'Appennino Settentrionale, CNR, Via S. Maria 53, I-56126 Pisa, Italy

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ABSTRACT. — Trace element (Sr, Mn, Rb, Cu, Zn, and Pb) and stable isotope ($^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) analyses were performed on calcite from profiles across high angle brittle faults developed in the Carrara marble of Alpi Apuane, in order to investigate the role and origin of fluids possibly involved during deformation. The tectonic structures studied are characterized by an inner cataclasite core grading outwards through cataclastic marble to fractured or undeformed host marble.

The $\delta^{18}\text{O}$ values indicate that large amounts of water were involved during formation of the cataclasite calcite at the inner core of the structure. With respect to the host marble, this calcite is depleted in both ^{18}O and ^{13}C , is enriched in base metals and in radiogenic ^{87}Sr . These features concur to suggest that the Palaeozoic siliciclastic basement of Alpi Apuane may have been the source of metals, ^{13}C -depleted carbon and radiogenic Sr.

RIASSUNTO. — Sono state effettuate analisi chimiche (Sr, Mn, Rb, Cu, Zn e Pb) ed isotopiche ($^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$) sulla calcite prelevata lungo profili a cavallo di faglie ad alto angolo ospitate all'interno del marmo di Carrara nelle Alpi Apuane, con l'intento di verificare il ruolo e l'origine dei fluidi eventualmente coinvolti nell'evento deformativo. Le strutture tettoniche

studiate sono costituite da una cataclasite centrale a composizione calcitica, dalla quale si passa esternamente a marmo cataclastico, a marmo fratturato ed infine al marmo indeformato.

I valori di $\delta^{18}\text{O}$ indicano il coinvolgimento di quantità importanti di acqua durante la formazione del nucleo cataclastico. Rispetto al marmo, questa calcite è impoverita in ^{18}O e ^{13}C , ed arricchita in ^{87}Sr e nei metalli di base. L'insieme dei risultati suggerisce che la sorgente dei metalli, del carbonio impoverito in ^{13}C e dello Sr radiogenico sia da ricercarsi nel basamento Paleozoico silicoclastico delle Alpi Apuane.

PAROLE CHIAVE: *faglie ad alto angolo, interazione fluido-roccia, geochimica, Carrara marble, Alpi Apuane.*

KEY WORDS: *high angle fault, fluid-rock interaction, geochemistry, Carrara marble, Alpi Apuane.*

INTRODUCTION

Trace element and isotope analyses on sedimentary and metamorphic carbonates may constrain past water-rock interaction processes during diagenesis and metamorphism, due to redistribution of elements and isotopes between fluid and mineral (e.g. Veizer, 1983; Rye *et al.*, 1976).

* Corresponding author, E-mail: cortecci@geomun.unibo.it

In the present paper, this geochemical approach was applied to high angle faults occurring in the Alpi Apuane within the homogeneous Hettangian Carrara marble to investigate the potential role of fluids involved in the tectonic event. The faults most likely developed during the latest phase of the Apenninic orogeny. These tectonic structures show a gradual transition in fabric from undeformed marble, to fractured marble and to the cataclastic core of the fault. Cataclasite is composed of angular/subangular clasts of marble hosted within an orange to brownish matrix prevalently consisting of fine grained calcite. This calcite displays a variety of deformation features which may have been enhanced by fluids.

Along with major, minor and trace elements and stable isotopes, some selected samples were also analysed for strontium isotopes. These samples refer to the tectonic structure showing the highest concentrations of base metals in the cataclastic facies.

GEOLOGICAL SETTING

A large amount of work was done in the last decades on the tectonic deformation (e.g. Carmignani *et al.*, 1978; Carmignani and Kligfield, 1990) and ore deposits (Benvenuti *et al.*, 1992 and references therein; Cortecci *et al.*, 1992) in the Alpi Apuane metamorphic complex. These belong to the northern Apennine thrust- and fold-belt, which derives from the tectonic stacking of the Ligurian-Piemontese oceanic units, and ocean-continent transition units (Ligurian and sub-Ligurian units), onto the Adriatic continental margin (Tuscan units). In the Alpi Apuane area (fig. 1), the entire nappe system of the northern Apennines is exposed, including the Tuscan metamorphic units (Apuane Unit and Massa Unit), that are composed of a Paleozoic basement (e.g. Conti *et al.*, 1991) and metasedimentary sequences (e.g. Carmignani and Giglia, 1984). The metamorphism of Alpi Apuane took place

between 27 and 12 Ma (Carmignani and Kligfield, 1990), and reached peak temperatures of 380 to 450°C, and pressures of 3 to 4 kbar (Di Pisa *et al.*, 1985) or 6 to 8 kbar according to Jolivet *et al.* (1998) (see discussion in Molli *et al.*, 2000). As a whole, the structural evolution of the Alpi Apuane can be divided in two main tectono-metamorphic events (Carmignani and Kligfield, 1990; Molli and Meccheri, 2000 and references therein). The earliest D1 compressive event produced the overthrusting of the Ligurian units and a regional syn-metamorphic schistosity. The subsequent (D2) event caused deformation of the D1 structures and the progressive exhumation of the massif under retrograde metamorphic conditions. Post-D2 deformation events generated brittle structures which, according to Ottria and Molli (2000), should be related to a polyphase deformation history, with an older stage responsible for strike slip and normal faults, and a younger stage developing normal faults locally showing the NW-SE Apenninic trend. These structures were related to the Late Pliocene-Middle Pleistocene extensional evolution of the Tyrrhenian side of the northern Apennines (Ottria and Molli, 2000).

Relevant for the present work is the presence in the Paleozoic basement of 1) vein Pb-Zn-Cu (Ag) sulfide ore deposits (Bottino and S. Barbara mines; see Benvenuti *et al.*, 1991 and 1992), 2) dolomite lenses ($\delta^{13}\text{C} = -4.7\text{‰}$ and $\delta^{18}\text{O} = +16.3\text{‰}$, in the Levigliani locality; Cortecci *et al.*, 1994), and 3) carbonaceous (organic) matter (Dallan Nardi and Nardi, 1974). Moreover, carbonate minerals (calcite, dolomite and siderite) from the Bottino mine have $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the ranges -3.8 to -9.5‰ and $+12.7$ to $+21.4\text{‰}$, respectively (Benvenuti *et al.*, 1991).

SAMPLING AND ANALYTICAL METHODS

The sampling sites are shown in figs. 1 and 2, and an example of the studied fault zones is sketched in fig. 3. In the fault zone we distin-

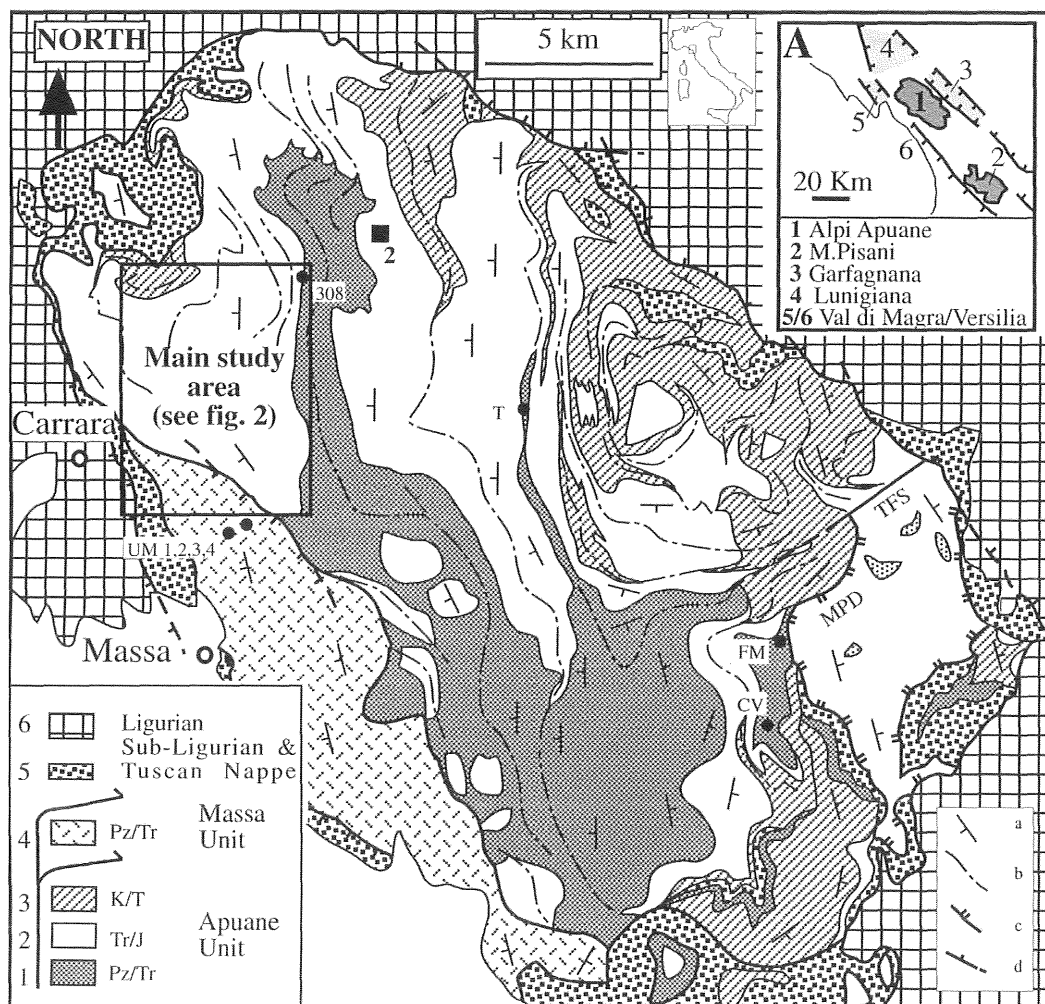


Fig. 1 – Schematic structural map of the Alpi Apuane region. Studied site 2 is shown in this figure, as it is out of Fig. 2. Legenda: 1) Paleozoic to Triassic: metavolcanics (porphyroids), phyllites, quartzites and metaconglomerates; 2) Upper Triassic to Liassic carbonate platform deposits, mainly metadolostones, marbles and cherty metalimestones; 3) Cretaceous to Tertiary phyllites and metasandstones; 4) Massa Unit; 5) breccias and cataclasites largely derived from the Triassic evaporites («Calcare Cavernoso») at the base of the Tuscan Nappe; 6) Tuscan nappe, and Ligurian and sub-Ligurian units; a) strike and dip of the main regional schistosity; b) axial plane traces of major D1 structures; c) low angle detachment; d) high angle faults.

guish structures composed of undeformed host marble in the outer part, followed by fractured marble with centimeter spacings and then cataclasite in the inner part. These distinctions match the fault zone architecture (protolith, damage zone and fault core) of Caine *et al.*,

(1996), and are particularly relevant to the understanding of fluid flow properties and relationships with brittle faulting. The damage zone consists of marbles with centimetre-scale fracture spacings, the latter increasing towards the fault core. The core is typically formed by

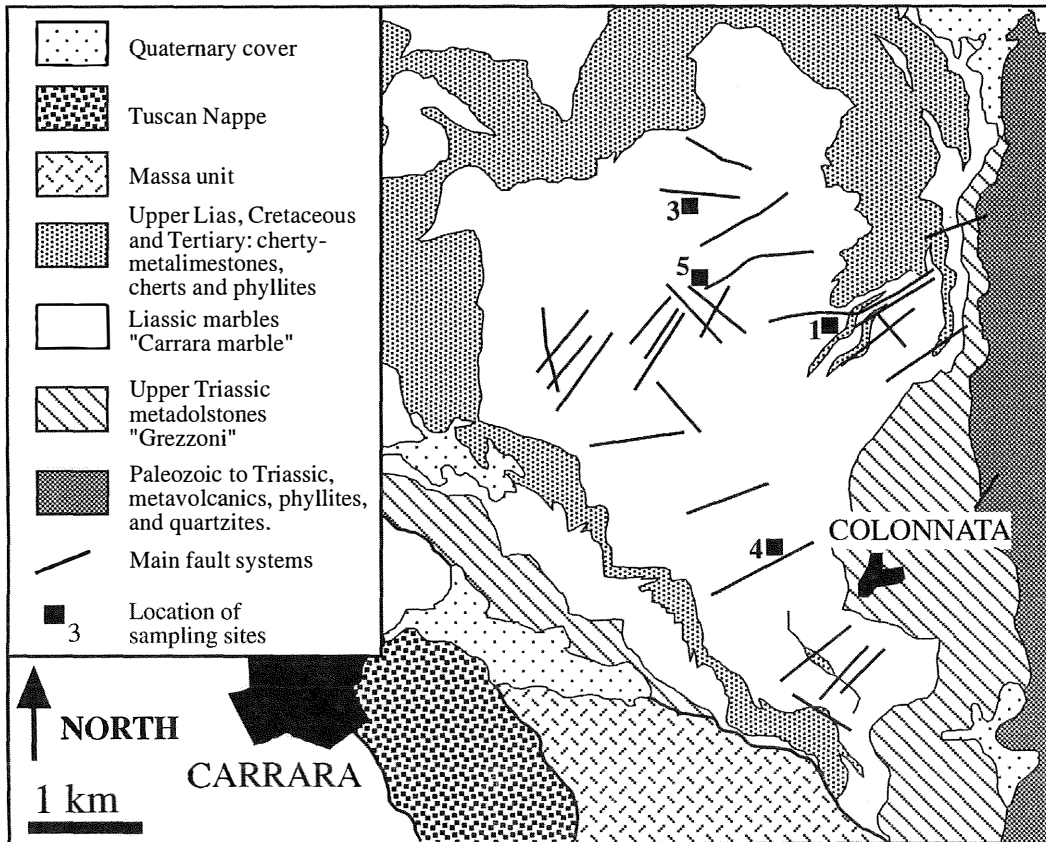


Fig. 2 – Geological map of the Carrara area with location of the sampling sites (numbers correspond to the analysed cataclasites reported in Table 1). The location of the sampling site 2 is shown in Fig. 1.

marble cataclasite/ultracataclasite, composed of millimetre/submillimetre-sized angular/subangular clasts of marble embedded within an orange to brownish matrix, made up of fine-grained calcite with minor clay minerals.

Analysed carbonate samples include the undeformed marble, the fractured marble and the cataclasite (both clasts and matrix). Clasts were separated from the matrix and the matrix purified from clasts by handpicking under the binocular microscope. Siliciclastic rocks from the basement were also analysed for major and selected minor elements, and for the content and carbon isotopic composition of the organic matter.

Chemical and isotopic analyses

Contents of major and minor elements in carbonates and siliciclastic rocks were determined by X-ray fluorescence spectrometry. Loss on ignition (LOI) was determined by keeping the sample at 950°C until the weight remained unchanged. Carbon dioxide was extracted from calcite by reaction with anhydrous H_3PO_4 at 25°C following the method of McCrea (1950), and analysed for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios by mass spectrometry. The carbon and oxygen isotope ratios are reported in the δ -notation in per mil (‰) relative to V-PDB and V-SMOW

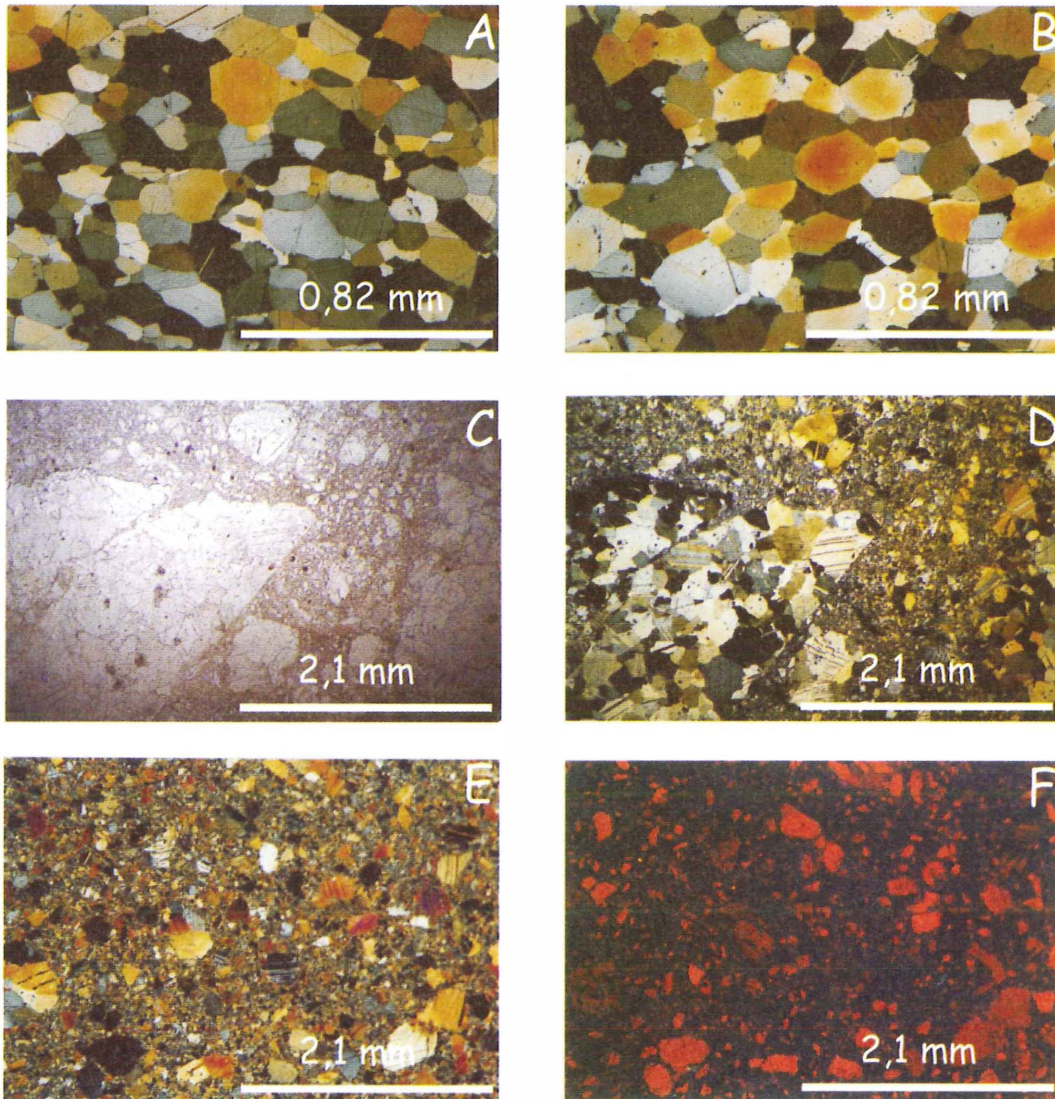


Fig. 4 – A, B: ultrathin section (cross polarized light) of undeformed marble protolith with granoblastic microfabric from the side part of the fault zone shown in Fig. 3. C, D: ultrathin sections showing microstructures of cataclastic marble in the damage zone towards the fault core (C: natural light, D: cross polarized light). E, F: ultrathin sections showing microstructures of the cataclasite core matrix (E: cross polarized light, F: cathodoluminescence micrograph).

microstructures and fluid infiltration, we show here an example of fault zone (fig. 3), where the marble protolith is characterized by type-A and type-B microstructures; the marble shows (fig. 4 A, B) equant polygonal grains with

predominantly straight grain boundaries on both sides that meet in triple points at angles of nearly 120° . The grain size is around $200\text{--}250\ \mu\text{m}$. C-axis displays a nearly random distribution along a crystallographic preferred

orientation. Thin *e*-twins can be recognized.

In the damage zone, the marble microstructures are the same as those of the protolith, with the additional presence of fractures. The fault core is composed of angular/sub-angular marble clasts with largely variable grain size. They are embedded in a very fine matrix (fig. 4 C, D). The matrix is formed mostly by calcite both as sub-crystal scale of crushed protolith marble and as newly formed calcite. The latter can be easily identified by cathodoluminescence analysis due to its blue color compared to the red/orange one of the marble protolith (fig. 4 E, F).

RESULTS AND DISCUSSION

The results of the chemical and isotopic analyses are reported in Tables 1 and 2. The data on the different types of carbonates involved in the studied tectonic structures will be presented and discussed separately.

Undeformed marble (samples 1, APa-1, APb-1, 10, 13a) and fractured marble (samples 2a, 2b, 11 and 13b)

Analysed undeformed marble specimens are white and massive. Their [CaO + MgO + LOI] values range between 99.4 and 99.8%. Strontium (137-211 ppm) and manganese (12-31 ppm) concentrations are consistent with those measured by X-ray fluorescence in the Carrara marble from several quarries in the Alpi Apuane (mean values of 164 ± 40 ppm Sr and 30 ± 14 ppm Mn; Herz and Dean, 1986). Zinc (31-41 ppm) is strongly enriched compared with that of 6.7 ± 1.2 ppm observed in all but one Carrara marble quarries investigated by Herz and Dean (1986); its concentration matches the one (33 ppm) measured in marble from the mineralised (pyrite and magnetite) Mandria quarry in the Torano district of the Alpi Apuane. Finally, no Pb was detected in the studied samples. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.707871 in marble APb-1 is within the range obtained by Herz and Dean

(1986) for Carrara marble specimens from some quarries.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of undeformed marbles bordering all the studied cataclasites vary between +1.3 and +2.7‰ (mean $+2.1 \pm 0.6$ ‰) and +28.5 and +30.1‰ (mean $+29.1 \pm 0.6$ ‰), respectively. By comparison, many samples from several Carrara marble quarries have $\delta^{13}\text{C}$ values of +1.6 to +2.5‰ and $\delta^{18}\text{O}$ values of +27 to +30‰ (Cortecchi and Orlandi, 1975; Herz and Dean, 1986). These narrow variations point to a quite homogeneous isotopic composition for the marble precursor of cataclasites.

The analysed samples of fractured marbles are similar to the undeformed marble both chemically (major and trace elements) and isotopically. Only sample 11 from the cataclasite #4 appear to be slightly depleted in ^{13}C and ^{18}O .

Cataclastic marble (samples APb-2 and APb-2bis)

This marble occurs at the rims of the cataclasite core of the studied tectonic structure APb at site #3. The [CaO + MgO + LOI] values are 93.5 and 95.5%. With respect to the undeformed protolith, this type of marble is appreciably enriched in Si, Al, Fe and K. It is also enriched in Zn and Mn. With respect to undeformed marble, the clasts are depleted in ^{18}O by 5.3 to 6.9‰, as well as in ^{13}C by about 0.7‰. These features indicate exchange of the marble with fluids, which most likely took place during the faulting event. The chemical process basically involved carbonate carbon from dissolution of marble and was accompanied by neoformation of Fe/Mn oxides and additional phyllosilicate minerals compared to the protolith, as evidenced by XRD analysis. The high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.708559 in the calcitic fraction suggests crystallization from fluids rich in radiogenic Sr and may support derivation of fluid from deeper siliciclastic metamorphic units. The source of isotopically light carbon in the fluids can be searched in the Paleozoic basement of the Alpi Apuane edifice, where ^{13}C -depleted

TABLE 1

Chemical and isotopic composition of studied carbonate cataclasites and Carrara marble host.

Sample	Notes	SiO ₂ wt%	TiO ₂ wt%	Al ₂ O ₃ wt%	Fe ₂ O ₃ wt%	MgO wt%	CaO wt%	K ₂ O wt%	P ₂ O ₅ wt%	LOI wt%	Rb ppm	Sr ppm	Mn ppm	Cu ppm	Zn ppm	Pb ppm	δ ¹³ C ‰	δ ¹⁸ O ‰	⁸⁷ Sr/ ⁸⁶ Sr
<i>Cataclasite # 1</i>																			
1	U	—	0.02	—	0.16	0.51	55.36	—	—	43.88	12	141	—	27	34	—	2.7	30.1	
2a	FM	—	0.02	—	0.19	0.48	55.27	—	—	43.96	10	131	—	26	35	—	2.7	30.3	
2b	FM	—	0.03	—	1.47	0.42	54.79	—	—	44.22	11	130	28	27	32	—	2.6	30.1	
3a	C	—	0.03	—	0.27	0.32	53.92	—	—	45.39	13	128	21	29	45	7	1.9	28.0	
3b	M	—	0.02	0.23	0.53	0.28	52.00	0.04	—	46.81	17	123	90	31	59	14	1.1	26.1	
3c	M	—	0.02	—	0.30	0.19	55.00	—	—	44.41	10	113	7	27	48	11	0.9	26.5	
<i>Cataclasite # 2</i>																			
AP(a)-1	U	—	0.02	—	0.14	0.53	55.26	—	—	43.97	13	137	—	28	31	—	2.7	29.5	
AP(a)-2	M	14.28	0.26	6.10	1.90	2.26	39.40	1.30	0.04	34.36	51	92	679	361	248	5	0.5	25.0	
AP(a)-2b	C	—	0.02	—	0.15	0.08	56.18	—	—	43.49	14	66	—	32	40	—	0.3	25.0	
<i>Cataclasite # 3</i>																			
AP(b)-1	U	—	0.02	—	0.15	0.48	55.80	—	—	43.47	13	166	12	31	41	—	2.1	28.7	0.707871
AP(b)-2	CM	1.25	0.09	2.07	0.46	0.79	53.05	0.45	0.10	41.67	26	146	82	31	158	—	1.4	21.8	
AP(b)-2bis	CM	2.21	0.11	2.71	0.58	0.95	51.40	0.66	0.13	41.19	35	151	83	26	166	11	1.3	23.4	0.708559
AP(b)-3	M	0.82	0.09	1.75	1.16	0.56	52.97	0.36	0.50	41.70	22	208	219	77	297	450	0.9	16.7	0.709035
<i>Cataclasite # 4</i>																			
10	U	—	0.02	—	0.16	0.50	55.81	—	—	43.43	12	138	31	31	36	—	1.3	28.5	
11	FM	—	0.02	—	0.14	0.34	55.60	—	—	43.82	11	116	—	28	32	—	0.9	28.1	
12(2)	C	—	0.03	—	0.19	0.02	57.54	—	—	42.14	11	104	—	32	42	38	-0.6	24.1	
12(1)	M	—	0.05	0.46	0.41	0.09	56.27	0.07	—	42.56	17	99	88	37	49	75	-0.2	24.7	
12(3)	M	—	0.04	0.18	0.28	0.04	55.91	—	—	43.48	13	90	47	36	45	67	-0.6	24.7	
<i>Cataclasite # 5</i>																			
13a	U	—	0.03	—	0.18	0.57	54.70	—	—	44.45	15	211	—	30	34	—	1.9	28.7	
13b	FM	—	0.05	0.59	0.36	0.59	54.98	0.06	—	43.29	15	191	94	29	37	—	1.7	28.5	
14	M	3.12	0.13	3.47	0.97	1.01	49.68	0.54	0.01	40.97	29	116	386	40	61	3	0.0	28.2	
15	C	—	0.06	1.04	0.34	0.68	54.65	0.08	—	43.07	15	204	111	35	38	—	1.8	28.9	

Key to notes: U = undeformed marble; FM = fractured marble; CM = cataclastic marble; C = marble clasts from cataclasite core; M = cataclasite core matrix (± impure of very small marble clasts). Sodium was not detected in the samples. — not detected.

TABLE 2
*Rocks from the basement of Alpi Apuane: chemical composition of major (wt%) and trace (ppm) elements,
and content and carbon isotope composition of organic matter.*

Sample ¹	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Rb	Sr	Cu	Zn	Pb	Corg wt%	δ ¹³ C ‰
UM1	54.55	1.22	26.94	2.24	0.05	1.18	0.26	0.07	8.90	0.13	4.46	352	47	46	15	6	0.07	-18.9
UM2	51.74	1.08	24.12	8.52	0.08	2.52	0.21	n.d.	6.71	0.12	4.89	277	48	43	83	14	0.05	-19.5
UM3	54.88	1.12	23.80	7.12	0.08	1.87	0.18	0.01	6.19	0.11	4.64	256	45	39	84	16	0.25	-19.3
UM4	59.13	1.04	23.12	7.20	0.11	1.60	0.21	0.32	4.84	0.13	2.32	199	73	26	75	13	0.28	-20.3
FM	72.11	0.58	14.53	0.88	0.04	1.08	0.07	n.d.	3.48	0.01	7.21	147	11	n.d.	20	3	4.26	-26.4
308	76.94	0.49	13.26	1.48	0.04	1.03	0.19	n.d.	4.38	0.09	2.10	127	21	6	38	7	0.08	-19.8
CV	19.33	0.38	8.79	3.70	0.27	11.40	20.27	n.d.	1.79	0.33	33.73	78	73	136	25	23	3.25	-21.7
T	0.97	0.30	4.54	83.16	0.08	4.88	3.64	n.d.	0.11	1.14	1.18	32	6	26	244	4	0.015	-25.7 ²

¹ Details: UM1,2 = metasilstones from Massa Unit; UM3,4 = chloritoid-metapelites from Massa Unit; FM = graphitic slate; 308 = black qtz-phyllite; CV = black phyllite; T = heavily mineralized phyllite. ² Analytical uncertainty of about 1‰. n.d. = not detected.

dolomite (see section on geological setting) and organic matter ($\delta^{13}\text{C} = -26.5$ to -19.3‰ ; Table 2) were recognized. These fluids may have also dissolved metallic sulfides occurrences in the basement from ore deposits (see section on geological setting) and mineralized rocks (see metal contents of rocks CV and T in Table 2).

Marble clasts from cataclasite cores (samples 3a, 12-2, 15, APa-2b)

They consist essentially of calcite, the $[\text{CaO} + \text{MgO} + \text{LOI}]$ values of 98.4 to 99.8% being nearly identical to those of the undeformed marble. Major and trace elements (Sr, Mn, Zn) also display comparable concentration values. These chemical features are in conflict with the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, which vary considerably from -0.6 to $+1.9\text{‰}$ (mean $+0.9 \pm 1.2\text{‰}$) and $+24.1$ to $+28.9\text{‰}$ (mean $+26.6 \pm 2.1\text{‰}$), respectively. Probably, the clasts interacted with fluids depleted in ^{13}C and ^{18}O , as those expected to derive from the basement. The high Pb concentration of 38 ppm in the clast 12-2 would seem to support such an origin of the fluids. Before interacting with marble, these fluids were possibly low in carbonate, so that the recrystallization mainly involved carbonate carbon from host marble. This interpretation might explain the decoupling between the base metal content and the carbon isotope composition.

Cataclasite matrix (samples 3b, 3c, 12-1, 12-3, 14, APa-2, APb-3)

Along with millimetric to submillimetric marble clasts, the matrix constitutes the core of the studied tectonic structures. Before analysis, the matrix was largely (but not completely) purified from clasts by hand-picking. All but one separate samples consist mainly of calcite (from 92 to more than 99%) and subordinate amounts of phyllosilicates and Fe/Mn oxides. In sample APa-2 the non-carbonate fraction is about 24%, with $[\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{K}_2\text{O}]$ and $[\text{Fe}_2\text{O}_3 + \text{MnO}]$ summing to 21.7% and 2.0%,

respectively. Copper and zinc are enriched in the matrix, with concentrations as high as 361 ppm Cu and 248 ppm Zn in sample APa-2. The concentration of Pb is just above the detection limit in samples APa-2 and 14, and much higher up to 450 ppm (sample APb-3) in the other samples. Sample APb-3 also contains high Cu (77 ppm) and Zn (297 ppm). Manganese correlates positively with Fe ($r^2 = 0.90$), and displays concentration values as high as 679 ppm in sample APa-2.

The $\delta^{13}\text{C}$ values vary between -0.6 and $+1.1\text{‰}$ (mean $+0.4 \pm 0.6\text{‰}$); this range of values is slightly lower than that observed in the clasts, and may reflect the syntectonic origin of most calcite in the matrix. The $\delta^{18}\text{O}$ values are in the range $+16.7$ to $+28.2\text{‰}$ (mean $+24.6 \pm 3.7\text{‰}$), likely denoting mixtures of newly formed calcite during the tectonic deformation with original carbonate, that in turn may have exchanged with the fluid. The lowest $\delta^{18}\text{O}$ value occurs in sample APb-3, which also shows high concentrations of metals. This sample was analysed for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, and the resulting high 0.709035 value (compared to the 0.707871 in the undeformed marble and 0.708559 in the cataclastic marble from the same cataclasite; see Table 1) agrees with the precipitation of calcite from fluids rich in radiogenic strontium and probably rising from the siliciclastic basement.

Isotopic composition and metal contents

A clear-cut overall relationship does not exist between oxygen and carbon isotopes in analysed carbonates, even if samples from individual sites show good linear correlations (fig. 5a). Furthermore, most samples cluster along a «mixing» trend (fig. 5b), with endmembers represented by massive marble relatively enriched in heavy isotopes and calcite in the matrix enriched in light isotopes. Isolated calcites refer to cataclasite from site #3, and distinguish themselves for their low $\delta^{18}\text{O}$ values. At this site, cataclastic marble lies

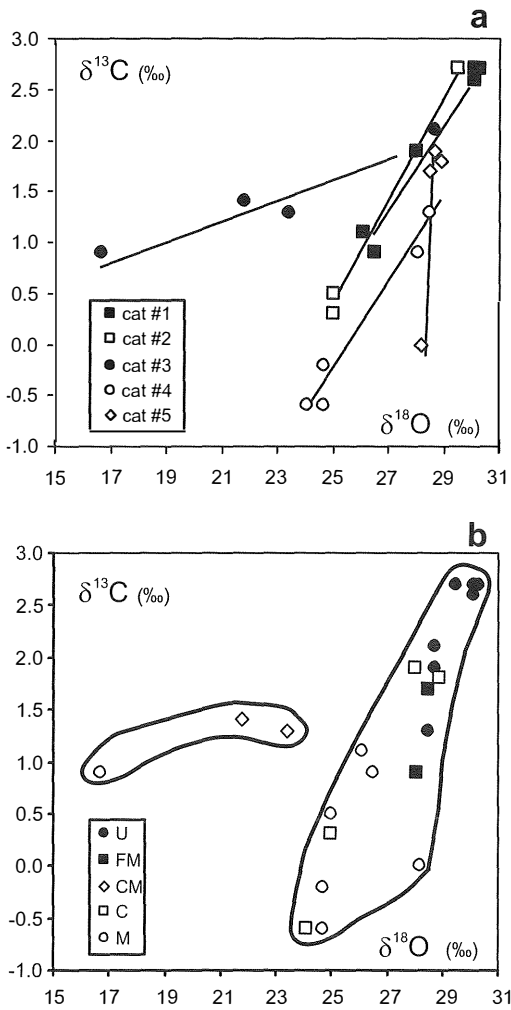


Fig. 5 – a: $\delta^{18}\text{O}$ vs $\delta^{13}\text{C}$ values for individual cataclastics, with interpolation lines showing positive trends. b: $\delta^{18}\text{O}$ vs $\delta^{13}\text{C}$ values of calcites from the different facies studied (the labelling is explained in Table 1). Majority of samples cluster along a positive trend, three deviating samples being considerably depleted in ^{18}O .

in the middle between the isotopic compositions of massive, undeformed marble and cataclastic matrix. It is likely that the isotopically depleted endmember for all studied structures is represented by calcite newly formed during deformation; this calcite

can have different oxygen and/or carbon isotopic composition depending on the several factors that may play a role during the interaction of fluids with carbonate rocks. These factors include the fluid to rock ratio during crystallization and the relative proportions of carbon and oxygen from the different sources involved, and can vary in space and time.

Zinc and copper show a wide range of concentrations, and the highest values appear to be related with the samples most depleted in ^{18}O (fig. 6). This suggests that metal content in the studied calcites positively depends on the original composition of the fluid involved in the faulting as well as on the water to calcite ratio during the recrystallization of pre-existing marble or the deposition of newly formed calcite (i.e. vein calcite, that normally implies the highest water to calcite ratio). This relation is not manifest for Pb, even if the highest concentration of the element is shown by a cataclastic matrix sample.

In conclusion, precipitation of newly formed calcite from the fluids (chemical reaction) during the deformation event was probably the

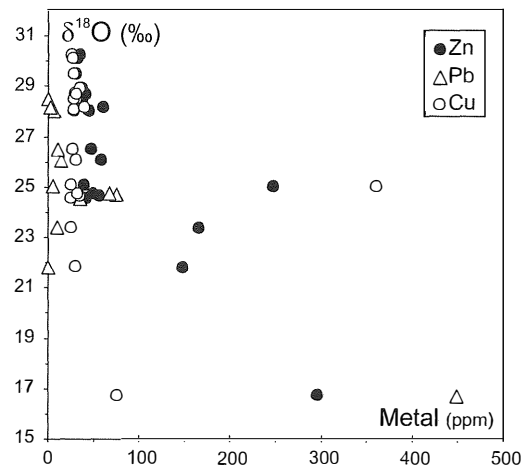


Fig. 6 – Calcite $\delta^{18}\text{O}$ values compared to the metal content of samples. The enrichment order is generally $\text{Zn} > \text{Cu} > \text{Pb}$, with a notable exception represented by the most ^{18}O -depleted sample that shows $\text{Pb} > \text{Zn} > \text{Cu}$.

main process of isotopic and elemental change within the cataclasite structures, i.e. formation of new calcite in the cataclasite matrix and partial breakdown of the original calcite crystal and substitution by new calcite in the cataclastic marble and marble clasts. Recrystallization (solution-precipitation) and diffusion (exchange at the interface between the crystal and the fluid) may have played only subordinate roles. In fact, the observed linear $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ trends support binary mixing between calcite endmembers as the prevailing exchange mechanism rather than recrystallization or diffusion, the latter processes being described by curved trends (Zeng and Hoefs, 1993). The decoupling of stable isotopes and base metals in the clasts may be due to interaction with fluids comparatively low in carbonate, as well as under small water to rock ratios.

Origin of water

As faulting occurred after peak metamorphism, dehydration of OH-bearing minerals in the basement could not have been involved in the genesis of secondary calcite in the cataclasite matrix. Seawater can also be excluded, due to the paleotectonic setting at the time of the brittle deformation, when regions surrounding the studied area (Garfagnana, Val di Magra/Versilia and Lunigiana; see fig. 1) were affected by sediment deposition fed by the presently eroded Alpi Apuane cover units (Carmignani and Kligfield, 1990; Ottria and Molli, 2000 and references therein). Therefore, one may infer that the water involved in the faulting was meteoric and possibly backflooded from the basement.

We may speculate that the lowest $\delta^{18}\text{O}$ value of +16.7‰ observed in the matrix APb-3 corresponds to a very high water to calcite ratio, that is the $\delta^{18}\text{O}$ of water in equilibrium with calcite closely approach the original meteoric one, i.e. tentatively -5.8 to -7.2‰ according to the average values of present-day precipitation sampled on the West Apuane slope (Mussi *et al.*, 1998). By these data, a

calcite-water isotopic temperature of $55 \pm 3^\circ\text{C}$ is calculated based on fractionation factors from O'Neil *et al.* (1969). This temperature may be somewhat underestimated, as the analysed matrix may contain some small (unremoved) marble clasts enriched in ^{18}O with respect to secondary calcite and the original $\delta^{18}\text{O}$ of water may have increased by interaction with the basement rocks.

CONCLUSIONS

The results of our study indicate that fluids were involved during the development of brittle faults hosted within the Liassic marble of the Alpi Apuane metamorphic complex.

Compared to the host marble, newly formed calcite from the cataclasite cores is on average considerably depleted in ^{18}O and depleted in ^{13}C , and even largely enriched in base metals with respect to host marble. Marble clasts from the cataclasite cores and surrounding cataclastic marble show notable variability in the chemical and isotopic compositions relative to their protoliths as a result of fluid-rock interaction processes.

The fluids are interpreted as rising from the siliciclastic basement of the Alpi Apuane, where ^{13}C -depleted carbon sources and mineralized rocks (and ore deposits) occur. This interpretation is supported by the enrichment in radiogenic ^{87}Sr observed in calcite from the cataclasite matrix (as well as the cataclastic marble), as expected for crystallization in the presence of fluids that leached old rocks in the basement.

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