Dating Thrust Events Using ^{87}Sr/^{86}Sr: An Example from the Northern Apennines, Italy[1]

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ABSTRACT

Isotopic and petrographic analyses of the major thrust zone (Calcare Cavernoso) in the Apuane region of the Northern Apennines are used to date the timing of motion on that thrust zone and to document the type and the amount of fluid focused there. The thrust zone consists of a porous cataclasite composed of polylithologic clasts and finely crystalline dolomite included within a recrystallized calcite matrix that shows no affect of subsequent brittle or ductile deformation. ^{87}Sr/^{86}Sr isotopic compositions of clasts and matrix from around the entire Apuane region (1000 km^2) are very uniform, with values that average 0.70811. The strontium data suggest recrystallization of the entire thrust zone by huge volumes of focused fluid flow that caused complete and uniform resetting of the original Triassic Sr isotopic signature by Oligocene sea water during Oligocene thrusting. Preservation of fragile vein networks that also yield the Oligocene sea water Sr ratios suggests that significant post-thrusting deformation or fluid influence within this level of the thrust zone did not occur.

Introduction

Accurately determining the timing of motion on discrete movement zones in deformed terranes is critical to understanding the deformational history of those regions, yet is problematical. In many cases such zones are overprinted by subsequent deformational or metamorphic events, or the host rock composition is not suitable for dating. Many studies, therefore, have focused on the paleontology and palynology of the youngest strata not involved in deformation to provide either an upper age limit before which deformation must have occurred or a broad interval of time during which deformation probably occurred. Recently, radiometric dating techniques of suitable minerals in deformed metamorphic rocks have been used to pinpoint precise ages of deformational events to which thrusting can be related and thereby be indirectly dated (e.g., Kligfield et al. 1986). In addition, stable isotope studies have been used to document the type and amount of fluids linked to dated deformational events (Wickham and Taylor 1985; Dipple and Ferry 1992). However, where thrusts are localized in carbonate rocks, these geologic techniques are often not adequate to constrain the time of thrusting nor the nature of fluid interaction during thrusting.

In this paper, we suggest that movement on thrust zones in carbonate rocks can be directly dated by measuring the ^{87}Sr/^{86}Sr of mineral phases within the movement zone, if the rocks underwent complete Sr isotopic exchange with sea water during thrusting, and that the chemical conditions accompanying thrusting can be constrained by geochemical analyses. We use, as an example, a carbonate thrust zone (Calcare Cavernoso) from the Apuane Alps of the Northern Apennines, Italy, to document the timing of thrusting in that region.

Geologic Setting

The Northern Apennines have been called a thin-skinned thrust-nappe belt that formed in response to the late Oligocene collision between the Corsica-Sardinia and Adriatic plates (Boccaletti et al. 1971, 1980; Alvarez et al. 1974; Dallan-Nardi and Nardi 1978; Reutter et al. 1978; Boccaletti and Coli 1983; Kligfield et al. 1986). Cover sequences of Mesozoic and Tertiary sedimentary rocks of the Tuscan and Ligurian units were transported northeast (Abbatte et al. 1970) and are characterized by overturned folds, thrusts, and reverse and normal faults. Deformation proceeded from west to east

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as determined from sequentially younger deformed sediments toward the east (Merla 1952; Bortolotti et al. 1970). The Liguride units represent remnant Tethyan oceanic crust (Decandia and Elter 1972; Bernoulli and Lemoine 1980) and flysch sediments obducted onto the continental margin during the Eocene (Decandia and Elter 1972; Elter and Trevisan 1973; Elter 1975). The underlying Tuscan sequences are composed of two parts: the lower consists of a Paleozoic to Oligocene metamorphic sequence (the "Apuane Metamorphic Complex") and the upper, a late Triassic to late Oligocene very low-grade to non-metamorphic sedimentary sequence (the "Tuscan Nappe": Baldacci et al. 1967, 1972; Carmignani et al. 1978).

Microplate collision and subsequent compression in the late Oligocene caused stacking of the Ligurian unit and Tuscan Nappe onto the Apuane Paleozoic to Oligocene core along the Calcare Cavernoso, which resulted in its brecciation as well as the formation of the underlying Apuane intracontinental ductile shear zone (Carmignani et al. 1978; Kligfield 1980; Kligfield et al. 1981). In addition, the load supplied by the Tuscan Nappe and Ligurian units created the P-T conditions that resulted in greenschist facies metamorphism of the

Apuane Metamorphic Complex (Carmignani et al. 1978). The youngest rocks (the "Pseudomacigno" Formation) deformed in the shear zone are late Oligocene flysch deposits (Dallan Nardi and Nardi 1978) and are the metamorphic equivalent of the arenaceous flysch sequence (the "Macigno" formation) deposited on the Adriatic plate margin.

The Calcare Cavernoso in the Apuane Alps (figure 1) is an Upper Triassic evaporitic deposit based on (1) its location at the base of the Tuscan Nappe (Upper Triassic through Miocene sequences), (2) well-established stratigraphic correlation throughout northern Italy (see Merla 1952 and Boccaletti et al. 1987a), and (3) the presence, in some places, of evaporites (Boccaletti et al. 1987b). In addition, structures above and below the Calcare Cavernoso indicate that this unit was the focus of extensive movement either as a simple thrust (Carmignani et al. 1978) or as a thrust reactivated as a normal detachment zone (core complex, Carmignani and Kligfield 1990). Timing of the shortening and synmetamorphic extensional phases have been reported as 27 Ma and 14 Ma, respectively, based upon K-Ar and Ar-Ar ages from micas within the metamorphic core (Kligfield et al. 1980). These dates reflect cooling ages of micas
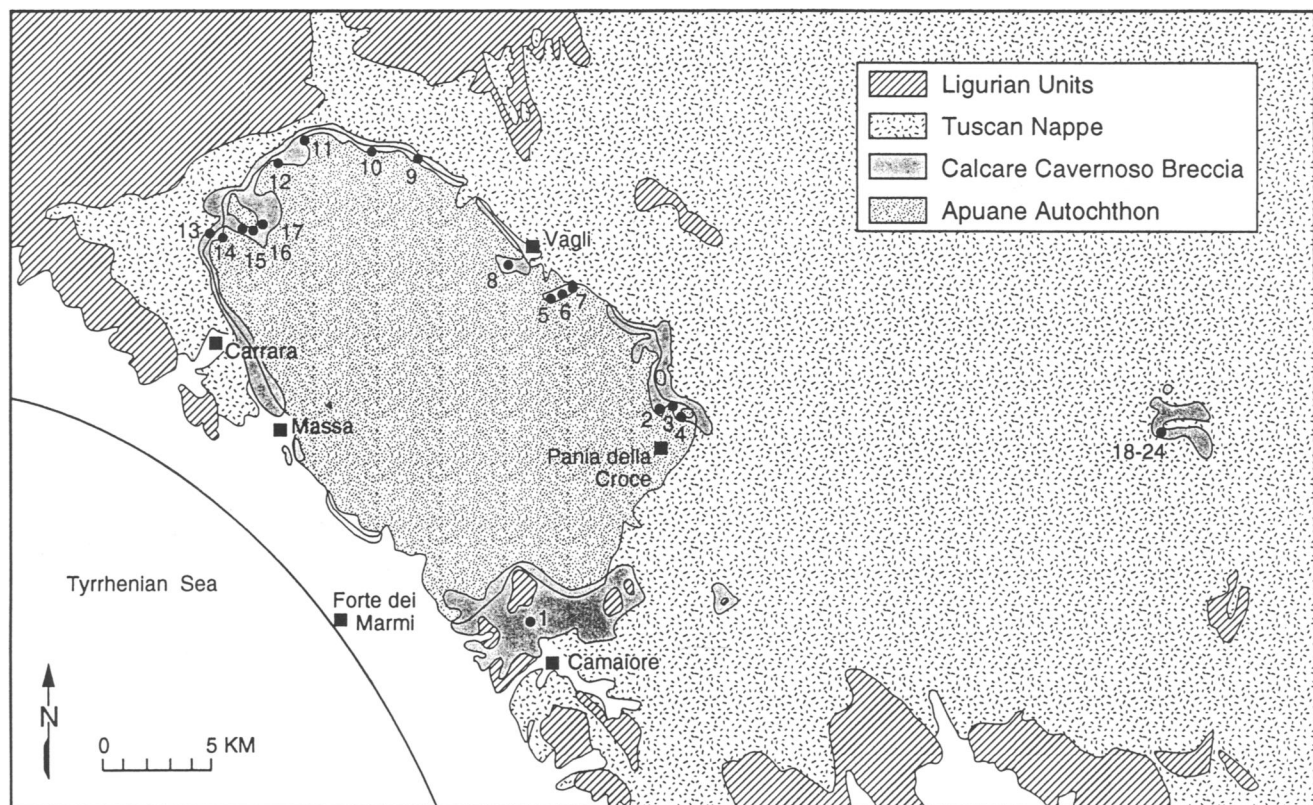

Figure 1. Generalized geologic map of the Apuane Alps region of the Northern Apennines (modified from Boccaletti et al. 1987a). Location of samples 1 through 24 indicated.

in greenschist facies rocks in the core and have been used to infer the timing of NE-directed transport of nappes along the Calcare Cavernoso evaporite above the core. There has recently been some debate over the nature and age of alteration of this Triassic layer (Federici and Raggi 1974; Feroni et al. 1976; Dallan Nardi 1979; Sani 1985; Chicchi et al. 1985). Determining the deformational and fluid history of this zone, therefore, will be important to understanding this part of a major thrust belt in terms of timing of thrusting as well as of mechanisms, sequence of events, and fluid-rock interaction.

Petrographic Characteristics of the Calcare Cavernoso

The Calcare Cavernoso is nearly everywhere a very porous carbonate breccia whose thickness varies from several meters to several hundreds of meters (Boccaletti et al. 1987) and whose aerial extent covers a large part of the Northern Apennines (figure 1). Most commonly the Calcare Cavernoso is a cataclasite composed of calcite-cemented carbonate clasts but, in some locations (18–24 of figure 1), the original, finely laminated host rock is visible. Clasts in the breccia in some places preserve this lamination and are primarily composed of 5 to 10 μ rhombic to anhedral dolomite crystals (figure 2a) that in some cases contain inclusions of anhydrite. Typically, the dolomite crystals within clasts are not cemented with calcite, and therefore, the dolomite is pulverulitic and easily eroded from the rock, resulting in the large pore spaces commonly found in the Calcare Cavernoso (figure 2b). A few of the clasts are composed of metamorphic rock fragments derived from the underlying metamorphic core or are carbonate clasts that show a grain-shape fabric indicating they experienced a previous ductile deformation. Authigenic quartz, although rarely present in the calcite matrix, contains anhydrite inclusions.

The calcite cement forming the matrix of this breccia consists of coarse (up to 0.5 mm), anhedral crystals that are not fractured or twinned and show no intracrystalline deformation (figure 2c). In many samples, the matrix consists of swarms of narrow (1 mm) calcite veins (figure 2d) that cement the surrounding dolomite crystals and form a boxwork texture. These veins also show no evidence of deformation.

Methods

Isotopic analyses were performed on 24 samples of the Calcare Cavernoso from a 1000 km^2 area around the Apuane region (figure 1). Clasts, matrix, and whole rock samples were analyzed for their Sr, C, and O isotopic compositions and X-ray diffraction analyses determined their mineralogy (table 1). Samples for C and O isotopic analysis were reacted with anhydrous H_3PO_4 according to standard techniques (McCrea 1950), and analysis was conducted on a Nuclide mass spectrometer. Analytical reproducibility for $\delta^{18}O$ and $\delta^{13}C$ values is within ±0.1 per mil.

Strontium isotope analysis was performed by simultaneous multicollection on a MAT 261 mass spectrometer. Fractionation in the mass spectrometer was corrected using $^{87}Sr/^{86}Sr$ = 0.1194. Standard NBS 987 was routinely analyzed and yielded 0.710236 ± 0.000029 (n = 5). $^{87}Sr/^{86}Sr$ ratios presented in this paper have been adjusted to NBS 987 = 0.71030 in order to compare with the $^{87}Sr/^{86}Sr$ curve of DePaolo and Ingram (1985).
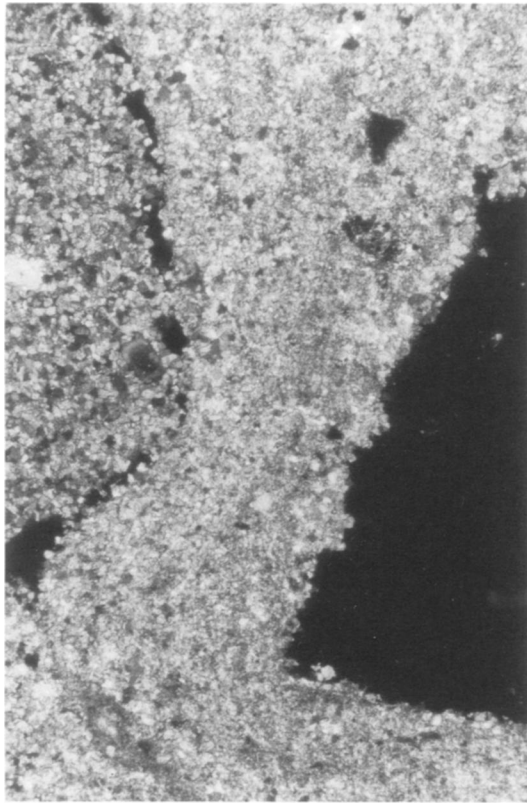
Geochemical Results

The Sr isotopic composition of all carbonate components in the Calcare Cavernoso are statistically indistinguishable. The $^{87}Sr/^{86}Sr$ ratios for laminated dolomite, pulverulitic dolomite, and the calcite matrix average 0.70811 ± 0.00006 (table 1). Such consistent Sr ratios over such a large area suggest that the Sr within the Calcare Cavernoso was derived from a fluid with a homogenous Sr isotopic composition.
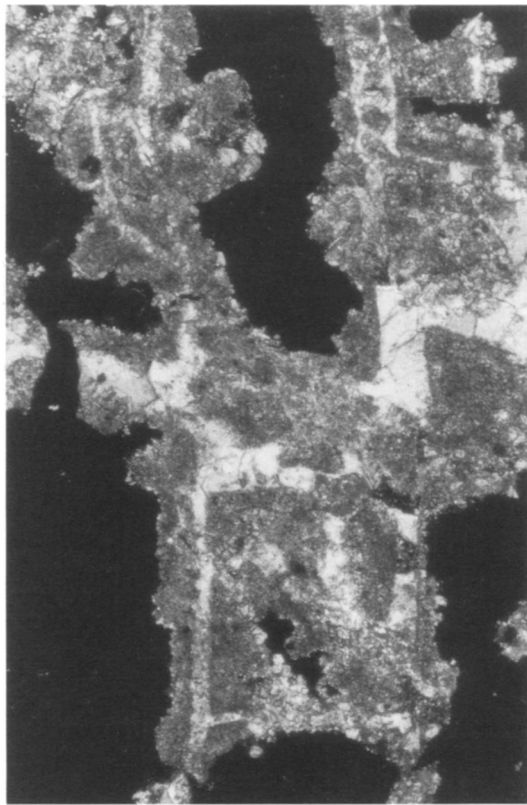
Dolomite from the laminated host rock and from the pulverulitic dolomitic clasts has oxygen and carbon isotopic compositions that average −2.1 and +2.8 per mil PDB, respectively (figure 3b). Matrix calcite has an average oxygen isotopic composition of −5.8 per mil PDB and an average carbon signature of −3.6 per mil PDB (figure 3b). Preliminary trace element analysis reveals that Sr concentrations in both calcite and dolomite are below the detection limit (160 ppm) of the electron microprobe.

Synthesis

Small anhydrite inclusions in the dolomite and authigenic quartz indicates that evaporite minerals were, at one time, present in the Calcare Cavernoso and have since been nearly completely dissolved. Rounded dolomite crystals and euhedral authigenic quartz crystals, commonly found in sediments that originally contained evaporites (Folk pers. comm.), are also present. The presence of evaporite minerals in conjunction with thinly laminated dolomite suggests that the Calcare Cavernoso was originally deposited in an evaporitic
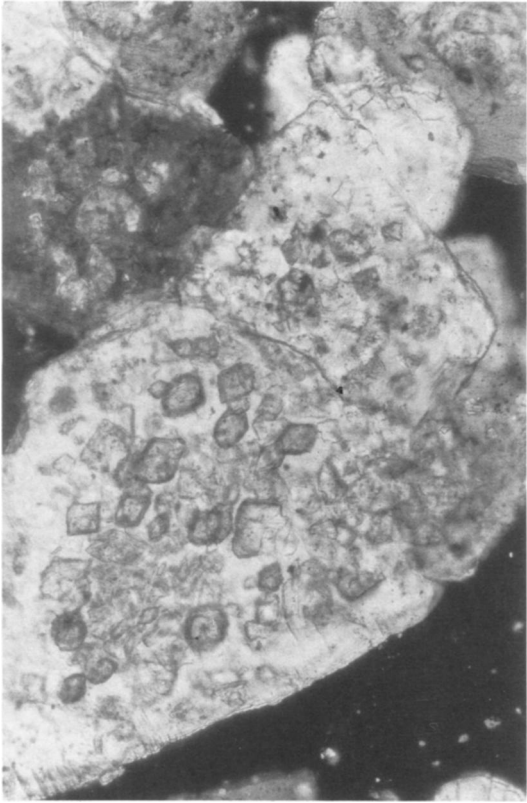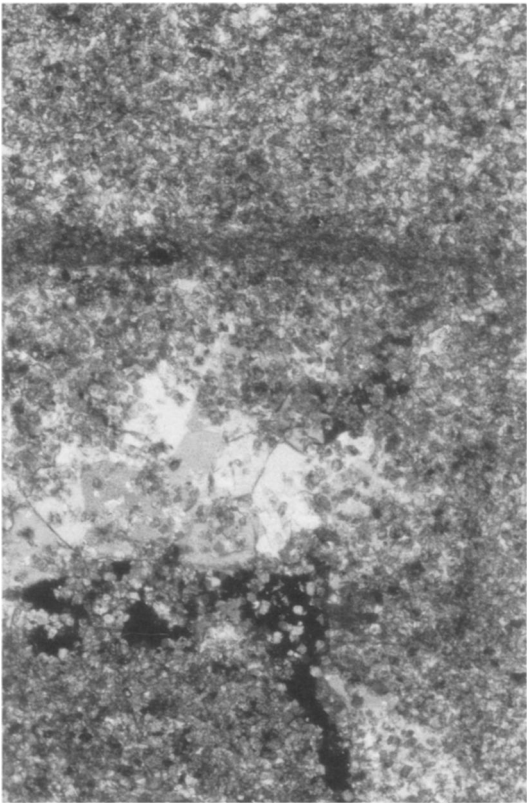
Figure 2. Photomicrographs of the Calcare Cavernoso. (*a*) Rhombic to corroded dolomite crystals included within the younger, undeformed calcite matrix. Long dimension of photograph is 1.1 mm. (*b*) Uncemented dolomite within breccia clasts with large pore spaces (dark area at bottom). A more well-cemented clast (upper third of photograph, rimmed by thin, dark void) maintained its integrity. Long dimension of photograph is 3.3 mm. (*c*) Calcite cement (matrix) consists of coarse (up to 0.5 mm), anhedral crystals that are not fractured or twinned and show no intracrystalline deformation. Long dimension of photograph is 3.3 mm. (*d*) Swarms of narrow calcite veins surrounding dolomite crystals to form a box-work texture. These veins show no evidence of deformation. Long dimension of photograph is 3.3 mm.

Table 1. Calcare Cavernoso Isotopic Compositions

Sample	[87]Sr/[86]Sr	$\delta^{18}O$	$\delta^{13}C$	Mineralogy
1	.70821	−4.08	−3.28	C
2		−4.99	1.47	M
3		−4.81	1.80	M
4		−6.44	0.47	C
5	.70818	−4.41	−1.21	M
6	.70821	−4.56	−1.69	M
7	.70808	−4.00	−.76	M
8	.70811	−3.47	−4.51	M
9	.70811	−4.66	−2.83	M
10	.70808			M
11	.70804			D
12	.70817			C
13	.70812	−6.83	−4.41	C
14	.70806	−7.89	−0.77	C
15	.70812	−6.87	−5.17	C
16	.70802			M
17	.70812	−4.35	−5.3	C
18	.70815	−5.20	−3.71	C
19	.70809	−5.52	−2.67	C
20	.70806	−2.87	3.15	Dp
21	.70804	−2.68	3.23	D
22	.70815	−2.92	2.31	Dp
23	.70810			D
24	.70802	−1.01	2.63	Dp

Note. C = calcite matrix; D = laminated dolomite; Dp = pulverulitic dolomite; M = whole rock.

Figure 3. Isotopic compositions of whole rock, matrix, and clasts from the Calcare Cavernoso from locations 1 through 24 of figure 1. (A) Sr isotopic compositions. Horizontal line represents the average [87]Sr/[86]Sr value of 0.70811 ± .00006. (B) C and O isotopic compositions of calcite (dots) and dolomite (squares). Isotopic compositions of polymineralic carbonate samples are not shown.

tidal flat. This zone is correlative with Late Triassic evaporites throughout the Northern Apennines (Boccaletti et al., 1987) and appears to be correlative with other Late Triassic evaporitic zones in many regions of central Europe (cf. Grandjacquet and Haccard 1975; Jeanbourquin 1988). It is therefore reasonable to suggest that the Calcare Cavernoso was originally composed of gypsum and dolomite and that the present texture and mineralogy reflect dissolution of gypsum and its replacement by the calcite matrix. The pulverulitic dolomite may represent areas that were never cemented with calcite or alternatively, they could be areas in which late dissolution of anhydrite or calcite occurred.

The range of oxygen isotopic values in the calcite and dolomite indicates that they may be in oxygen isotopic equilibrium. Both the dolomite and the calcite have oxygen isotopic signatures lighter than would be expected if these phases were derived directly from sea water at earth surface temperatures. These light values may be the result of interaction with meteoric water or might represent precipitation or recrystallization at elevated temperatures. It has recently been suggested by Lugli (1992) and Hodgkins and Stewart (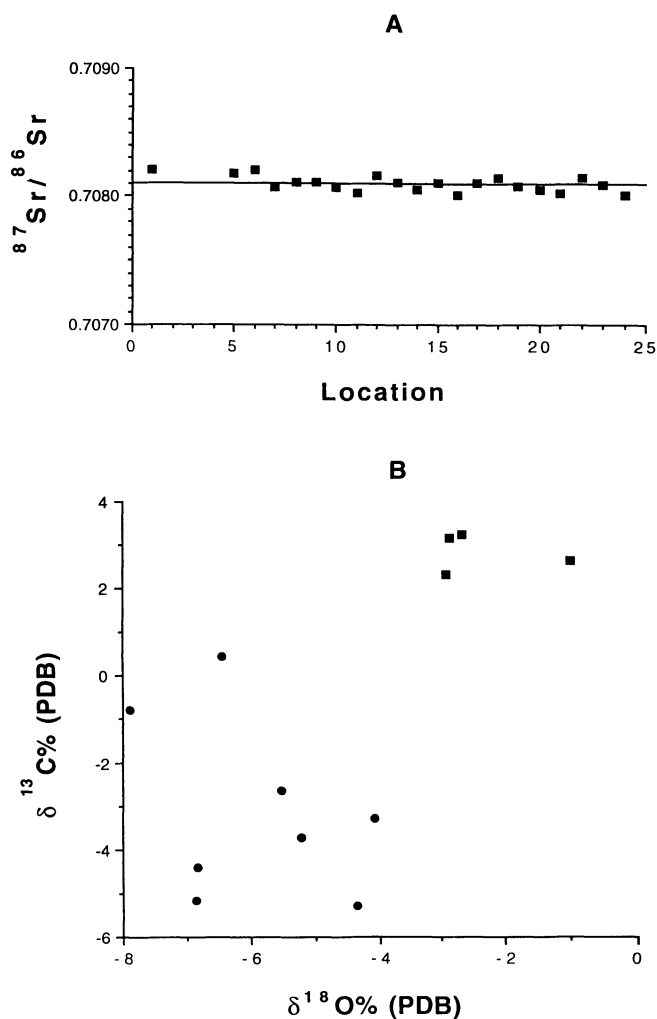1991) on the basis of fluid inclusions that this zone had experienced elevated temperatures (perhaps between 250 and 300°C) at some point during its evolution.

The carbon isotopic compositions of the two carbonate phases are distinctly different. The heavy values obtained from the dolomite indicate inorganic carbon. In contrast, the light carbon values of the calcite suggest that nearby organic material was being oxidized during the formation of the calcite matrix. Regardless of the origin of the carbon, the difference in carbon compositions of the two carbonates indicates that they formed from different fluids.

The oxygen isotopic compositions of the carbonate phases probably record the last phase of diagenesis, which was apparently controlled by meteoric

fluids. Although the Calcare Cavernoso experienced considerable burial accompanied by high temperatures (Carmignani et al. 1978), the oxygen ratios are relatively heavy and, therefore, probably do not record burial diagenesis. Heavy oxygen ratios could be maintained in closed systems even at high temperatures. As will be discussed, however, the Calcare Cavernoso at some time did experience extreme open-system conditions. The average oxygen isotopic compositions of both the calcite and the dolomite suggest equilibrium conditions with light waters (-4 to -6) at conditions ranging from the earth's surface to slightly elevated temperatures (25°C to 40°C). The distinctly different carbon isotopic compositions between the dolomite and calcite support the petrographic observations that the minerals formed at different times. The positive carbon values of the dolomite apparently represent inorganic carbon derived from sea water. The light carbon composition of the calcite matrix indicates the contribution of organic carbon probably generated from thermally oxidized organic material during burial. The final interaction of both carbonate phases with meteoric waters probably reset the oxygen ratios but left the carbon ratios essentially unchanged from their original values due to the small amount of dissolved carbon in aqueous fluids.

Uniform values of $^{87}Sr/^{86}Sr$ in all carbonate portions (clasts, matrix, and whole rock) of the Calcare Cavernoso over a large area suggest that the rocks derived their strontium from an aqueous reservoir with a homogenous strontium isotopic composition. Ground waters and basinal brines from other locations have been shown to have areally inhomogeneous strontium isotopic compositions (Steuber et al. 1984; Muskgrove and Banner 1992) and, therefore, it is most reasonable to assume that strontium in the Calcare Cavernoso is derived from sea water, probably the only large aqueous reservoir with a uniform strontium isotopic composition (Veizer 1989). The $^{87}Sr/^{86}Sr$ in the Calcare Cavernoso is areally uniform; however, it is not representative of the value cited for Late Triassic sea water (0.7075–0.7076; Burke et al. 1982), from which the host rock was reportedly deposited. Rather, the $^{87}Sr/^{86}Sr$ corresponds to a Middle Oligocene (ca. 30 Ma) sea water ratio (Burke et al. 1982; DePaolo and Ingram 1985). This is in contrast to the surrounding Mesozoic rocks, which apparently retain their depositional strontium ratio; for example, the overlying Portoro Triassic limestone has a strontium ratio of 0.7076 which reflects a late Triassic sea water origin (Carter and Dworkin 1990).

It appears, therefore, that the depositional $^{87}Sr/^{86}Sr$ of the Late Triassic Calcare Cavernoso was reset. In general, strontium ratios in carbonate rocks that differ from the whole rock depositional values occur in cements or dolomitized portions of the rock. Whole rock strontium isotopic ratio modification has been observed in carbonate rocks but usually occurs as areally inconsistent ratios that range between the depositional ratio and the ratio of the diagenetic fluid (Gao 1990). This is probably caused by inhomogeneous strontium ratios in the invading fluids as well as by different amounts of water-rock interaction throughout the formation. Consistently and uniformly reset whole rock strontium ratios in the Calcare Cavernoso suggest that large volumes of water interacted with the rock and that the rock was completely equilibrated with the new fluid. Estimates of the water-rock (volume to volume) ratio needed to accomplish such equilibration vary from 60 to 100 depending on the assumed initial Sr concentration of the rocks. These water-rock ratios were generated using the mass balance equation and program developed by Banner and Hanson (1990). The model simulates resetting the strontium ratio in dolomite from a Jurassic sea water value to that of an Oligocene sea water value. We therefore propose that sea water flowed through this thrust zone within the Calcare Cavernoso during thrusting, because the age of sea water with the appropriate Sr isotopic composition (i.e., Oligocene) corresponds precisely to the timing of deformation determined by radiometric techniques (ca. 27 Ma, Kligfield et al. 1980) and by the age of the youngest rocks (Pseudomacigno Formation) involved in deformation. Such focused sea water flow through a thrust fault has not been documented before and could have implications about the structural level and style of thrusting in this area.

Conclusions

The geochemical and petrographic analyses of carbonate minerals in the Calcare Cavernoso suggest that it has undergone a complex diagenetic and tectonic history. The rocks were initially deposited in evaporitic conditions as gypsiferous and dolomitic sediments (Merla 1952; and see Boccaletti et al. 1987a, 48). After deposition, the sediments were buried by a Mesozoic and Cenozoic cover, and most of the gypsum was dissolved. Thrusting of the Tuscan Nappe in the Oligocene caused intense brecciation that destroyed most of the original fabric (i.e., fine laminations) of the rock. During this phase, Oligocene sea water was focused through

and interacted with carbonates in the fault zone. These fluids were responsible for resetting the ^{87}Sr/^{86}Sr value in the remaining dolomite and also provided the constituents needed for precipitation of the calcite cement that lithified parts of the rock.

Focused sea water flow during thrusting in carbonate rocks is significant because its effects can be used to determine accurately the timing of thrusting. In this case, the timing of thrusting, as determined by measuring ^{87}Sr/^{86}Sr in the thrust zone, is in agreement with the age of the deformational event to which thrusting has been related (Kligfield et al. 1986). Such independent verification suggests that using strontium ratios to date thrusting, or any movement event within carbonate rocks that have recrystallized in the presence of sea water, is a useful endeavor. If sea water flow through movement zones is a common phenomenon during tectonism, this technique may be useful in unraveling geologic histories in areas where no other age determination methods are viable. The Alpine "cornieules" (see Bruckner 1941) would be another location to test this hypothesis.

The mechanism by which fluid could be focused through a thrust zone is unclear, but three possibilities can be suggested: (1) Oliver (1986) has suggested the "squeegee" method in which fluids in thrust belts are expelled toward the foreland. This might not have been the functioning mechanism in Northern Apennine thrusting because the volume of fluid needed to reset the Calcare Cavernoso would have been too large to have been obtained solely from pore fluids. In addition, pore fluids generally have inhomogeneous ^{87}Sr/^{86}Sr values controlled by the lithology of the rocks in which they reside (Steuber et al. 1984). (2) Thermal anomalies have been suggested as the driving force behind the circulation of fluids in many crustal environments (Bjorlykke 1984; Wickham and Taylor 1985). It might not be unreasonable to hypothesize that dense, cold, sea water could sink into and flow through a highly permeable zone and then be expelled into other areas following heating at depth. In fact, brecciation of the Calcare Cavernoso as a result of thrusting may have created just such a porous zone. Finally, (3) it seems possible that waters could be periodically drawn into a zone by vacuum suction if that zone were repeatedly opened and closed during fracturing. Perhaps, as is often the case, the driving mechanism is some combination of these three possibilities.

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