Int J Earth Sci (Geol Rundsch) (2006) 95: 413–430
DOI 10.1007/s00531-005-0040-z

ORIGINAL PAPER

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Thrusting and faulting in metamorphic and sedimentary units of Ligurian Alps: an example of integrated field work and geochemical analyses

Received: 2 December 2004 / Accepted: 18 June 2005 / Published online: 27 September 2005

Abstract In a sector placed in the SE part of the Alps–Apennine junction, a kilometre-scale shear zone has been identified as the Grognardo thrust zone (GTZ), which caused the NE-directed thrusting of metaophiolites (Voltri Group) and polymetamorphic continental crust slices (Valosio Unit) of Ligurian Alps onto Oligocene sediments of an episutural basin known as "Tertiary Piemonte Basin". The structural setting of the GTZ is due to syn- to late-metamorphic deformation, followed by a brittle thrusting that occurred in the Late Aquitanian times and can thus be related to one of the main contractional tectonic events suffered by northern Apennines. The GTZ was then sealed by Lower Burdigalian carbonate platform sediments (Visone Formation). Transtensive faulting followed in post-Burdigalian times along NW–SE regional faults and displaced the previously coupled sedimentary and metamorphic units. The GTZ thus underwent a plastic-to-brittle evolution, during which carbonate-rich fluids largely sustained the deformation. In these stages, a complex vein network originated within both the metamorphic and sedimentary rocks. Field data and stable isotopic analyses (^{13}C and ^{18}O) of bulk rocks and veins show that fluid–rock interaction caused the carbonatisation of the rocks in the late-metamorphic stages and the cataclasis and recementation, by the action of isochemical cold carbonate groundwater during the thrusting events. Carbonate veins largely developed also during the transtensive faulting stages, with composition clearly different from that of the veins associated to thrust faults, as indicated by the strong depletion in ^{13}C of carbonate fillings, suggesting the presence of exotic fluids, characterised by a high content of organic matter.

Keywords Ligurian Alps · Tertiary Piemonte Basin · Miocene tectonics · Faulting · Methane-bearing fluids · Stable isotopes

Introduction

The exhumation of the Alpine chain has been intensively studied in recent years. The reconstruction of the exhumation path of the Alpine metamorphic units can be derived by recognition of the chronological order of deformational events that occurred in progressively shallower crustal levels. Unfortunately, this approach sometimes fails in its goals due to the paucity of chronological data to constrain the age of the deformational events. In fact, absolute ages can be obtained only by means of expensive or wasting-time procedures such as radiometric dating, while the relative chronology of the deformational events is often difficult to establish since the overprinting relations between the main penetrative structural elements are not always clear.

The possibility to date the post-metamorphic tectonic events and/or to establish chronological relations between different structural associations has been given in the study area (Fig. 1) by the occurrence of several geological conditions such as:

- The presence of relatively well-dated Oligocene–Early Miocene stratigraphic successions, belonging to an episutural basin known as Tertiary Piemonte Basin (TPB), that unconformably covers the metamorphic units of the Ligurian Alps
- The presence of dated regional stratigraphic unconformities within these successions that record the tectonic events suffered by their basement
- The possibility to establish geometrical correlations between tectonic structures in sedimentary and metamorphic units

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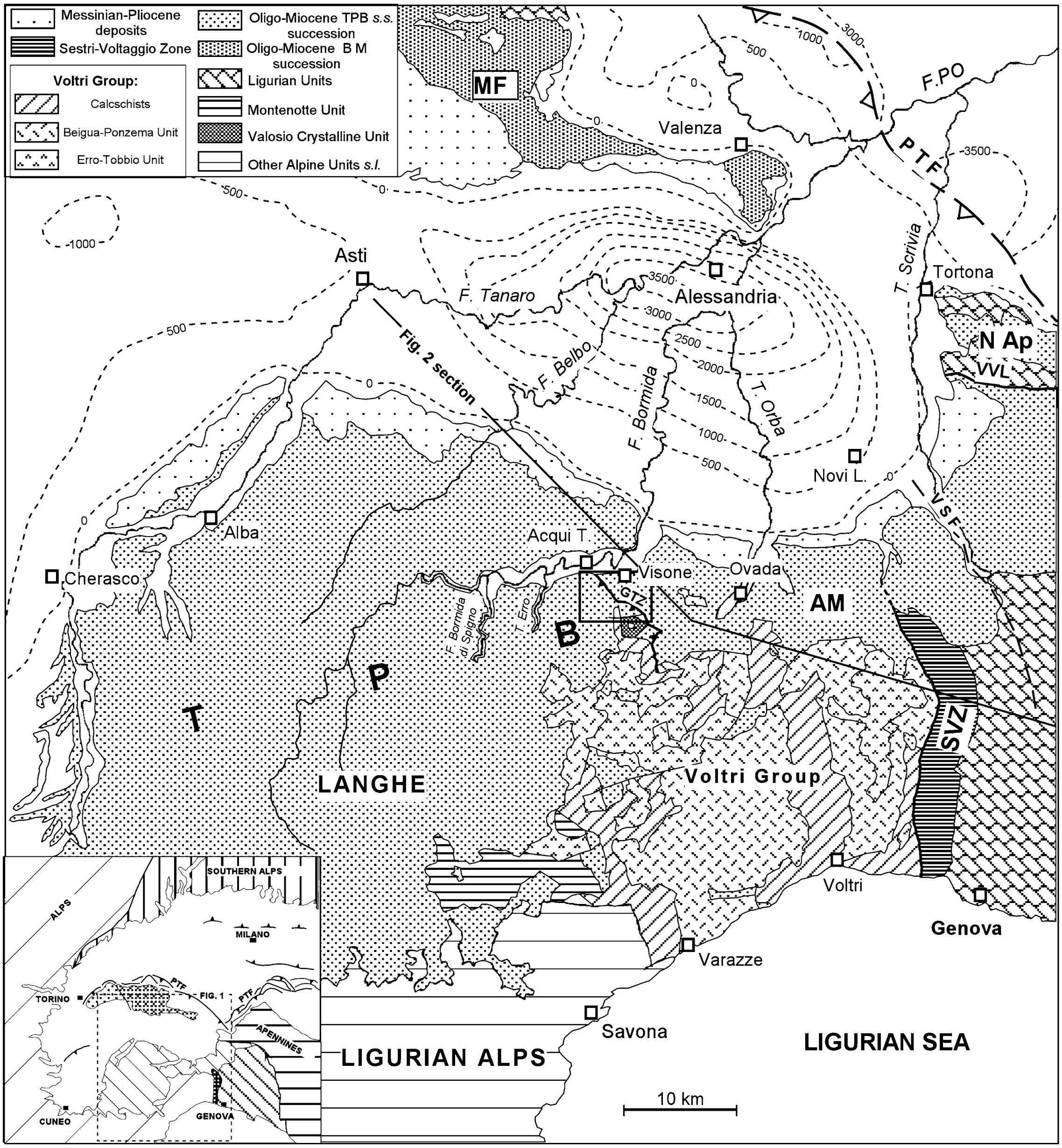


Fig. 1 Structural sketch of part of the Tertiary Piemonte Basin domain and adjoining regions. In the *inset* the studied area. *PTF* Padan thrust front, *SVZ* Sestri Voltaggio zone, *VVL* Villalvernia-Varzi line, *AM* Alto Monferrato, *MF* Monferrato, *N Ap* Northern Apennine, *VSF* Valle Scrivia Fault, *GTZ* Grognardo thrust zone. *Dotted lines* indicate the depth (in metre) of the base of the Pliocene (after CNR 1990)

In the study area (Fig. 1), a reconstruction of the regional Oligocene–Early Miocene tectono-sedimentary evolution of the Alto Monferrato sedimentary succession and relative basement has been recently proposed (d'Atri et al. 1997; Piana et al. 1997). In this work, a better description of this model is pointed out; it mainly regards the structural topics and is grounded on the analysis of the relations between pre- and post-metamorphic deformations and on the role of fluids during faulting.

The chronology of the syn- and post-metamorphic deformations of the study area has been inferred on the basis of overprinting relations between the tectonic structures and on their relations with the unconformities of the Alto Monferrato sedimentary succession. Different tools or methods have been used for structural correlations, such as: (1) the presence of regional persistent structural elements or penetrative macroscopic fabrics, (2) the kinematic consistency of the different structural associations.

Furthermore, the structural evolutfion has also been reconstructed by comparisons between the geochemical-isotopic compositions of the vein-infillings on the main structures, since large occurrences of fluids, mainly concentrated in wide regional shear zones, sustained the deformational processes in both the metamorphic and sedimentary units.

In fact, the metamorphic rocks underlying the Alto Monferrato succession were metasomatised by hydrothermal carbonate fluids, which gave rise to intensively recemented fault rocks. The abundance of carbonate in the rocks enabled the development of diffuse vein systems also during the post-metamorphic brittle deformations. In the light of the importance of fluids in promoting the displacement of rock bodies along thrusts and faults (Oliver 1986; Burkhard and Kerrick 1990; Behrmann 1991), stable isotope analyses were carried out on the carbonate veins and corresponding host rocks to obtain additional information on the deformational processes (i.e., the physico-chemical conditions during fracture infilling) and to achieve a better understanding of the temporal relations existing between the structural associations.

Geological setting

The exhumation of the metamorphic units of the Ligurian Alps occurred in the frame of the post-collisional evolution of the Western Alps. This evolution was first driven by Eocene meso-alpine North-directed backvergent thrusts developed in a retroforeland domain made up of Insubric–Adriatic crust and Ligurian Mesozoic–Paleogene covers (Polino et al. 1994; Roure et al. 1990). Linked sedimentary basins developed, during these events, on both the Alpine thrust belt and the retroforeland domain, to form the so-called Piemonte Tertiary Basin (Gelati and Gnaccolini 1988 and references therein; Fig. 1). These basins experienced Oligocene–Neogene syn-sedimentary tectonics that incorporated them into the western termination of the Apennine chain (Elter and Pertusati 1973; Cassano et al. 1986; Biella et al. 1988, 1997; Bozzo et al. 1992; Laubscher et al. 1992; Castellarin 1994; Polino et al. 1994; Falletti et al. 1995; Mutti et al. 1995). This tectonic evolution, thought as driven at large scale by the Western Mediterranean opening (Boccaletti et al. 1990) induced the NE-ward translation of the basins and relative detached basement slices, while coeval left-lateral NW-directed movement occurred along the main thrust fronts (Castellarin 1994; Piana and Polino 1995). As the outward migration of the Apennine thrust front proceeded, in the inner parts of the thrust belt the TPB differentiated into distinct tectono-stratigraphic domains (Fig. 1): Torino Hill, Monferrato, Borbera-Grue, Langhe Basin and Alto Monferrato which comprehends the study area (Gelati and Gnaccolini 1988).

The Alto Monferrato domain is characterised by a sedimentary, mainly terrigenous succession, deposited since Early Oligocene onto a metamorphic substratum made up of metaophiolites (Voltri Group) and polymetamorphic continental crust slices (Valosio Crystalline Unit) that have been previously coupled by meso-alpine tectonics (Forcella and Rossi 1980; Hoogerduijn Strating 1994; Capponi et al. 1999; Fig. 2). The uplifting of the metamorphic Alpine units continued through Oligocene, since they overthrust a part of the Alto Monferrato succession in Late Aquitanian times (d'Atri et al. 1997; Piana et al. 1997). This thrusting event, which was sealed by a regional unconformity at the base of Burdigalian platform sediments (Visone Formation), inherited the structural features due to the eo-alpine and meso-alpine events and led to the development of penetrative brittle fabrics both in metamorphic and sedimentary units (Piana and Tallone 1997). Transtensional tectonics followed in the post-Burdigalian times, which gave rise to well-developed normal and strike-slip fault systems. These faults accommodated the Late Burdigalian–Langhian regional subsidence of the Alto Monferrato domain, although their activity continued probably until late Serravallian times mainly as strike-slip faults. The regional tectonic evolution continued until the Pliocene–Pleistocene, when the Alpine metamorphic units, the Ligurian units and the Oligocene–Miocene TPB successions were translated N- and NE-ward onto the Insubric foreland, along the Padan thrust front (Pieri and Groppi 1981).

The metamorphic units of the Voltri Group and Valosio Crystalline Unit

The metamorphic substratum of the TPB succession crops out in the SE part of the study area (Fig. 3). It is made up of metaophiolites and associated metasediments of the Voltri Group that underwent a polyphase tectono-metamorphic evolution, from high-pressure conditions to greenschist-facies conditions (Capponi et al. 1994 and references therein). A slice of polymetamorphic rocks (paraderivates and gneisses of the "Massiccio Cristallino di Valosio" sensu Forcella et al. 1973, here designated as "Valosio Crystalline Unit") is at present tectonically stacked between different geometrical units of the Voltri Group (Cabella et al. 1991 and references therein; d'Atri et al. 1997; Piana et al. 1997) by brittle shears of a larger fault zone, the Grognardo thrust zone (GTZ, see The Grognardo thrust zone and Figs. 3, 4).

The Voltri and Valosio Units underwent syn-metamorphic eo-alpine and meso-alpine ductile deformations, which generated regional transpositive foliations deformed by several folding phases. All these rocks present syn-metamorphic tight folds refolded by open coaxial folds, whose axial planes are defined by a centimetre-spaced crenulation cleavage. In the upper slices of the GTZ, the older folds mainly trend NW–SE; these folds are particularly well preserved in the metabasites of the Voltri Group. In the lower slices of the GTZ, ENE-WSW-trending tight folds are prevalent, which can be observed mainly within the tectonic slices of Valosio quartz-micaschists (Fig. 5). Penetrative brittle fabrics were then superimposed on the syn- to late-metamorphic structures.

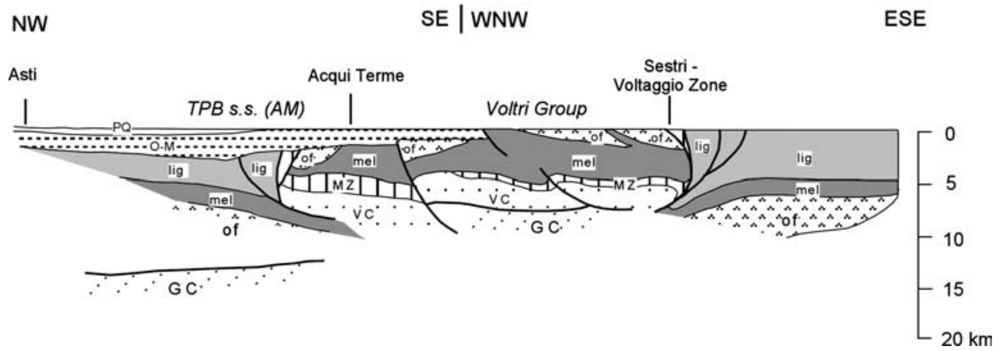


Fig. 2 Geologic interpretation of a seismic line across the Tertiary Piemonte Basin, after Biella et al. (1988). Location in Fig. 1: *GC* "Granite-type" crust, *VC* metamorphic Paleozoic units (i.e. Valosio Crystalline Unit), *of* main ultramafic units, *mel* calcschists and ophiolitic mélange, *lig* Ligurian and subligurian units, *MZ* carbonate Meso-Cainozoic successions, *OM*: Oligocene–Miocene succession of Tertiary Piemonte Basin, *PQ* Plio-Quaternary sediments

The Alto Monferrato Oligocene–Lower Miocene succession

In the study area, the Alto Monferrato Oligocene–Lower Miocene succession consists of continental conglomerates and sandstones followed by marine arenite–microconglomerate successions (Molare Formation, Lowermost Oligocene; Lorenz 1969; Gnaccolini 1974), which pass gradually to a slope-basinal hemipelagic, silty-marly succession (Rocchetta Formation, Lower Oligocene–Upper Oligocene; Gelati and Gnaccolini 1980; d'Atri 1995). Transgressive-shelf biocalcarenites and outer-shelf glaucony-rich arenites (Visone Formation, Lower Burdigalian–Upper Burdigalian; Gelati 1969; d'Atri 1990b) unconformably follow these sediments (d'Atri 1990a). Above the Visone Formation, a thick succession consisting of basin plain turbidite deposits is present (Cortemilia Formation, Upper Burdigalian–Lower Langhian; Gelati and Gnaccolini 1988; d'Atri 1995).

The stratigraphic features of the study area show that Early Miocene sedimentation was controlled by tectonics mainly in two periods:

- The Late Aquitanian, when the uplift of the depositional area (slope) of the Rocchetta Formation was driven by transpressive tectonics (Piana et al. 1997)
- The Langhian, when transtensional tectonics induced fast collapse in the study area, restoring the deep-water sedimentation

These two tectonic events originated, respectively, from distinct fault systems:

- A Late Aquitanian system that mainly consists of NNW–SSE striking thrusts and associated strike-slip faults, which are currently sealed by the erosional angular unconformity at the base of the Visone Formation. The major fault zone that belongs to this system is the Grognardo thrust zone.
- A post-Burdigalian system, characterised by NW–SE and E–W transtensional faults that were successively reactivated and tilted by late Serravallian transcurrent tectonics, probably related to the outward migration of TPB thrust front at regional scale (Falletti et al. 1995). At present, the post-Burdigalian fault system is thus characterised by interconnected fault segments originated by both the Langhian transtensional and late Serravallian strike-slip faulting.

All these faults displaced both the Alto Monferrato sedimentary succession and the Valosio and Voltri metamorphic units and partially reactivated most of the pre-existing syn-metamorphic shear zones.

The Grognardo thrust zone

The GTZ is well exposed along the River Visone, south of Acqui Terme (Fig. 3), and its description is the main topic of this work. It represents a late-metamorphic shear zone reactivated by brittle shearing related to the Late Aquitanian transpressive tectonics. It is bounded at the top by the Ciglione ductile-to-brittle thrust (CGT) that records the early stages of the GTZ deformation, and at the foot by the Val Gorrini brittle thrust (VGT, Figs. 3, 4).

The CGT and the VGTt are roughly subparallel, on a map, at a kilometric scale. An older syn- to late-metamorphic shear zone is preserved within the GTZ, as described below (see The Musotto–Sappagliano shear zone)

The amount of shortening or the total displacement of the GTZ cannot be precisely determined, since reflection seismic lines are not available for the study area or surroundings, and good geometrical markers are lacking in the metamorphic units. On the basis of field data and by comparisons with logs available for Acqui Terme hot springs sites (Bortolami et al. 1982), the vertical displacement could be at least 300–400 m and the horizontal displacement about 2 km. The depth at

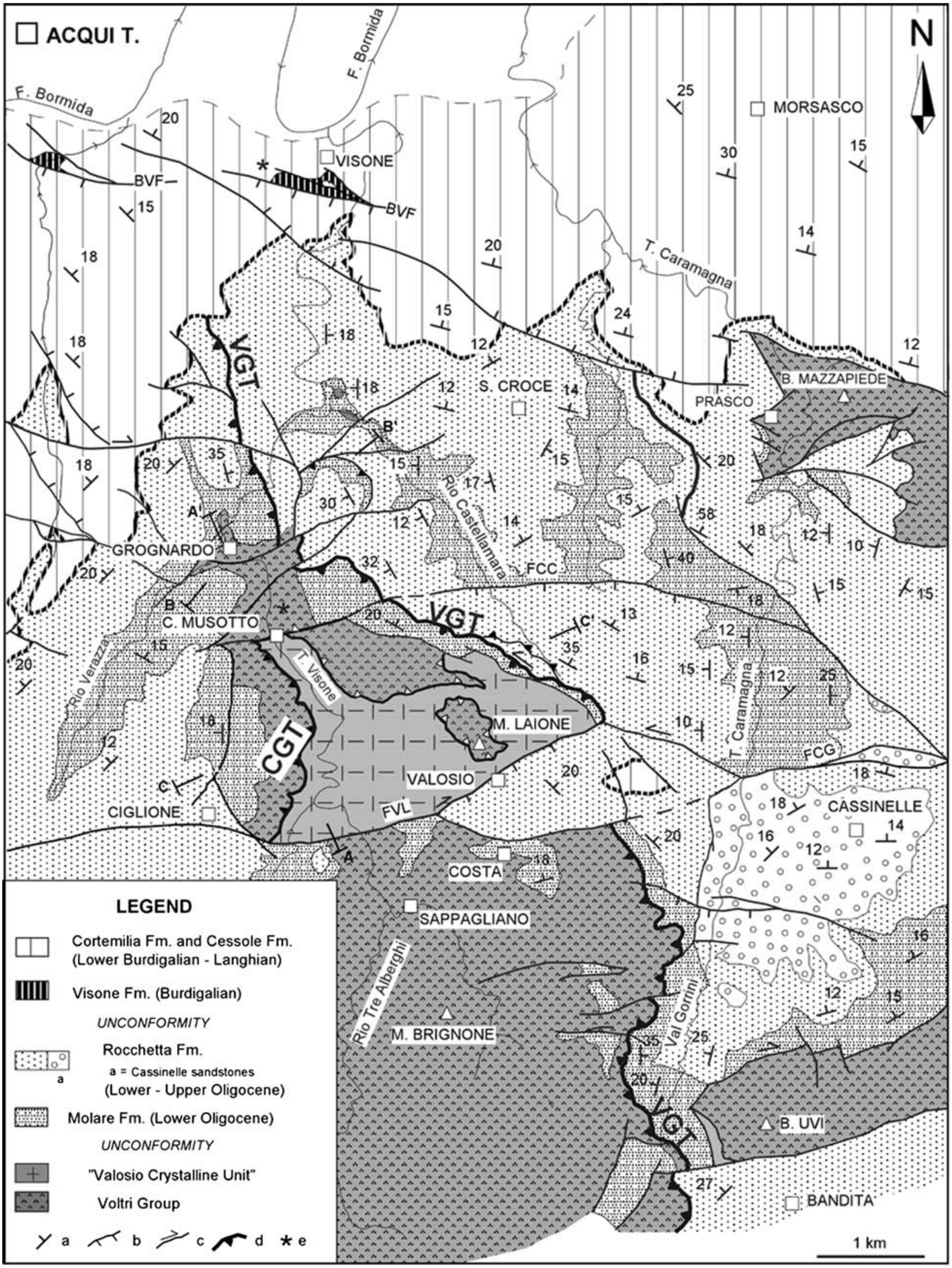


Fig. 3 Geological sketch map of the studied area. The Ciglione and Val Gorrini thrusts depict a large fault zone, here named Grognardo thrust zone. *CGT* Ciglione thrust, *VGT* Val Gorrini thrust, *BVF* Bagni-Visone fault. **a** Bedding and/or regional schistosity attitude, **b** normal faults, **c** strike-slip faults, **d** thrusts (*triangles on the upper side*), **e** sampling localities **A**–**A′**, **B**–**B′**, **C**–**C′**: geological sections reported in Fig. 4

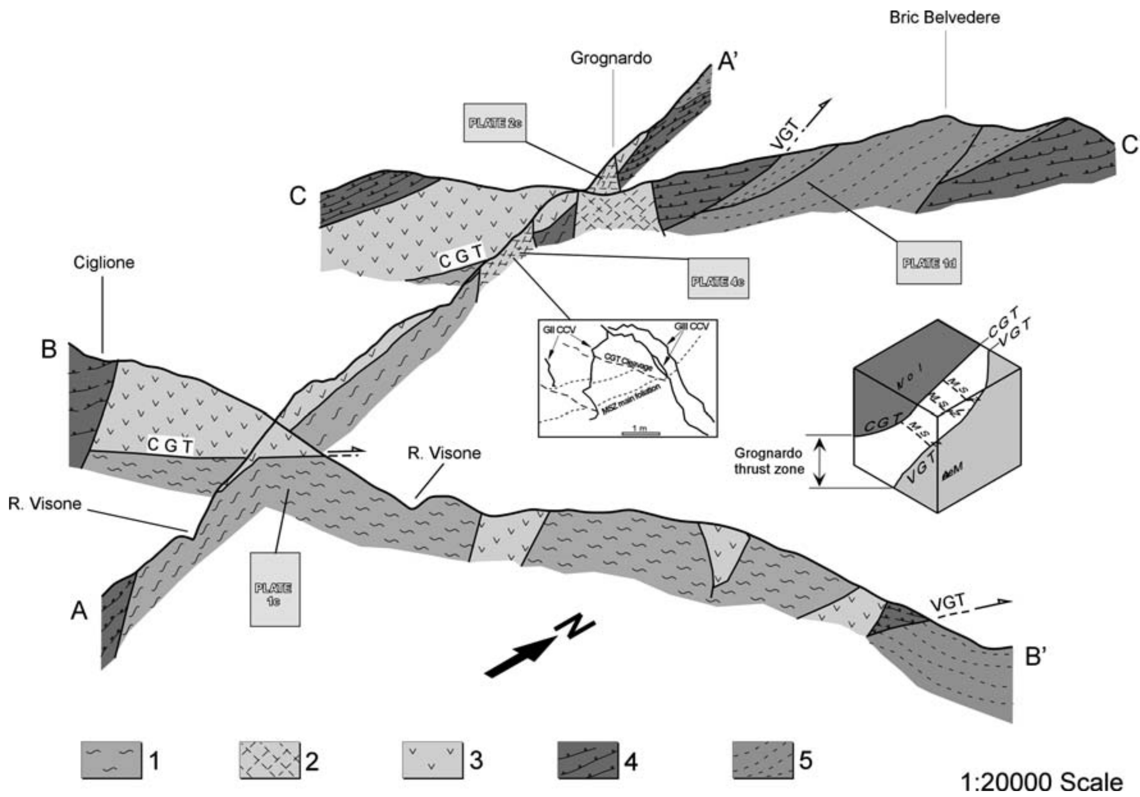


Fig. 4 Fence diagram resulting from intersections of the geological sections **A**–**A′**, **B**–**B′** and **C**–**C′** (see traces in Fig. 3). *1* Valosio Unit, *2* listwaenites and carbonatised micaschists within the Grognardo thrust zone, *3* Voltri Group, *4* Molare Formation (Lower Oligocene), *5* Rocchetta Formation (Lower Oligocene-Aquitanian), *CGT* Ciglione thrust, *VGT* Val Gorrini thrust

which the basal thrust could have originally worked is constrained by the thickness of Molare and Rocchetta (see legend in Fig. 3) plus the vertical offset of the whole GTZ (see geological map in Fig. 3 and cross-sections in Fig. 4). It is here assumed that it could be of the order of 2–3 km.

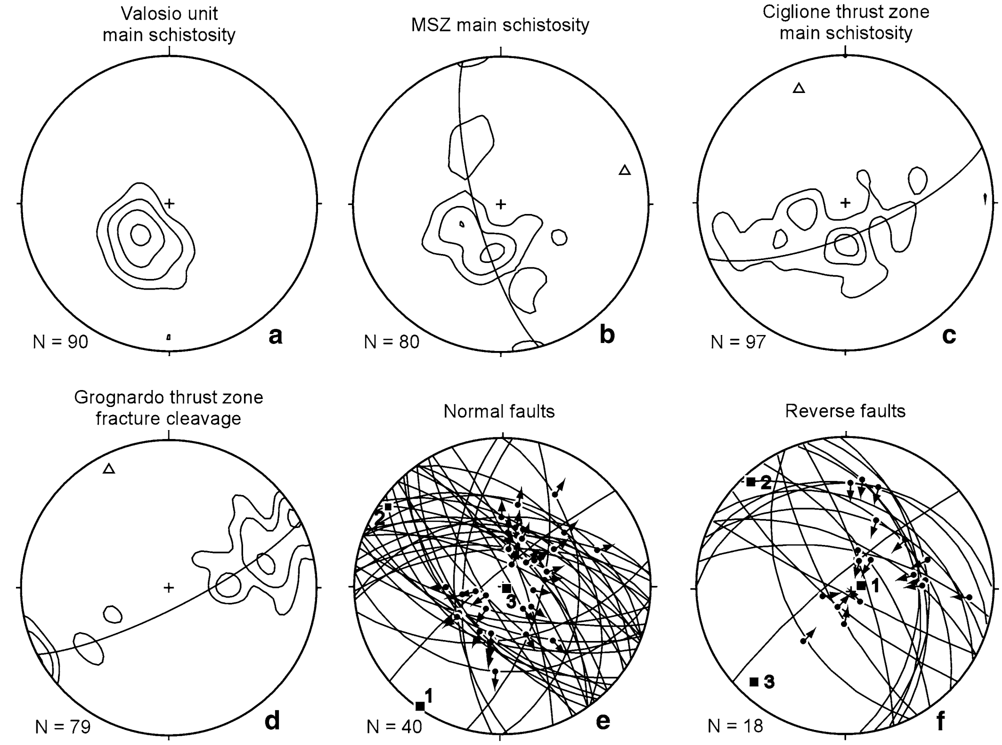


Fig. 5 Schmidt and Wulff diagrams (*lower hemisphere*) of mesoscopic structural data. Plots **a**–**d** report the poles to macroscopic penetrative surfaces (regional schistosity or macroscale cleavages). They are probability density diagrams and the *curves* represent density isolines within a uniform distribution of orientations. Plots **e** and **f** show *great circles* of fault planes. *Arrows on great circles* show the slip vector on the fault planes. *Numbered squares* show the maximum (*1*), intermediate (*2*) and minimum (*3*) shortening axes. *Great circles* and *triangles* in plots **a**–**c** refer, respectively, to the calculated best-fit circle and distribution axes (i.e. large-scale folding axes)

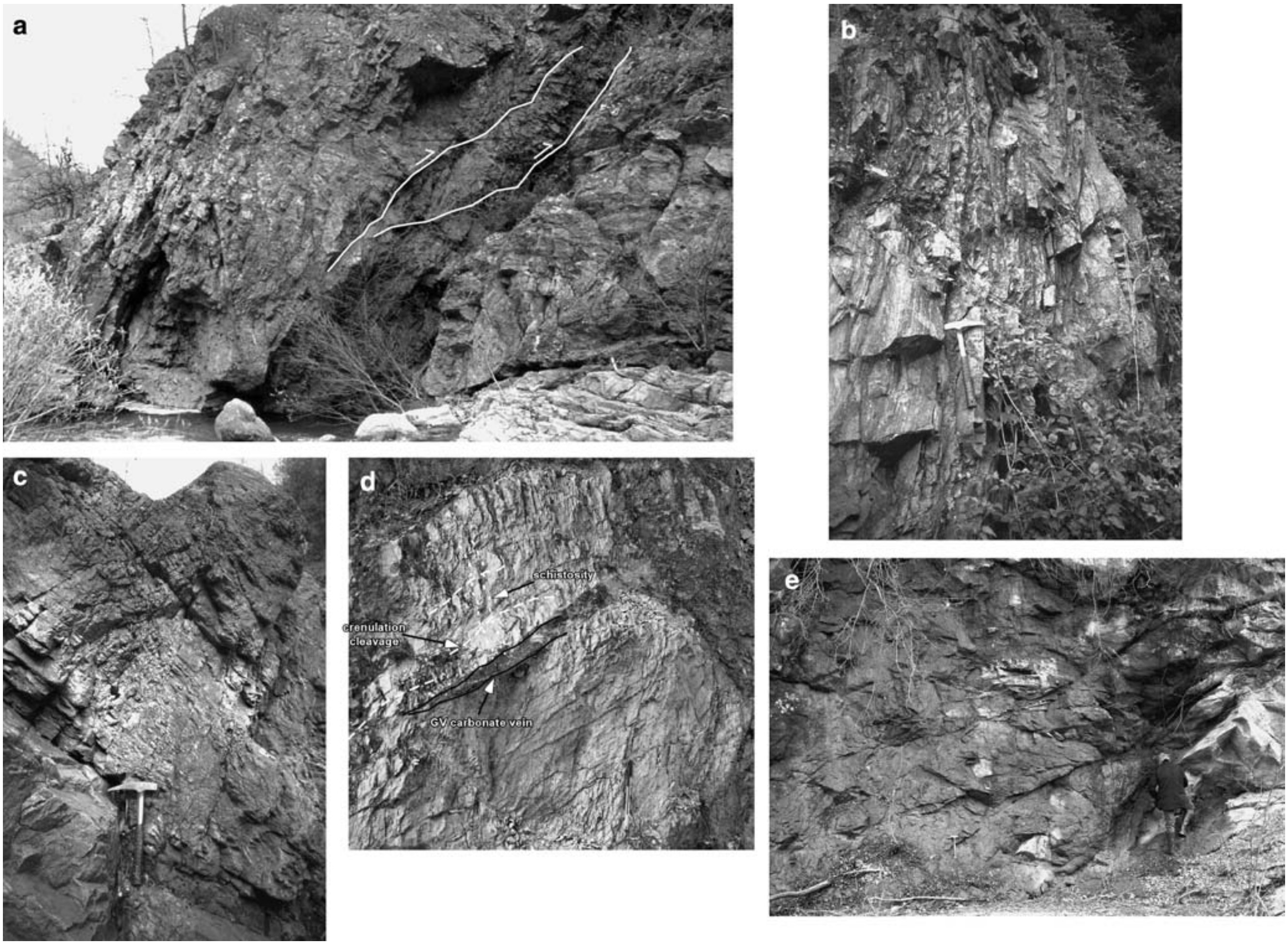


Plate 1 **a** Ciglione thrust. Decametric shear zone and associated fault breccia along the Visone river. The spaced fracture cleavage dips to WSW. **b** Hangingwall of the Ciglione thrust—metabasites of the Voltri Group refolded by chevron-like folds with subvertical axial surfaces. **c** Spaced fracture cleavage in quartzites of the Valosio Unit in the footwall of the Ciglione thrust (Visone River). **d** Deformed serpentinites in the Ciglione thrust zone. Rocks are cut by a centimetre-spaced NW–SE striking crenulation cleavage that often corresponds to brittle shear planes of the Ciglione thrust front. It became a fracture cleavage in some places, where the fractures opened and were filled by carbonates similar to those of the listwaenites involved in the thrust zone (see para 3 in The Ciglione thrust). **e** Val Gorrini thrust. Molare Formation has been displaced by metre-spaced, low-angle reverse faults that are in turn cut by steeply dipping normal faults

The Ciglione thrust

The CGT is a NNW–SSE striking shear zone that can be traced for about 4 km and records all the faulting stages of the GTZ, at least since the early semibrittle deformation stages (Plate 1a).

In the CGT zone the fault-bounded domains mainly consist of folded and sheared metamorphic rocks pervasively displaced by all-scale brittle shear zones parallel to the main strike of the thrust. The metamorphic foliation is refolded mainly by mesoscale chevron-like and open flexural folds. These folds verge ENE and are characterised by NNW–SSE trending axes, and hence the ones parallel to the average strike (NNW–SSE) of the thrust plane (Plate 1b). The fold axial surfaces generally correspond to a centimetre-spaced crenulation cleavage, which was brittlely reactivated as a subparallel, N150-striking fracture cleavage. This fracture cleavage is often associated with cataclastic zones (Plate 1c, d) and is understood here as the main and readily correlatable field evidence of the CGT. The N150 fracture cleavage was in turn reactivated by later strike-slip and extensional faults (see below, The post-Burdigalian transtensive fault system).

In the CGT zone extensive fluid circulation occurred, giving rise to complex carbonate vein systems, which in most cases displaced the metamorphic foliation (Plate 2d). These veins and the N150 spaced cleavage crosscut each other at all scales.

The Val Gorrini thrust

The VGT (d'Atri et al. 1997; Piana et al. 1997) is a purely brittle shear zone that can be traced for at least 6 km and caused the NE-verging superposition of the

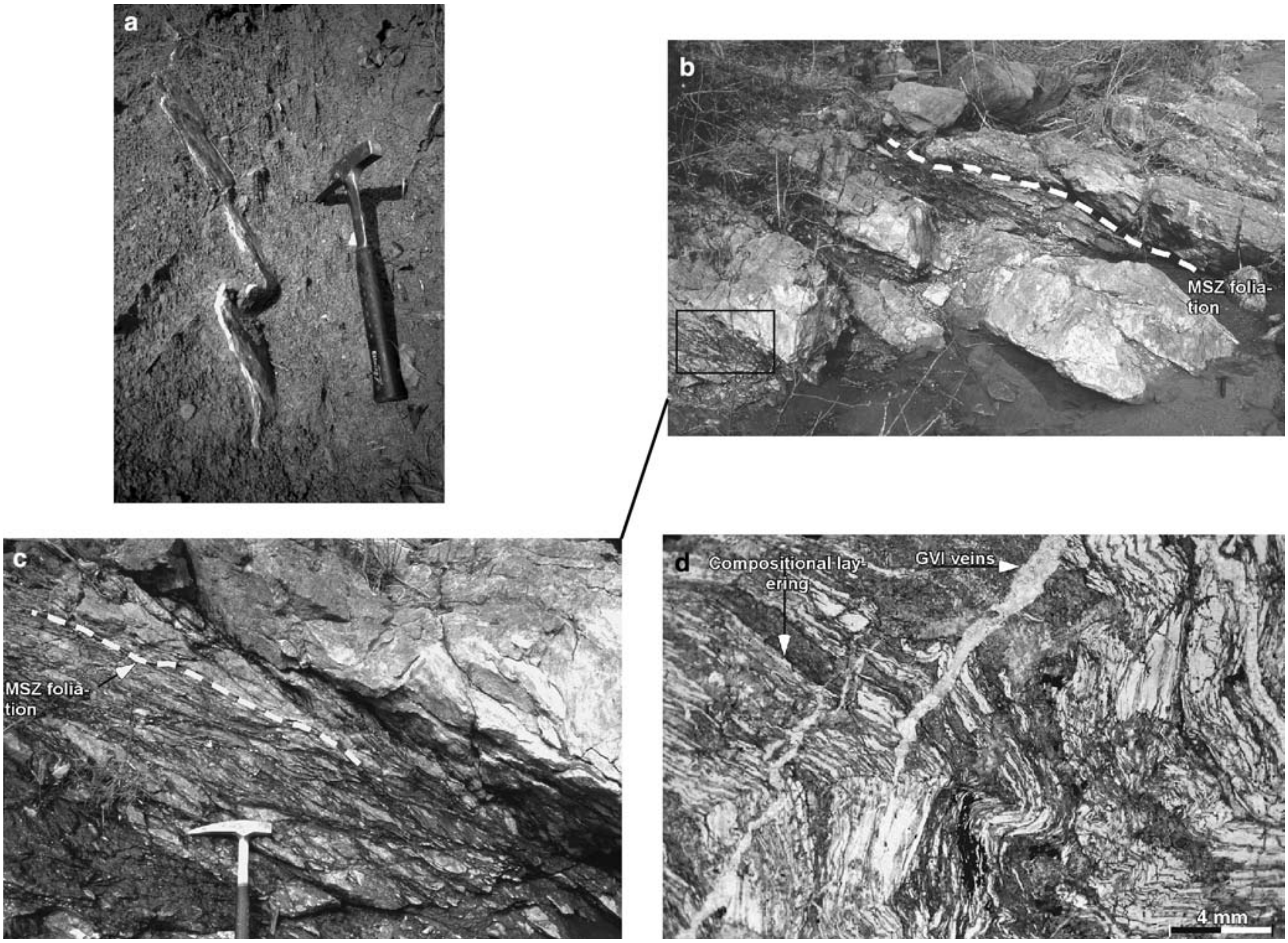


Plate 2 **a** Folded carbonate veins in the Val Gorrini thrust zone. **b** The most striking feature of the MSZ is a composite fabric resulting from the reactivation and cataclasis of an older schistosity. Nevertheless, the orientation of this foliation is quite constant, as roughly distributed about E–W direction. **c** Detailed view of **b**. An older planar fabric is displaced by sets of spaced shear zones. Here the foliation roughly corresponds to "C planes" that drag an older schistosity. **d** Serpentine-carbonate compositional layering folded by microscale chevron folds, in the listwaenites of the Musotto–Sappagliano shear zone (MSZ). The compositional layering is displaced by carbonate veins (GVI in Fig. 6, see text for details)

Voltri Group and Valosio Crystalline Unit onto the Molare and Rocchetta Formations (Figs. 3, 4). The VGT belongs to a regional fault system responsible, at the regional scale, for overthrusting of the Voltri Group and Montenotte Unit onto the Alto Monferrato succession (Pasquare' 1968; Forcella et al. 1973; Forcella 1976; Capponi and Giammarino 1982; Forcella and Rossi 1980). The VGT (Plate 1e) is roughly subparallel to and kinematically consistent with the CGT and can be considered as a major structural field evidence of the regional Early Miocene tectonics that induced the Late Aquitanian uplift of the Alto Monferrato domain. The VGT movement was partitioned by kilometre-scale, roughly E-W-striking faults. Late Burdigalian Visone and Cortemilia Formations seal the VGT-related deformation as they regularly deepen to N–NE (Fig. 3).

Calcite veins have often been found within strongly damaged zones near the main reverse faults of the VGT. In particular, these veins have been observed along the boundary slip planes of many mesoscale shear zones. In some cases, these veins were rotated inside the shear zones, and sometimes they were dragged or folded (Plate 2a).

The Musotto–Sappagliano shear zone (MSZ)

This several hundred metre thick shear zone is exposed along the Visone River (Musotto and Sappagliano sites) in between the CGT and VGT zones. It represents a relic of syn- to late-metamorphic deformation processes. The MSZ includes highly strained serpentinites of the Voltri Group and micaschists of the Valosio Unit. Carbonaceous fluids permeated these rocks and gave origin to peculiar rock types (Plate 2b, c), such as carbonate micaschists and carbonate serpentinites (listwaenites, see below, Carbonate veins on the fault zones).

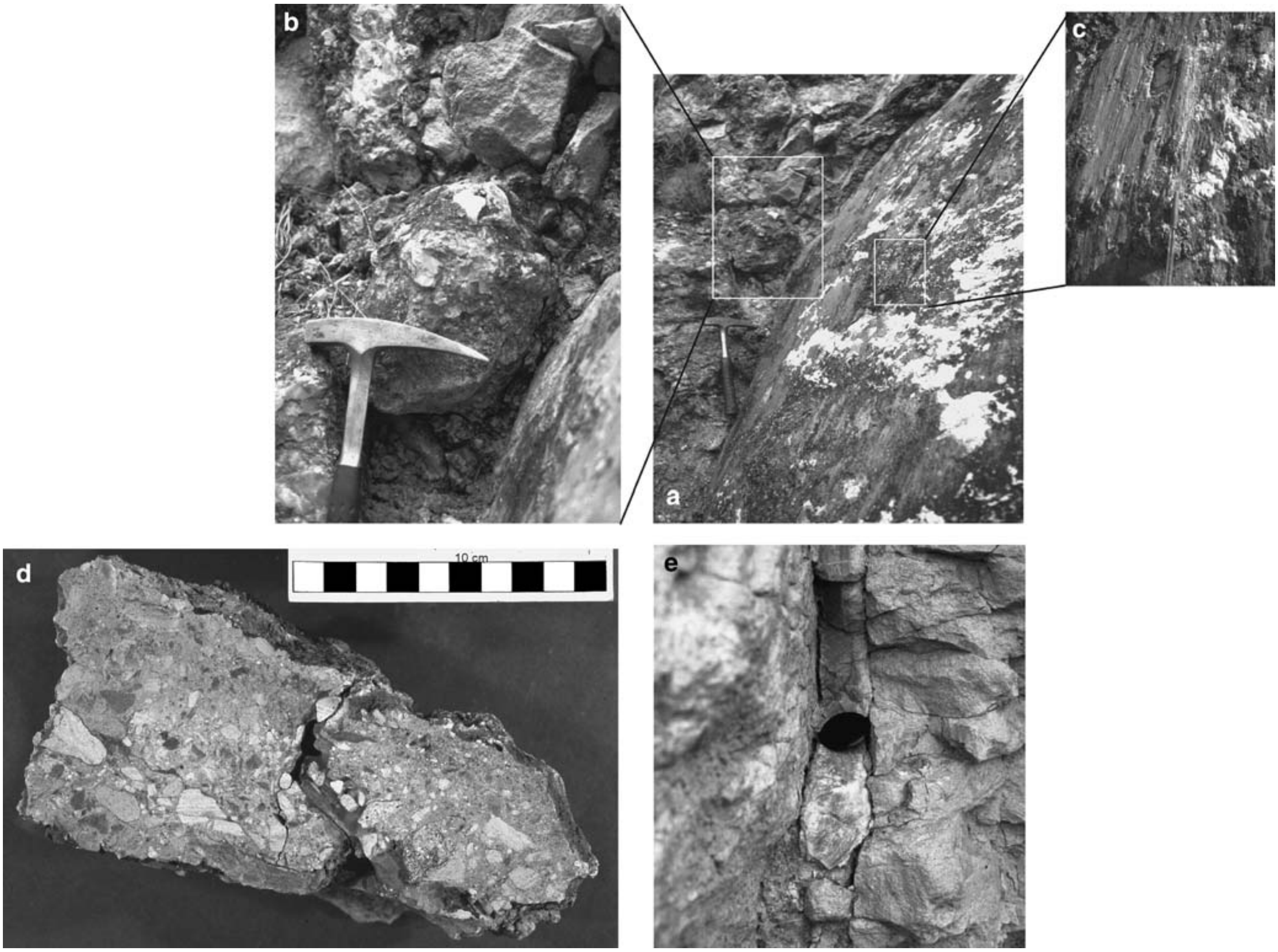


Plate 3 **a** NNW–SSE normal faults in the biocalcarenites of the Visone Formation (Zanoletti quarry, Visone site). Calcite slickenfibres have grown over extensional veins (white sparry calcite) on the fault planes. **b** Chaotic breccias have filled large open fractures developed along the main fault surfaces. See the centimetre-size calcite crystal (GVIII in Fig.7). **c** Abrasion sliccolites and fibrous calcite preserved on the slickensided fault planes. These post-date large white spatic calcite crystals due to early growing of extensional veins (EXV) on the fracture plane. **d** Detail of the chaotic breccia of **b**. **e** Decimetre-thick carbonate extensional veins consisting of white (external) and grey calcite crystals

The most striking structural feature of the MSZ is a pervasive foliation, moderately dipping to N, which is parallel to the contact between micaschists and serpentinite rock slices. This foliation is a composite fabric originated by syn-metamorphic plastic deformations which was intensively reactivated by semibrittle and purely frictional processes. The geometrical features of the foliation and the large occurrence of fluids suggest that the MSZ is a long-lived shear zone.

The MSZ foliation is displaced by the CGT-related N150 spaced cleavage (Plate 1a, c, d) and it can still be recognised only where it has not been overprinted by the CGT- and VGT-related brittle deformation.

Carbonate-rich fluids largely occurred along the MSZ since the older deformation events, as evidenced by the presence of millimetre-thick carbonate-serpentine compositional layering and several interconnected carbonate vein systems (Plate 2d). This layering is the oldest recognisable foliation and represents the main foliation of the MSZ, even though the chronological relations with the regional metamorphic foliation of the Valosio Crystalline Unit cannot be clearly assessed.

Since mesoscale tectonic slices of Valosio and Voltri Units are bounded and subparallel to the main MSZ foliation (Plate 2b, c), and also to the boundary slip planes of the MSZ, it is suggested here that the Valosio and Voltri Units were coupled along the MSZ at least since the carbonatisation events that gave origin to the carbonate-serpentine layering.

The post-Burdigalian transtensive fault system

Post-Burdigalian, interconnected NNW–SSE transtensive faults cut off the GTZ and induced a pervasive jointing of both the sedimentary and the metamorphic

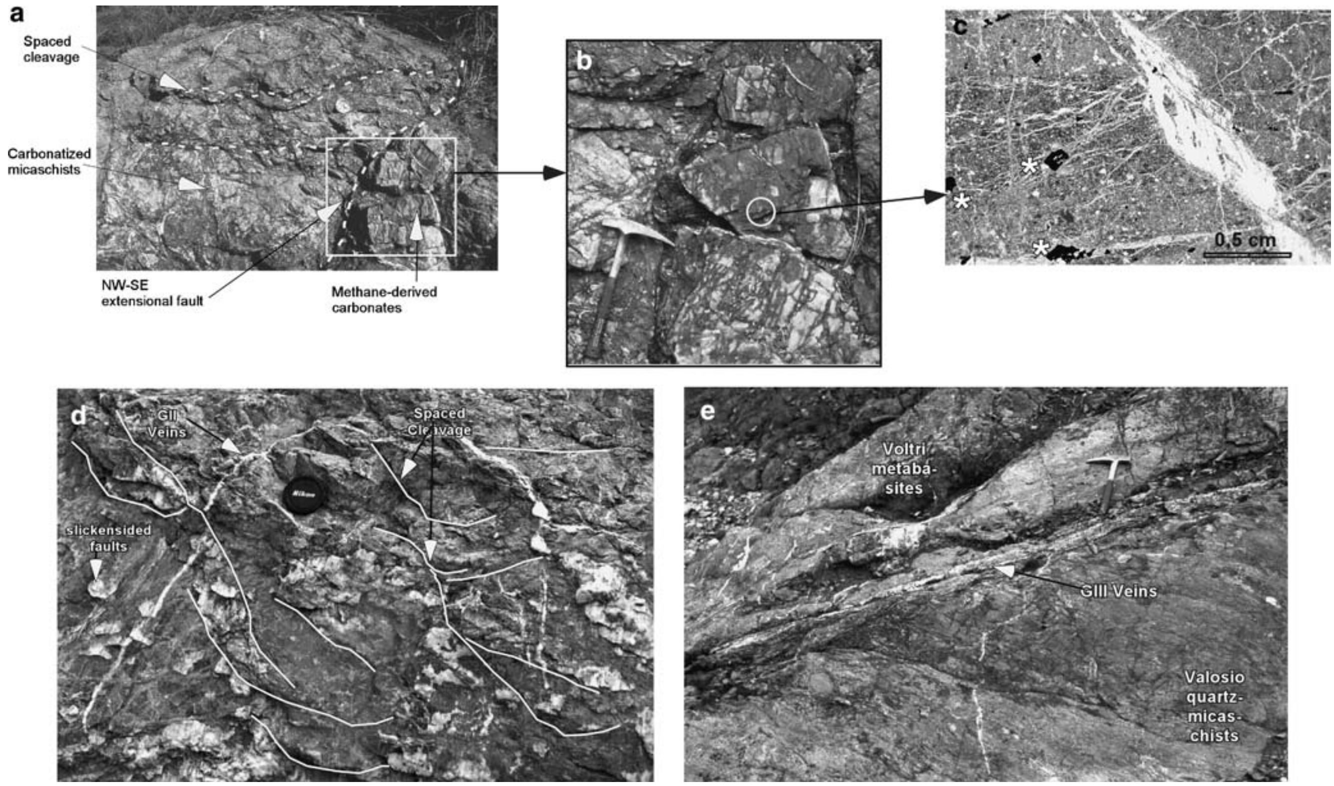


Plate 4 a, **b** Ciglione thrust zone (Case Musotto, Visone river)—anomalously cemented, pyrite-bearing sedimentary rocks (siltites, pelites). These rocks have been interpreted as methane-derived carbonates in the sense of Clari et al. (1988). They are characterised by the presence of thin, interconnected veins and bounded by later mesoscale faults which spare them from the foliated carbonatised micaschist largely involved in the thrust zone. **c** Microfacies of the rock of **a**. The rock is cross-cut by pervasive network of carbonate veins. *Stars* indicate pyrite grains. **d** Ciglione thrust zone near Cascina Musotto (Visone river). Spaced cleavage displacing carbonatised micaschist of the Valosio Unit. This cleavage is cross-cut by carbonate veins (CCV). Fibrous calcite (FBC) lenses are preserved on the slickensided fault planes that cut all the above described structures. **e** Visone river (MSZ) brittle shear zone where metabasites of the Voltri group (hangingwall) and quartz-micaschists of the Valosio Unit are coupled. The micaschist schistosity is dragged by the shear zone. Centimetric calcite veins are well developed along the brittle contacts. The carbonatic infillings of these veins (GIII values) are characterised by different isotopic values suggesting a multistage evolution

units (Figs. 3, 4). The transtensive deformation was partitioned by left-lateral and normal faults striking from N100 to N150. These faults also reactivated, and further steepened, most of the older reverse, low-angle faults of the GTZ. The original lozenge-type geometry of the thrust-related fracture network was thus partially obliterated. Opposite senses of movement recorded on the E–W strike-slip faults suggest that reactivation largely occurred also on this fault system. The NW–SE normal fault system is particularly evident where it truncates the Visone Formation, even though it displaces at least the whole overlying Langhian succession. Faulting was sustained by a large amount of fluids, as evidenced by centimetre-thick fibrous calcite lenses preserved on many slickensided fault planes (Plate 3a, b). Carbonate-rich fluids circulated along these faults also after their main slip events, as evidenced by the post-kinematic growing of large (up to 4–5 cm) calcite crystals within the chaotic breccias (see Carbonate veins in the post-Burdigalian transtensive fault system) that developed along fractures roughly parallel to this fault system (Plate 3a, b, d). Decimetre-thick extensional veins also developed along the fault-related fracture network. (Plate 3e).

Carbonate veins on the fault zones

The kinematic evolution of the study area was characterised by localisation of the deformation in long-lived shear zones (CGT, VGT, MSZ). These shear zones underwent a multistage tectonic evolution, during which carbonaceous fluids were largely concentrated within them.

Analyses were conducted on the complex vein systems that originated during the fluid-sustained deformational events, in order to discriminate the geochemical composition of fluids during each tectonic stage and to trace the relations between the provenance of the fluids and the local tectonic setting.

Carbonate veins were sampled in both the metamorphic and the sedimentary rocks involved in the GTZ, as well as along the post-Burdigalian transtensive fault system.

Table 1 $\delta^{13}C$ and $\delta^{18}O$ values for different vein types, fibrous calcites and related host rock sampled in the Grognardo thrust zone (Musotto sampling site) are reported

Sampling locality	Vein type/rock group	$\delta^{13}C$ versus PDB	$\delta^{18}O$ versus PDB
Musotto	Fibrous calcite (FBC)	−24.47	−6.60
Musotto	Fibrous calcite (FBC)	−32.37	−12.89
Musotto	Fibrous calcite (FBC)	−12.89	−13.93
Musotto	Cross-cutting veins (CCV)	−5.78	−9.71
Musotto	Cross-cutting veins (CCV)	−16.00	−9.12
Musotto	Cross-cutting veins (CCV)	−2.86	−12.25
Musotto	Cross-cutting veins (CCV)	−2.91	−13.18
Musotto	Cross-cutting veins (CCV)	−21.43	−13.45
Musotto	Cross-cutting veins (CCV)	−4.64	−14.46
Musotto	Cross-cutting veins (CCV)	−14.55	−9.87
Musotto	Cross-cutting veins (CCV)	−18.51	−8.11
Musotto	Cross-cutting veins (CCV)	−17.91	−9.04
Musotto	Cross-cutting veins (CCV)	−17.44	−7.97
Musotto	Cross-cutting veins (CCV)	2.02	−17.29
Musotto	Cross-cutting veins (CCV)	−14.75	−10.99
Musotto	Cross-cutting veins (CCV)	−14.84	−9.46
Musotto	Cross-cutting veins (CCV)	−1.61	−8.06
Musotto	Cross-cutting veins (CCV)	−4.89	−14.47
Musotto	Cross-cutting veins (CCV)	−6.00	−12.13
Musotto	Cross-cutting veins (CCV)	−20.79	−13.99
Musotto	Cross-cutting veins (CCV)	−15.44	−8.05
Musotto	Cross-cutting veins (CCV)	−16.01	−9.57
Musotto	Cross-cutting veins (CCV)	1.18	−14.98
Musotto	Cross-cutting veins (CCV)	0.89	−8.02
Musotto	Cross-cutting veins (CCV)	−15.00	−7.96
Musotto	Cross-cutting veins (CCV)	1.51	−12.25
Musotto	Cross-cutting veins (CCV)	3.61	−12.39
Musotto	Valosio carbonatised micaschists	−3.23	−11.10
Musotto	Valosio carbonatised micaschists	−5.02	−9.44
Musotto	Valosio carbonatised micaschists	−4.37	−9.62
Musotto	Valosio carbonatised micaschists	−7.26	−9.84
Musotto	Valosio carbonatised micaschists	−6.59	−15.19
Musotto	Valosio carbonatised micaschists	−4.49	−19.59
Musotto	Voltri carbonatised serpentinites	1.19	−13.83
Musotto	Voltri carbonatised serpentinites	−3.51	−13.49
Musotto	GTZ recemented sedimentary rocks	−3.76	−18.75

Isotopic data are referred to the PDB standard (see text for analytical precision)

The metamorphic rock samples came from a sector of the GTZ (C.na Musotto, Fig. 3) where carbonatised quartzite and micaschists of the Valosio Crystalline Unit, presently transformed into foliated cataclasites by frictional processes, are interlayered with carbonatised serpentinites (listwaenites sensu Aydal 1990, with references therein) of the Voltri Group (Plates 1d, 2b).

Sampling was also carried out along the post-Burdigalian transtensive fault system, which displaces all the lithostratigraphic units of the study area. Two different rock units were sampled, both of which contained several vein systems: the biocalcarenites and glaucony-rich arenites of the Visone Formation and a plurimetric, wide chaotic breccia within the same formation.

Carbonate veins in the Grognardo thrust zone

Different types of carbonate veins are recognisable here:

- Cross-cutting veins (CCV) are steeply dipping veins whose distribution and geometry seem to be related both to thrusting and to transtensional faulting, and mainly strike NW–SE to N–S.
- Fibrous calcite slickensides (FBC) preserved on the fault planes (Plate 4d).

Sedimentary rocks (recemented, pyrite-bearing siltites and pelites) are also involved in the thrust zone, where they presently crop out as rock slices bounded by mesoscale faults (Plate 4a). These rocks were recemented by intergranular carbonate cement anomalously depleted in ^{13}C (about −30‰) and they are diffusely cross-cut by veins characterised by polyphasic infillings (Plate 4c). They have been here interpreted as “methane-derived carbonates”, since they are similar to the ones described by Clari et al. (1988, 1994) in the Miocene succession of the Monferrato domain and to the ones found in the present-day settings near hydrocarbon-rich fluid emissions (Kulm and Suess 1990; Paull et al. 1992; Ritger et al. 1987). Consequently, hydrocarbon-bearing rocks are likely to be present in the underground of the study region, as also argued by Marini et al. (2000), who, on the basis of extensive geochemical analyses, interpreted the peculiar characteristics of the present-day hot-water springs (76°C) in Acqui Terme as being due to the interaction between water and oil.

Table 2 The $\delta^{13}C$ and $\delta^{18}O$ values for vein fillings, fibrous calcites and related host rock belonging to the post-Burdigalian transtensive fault system in the Visone Formation (Visone Zanoletti quarry)

Sampling site	Vein type/rock group	$\delta^{13}C$ versus PDB	$\delta^{18}O$ versus PDB
Visone quarry	Fibrous calcite (FBC)	−0.84	−13.21
Visone quarry	Extensional veins (EXV)	−3.33	−12.43
Visone quarry	Extensional veins (EXV)	−1.27	−13.52
Visone quarry	Extensional veins (EXV)	−0.17	−11.22
Visone quarry	Extensional veins (EXV)	−0.87	−11.87
Visone quarry	Extensional veins (EXV)	−0.31	−12.01
Visone quarry	Extensional veins (EXV)	−0.56	−11.74
Visone quarry	Extensional veins (EXV)	−0.02	−11.49
Visone quarry	Extensional veins (EXV)	−4.24	−11.77
Visone quarry	Extensional veins (EXV)	−0.06	−12.33
Visone quarry	Extensional veins (EXV)	−1.2	−10.67
Visone quarry	Extensional veins (EXV)	1.43	−12.23
Visone quarry	Extensional veins (EXV)	0.07	−11.06
Visone quarry	Extensional veins (EXV)	0.04	−10.76
Visone quarry	Extensional veins (EXV)	−0.01	−10.52
Visone quarry	Extensional veins (EXV)	−1.82	−12.56
Visone quarry	Extensional veins (EXV)	−17.45	−15.37
Visone quarry	Extensional veins (EXV)	−20.70	−17.31
Visone quarry	Extensional veins (EXV)	−20.54	−18.02
Visone quarry	Extensional veins (EXV)	−20.03	−17.16
Visone quarry	Extensional veins (EXV)	−20.16	−16.65
Visone quarry	Extensional veins (EXV)	−21.72	−16.95
Visone quarry	Extensional veins (EXV)	−20.54	−18.02
Visone quarry	Visone Fm. biocalcarenites	−0.71	−7.53
Visone quarry	Visone Fm. biocalcarenites	1.26	−5.89
Visone quarry	Visone Fm. biocalcarenites	0.10	−7.00
Visone quarry	Visone Fm. biocalcarenites	−0.33	−7.69
Visone quarry	Visone Fm. biocalcarenites	−0.80	−7.55
Visone quarry	Visone Fm. chaotic breccia	−8.74	−10.95
Visone quarry	Visone Fm. chaotic breccia	−6.22	−11.70
Visone quarry	Visone Fm. chaotic breccia	−3.01	−10.90
Visone quarry	Visone Fm. chaotic breccia	3.75	−9.89
Visone quarry	Visone Fm. chaotic breccia	−0.34	−12.31
Visone quarry	Visone Fm. chaotic breccia	−3.31	−8.28
Visone quarry	Visone Fm. chaotic breccia	−1.44	−9.98

Isotopic data are reported versus the PDB standard (see text for analytical precision)

Carbonate veins in the post-Burdigalian transtensive fault system

Sampling was carried out mainly in the biocalcarenites of the Visone Formation in the Zanoletti quarry (Visone site), which is clearly displaced by N100-150-striking normal and left-lateral faults (Bagni-Visone fault, Fig. 3). Here, centimetre-thick to decimetre-thick calcite veins developed along these faults and associated fractures.

Different types of veins are recognisable:

– Decimetre-thick carbonate extensional veins consisting of white-to-grey calcite crystals (EXV) (Plate 3e)
– Fibrous calcite (FBC) preserved on the slickensided fault planes (Plates 3c, 4d)
– Yellow-to-brown calcite crystals and veins (also indicated with EXV acronym)

The vein thickness ranges from 5 to 50 cm. The veins were sampled in a metre-wide chaotic brecciated rock body without any recognisable tectonic displacement at its edges. The samples are made up of angular clasts floating in a carbonate-rich matrix. The clasts display the same composition as the surrounding rocks; the whole rock is strongly cemented by amber-coloured and euhedral calcite, which fills the intergranular pores and the voids (Plate 3d).

Isotope analyses

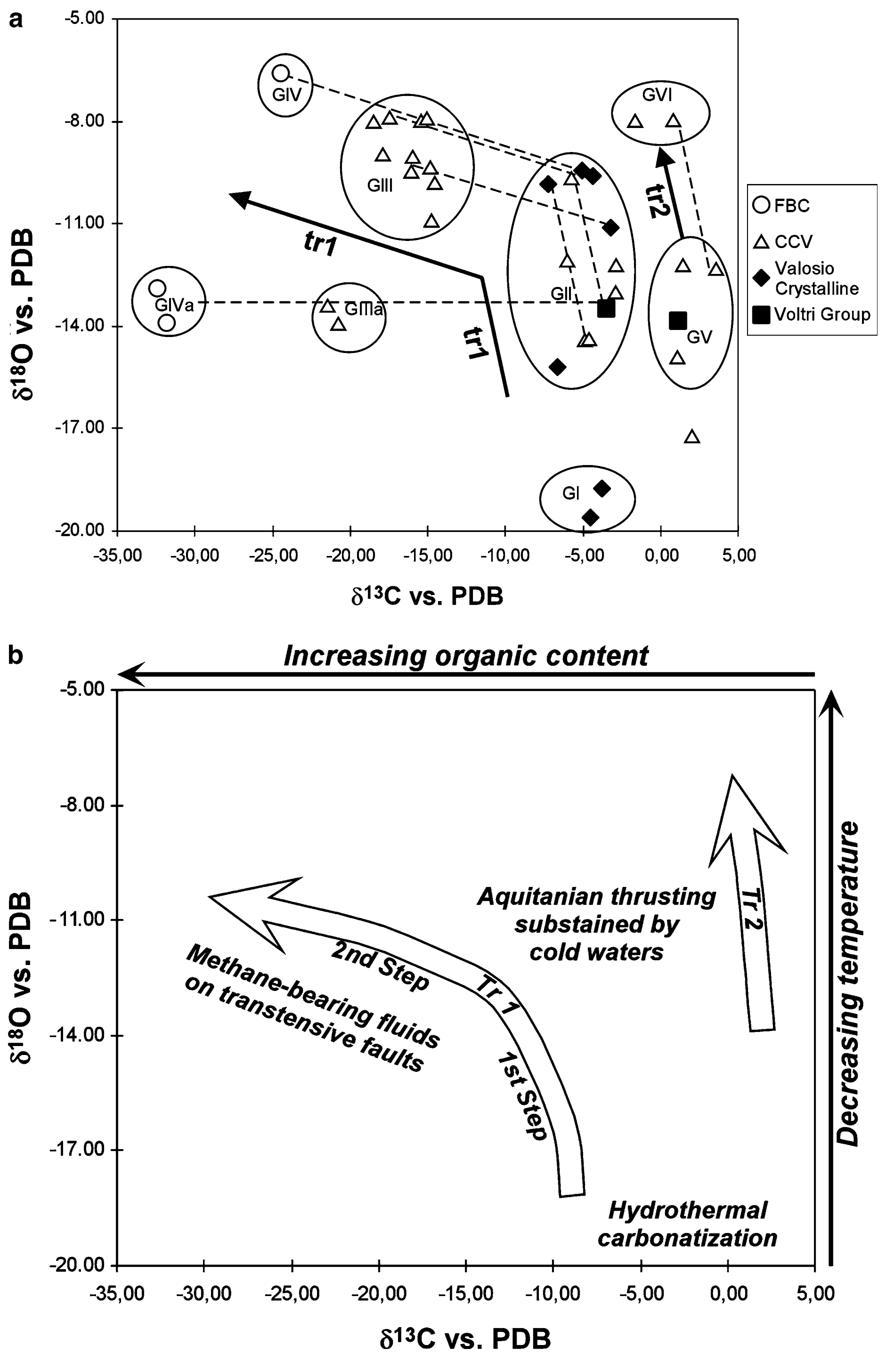
Methodology

The carbonate fraction of vein fillings was analysed after carbonate powder was reacted in vacuum conditions with 99% orthophosphoric acid at 25°C (McCrea 1950). The $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios of the CO_2 obtained were analysed by a MAT 250 mass spectrometer (Laboratory of Hydrology and Applied Geochemistry, University of Turin). The isotopic ratios are expressed as $\delta^{13}C$ and $\delta^{18}O$ per mil versus the PDB standard; the analytical error is ± 0.5 and $\pm 0.1‰$ for $\delta^{13}C$ and $\delta^{18}O$, respectively.

Results

The results are summarised in Tables 1 and 2 and in the corresponding $\delta^{13}C/\delta^{18}O$ diagrams (Figs. 6a, b, 7a, b).

Fig. 6 **a** δ^{13}C versus δ^{18}O diagram showing the geochemical trends in veins and related host rocks in the Grognardo thrust zone. *Dotted lines* connect veins/fibrous calcites and the relative host rock, *heavy lines* underline the main geochemical trends. *Circles* show compositional fields for both vein samples and host rocks. **b** Relationships between fluid circulation and main tectonic events are depicted here



The Grognardo thrust zone

The δ^{13}C values of the calcite fracture fillings associated with the GTZ range from −24.47 to −4.64‰, and the δ^{18}O values range from −14.46 to −6.60‰.

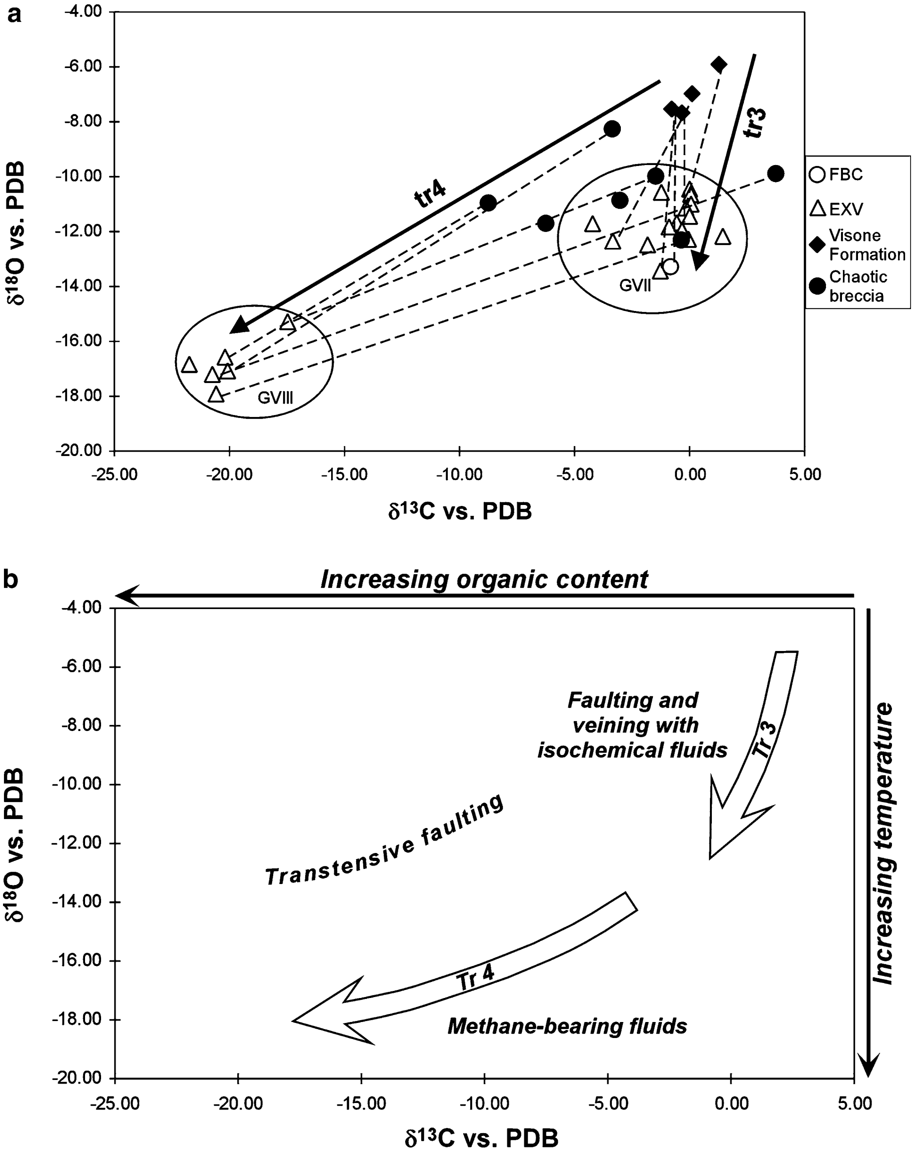
The isotopic characterisation of the veins associated with the CGT (CCV in Fig. 6) is marked by a sharp depletion in ^{13}C and by an appreciable enrichment in ^{18}O of the fracture fillings as compared to the country rock units.

The compositional range of the host rocks and veins can be subdivided into six separate groups (GI–GVI), which represent different fluid compositions and precipitation conditions (Fig. 6).

The post-Burdigalian faults

The composition of the veins associated with the post-Burdigalian faults is rather sharply divided into two compositional ranges (GVII and GVIII), which present δ^{13}C values ranging from −4 to +2‰ and from −20 to −17‰, respectively, and δ^{18}O values ranging from −14 to −10‰ and from −18 to −15‰, respectively. The δ^{13}C

Fig. 7 **a** $\delta^{13}C$ versus $\delta^{18}O$ diagram showing the geochemical trends in veins and related host rocks in the post-Burdigalian transtensive fault system. *Dotted lines* connect veins and calcite fibres to the relative host rock, *heavy lines* underline the main geochemical trends. *Circles* show compositional fields for the two main vein groups. **b** Relationships between fluid circulation and main tectonic events are depicted here



and $\delta^{18}O$ values of the host rocks range from −19.44 to +3.75‰ and from −12.31 to −5.89‰, respectively (Fig. 7).

Discussion

This section compares the isotopic compositions of different vein fillings and enclosing rocks that recorded distinct faulting stages during the deformational path of GTZ toward more shallow crustal levels. Furthermore, the discussion focuses on the relations between GTZ rocks and veins and isotopic composition of veins and fault rocks developed along post-Burdigalian transtensive faults. Lines have been drawn to connect different compositional ranges that record distinct stages of tectonic history, each one characterised by peculiar T conditions and/or fluid composition (tr1 and tr2 in Fig. 6 and tr3 and tr4 in Fig. 7).

Fluid–rock interaction in the Grognardo thrust zones

In the following carbonate veins and enclosing rocks will be described referring to Fig. 6.

Trend tr1 is characterised by two compositional steps. The first step connects the GI and GII ranges and reveals a sharp increase in $\delta^{18}O$ values, with a moderate decrease in $\delta^{13}C$ values in both host rocks and veins. $\delta^{18}O$ values of group GI could be interpreted as due to the carbonatation of the Valosio rock slices involved in the GTZ that occurred in hydrothermal conditions, as confirmed by the presence of listwaenites within the GTZ. In fact, the GI compositional range yields the end member of tr1 that could represent the oldest carbonatation event, which transformed the micaschists of the Valosio Crystalline Unit. Conversely, $\delta^{18}O$ values of group GII could be interpreted as related to the thrusting event that occurred in the GTZ at shallower crustal level (i.e. at lower temperatures) than those that should have characterised the GI carbonatation. The regional tectonic context (see before) allows to suggest that the fluid involved in the thrust zone was meteoric groundwater. In this case, with an original $\delta^{18}O$ of about $-10‰$, the precipitation temperature of the carbonate, calculated by means of the equation proposed by O'Neill et al. (1969), would be approximately 90°C. Otherwise, if the fluid was a marine-type water, the temperature of precipitation would be approximately 190°C.

The values of $\delta^{13}C$ of GI and GII groups are similar; this indicates that host rocks have supplied the carbonate that is now present in veins, suggesting local origin of syn-tectonic fluids.

The second step reveals a strong depletion in $\delta^{13}C$ of vein samples and a moderate increase in $\delta^{18}O$. It connects the compositional range of Group II with the veins (CCV) of Group III and the fault calcite fibres (FBC) of Group IV, which are both associated with plurimetric transtensive faults that cut off the metamorphic foliation (Plate 4d). This step testifies slight variations in temperatures with respect to those of GII samples, whilst the depletion in $\delta^{13}C$ of vein filling with respect to the enclosing rock is important. This suggests that the precipitation still occurred at shallow crustal levels, since the inferred re-equilibrium temperatures (about 140°C) are slightly lower than those of GII group. On the other hand, $\delta^{13}C$ values document the presence of fluid characterised by high content of organic C. Negative $\delta^{13}C$ values in carbonates are generally explained by a ^{13}C depletion of oxidised phases that are involved in the precipitation. The mechanism that could be responsible for such depletion is the fractionation between light hydrocarbons and CO_2, HCO_3^-, $CO_3^=$, resulting in a ^{13}C depletion of these oxidised phases. The finding, within the CGT zone, of lozenge-shaped rock slices that, for their petrographical and isotopic characteristics have been here interpreted as methane-derived carbonates, also supports the hypothesis of the presence of methane-bearing fluids along the transtensive fault network (Plate 4a–c). Methane is the lightest carbon compound in nature: thermogenic methane shows $\delta^{13}C$ values ranging from -30 to $-60‰$ PDB. Biogenic methane is even more depleted and can reach values lighter than $-80‰$ (Fritz and Fontes 1989).

A similar trend characterised by comparable $\delta^{13}C$ values and more depleted $\delta^{18}O$ values connects the compositional range of GII group with the veins of GIIIa group and the fault calcite fibres of GIVa group. The composition of the original methane-bearing fluids, as regards C composition, could be close to the FBC value of GIVa ($-32‰$). It is suggested that the calcite fibres on the faults could originate from dissolution of the pre-existing carbonate present in the veins, since the calcite fibres grow directly on the veins (Plate 4d).

Trend tr2 connects the compositional GV and GVI groups. GV group is characterised by positive values of $\delta^{13}C$, whilst $\delta^{18}O$ spans a rather wide range. GVI group is instead characterised by more ^{18}O-enriched compositions. Trend tr2 shows an isotopic evolution similar to that of the first step of tr1. It describes a vein-formation process that occurred under conditions of diminishing temperature and starts from the isotopic composition of the carbonate that gave rise to listwaenites of the Voltri Group.

On the basis of the isotopic evolution, it would seem that carbonate precipitation in these veins was controlled by the composition of the ultrabasites, originally enriched in ^{13}C during the metasomatic and late-metamorphic stages, as suggested by the presence of the serpentine-carbonate layering (Plate 2d). The depletion in $\delta^{18}O$ of the GVI vein samples with respect to those of GV is probably due to calcite re-precipitation in lower temperature regimes, consistent with the brittle reactivation that the rocks of the Musotto–Sappagliano shear zone underwent when involved in the post-metamorphic GTZ.

Fluid–rock interaction along the post-Burdigalian transtensive fault system

The isotopic compositions ($\delta^{18}O$ versus $\delta^{13}C$) of the millimetre- to centimetre-thick veins associated with the NW–SE normal and strike-slip faults that displace the Visone Formation are divided into Groups VII and VIII (Fig. 7). Group VII refers to extensional veins (EXV) and corresponding enclosing rocks of the Visone Formation, whilst Group VIII is represented by yellow-brown centimetre-size calcite crystals enclosed in a plurimetric chaotic breccia subparallel to, and bounded by, the main fault system.

The fluid–rock interaction is represented by two main trends of isotopic evolution:

- The first trend (tr3) is characterised by a depletion in ^{18}O of the vein carbonates with respect to the enclosing biocalcarenites, while the ^{13}C content remains practically unchanged. This trend suggests a strong fluid–rock interaction with little differentiation in $\delta^{13}C$ values between the biocalcarenites and veins. The isotopic composition of the veins indicates that the carbonate infillings derive from the enclosing rocks. Furthermore, it must be stressed that carbonate isotopic compositions of the sampled enclosing rocks do not represent the original carbonate composition of the Visone biocalcarenites, in so far as the samples display $\delta^{18}O$ values that are too low as compared to a normal marine carbonate. This suggests that the sampled enclosing rocks could have experienced a previous (pre-faulting) chemical re-equilibration by the action of permeating fluids under increasing temperature. Depletion in ^{18}O of vein carbonates could be either related to rather a high T during vein formation or to the presence of fresh waters in the system.
- The second trend (tr4) connects the composition of the chaotic, brecciated enclosing rocks to the composition of the veins found within the breccia itself. This trend indicates a strong depletion in heavy

isotopes, in particular in ^{13}C, of the vein carbonates with respect to the enclosing rocks. The low values of $\delta^{13}C$ of the veins of Group VIII suggest the presence of hydrocarbon-rich fluids, which can be explained by the release of reduced carbon species from levels rich in organic matter. It would appear that the temperature of formation of the veins was sensibly higher than the temperature that governed the precipitation of the veins of Group VII, even in the case where a freshwater component was involved in the process. These veins formed in the presence of higher fluid/rock ratios, as is also suggested by the large thickness of the veins and the large size of their calcite crystals (Plate 3d).

Concluding remarks

In the Ligurian Alps, neo-alpine tectonics led to the overthrusting of previously coupled metaophiolites (Voltri Group) and slices of polymetamorphic continental crust (Valosio Crystalline Unit) onto Oligocene–Miocene sediments of the Alto Monferrato domain (TPB) along a kilometre-wide shear zone (GTZ), exposed south of Acqui Terme. In the GTZ, late-metamorphic shear zones are also preserved and cut off by Aquitanian NW–SE striking thrust that formed by E–NE vergent contractional tectonic activity (paleo Apenninic phase sensu Schumacher and Laubscher 1996); the GTZ was then displaced by subparallel transtensive faults developed in response to a regional scale extension that led to the formation of a localised basin infilled by turbidites.

The GTZ thus suffered a multistage tectonic evolution characterised by plastic, semibrittle and brittle deformations. Syn-tectonic fluids largely sustained the deformational stages and deeply carbonatised the enclosing rocks, although fluid sources changed over time in response to changes in the stress field and in the fracture-system geometry.

These peculiar geological conditions allowed to usefully integrate field work and geochemical analyses. Stable isotope analyses ($\delta^{13}C$ and $\delta^{18}O$ of carbonate veins and host rock) allowed to characterise the variation of fluid compositions that occurred during the three main steps of the post-metamorphic history recognised by field work.

These steps are:

(a) Late-metamorphic, hydrothermal (150°C?) metasomatic carbonatisation of the rocks that occurred by means of carbonate-rich groundwater pumped into the thrust zone under a semibrittle deformational regime. This caused the reactivation of the fault contacts (i.e. Musotto–Sappagliano shear zone) related to Voltri and Valosio Unit coupling and resulted in the formation of carbonated quartz-micaschist in the Valosio Unit and carbonated serpentines (listwaenites) in the Voltri Group, as well as in the formation of a vein system proper in some places.

(b) Brittle thrusting of the previously coupled Voltri and Valosio Units onto the Alto Monferrato succession, which occurred starting from the Late Oligocene up to the Late Aquitanian (Piana et al. 1997) by means of two minor thrusts, referred to here as the Ciglione thrust (CGT) and the Val Gorrini thrust (VGT). Thrusting was probably sustained by meteoric waters that entered the GTZ through subaerially exposed areas of the Ligurian Alps and easily circulated within the Voltri and Valosio cataclastic rocks due to their high fracture permeability. Origin of these fluids is inferred to be local, as the composition of C in veins is very close to that of the carbonate that previously recemented the enclosing metamorphic rocks during the hydrothermal carbonatation. The large occurrence of carbonate veins, as well as the dispersion of their orientation and the complex cross-cutting relations with the tectonic foliations *l.s.*, suggests that the fluid pressure was relatively high as compared to the confining pressure and/or the tectonic differential stress. The relatively low temperature of the thrust-related fluids (about 90°C, as indicated by the $\delta^{18}O$ values, Fig. 6, Table 1) could be related to the shallow crustal level where the emplacement occurred. This shallow position could also explain the relatively low horizontal displacement (some kilometres) of these structures. On the other hand, it is known that thrust faults channelling great amounts of fluids (like the ones here described) are usually characterised by relatively low displacements (Sibson 2001).

(c) Transtensive faulting along plurikilometres faults that occurred since Late Burdigalian in response to Langhian regional subsidence of the western part of the Alto Monferrato and Langhe Basin and to subsequent (late Serravallian?) strike-slip motion along the same faults.

Larger amounts of fluids circulated along the transtensive post-Burdigalian faults than the ones that circulated on the GTZ thrust-related fractures. The fluids, which would appear to have been pumped into decimetre-centimetre steeply dipping fault zones, crossed both the marly sedimentary succession and the coupled cataclastic metamorphic rocks of the GTZ. The different rock permeabilities that can be inferred as $k < 10^{-4}$ for the metamorphic rocks (i.e. serpentinites and metabasites of the Voltri Group) and $k < 10^{-7}$ for the sedimentary rocks (i.e. Rocchetta marls) and thermal conductivity of these two distinct structural contexts could explain the different fluid-precipitation temperatures suggested by the $\delta^{18}O$ values (Figs. 6, 7). These values indicate that precipitation occurred at a lower temperature in the cataclastic metamorphic rocks than in the tectonites of the marly sedimentary succession. In the latter, the temperatures of the syn-tectonic fluids were higher, probably because the faults were extended at greater depth in the GTZ footwall. This interpretation is also supported by paleo-circulation of methane-bearing fluids along these faults, as revealed by δ^{13}C isotopic data of fault rocks and veins.

In conclusion, this paper provides an example of an integrated study grounded on field work and stable isotope analyses in a structurally complex area, where different tectonic events, each one characterised by syntectonic fluids of different composition, occurred during the exhumation of Ligurian Alps.

Hydrothermal carbon-rich fluids sustained the late-metamorphic deformation stages suffered by Ligurian Alps metaphiolites (Voltri Group), whilst cold meteoric waters circulated along the brittle thrusts that caused the superposition of Voltri Group onto Oligocene sediments of TPB succession. A dramatic change in syn-tectonic fluid composition occurred later, when methane-rich fluids were channelled along post-Burdigalian transtensive regional faults that displaced both the above-described metamorphic and sedimentary units.

Acknowledgements The authors thank G. Bodrato and M. Roz Gastaldi for their support during fieldwork and laboratory analyses. We also wish to thank Paola Cadoppi, Anna d'Atri, Francesco Dela Pierre, Luigi Marini, Giorgio Martinotti, Riccardo Polino and Livio Vezzani for their critical suggestions.

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