Fault weakening due to CO$_2$ degassing in the Northern Apennines: short- and long-term processes

C. COLLETTINI$^1$, C. CARDELLINI$^1$; G. CHIODINI$^2$, N. DE PAOLA$^1$, R.E. HOLDSWORTH$^3$ & S.A.F. SMITH$^3$

$^1$Dipartimento di Scienze della Terra, Università di Perugia, Piazza dell’Università 1, 06100, Perugia, Italia.
$^3$Reactivation Research Group, Department of Earth Sciences, University of Durham, Durham, DH1 3LE, UK

Corresponding author: Cristiano Collettini (e-mail: colle@unipg.it)

The influx of fluids into fault zones can trigger two main types of weakening processes that operate over different timescales and facilitate fault movement and earthquake nucleation.

Short-term and long-term weakening mechanisms along faults require a continuous fluid supply near the base of the brittle crust, a condition satisfied in the extended/extending area of the Northern Apennines of Italy. Here carbon mass balance calculations, coupling aquifer geochemistry to isotopic and hydrological data, define the presence of a large flux ($\sim$12,160 t d$^{-1}$) of deep-seated CO$_2$ centred in the extended sector of the area. In the currently active extending area, CO$_2$ fluid overpressures at $\sim$85% of the lithostatic load have been documented in two deep (4-5 km) boreholes.

In the long-term, field studies on an exhumed regional low-angle normal fault show that during the entire fault history, fluids reacted with fine-grained cataclasites in the fault core to produce aggregates of weak, phyllosilicate-rich fault rocks that deform by fluid assisted frictional-viscous creep at sub-Byerlee friction values ($\mu < 0.3$). In the short-term, fluids can be stored in structural traps, such as beneath mature faults, and stratigraphical traps such as Triassic evaporites. Both examples preserve evidence for multiple episodes of hydrofracturing induced by short-term cycles of fluid pressure build-up and release.

Geochemical data on the regional-scale CO$_2$ degassing process can therefore be related to field observations on fluid rock interactions to provide new insights into the deformation processes responsible for active seismicity in the Northern Apennines.
The involvement of fluids in faulting has been recognized for over 250 years, particularly in the mining industry (e.g. Von Oppel 1749). Direct evidence of large fluxes of fluids into fault zones comes from oil exploration (e.g. Gaarenstroom et al. 1993) and from widespread recognition of fault-hosted vein complexes and hydrothermal alteration (e.g. Hulin 1925; Knopf 1929; Cox et al. 1986; Boullier & Robert 1992).

Fluid flow into fault zones can trigger two main types of weakening mechanism that operate over different timescales and facilitate fault movement by reducing the shear stress or frictional resistance to slip.

In the short term, i.e. during the seismic cycle, which for large earthquakes means timescales of 100- to 10,000-years, crustal fluids can be trapped by low permeability mature fault zone seals or stratigraphic barriers. The development of fluid overpressures at the base of the fault zone during the interseismic period can help to facilitate fault slip. Once the seal is ruptured by an earthquake, permeability increases and fluids are redistributed from high to low pressure areas. In this model, a fault is considered to act as a valve (Sibson 1981; 1992). The widespread development of crack-seal textures in mineral veins (Ramsay 1980) seems to be consistent with such behaviour, as they suggest repeated cyclic build-ups in fluid pressure, hydrofracture development and fluid pressure release (Secor 1965; Fyfe 1978). Similar trends in fluid pressure have been inferred using fluid inclusion studies in the hydrothermally altered footwall rocks of active normal faults (Parry & Bruhn 1990).

Over longer timescales, i.e. during the entire fault history (thousands to millions of years), fluids can react with fine-grained cataclasites in the fault core to produce interconnected and aligned aggregates of phyllosilicate-rich fault rock (e.g.
Evans & Chester 1995; Wintsch et al. 1995; Wibberley 1999; Holdsworth 2004; Jefferies et al. 2006a). The phyllosilicate-rich fault rocks are weak (a) due to reaction softening during low-grade alteration and (b) due to the onset of pressure solution. Laboratory experiments, underpinned by theoretical and field observations have shown that pressure solution-facilitated creep is important in reducing long-term fault strength and in promoting aseismic slip along faults (Rutter & Mainprice 1979; Bos & Spiers; 2002; Collettini & Holdsworth 2004). The frequently observed localization of later fault displacements along the foliated phyllosilicate-rich layers suggests that these processes lead to important fault weakening (Imber et al. 2001; Jefferies et al. 2006b).

All these weakening mechanisms require a continuous fluid supply near to the base of the brittle crust. In this paper, we present new arguments for regional scale fluid involvement during ongoing extension of the Northern Apennine region in Italy based on the integration of new and recently published data. We then use two field examples to illustrate fluid-assisted weakening processes along exhumed normal faults, e.g. the low-angle Zuccale detachment exposed on the isle of Elba, and within the Triassic evaporites in Tuscany, mainland Italy. Finally, we link these observations made at different scales to assess long-term and short-term weakening processes in the extending area of the Northern Apennines.

**Regional Setting**

The Northern Apennines consist of a NE-verging compressional belt formed as a result of the collision between the European continental margin (Sardinia-Corsica block) and the Adriatic microplate (e.g. Alvarez 1972; Reutter et al. 1980). The NE migration of active shortening towards the foreland is followed closely by a phase of
asymmetric extension in the hinterland, resulting in two spatially and kinematically distinct structural domains in the present day Apennines (e.g. Pauselli et al. 2006). Extension within the brittle upper crust is accommodated by a set of major east-dipping low-angle normal faults (LANF; Banchi et al. 1998; Decandia et al. 1998) and associated high angle structures (Fig. 1). Extension, now active in the inner zone of the Umbria-Marche Apennines, generates moderate to large earthquakes, 5.0<M<7.0 (Boschi et al. 1999), with a regional extension rate of 2.5 mm/yr measured using geodetic techniques (Hunstad et al. 2003). In Tuscany, older parts of the extensional system are significantly exhumed due to the combined effects of extension and associated regional uplift. As a result, it is possible to examine extension-related deformation processes at different crustal depths (Collettini et al. 2006a). In addition, in Tuscany extension has been active for enough time to change the geological and geophysical character of the area: the Moho is shallow (Ponziani et al. 1995; Banchi et al. 1998), heat flow is high (Mongelli & Zito 1991) and magmatism is widespread (Serri et al. 1993).

The extended/extending sector of the Apennines, including most of central and south Italy, is affected by a widespread and vigorous episode of deep-seated CO\textsubscript{2} degassing (Chiodini et al. 2004) that seems to have a close association with the regional patterns of seismicity (Collettini & Banchi 2002; Chiodini et al. 2004; Miller et al. 2004). A similar region where deep seated CO\textsubscript{2} has been invoked to explain the swarm-like seismicity has been discovered in NW Bohemia at the German/Czech border (Parotidis et al. 2003).
Geochemical evidence of fluid involvement during extension

In this section, the evidence for the occurrence of CO₂ degassing processes in the northern Apennines is discussed. The gas-water-rock interaction processes involving the deeply-derived gases and shallow fluids are investigated to explain the surface expressions of degassing, to derive a map of the regional CO₂ flux and to quantify the amounts of CO₂ involved in the process.

Recent regional-scale studies have shown that the western regions of Italy are affected by an intense CO₂ degassing process which results at the surface in numerous cold, CO₂-rich gas emissions (Fig. 2a, e.g., Chiodini et al. 2000, 2004; Minissale 2004; Rogie et al. 2000). The main component of the gas is CO₂, together with lesser amounts of N₂, H₂S, CH₄, H₂, Ar, He, and CO (Table 1). The gas flow rates (Table 1) are very high; for example, the biggest gas emissions release amounts of CO₂ similar to diffuse degassing from active volcanoes worldwide (CO₂ fluxes from 6 t d⁻¹ to 2800 t d⁻¹, mean of 430 t d⁻¹, Mörner & Etiöpe 2002)

Because of the relatively high CO₂ solubility in water, the occurrence of gas emissions at the surface depends in some way on the quantitative ratio of groundwater volumes circulating in the sub-surface relative to the amount of gas arriving from depth. The relationship between the injected and dissolved/degassed gasses has been investigated using a gas-water-rock interaction path model (GWRI) that simulates the chemical and isotopic composition of groundwater affected by the input of a CO₂ rich gas phase. The computational details are discussed in Chiodini et al. (2000), Cardellini (2003) and Caliro et al. (2005). The results (Fig 2.b) show that for low CO₂ input values almost all the CO₂ is dissolved by the groundwater (i.e. fraction of degassed CO₂, \( f_{\text{deg}} \approx 0 \)) because the solution degasses the atmospheric gas
components dissolved in the groundwater as these are less soluble than the CO₂. As CO₂ input passes a critical threshold value, $f_{\text{deg}}$ increases quickly indicating that the solution degasses CO₂ as it moves close to saturation point (i.e., $P_{\text{CO}_2} \approx 1$ bar). Beyond this point, the curves flatten out at $f_{\text{deg}} \approx 1$, since any further input of CO₂ cannot be dissolved and is totally degassed from the groundwater (CO₂ saturation condition).

Because the gas input necessary for the achievement of CO₂ saturation depends also on the amount of water circulating in the aquifers (which is here assumed to be equal to the effective infiltration), the three curves in Fig. 2b were derived for the different hydrogeological conditions of the study area: (i) flysch (or Neogene deposits) formations; (ii) volcanic formations; and (iii) carbonate formations, which are assumed to be characterised by mean effective infiltrations of 2 l s⁻¹ km⁻², 8 l s⁻¹ km⁻² and 20 l s⁻¹ km⁻², respectively (Boni et al. 1986; Capelli et al. 2005; Di Matteo et al. 2006).

The results confirm that gas emissions at the surface are possible (i.e., $f_{\text{deg}} > 0.5$) only when the CO₂ influx is higher than ~ 0.5 t d⁻¹ km⁻², 2 t d⁻¹ km⁻² and 5 t d⁻¹ km⁻² for the flysch, volcanic and carbonate aquifers respectively.

The CO₂ flux threshold value is ten times higher for the carbonates cropping out in the eastern part of Central Italy, compared to the flysch and volcanic aquifers located in the western sector. Therefore, in the western sector, the rising CO₂ can more easily reach the surface as a free gas phase generating the strong emissions observed at the surface. By contrast, the carbonate aquifers of the eastern sector can dissolve very large amounts of deeply-derived CO₂ preventing the formation of gas emissions.

These findings allow a map and an estimation of the deeply-derived CO₂ flux to be made for central Italy based on the concentration ($C_{\text{ext}}$) and the isotopic composition
(δ^{13}C_{ext}) of the fraction of carbon dissolved in the groundwaters which does not derive from carbonate mineral dissolution (Chiodini et al. 2000). Fig. 3a shows the C_{ext} and δ^{13}C_{ext} computed for 88 samples from the larger springs in carbonate regional aquifers of the Apennines and of Tuscany (Chiodini et al. 2000; Frondini et al. 2006; Fig. 2a).

In Fig. 3a the samples fall in a hyperbolic domain, highlighted by the grey area, that represents the theoretical compositions of infiltrating waters to which are added variable amounts of CO_{2} with an isotopic composition in the range typical of the deeply derived CO_{2} released in the study area (Table 1).

The flux of CO_{2} into the aquifers (ϕ_{CO_{2-ext}, t d^{-1} km^{-2}}) was computed for each spring on the basis of the C_{ext}, of the flow rates of the springs and of the corresponding extension of the hydrogeological basin. The probability distribution of ϕ_{CO_{2-ext}} (Fig. 3b) shows the presence of two statistical flux populations that can be partitioned using the method of Sinclaire (1974). Population A, with lower values, represents the CO_{2} flux connected only to the biogenic CO_{2} dissolved by groundwater during surface infiltration. Fig. 3b shows that a value of 0.4 t d^{-1} km^{-2} is a reliable upper limit for Population A. The highest values of the Population B represent the addition of deeply-derived CO_{2}.

The calculated values of ϕ_{CO_{2-ext}} for each spring were used to draw a map of the CO_{2} flux using an algorithm of sequential Gaussian simulation (Deutsch & Journel 1998). The map (Fig. 4a) highlights the presence of a large region where the CO_{2} flux is due to deeply derived CO_{2} (i.e. CO_{2} flux higher than 0.4 t d^{-1} km^{-2}) that includes Tuscany, Latium and the western sector of the Umbria-Marche Apennines (Fig. 4a).

The presence of this regional degassing structure was previously reported by Chiodini et al. (2004) using a probability map. The improved version shown here allows the
total flux of external CO2 affecting the study area to be derived for the entire region (an area of 45512 km2).

The total CO2 flux results in 22630 t d\(^{-1}\). This includes both the biogenic and deeply-derived CO2. If we assume a constant flux of biogenic CO2 over the area, equal to the mean of Population A (Fig. 3b), the total amount of deeply-derived CO2 is estimated to be 12160 t d\(^{-1}\). Given that the eventual CO2 degassing from the groundwater is neglected, this value has to be considered a minimum estimation.

**Origin and circulation of deep fluids**

The origin of the deeply-derived CO2 is still a matter of debate. From petrological and petrographical investigations Gianelli (1985) proposed a metamorphic origin for the CO2 based on the nature of decarbonation reactions of impure limestones (T > 200 °C) within the Paleozoic metamorphic basement located at shallow depths (e.g., 4-8 km at Larderello geothermal field). However a shallow crustal metamorphic source for the whole regional CO2 Earth degassing seems to be inconsistent with other evidence. For example, the isotopic compositions of the carbon in the gas emissions (Table 1) and dissolved in the groundwater are not compatible with a CO2 derivation only from shallow crustal metamorphic reactions involving carbonate formation (e.g., Marini & Chiodini 1994; Chiodini *et al.* 2000). In addition, the CO2 pressures and temperatures encountered in the geothermal reservoirs of Tuscany and Latium, and in deep wells located in the western sector of the Umbria-Marche Apennines (San Donato and Santo Stefano wells, see location in Fig. 4a), are not compatible with any of the typical thermo-metamorphic reactions involving silicate and carbonate, or with hydrothermal reactions producing CO2. In general, the CO2 fugacity (\(f_{CO2}\)) of the deep well fluids is 2-3 orders of magnitude higher than that expected for a hydrothermal-
metamorphic derivation within the reservoirs (Fig. 4b). A partial origin for the CO$_2$ from hydrothermal-metamorphic reactions within the reservoir is thermodynamically possible only in the high temperature geothermal systems like Larderello and Mt. Amiata. Therefore, excluding these extreme cases, Fig. 4b suggests that the CO$_2$ is mainly supplied by external and deep sources. In addition, the P$_{CO2}$ of these systems can be closely correlated with the depth of the reservoirs. Thus the P$_{CO2}$ values are close to hydrostatic at shallow crustal levels (1-2 km) and approach lithostatic values at greater depths (3-5 km; Fig. 4c). This suggests that the buried reservoirs in central Italy act as traps for CO$_2$ of external, deep provenance and contain as much gas as possible for their depth (Marini & Chiodini, 1994; Chiodini et al. 1995, 1999).

Chiodini et al. (2004) have suggested that the CO$_2$ was derived from mantle rocks overlying the Adriatic subduction zone which were metasomatised by crustal fluids originating from the down-going slab. This hypothesis is supported by the relatively low $^{3}$He/$^{4}$He ratios (0.019 R/Ra to 1.5 R/Ra) of gas emissions in central Italy (e.g., Table 1) which fall in the same range as the He (0.44 R/Ra to 1.73 R/Ra, Martelli et al. 2004) recorded from fluid inclusions trapped within olivine and pyroxene phenocrysts associated with mantle-derived basic lavas and pyroclastic rocks from the volcanic districts of central Italy (e.g., Albani and Vulsini in Latium region, Martelli et al. 2004).

**Geological evidence of fluid involvement during extension**

Here we document and analyze field examples of fluid-assisted weakening processes along exposed fault zones in the Apennine region. In particular we focus on the Zuccale LANF cropping out on the isle of Elba and on evaporite-bearing outcrops located in the footwalls of major normal faults in Tuscany. These localities give a
direct insight into the mechanics of earthquakes responsible for the Umbria-Marche seismicity during crustal extension. The seismicity in this part of the Apennines is noteworthy in two main ways: 1) an active LANF – the Altotiberina Fault (ATF) - can be shown to exist at depth from the integration of seismic profiles with data recorded during two detailed microseismic surveys (Boncio et al. 2000; Collettini & Barchi 2002; Piccinini et al. 2003) and, 2) the recent seismic sequences which affected the Umbria-Marche Apennines (Colfiorito M_w=6.0 1997; Gualdo Tadino M_w=5.1 1998) nucleated at a depth of ~6 km within Triassic evaporites, as shown by the integration of seismic reflection profiles with well-located earthquakes (Barchi 2002; Mirabella & Pucci 2002; Miller et al. 2004; Ciaccio et al. 2005).

The Zuccale Low-Angle Normal Fault

The Zuccale fault (ZF) is a regional fault cropping out on the isle of Elba (Fig. 5a). On a regional scale, it dips on average 15° east and cuts down-section through an earlier thrust stack formed during the late Cretaceous to early Miocene compressional phase (Trevisan et al. 1967; Keller & Pialli 1990). Eastward-directed displacement, in the range of 7-8 km (Keller & Coward 1996), occurred along the fault from the middle Miocene to the early Pliocene, and the fault has been exhumed from a depth of 3-6 km. Details of the structural geology of the fault including fault zone architecture, geometry and kinematics are illustrated in Collettini & Holdsworth (2004). These authors used field observations, fault rock distribution and microstructures to assess fluid assisted weakening mechanisms along the fault zone. One key feature of the Zuccale fault is the development of a pervasively foliated fault core, generally 3-8 m thick, sandwiched between footwall and hangingwall blocks in which the normal fault-related deformation is exclusively brittle (Fig. 6). In the hangingwall, brittle
normal faults are observed to link directly downwards into the detachment and commonly show dip-slip kinematics with top-to-the-east shear sense. Similarly, small displacement normal faults in the footwall of the main detachment, which may have listric geometries, are observed to control fault zone thickness and the internal distribution of fault rocks within the core of the Zuccale Fault (Fig. 6a-b). Footwall structures appear to have been active throughout the history of the Zuccale Fault, indicating that high- and low-angle normal faults were active contemporaneously. The fault rock distribution, moving from the low-strain footwall domain towards the high-strain fault core, changes very markedly. Immediately below the detachment we observe a heterogeneous quartz cataclasite set in a carbonate-chlorite-quartz-rich matrix and containing localized brittle faults due to the presence of minor, steeply-dipping normal faults and linking transfer faults (Fig. 7a). At the footwall-to-fault core transition, we observe a collapse of the cataclastic microstructure triggered by reaction softening and the onset of ductile deformation (Fig. 7b). Moving into the high strain regions of the fault core a highly foliated unit of green serpentinites plus tremolite-talc-chlorite schists (Fig. 7c) occurs and is associated with a heterogeneous unit of chlorite phyllonites (Fig. 7d). In these rocks, the main grain-scale deformation processes are pressure solution and precipitation which are indicated by the presence of dark dissolution seams and fibrous overgrowth of tremolite, talc and calcite wrapping the carbonate clasts (e.g. Fig. 7d). The observed fault rock textures appear to record a switch in deformation processes from cataclasis to pressure solution-accommodated slip as one moves into the fault core (Collettini & Holdsworth 2004). This switch appears to be triggered by cataclastic grain-size reduction and simultaneous influx of hydrous fluids into the fault zone, together with reaction
softening due to the effects of secondary alteration of strong minerals into fine-grained, highly aligned aggregates of weak phyllosilicates.

The fault zone is also characterized by a complex system of carbonate-infilled syntectonic hydrofractures (Fig. 6c) formed during repeated cycles of fluid pressure build up and release (Collettini & Holdsworth 2004). Many of these hydrofractures link directly into footwall normal faults, indicating that footwall structures are able to periodically tap and release fluids. The latest veins preserve good crack-seal textures whilst earlier veins are sheared and reworked into the fault zone. The thick, ∼2cm, sub-horizontal vein located at the footwall block - fault core boundary (Fig. 6c) preserves crack-seal textures and shows vertically oriented calcite fibers, suggesting the local attainment of lithostatic fluid pressures during fault activity (Collettini et al. 2006b).

The footwall evaporites of Tuscany

In Tuscany, the Triassic evaporites form a thick sequence, up to 2-2.5 km, composed of decimetric-to-decameter scale interbeds of gypsum-anhydrite and dolostone, with minor halite (Fig. 8a-b; Ciarapica & Passeri 1976; Lugli 2001). This unit is interposed between the Permian-Triassic phyllitic basement and the Mesozoic carbonate multilayer sequences and has been affected by diagenetic processes and post-depositional tectonics. The diagenetic history of the evaporites began during the early Jurassic/late Cretaceous, after about 1km of burial, when gypsum, originally deposited within shallow water environments, became unstable and was replaced by anhydrite (Murray 1964; Ciarapica & Passeri 1976; Lugli 2001). The evaporites experienced the two main eastward-migrating tectonic phases that affected the Northern Apennines, with extension superimposed on shortening (for
details see Pauselli et al. 2006). The mechanical behavior of the evaporites in the
tectonic evolution of the Northern Apennines is still not fully understood. They are
considered to be the relatively ductile décollément zone for the Umbria-Marche thrust
and fold belt (e.g. Bally et al. 1986). However, the integration of commercial seismic
reflection profiles with well-located earthquakes has recently shown that the main
seismic sequences of the Umbria region nucleated within the evaporites (e.g. Barchi
2002; Mirabella & Pucci 2002; Ciaccio et al. 2005), with the extensional mainshocks
triggered by fluid overpressures trapped within this sequence (Miller et al. 2004).

In order to determine the deformation processes operating at depth in the
seismogenic zone of the Umbria region, we studied exhumed outcrops of Triassic
evaporites in Tuscany (see location on Fig. 1). Here the evaporites extensively crop-
out due to the effects of extension (crustal thinning) and regional uplift. We focused
on two large exposures in the Roccastrada and Chianciano quarries, located in the
footwalls of large, moderately to steeply-dipping normal faults. During the early
compressional, syn-orogenic deformation, the evaporites developed a strong foliation
resulting from the shearing of an earlier compositional layering (Fig. 8b). This can be
observed within the sulphate layers which are characterized by flow structures (e.g.
iscoclinal folds) and dismembered original sedimentary layers forming a millimetric-
to-centimetric-scale transposed foliation (Fig. 8). The dolostone layers are
characterized by the intense development of gypsum-filled fractures and appear
strongly stretched with variably-sized boudins of dolostone set in a sulphate ground
mass (Fig. 8).

The style of deformation in the evaporites during the later, post-orogenic
extensional episode is strongly controlled by the pre-existing fabric and lithology.
Small displacement faults (up to few meters in throw) develop different fault zone
architecture as the fault zone cuts different rock types in the protolith. Faults developed within dolostone-rich layers display brittle features with well-defined striated fault planes and associated fault rocks (Fig. 9a-b). Fault zones here are characterized by a fault core with a thin layer of fine grained cataclasite (up to 1 cm) in contact with a relatively thicker, coarse grained cataclasite with a high to moderate clast/matrix ratio and rounded fragments suggesting that they have originated by frictional attrition of the wall rocks (Fig. 9c). A well developed damage zone extends for a few meters from the fault core. Small extensional faults preserved within the anhydrite- and gypsum-rich layers cut through the pre-existing fabric developed during the earlier compressional deformation event (Fig. 9d). Here the faults are characterized by a thin fault core and absence of a damage zone. The fault core consists of a dark, fine grained, cataclasite matrix with small dolostone clasts embedded within it (Fig. 9e). Dolostone clasts are observed here to be smeared out into the fault plane (Fig. 9f).

Large displacement faults (>100 m) cut across the entire multilayer stratigraphy with dips in the range of 40-50°. No significant changes in dip have been recorded due to changes in lithology (Fig. 10a). The fault cores, up to 2 m thick, are characterized by a grey fault gouge, dolostone-rich fault breccia and cataclasites, which, in some cases, evolve into foliated cataclasites with S-C fabrics. Damage zones of the major extensional faults are absent to poorly developed when the fault cuts gypsum/anhydrite bearing rocks. On the other hand, damage zones are well developed in thick dolostone layers. In this case, the damage zone structures are mainly controlled by penetrative (up to few meters thickness) and intense fault/fracture mesh development (Fig. 10). The fault/fracture mesh is composed of vein-rich normal faults forming dilational jogs, conjugate extensional shear fractures
and subvertical hydrofractures with crack-seal texture preserving evidence of multiple episodes of opening (Fig. 10b). Hydrofractures also developed during the earlier compression phase, but those formed by fluid-assisted processes during the post-orogenic extension can be distinguished because: 1) the hydrofractures possess the same strike as the associated normal faults with a majority indicating a vertical $\sigma_1$ orientation; 2) the fluid-rich normal faults possess the same orientation and kinematics as the regional extensional structures; and 3) the hydrofractures cut the earlier, syn-orogenic features such as transposed foliation and folds.

**Discussion**

*Fluids in the Northern Apennines*

Following slab retreat and roll-back beneath the Apennine chain (e.g. Doglioni et al. 1999) extension in the Northern Apennines migrated with time from the Tyrrhenian Sea to the Umbria–Marche Apennines from ca. 15 Ma to the present day. Extension is accommodated by east-dipping low-angle normal faults and antithetic structures. In the extended/extending region geochemical and isotopic data from CO$_2$ gas emissions and CO$_2$ dissolved in groundwaters circulating in the carbonate aquifers suggest that the area is affected by variable but generally large inputs of CO$_2$ derived from metasomatism of the mantle wedge overlying the Adriatic subducted slab (Chiodini et al. 2004).

Assuming that a mantle origin for the CO$_2$ rich fluid is correct, we suggest a simple conceptual model for fluid circulation within the extended/extending sector of the Northern Apennines (Fig. 11). In the western extended sector (Tuscany and Latium), characterised by a marked upwelling of the mantle, deeply-sourced fluids enter the ductile lower crust and infiltrate upwards through interconnected networks of
extensional fractures and normal faults. The fluids accumulate in shallow crustal traps and feed the high CO₂ flux region observed at the surface. In the eastern actively extending sector, we propose that the process of crustal thinning has not yet gone to completion, so that stratigraphic and/or structural seals can trap deeply-sourced CO₂-rich fluids to produce fluid overpressures. It is worth noting that the CO₂ flux anomaly at the surface seems to rapidly disappear close to the active extensional front (Fig. 4 and 11), where two deep wells, S. Donato and Pieve S. Stefano, encountered CO₂ pressures of about 98 MPa and 67 MPa at depths of 4750 and 3700 m b.s.l. respectively (i.e. ~ 0.8 of the lithostatic). In addition this area of high CO₂ fluid overpressure at depth corresponds closely to the area of active extension and seismicity (Fig 4a) suggesting that a key-role is played by trapped fluid pressures in earthquake triggering.

The presence of an intense and widespread deep-seated CO₂ Earth degassing process, produced by the eastward migration of extension following slab retreat, suggests a continuous fluid supply near to the base of the brittle crust. As we explain below, this allows both long and short term fluid-assisted weakening processes to occur widely (Fig. 12) and likely provides an explanation for the widespread development of LANF in the Northern Apennines.

Long term fluid assisted-weakening processes

From the microstructural evolution of the long-lived Zuccale fault zone we suggest the following model for long-term weakening (Fig. 12a). An initial phase of cataclasis increased fault zone permeability and helped focus fluid flow into the fault zone. Fluid interaction with the fine grained cataclasites lead to alteration, reaction
softening and the onset of fluid-assisted dissolution and precipitation processes, such as pressure solution, in the highly deformed fault core (Collettini & Holdsworth 2004). The deformation accommodated by pressure solution and slip along the phyllosilicate-rich foliae would reduce the shear strength of the fault by reducing the coefficient of sliding friction to $\mu_s < 0.3$, allowing fault slip under low values of shear stress (Fig. 12a). Similar weakening mechanisms have been demonstrated in deformation experiments on rock analogues of phyllosilicate-rich fault rocks (Bos & Spiers 2001, 2002), where the switch from cataclastic to pressure-solution accommodated deformation is accompanied by a decrease in friction coefficient. These weakening processes can be used to explain movements on LANF throughout the Northern Apennine region and also provide an explanation for the activity of the currently active Altotiberina low-angle normal fault located in the extending area of the Umbria-Marche Apennines (Fig. 11, see Collettini & Holdsworth 2004).

Short-term fluid assisted weakening processes

The influence of trapped fluid overpressure in promoting earthquake nucleation is well illustrated in the active area of the Umbria-Marche Apennines where overpressures have been recorded in two deep boreholes (San Donato & Santo Stefano, Fig. 4 & 11) within the Triassic evaporites at depth. Significantly, both wells are also located in the footwall block of the Altotiberina extensional detachment (Fig. 11). These data suggest that structural (e.g. large displacement LANF possessing a well developed fault core) and stratigraphical seals (e.g. the Triassic evaporites) can act as traps for the CO$_2$-rich fluids and promote the development of fluid overpressures that facilitate fault slip (Fig. 12b).
The short-term structural control on fluid overpressure is well illustrated by the presence of syntectonic hydrofractures in the immediate footwall and intervening fault core of the exhumed Zuccale detachment (Fig. 6c). We interpret the hydrofracture system formed during the ZF activity as indicating high fluid pressures and short term fluid-assisted weakening processes. In particular the development of the thick, ~2 cm, sub-horizontal vein located at the footwall block – fault core boundary testifies to the sealing capacity of the ZF foliated fault core, which was therefore able to trap crustal fluids during their ascent and promote fluid overpressure. Fluid overpressure facilitated brittle processes that transiently increased permeability favouring fluid release and fluid pressure drop.

Collettini & Barchi (2002) and Collettini & Holdsworth (2004) have used these field observations to explain the microseismicity observed along the Altotiberina fault, suggesting that cyclic build-up in fluid pressure below the fault zone promotes a temporary switch from the pressure-solution-accommodated deformation (the long term weakening process resulting in aseismic creep) to fluid-assisted brittle faulting, e.g. hydrofractures that can be interpreted as microseismic processes.

The evaporite-bearing outcrops in Tuscany provide an opportunity to investigate lithological controls on fluid overpressure development. Different rheological behaviours are recognized - ductile in the gypsum/anhydrite layers vs. brittle/ductile in the dolostones - leading to the development of a syn-orogenic transposed foliation which enhanced the low-permeability character of the gypsum/anhydrite units. This inherited lithological/structural anisotropy favored the build-up of fluid overpressures during the post-orogenic extensional phase by trapping CO₂ rich fluids during their ascent (Fig. 12b). Fluid overpressures loaded the evaporites-bearing faults and promoted fluid-assisted slip processes and associated fluid discharge. This process is
documented in the field by vein-rich brittle fault zones associated with well developed damage zones, with networks of subsidiary hydrofractures observed especially in correspondence with thick dolostone layers (Fig 10). Finally, the inferred fluid-assisted slip behavior observed in the field is consistent with the recognition of the fluid-driven nucleation of the largest events of the Umbria-Marche area within the Triassic evaporites (e.g. the 1997-98 M=6.0 Colfiorito seismic sequence Barchi, 2002; Miller et al., 2004).

The work presented in this paper benefits of continuous and stimulating discussions with M.R. Barchi. Field work on the Evaporites was supported by PRIN05 C. Collettini grant. We wish to thank F. Trippetta for his help in field work on the Evaporites. Comments and suggestions made by C. Vita-Finzi and S Shapiro helped to improve the quality of this manuscript.

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Fig 1. Block diagram and cross section of the northern Tyrrhenian Sea (Jolivet et al. 1998) and the northern Apennines based on the CROP 03 seismic traverse (Pialli et al. 1998). Ages of syntectonic basins in white boxes document eastward migration of extension. Suggested location of frictional-viscous transition after Pauselli & Federico (2002). Extension is accommodated by upper-crustal, east-dipping low-angle normal faults and high-angle, west dipping antithetic structures. Extension is active in the Umbria-Marche Apennines. ZF, Zuccale Fault; ATF, Altotiberina Fault. Ages of extension on Corsica include early core complex formation and late, high-angle faulting (Jolivet et al. 1998; Rosenbaum et al. 2005).
Fig. 2. (a). Location map of gas emissions and travertine deposits in central Italy, and of the main springs from carbonate aquifers used to compute the CO$_2$ flux affecting the region. (b) Diagram of the fraction of degassed CO$_2$ vs. the CO$_2$ input. The ratio between degassed and injected CO$_2$ (fraction of degassed CO$_2$, $f_{deg}$) is compared with the input of CO$_2$ (CO$_2$ input, expressed in t d$^{-1}$ km$^{-2}$). The three curves report the theoretical ratios between the input of CO$_2$ and the degassed CO$_2$ computed for a variable input of CO$_2$ in different hydrogeological conditions occurring in central Italy: flysch (and Neogene) formation aquifers, volcanic aquifers and carbonate aquifers.
Fig. 3. (a) Diagram of $\delta^{13}C_{\text{ext}}$‰ vs $C_{\text{ext}}$ of groundwater from Apennine and Tuscany carbonate aquifer. The grey area represents the theoretical compositions of infiltrating waters (i.e., where only biological CO$_2$ is dissolved) to which were added variable amounts of deeply derived CO$_2$, as computed by GWRI simulations. The isotopic composition of deeply derived CO$_2$ was considered in the range -6.1 ‰ to +1.5 ‰, that corresponds to the isotopic composition of CO$_2$ released by gas emission in the study area (horizontal, dashed lines). The samples with lower $C_{\text{ext}}$ and $\delta^{13}C_{\text{ext}}$ (-18‰ to -28‰) are compatible with infiltrating waters, while the samples with a relatively higher $C_{\text{ext}}$ and $\delta^{13}C_{\text{ext}}$ are compatible with a further input of deeply-derived CO$_2$. (b) Logarithmic probability plot of the CO$_2$ flux ($\varphi_{\text{CO}_2}$-$\text{ext}$) for the groundwater of Apennine and Tuscany carbonate aquifers. The $\varphi_{\text{CO}_2}$-$\text{ext}$ refers to the CO$_2$ from sources external to the aquifer. The computed values fit a curve with an inflection point. This shape is typical of bimodal distributions caused by the partial overlapping of two log-normal populations. Population A, which comprises 40% of the samples (mean = 0.23 t d$^{-1}$ km$^{-2}$, central 90% confidence interval = 0.21 t d$^{-1}$ km$^{-2}$ – 0.26 t d$^{-1}$ km$^{-2}$) represents the samples where carbon derives from biological CO$_2$. Population B (mean = 1.04 t d$^{-1}$ km$^{-2}$, central 90% confidence interval = 0.86 t d$^{-1}$ km$^{-2}$ – 1.35 t d$^{-1}$ km$^{-2}$) which includes 60% of the samples, represents the samples where the carbon partially derives from a deep source. The CO$_2$ flux value of 0.4 t d$^{-1}$ km$^{-2}$ chosen to discriminate the occurrence of deep CO$_2$ flux is highlighted.
(a) Map of the flux of CO$_2$. CO$_2$ fluxes above 0.4 t d$^{-1}$ km$^{-2}$ are related to the presence of a deep source of CO$_2$. The map was obtained by a point-wise linear averaging of all 100 realizations of the CO$_2$ flux distribution performed using an algorithm of sequential Gaussian simulation, in a computational domain of 11378 squared cells of 4 km$^2$. The locations of deep wells are also shown.  

(b) Plot of CO$_2$ fugacity ($f_{CO_2}$, at pressure and temperature of interest $P_{CO_2}$ and temperature measured in geothermal wells of Tuscany and Latium reservoirs and in deep wells located in the Apennines (San Donato and Santo Stefano wells). Values of $f_{CO_2}$ and temperature fixed by relevant metamorphic reactions and by the full equilibrium function of Giggenbach (1988) are also shown.  

(c) Depth vs. CO$_2$ pressure ($P_{CO_2}$) measured in the same wells.
Fig. 5. Geology of Elba (modified after Trevisan et al. 1967; Bortolotti et al. 2001; Collettini & Holdsworth 2004). (a) Schematic geological and structural map of the isle of Elba. Position of 2 main outcrops, at Punta Di Zuccale and Spiagge Nere, is indicated. Quaternary deposits are white. (b) Geological cross-section through central and eastern Elba, modified after Collettini & Holdsworth (2004). The position of the Zuccale Fault at depth is constrained using borehole data (Bortolotti et al. 2001).
Fig. 6. (a) Schematic representation of the Zuccale fault (ZF) architecture linking the Punta di Zuccale and Spiagge Nere outcrops (not to scale, see location in Fig. 5). Location of the structural log reported in Fig. 7. (b) Listric normal fault within the basement footwall of the ZF (see location in Fig. 6a). (c) Down-dip view of the syntectonic hydrofracture system: (h) sub-horizontal veins, (v) vertical veins. Note the thick subhorizontal hydrofracture at the footwall fault core boundary.
Fig. 7. Microstructural evolution along a transect from the footwall block up into the fault core. (a) Quartz rich cataclasites in a carbonate-chlorite-quartz rich matrix and a brittle fault plane. (b) Collapse of the cataclastic load-bearing microstructure at the footwall fault core boundary. (c) Foliated unit of green serpentinites plus tremolite-talc-chlorite schists containing a calcite-rich hydrofracture. (d) Heterogeneous unit of chlorite phyllonites with dark dissolution seams (s) and fibrous overgrowths of talc and calcite (g).
Fig. 8. (a) Massive stretched (boudinaged) and folded dolomitic mudstone (dark grey) between foliated and folded gypsum rocks after anhydrites (white). Syn-orogenic deformation of the Triassic evaporites produced a transposed foliation with flow structures within the sulphates and dismembered and stretched original layers within the more competent dolostone. (b) Thin stretched and folded dolostone layers intercalated with foliated/laminated gypsum rocks after anhydrites.

Fig. 9. (a) Striated normal fault plane within dolostone rocks. (b-c) Details of dolostone fault core architecture in the field (b) and saw-cut hand-specimen (c) show a fine grained cataclasite within the slip zone in contact with a coarse grained cataclasite. (d) Small displacement normal fault within gypsum rocks cutting through the pre-existing fabric (transposed foliation) developed during the syn-orogenic deformation event. (e) Saw-cut hand-specimen shows a thin fault zone with small dolostone clasts embedded within a dark and fine grained cataclasite. (f) Dolostone clasts are smeared out into a normal fault plane developed within gypsum rocks.
Fig. 10. (a) Normal fault cuts across the entire multicompetent stratigraphy. Note that no significant changes in dip have been observed as a function of lithology. Fault-fracture meshes have been observed within dolostone-bearing rocks adjacent to the fault zone. (b) Details of the fault-fracture mesh developed within the dolostone-bearing rocks in the footwall of the normal fault. Conjugate shear fractures and hydrofractures are consistent with extensional kinematics of the main fault.

Fig. 11. Comprehensive conceptual model integrating geochemical, geological and geophysical observations for the Northern Apennines. Mantle wedge metasomatized by crustal fluids derived from the subducted Adriatic plate (e.g. Doglioni et al. 1999; Di Stefano et al. 1999) represents the deep source of CO₂ rich fluids (Chiodini et al. 2004). The deeply sourced CO₂ degassing potentially represents a continuous fluid supply rising into the brittle crust that triggers long-term fluid rock interactions. In the extending portion of the Northern Apennines CO₂ rich fluids are trapped by stratigraphical (i.e. the evaporites) and/or structural seals (i.e. mature structures like the Altotiberina fault) and develop fluid overpressures (as documented in the San Donato, SD, and Santo Stefano, SS, wells). Trapped fluid overpressures represent a short-term weakening mechanism that strongly influences the nucleation of microearthquakes along the Altotiberina fault (e.g. Collettini & Barchi 2002; Piccinini et al. 2003) and major events, M > 5.0, on south-west dipping structures (e.g. the Colfiorito 1997 earthquakes, Miller et al. 2004).
Fig. 12. Long vs. short term fluid assisted weakening mechanisms. (a) Long term weakening processes observed along the Zuccale fault suggest that fluid influx into the fault zone triggered reaction softening and the onset of fluid-assisted dissolution and precipitation processes. The fault zone microstructure evolves from a cataclasite to a highly foliated fault rock with an associated decrease in friction coefficient at sub-Byerlee friction values ($\mu < 0.3$). (b) Short term weakening processes observed in the field and documented in deep boreholes suggest that mantle-derived CO$_2$-rich fluids can be easily trapped by structural and/or stratigraphical seals that promote fluid overpressures. Fluid overpressures produce a short term weakening since they reduce the differential stress required for faulting. Fluid assisted ruptures create permeability allowing fluid discharge with associated fluid pressure drop. The field analogue of this process is represented by the hydrofracture systems within the Zuccale and the evaporite-bearing faults (Fig. 6c & 10).
### Table 1. Chemical and isotopic composition of selected gas emission of central Italy, and measured CO2 flux.

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Chemical species are expressed in µmol/mol, %° = %o vs PDB, R/R_a = (3He/4He)sample/(3He/4He)air

† Data from Rogie et al. (2000) and references therein.
‡ Data from Frondini et al. (2006).