GEOCHEMISTRY OF THE HIGH-PRESSURE CO_2 SYSTEMS: THE PSS-1 WELL (CAPRESE MICHELANGELO, EASTERN TUSCANY), A NATURAL ANALOGUE OF CO_2 GEOLOGICAL SEQUESTRATION SITE

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INTRODUCTION AND AIMS

The peri-Tyrrhenian side of the Italian peninsula is characterized by strong CO_2 degassing (*e.g.*, Rogie *et al.*, 2000; Minissale, 2004), whose origin is twofold: (*i*) mantle and (*ii*) thermo-metamorphic processes at crustal depth (*e.g.*, Gianelli, 1985; Minissale *et al.*, 1997, 2000; Chiodini *et al.*, 2004; Minissale, 2004). The Tyrrhenian domain is dominated by an extensional regime (*e.g.*, Frepoli & Amato, 1997; Mariucci *et al.*, 1999) that has favored the uprising of these deep-seated CO_2-rich fluids to the surface. In Central Italy, the CO_2 degassing area corresponds to the so-called "Tuscan-Roman Degassing Structure" (TRDS; Chiodini *et al.*, 2000; 2004; 2011; Fig. 1). The axial zone of most Umbria Apennines in correspondence of the TRDS eastern margin (Fig. 1) is characterized by a tectonic system responsible for the relatively high seismicity in the area. Here, the main structural features are a main E-dipping low-angle fault, termed "Alto Tiberina Fault" (ATF; Fig. 2a), and SW-dipping antithetic faults (Boncio & Lavecchia, 2000; Ciaccio *et al.*, 2006; Bonini, 2009). At the boundary between the Tyrrhenian and Adriatic domains (Fig. 1), the arrangement of thrusts and normal faults creates suitable conditions for the development of structural traps generating pressurized CO_2-rich reservoirs (*e.g.*, Chiodini *et al.*, 2004), which are thought to cause seismic activity, such as the Colfiorito seismic sequence that occurred in 1997 (Chimera *et al.*, 2003; Miller *et al.*, 2004).

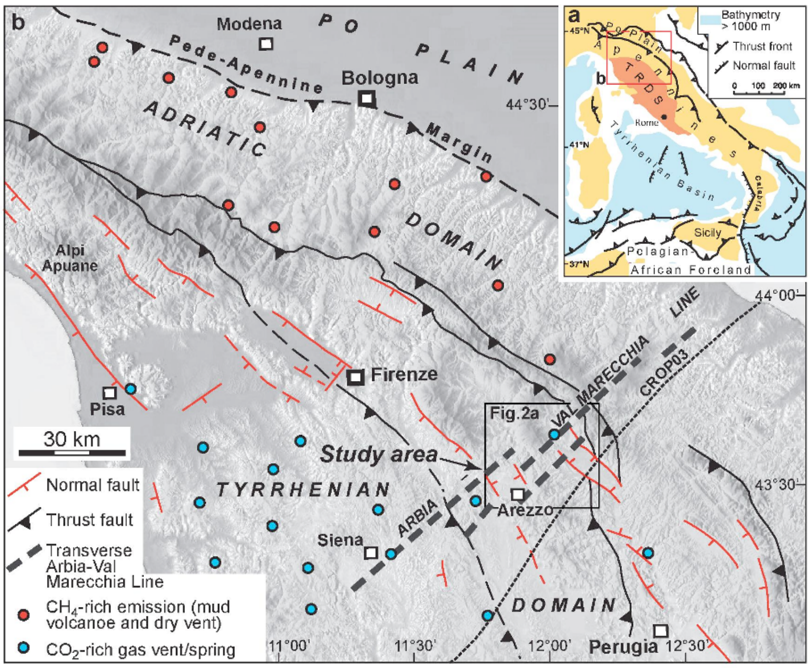

Fig. 1 - (a) Schematic map of Italy. The location of the Tuscan Roman Degassing Structure (TRDS; Chiodini *et al.*, 2004) is reported (red shaded area); the red square indicates the location of Fig. 1b; (b) map of gas manifestations (filled circles) in the Northern Apennines from Minissale *et al.* (2000). Note that the study area (black square; Fig. 2a) is located around the boundary between the Adriatic CH_4-dominated and the Tyrrhenian CO_2-dominated provinces.

One of these CO_2 reservoirs (hereafter "Caprese Reservoir", CR; Bicocchi *et al.*, 2013) was recognized during the drilling of the Pieve Santo Stefano 1 (PSS1) borehole in the San Cassiano depression, a small continental basin near Caprese Michelangelo (Eastern Tuscany). The CR is to be interpreted as the source of CO_2-rich gas emissions discharging from the nearby Mt. Fungaia area (*e.g.*, Vaselli *et al.*, 1997; Heinicke *et al.*, 2006; Bonini, 2009; Bicocchi *et al.*, 2013).

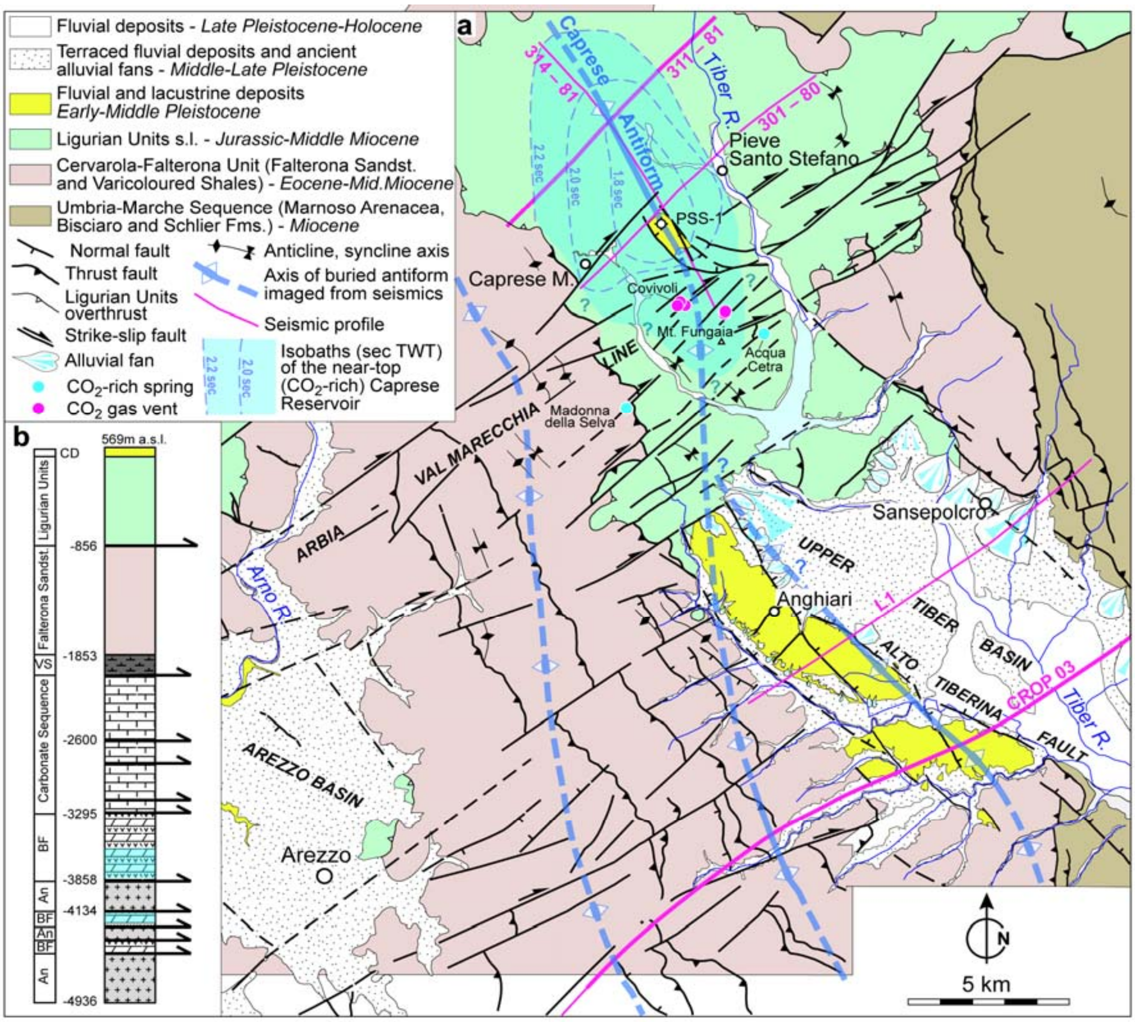

Fig. 2 - (a) Schematic geological-structural map of the area around the 'Pieve Santo Stefano 1' borehole (adapted from Bonini, 2009); (b) simplified stratigraphy of the "Pieve Santo Stefano 1" borehole (from: http://unmig.sviluppoeconomico.gov.it/videpi/; the light blue shading indicates the zones of CO_2-rich fluids. CD, Pleistocene continental deposits; VS, Varicolored Shales; BF, Burano Fm.; An, Andesite.

This research was focused on the geochemistry of (*i*) the fluids collected from the wellhead of the PSS1 borehole, (*ii*) the physical-chemical characteristics of the altered volcanic rocks available by PSS1 drill cores (the latter sampled at a depth of 3,864 to 3,871 m). CR top is located 3,300 m deep with respect to PSS1 log, the reservoir host rocks being represented by the altered volcanic products mentioned above and Burano Fm. evaporites. In addition, the study was extended to (*iii*) the CO_2-driven surficial manifestations and natural water discharges in nearby of PSS1 (samples collected repeatedly in the period 2009-2011), and (*iv*) the available geophysical data (*e.g.*, reflection seismic profiles such as CROP03; Finetti *et al.*, 2001; 2005) for defining the local structural setting. Overall, the data obtained have been merged to develop a conceptual model of the CR.

FLUID GEOCHEMISTRY

Caprese Reservoir fluids origin

CR fluids are composed of saline Na-Cl water (up to 82 g/L of TDS) circulating in the reservoir rocks and a CO_2-rich supercritical gas phase (density of 840 kg/m^3). At 3,700 m depth, these fluids are characterized by P-T conditions of 70 MPa and 120 °C, respectively. The isotopic signature (δ^2H, δ^{18}O, ^{3}H) highlighted that the saline water reservoir is part of a long hydrologic circuit fed by meteoric water, the main source of dissolved salt being represented by minerals of the Burano Fm. (*i.e.*, halite and anhydrite; Martinis & Pieri, 1964). Concerning the major gas phase components, CO_2 (915 mmol/mol, δ^{13}C-CO_2 of -3.4‰ V-PDB), N_2 (89.5 mmol/mol), and CH_4 (0.25 mmol/mol) are originated by a mixture of fluids sourced from both the upper-mantle and thermometamorphic degradation of the carbonate rocks and organic matter (*e.g.*, Chiodini & Marini, 1998), while H_2S (0.11 mmol/mol) is likely produced by thermochemical sulphate reduction (*e.g.*, Worden & Smalley, 1996). Information from seismic profiles suggests that the CR is basically controlled by the Caprese Antiform.

The anhydrites contained in the Burano Fm. act as a regional seal layer for the deep-sourced fluids (Trippetta *et al.*, 2010; 2013). Some tectonic structures (*i.e.*, regional thrusts) may represent suitable paths, where fluids originated at deeper levels by thermal degradation and mantle degassing could rise into the CR.

Caprese Reservoir past P-T-x conditions inferred from fluid inclusions

Similarly to the present-day conditions in the CR, fluid inclusions (FIs) from PSS1 borehole drill core contain a H_2O-NaCl phase and a CO_2-N_2 phase. Data retrieved from FIs indicate the occurrence of changes of P-T conditions in time (from 60 to 160 MPa and from 125 to 200 °C, respectively; Fig. 3).

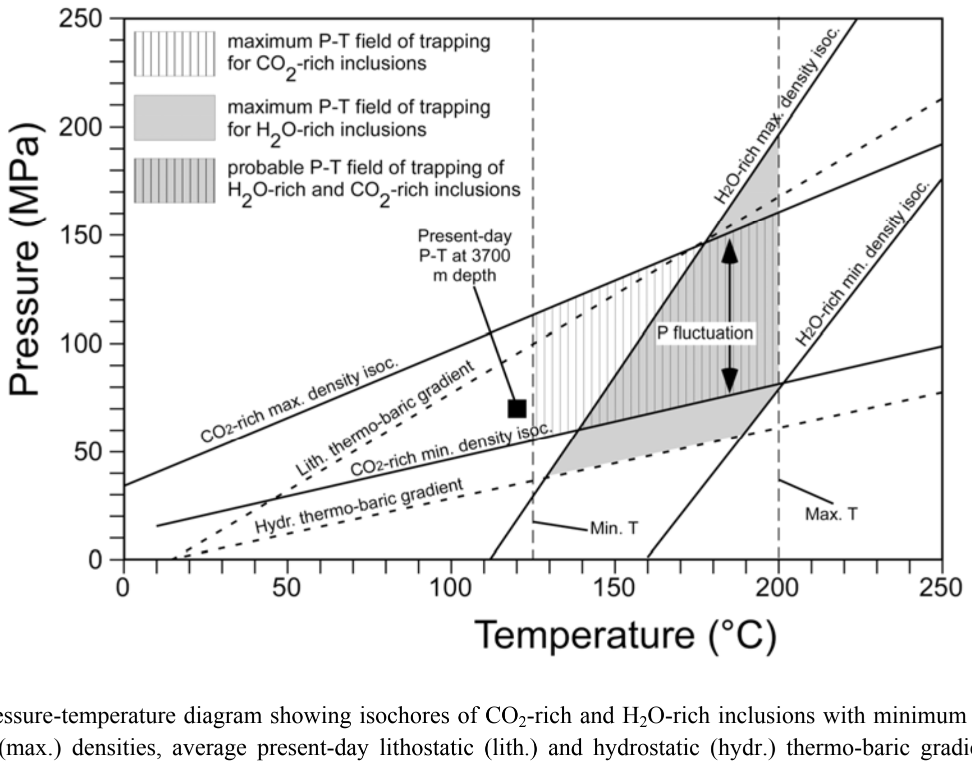

Fig. 3 - Pressure-temperature diagram showing isochores of CO_2-rich and H_2O-rich inclusions with minimum (min.) and maximum (max.) densities, average present-day lithostatic (lith.) and hydrostatic (hydr.) thermo-baric gradients in the PSS1 borehole (gradients computed at 28 °C/km and 26 MPa/km), estimated maximum temperature (max T) in the past, pressure-temperature (P-T) conditions in the reservoir at the depth of 3,700 m and estimated pressure-temperature during fluid inclusion trapping at about 3,865 m (Bicocchi *et al.*, 2013).

These changes could be related to the local development of the Apennine chain (*i.e.*, uplift and erosion; *e.g.*, Zattin *et al.*, 2002). Pressure variations indicated by CO_2-N_2 phase densities (from 645 to 914 kg/m^3) are supposedly caused either by erosion of rocks overlying the reservoir (thus the decrease of the related lithostatic pressure) or by seismic activity able to, episodically, depressurize or pressurize the reservoir. The wide range of salinity values (6-22% by wt. NaCl eq.) found in H_2O-rich inclusions likely indicates aquifer stratification. The CO_2-rich inclusions are characterized by variable contents of CO_2 and N_2 (85-97 and 3-15 mol%, respectively). These differences could be induced by variable contributions in time from the two main CO_2 and N_2 sources, *i.e.*, mantle degassing and metamorphism of sedimentary rocks, which are characterized by distinct CO_2/N_2 ratios. Also, differences in composition in different, coeval, part of the same reservoir (*e.g.*, Trippetta *et al.*, 2013) cannot be excluded and hardly distinguished from temporal variation in fluid composition.

Chemical-physical processes controlling natural discharges

The chemical and isotopic compositions of natural waters around PSS1 indicated that they are mainly fed by meteoric water and connected to a shallow hydrologic circuit. The major dissolved constituents of water (alkaline and alkaline-earth metals, carbon species, chlorine and sulphate) derive from the leakage of minerals present in the aquifers host rocks (mainly limestones and sandstones). Nitrogen species (NH_4^+ and NO_3^-) contents are rather variable and connected to the biogeochemical cycles. Chemical analyses and carbon isotopic signature in water and dissolved gas evidenced the presence of CO_2 deep input in two springs (Acqua Cetra and Madonna della Selva, CO_2 >10 mmol/L and $\delta^{13}C$-$CO_{2(aq)}$ > -10‰ V-PDB), whereas the majority of the water samples are interested only by biological production of CO_2 (contents < 5 mmol/L and $\delta^{13}C$-$CO_{2(aq)}$ < -18‰ V-PDB). Steep transverse faults pertaining to the Arbia Val-Marecchia Lines (AVML) represent favorable pathways connecting the CR with the Mt. Fungaia gas seeps and CO_2-rich springs (Fig. 2a). As a matter of fact, all these manifestations occur along the AVML structures (or at the intersection of these features with the axis of the Caprese Antiform; Bicocchi *et al.*, 2013). Interaction of the reservoir uprising gases with shallower aquifers cause an increase of CO_2/N_2 ratios (over 30 in Fungaia discharges *vs.* ~10 in the reservoir), due to N_2-CO_2 exchange in shallower CO_2-rich aquifer. Interaction of CO_2-rich fluids with ophiolite-bearing formations likely cause (*e.g.*, Boschetti & Toscani, 2008) the increase of H_2 (up to 0.411 mmol/mol) and consequently H_2S (up to 1.87 mmol/mol) in the Mt. Fungaia gases with respect to those of the PSS1 borehole. High contents of H_2 also favor the presence of CO (0.010 mmol/mol), usually absent in low temperature gas discharges such those of Mt. Fungaia. The addition of CH_4 (up to 2.87 mmol/mol) and light hydrocarbons mostly derive from thermogenic processes (*e.g.*, Whiticar, 1999; Tassi *et al.*, 2012) occurring within the Cervarola-Falterona Unit (*e.g.*, Botti *et al.*, 2004) underlying the Ligurian Units. Overall, these processes are resumed in a conceptual model (Fig. 4). The field surveys, aimed to determine the occurrence of compositional variations in waters and gases, led to the conclusion that these variations are mostly correlated with the weather (*i.e.*, the abundance of precipitations, soil moisture and insolation). Also, field observations provided evidences for a possible seismic triggered response in one of the gas discharges, which extruded a mud flow within a few weeks after an earthquake occurred nearby (M = 3.2 at a distance of approximately ~ 3.2 km from Mt. Fungaia).

ORIGIN AND PROCESSES AFFECTING RESERVOIR ROCKS

Rocks and mineral assemblage genesis

The volcanic rocks of PSS1drillcore (depth 3,864-3,871 m with respect to borehole log) were previously classified as "andesites" (by mean of the TAS diagram) and dated at 33.8±1.7 Ma through the K-Ar radiometric method (Anelli *et al.*, 1994). However, the main mineralogical assemblage (Fig. 5) is extremely inhomogeneous from point to point, overall consisting of illite and quartz (up to 95 wt.%), Ca-Fe-Mg carbonates (calcite and ankerite, up to ~ 10 wt.%), chlorite and hematite (< 5.5% wt.%), the primary minerals (presumably feldspars and pyroxenes) being completely obliterated by alteration processes. The last ones consist of water-gas-rock interactions promoted by fluids circulating, *i.e.*, to the aqueous Na-Cl brine, and to the CO_2-rich gas. A statistical study (Bicocchi *et al.*, 2011) was performed on calcite and ankerites compositions (*i.e.*, Ca-Fe-Mg contents retrieved by EMP analyses) by employing COmpositional Data Analysis (CODA) techniques (*e.g.*, Aitchison, 1986; Pawlowsky-Glahn & Buccianti, 2011).

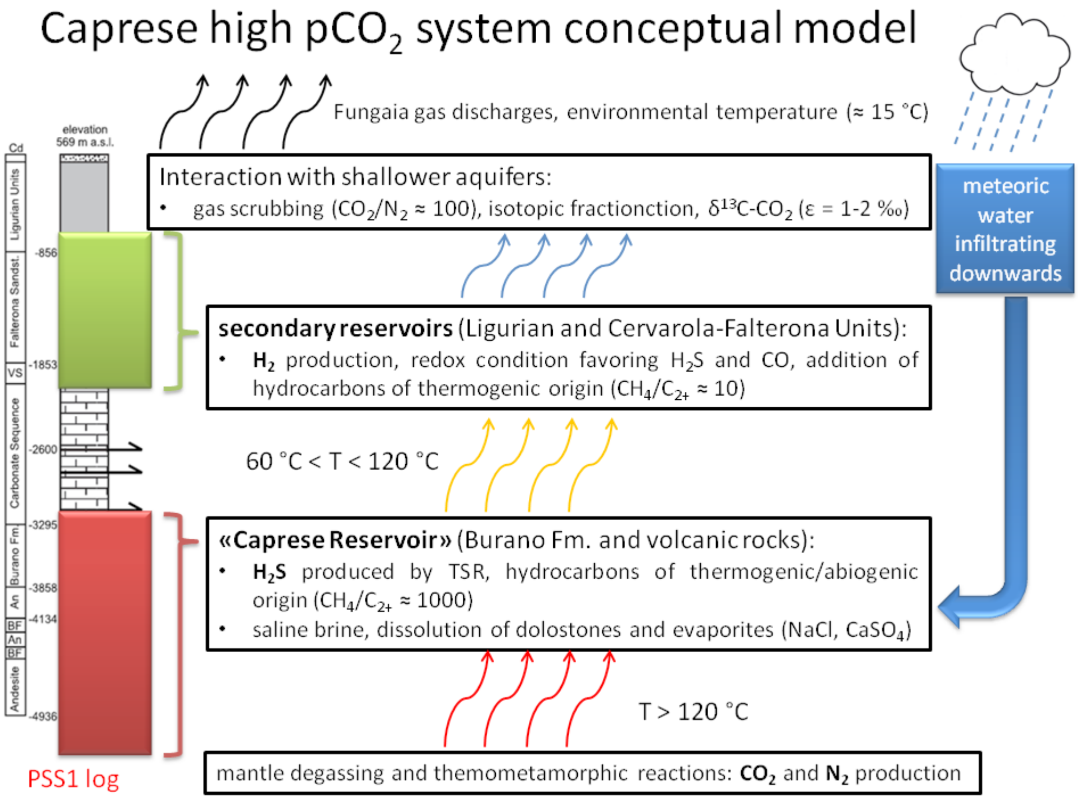

Fig. 4 - Conceptual model of Caprese Reservoir. See text for further detail.

The study revealed that composition of calcites is much more variable than that of ankerites, the latter likely replacing pristine calcites crystals, as observed also in some SEM images (Fig. 5). Indeed, while calcite precipitation may be not only related to CO_2 flooding, ankerite formation is likely due to the presence of the CO_2-rich fluids, which promote the dissolution of other mineralogical phases (*e.g.*, Kaszuba *et al.*, 2005) providing Fe and Mg ions, and supply carbonate ions for the formation of ankerite crystals. Overall, our data suggest the previous classification (*i.e.*, andesitic composition) and dating (Oligocene) of these rocks to be unrealistic. We instead hypothesized that they formed during the same period of time (*i.e.*, Upper Triassic) of the Burano Formation. PSS1 volcanic rocks could thus represent a layer of former basaltic rocks extruded during the volcanic activity related with the aborted Triassic rifting, as for other rocks of similar age found nearby the Tyrrhenian coast near La Spezia (*e.g.*, Martini *et al.*, 1986).

Physical-chemical characteristics of PSS1 borehole drill cores

Physical properties of the volcanic rocks have been investigated with the small angle neutron scattering (SANS) technique aiming to inspect their microporous structure (Bicocchi *et al.*, 2012). The fractal dimension D_s of pore-rock interfaces has been determined, as well as the mean dimension of pores. Values of D_s for the CO_2 altered volcanic rocks lay in a wide range (2.11-2.82) showing differences of more than 30%, whereas it was confined between 2.33 and 2.52 for rocks unaffected by CO_2 circulation. A similar dispersion of values is also present in the bulk chemical (ICP-MS analyses) and mineralogical composition (XRD Rietveld refinement) of the investigated rocks. In the wellbore rocks, the wide range of determined D_s values (and the corresponding difference in chemical and mineralogical composition) can be interpreted, considering that chemical alteration due to CO_2-rich fluids proceeded not homogenously, to be likely due to the circulation of fluids along preferential paths. For these rocks there is a direct correlation between the dimension of micropores and the D_s (*i.e.*, the higher are the surface fractal dimension values, the larger are the pore sizes) features that can be related to the alteration by CO_2-rich fluid (*e.g.*, Anovitz *et al.*, 2009).

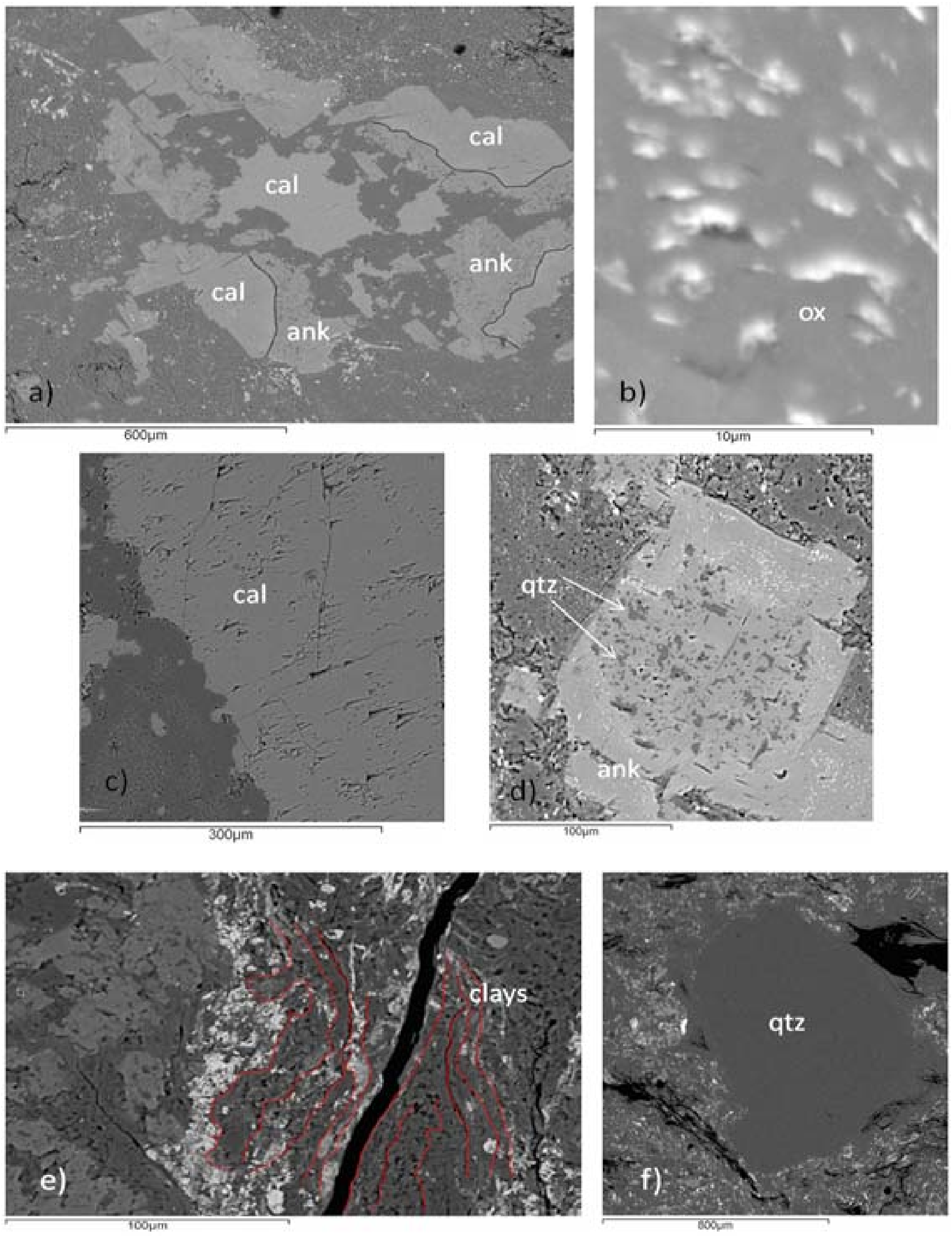

Fig. 5 - SEM images of PSS1 drill cores thin sections: (a) calcite (cal) and ankerite (ank) side by side forming crystals; (b) Fe-Ti oxides (ox) of small sizes (~10 µm); (c) calcite crystals partly interested by fractures and incipient dissolution processes; (d) ankerite crystals interested by re-precipitation of microcrystalline quartz (qtz) and Fe-Ti oxides healing the fractures; (e) clay minerals (clays) with some evidences (in red) of fluidal structures; (f) isolated quartz (qtz) crystal of millimetric dimension.

IMPLICATION FOR CO_2 GEOLOGICAL SEQUESTRATION FROM THE STUDY OF CAPRESE RESERVOIR NATURAL ANALOGUE

The investigation developed in this research has also given valuable indications for the Carbon Capture and Storage (CCS) projects. Experimental data needed for a geochemical model of CO_2 storage can be acquired from "natural analogs" (*i.e.*, natural deep reservoirs of CO_2), which are useful for identifying key mechanisms and processes relevant to long-term stability and fluids seepage associated with CO_2 geological sequestration (*e.g.*, IPCC, 2007; Oelkers *et al.*, 2008; Voltattorni *et al.*, 2009). Consequently, these systems, such as CR, are presently representing the easiest way to gather experimental data to be compared with scenarios provided by geochemical models.

A first indication for CCS from CR case study concern dawsonite, $NaAl(CO_3)_2$, a CO_2-fixing authigenic mineral. Dawsonite does not form under specific condition of high (> 30 MPa) pCO_2 and acidic *p*H of formation water. Accordingly, no dawsonite crystals were found in the analyzed samples although Na and Al were virtually available by circulating fluids and rocks of CR. Indeed, the stability of these minerals decreases with comparison to alumosilicates under these conditions, as highlighted by recent studies (*e.g.*, Hellevang *et al.*, 2011). Secondly, CR rocks analyzed give back other important experimental data useful to insert in chemical-physical numerical models. For instance, the pore-rock interface structure (*i.e.*, the estimation of a surface fractal dimensions) determined by Small Angle Neutron Scattering (SANS) can be regarded as valuable to describe the effect of CO_2-rich circulating fluids on the host rocks, circulation that affected the microporous structure. Indeed, for avoiding problems of scale, it has been proposed to adopt fractal dimensions in pore surface to describe the mineral surface reaction area. The information obtained through SANS could provide useful experimental data at this regard.

CONCLUSIONS

The research was aimed to inspect multiple aspects of a natural CO_2 reservoir in Northern Apennines. This study included: (*i*) a geochemical study of present and past circulating fluids, by analyzing water, gases and fluid inclusions, (*ii*) a comparison of chemical and isotopic composition of the deep reservoir fluids (available from PSS1 borehole) and the natural gas discharges of Mt. Fungaia fed by CR gas, (*iii*) the definition of the structural settings by interpreting available geophysical data, and (*iv*) the determination of physical-chemical features of reservoir rocks trough several experimental techniques, among them small angle neutron scattering (the latter provided by facilities sited in France, at LLB). Moreover, (*v*) the elaboration of data was performed adopting suitable tools for compositional data. All this work allowed to exhaustively characterizing the CR high pCO_2 system. The results improved the comprehension of the processes controlling the physical-chemical characteristics of deep fluids, as well as their relationships with the natural discharges. In addition, this kind of study could be beneficial for Carbon Capture and Storage projects (CCS). Indeed, analytical data from "natural analogues" (*i.e.*, natural deep reservoirs of CO_2 such as Caprese Reservoir) are useful for identifying key mechanisms and processes controlling long-term stability and fluid seepage in sites selected for CO_2 geological sequestration.

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