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The high pCO_2 Caprese Reservoir (Northern Apennines, Italy): Relationships between present- and paleo-fluid geochemistry and structural setting

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ABSTRACT

The chemical and isotopic compositions of (i) CO_2-rich fluids exploited from the ~5,000 m deep Pieve Santo Stefano 1 (PSS1) borehole located in the Upper Tiber Basin (Northern Apennines, Italy) and (ii) natural gas seeps located in its surroundings, mainly in the Mt. Fungaia ophiolitic-bearing complex (Ligurian Unit), are presented and discussed. Deep seismic profiles have allowed to identify a thrust-related antiform (Caprese Antiform), a regional geological structure trapping the pressurized deep fluids. Fluids from the Caprese Reservoir (CR) consist of a CO_2-, N_2-rich gas phase sourced by both mantle degassing and thermal degradation of carbonate rocks and organic-rich sediments of the Umbro–Tuscan sedimentary series and a Na–Cl saline (up to 82 g/L of TDS) brine. Gases naturally discharging in the study area are related to those present in the CR. These gases, during their uprising toward the surface, mix with shallow aquifers. Addition of (i) H_2 and H_2S, derived by the interaction with ophiolite-bearing Ligurian Units, and (ii) thermogenic hydrocarbons, originated from the degradation of organic matter contained in the turbiditic (sandstone-rich) formations (Cervarola–Falterona Unit) was also evidenced. Fluid inclusions, trapped in calcite and quartz crystals from the PSS1 drill-core at the depth of 3864 to 3867 m, contain CO_2–N_2 and H_2O–NaCl phases. The different paleo CO_2–N_2 contents and densities found with respect to the fluids currently exploited from the CR have been related to the evolution of the reservoir throughout the time. Compositional data of fluids exploited from PSS1 borehole provide a unique opportunity to better characterize chemical–physical processes and source regions of past and present deep fluids circulating in Northern Apennines.

1. Introduction

The peri-Tyrrhenian side of the Italian peninsula is characterized by strong CO_2 degassing (e.g. Rogie et al., 2000; Kerrick, 2001; 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 and 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., 2004, 2011; Fig. 1a). The axial zone of most Umbria Apennines in correspondence of the TRDS eastern margin (Fig. 1a) 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 and Lavecchia, 2000; Collettini and Barchi, 2002; Ciaccio et al., 2006; Bonini, 2009a,b). At the boundary between the Tyrrhenian and Adriatic domains (Fig. 1b), the arrangement of thrusts and normal faults creates favorable conditions for the development of structural traps generating pressurized CO_2-rich reservoirs (e.g. Minissale et al., 2000; 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).

One of these CO_2 reservoirs (hereafter "Caprese Reservoir") was recognized during the drilling of the 4936 m deep Pieve Santo Stefano 1 (PSS1) borehole in the San Cassiano depression, a small continental basin near Caprese Michelangelo (Eastern Tuscany) (Anelli et al., 1994; Fig. 2). The Caprese Reservoir was interpreted as the source of CO_2-rich gas emissions discharging from the nearby Mt. Fungaia area (Figs. 2a, 3) (Vaselli et al., 1997; Heinicke et al., 2006; Bonini, 2009a). In August 2011, Consorgas Ltd. has started the

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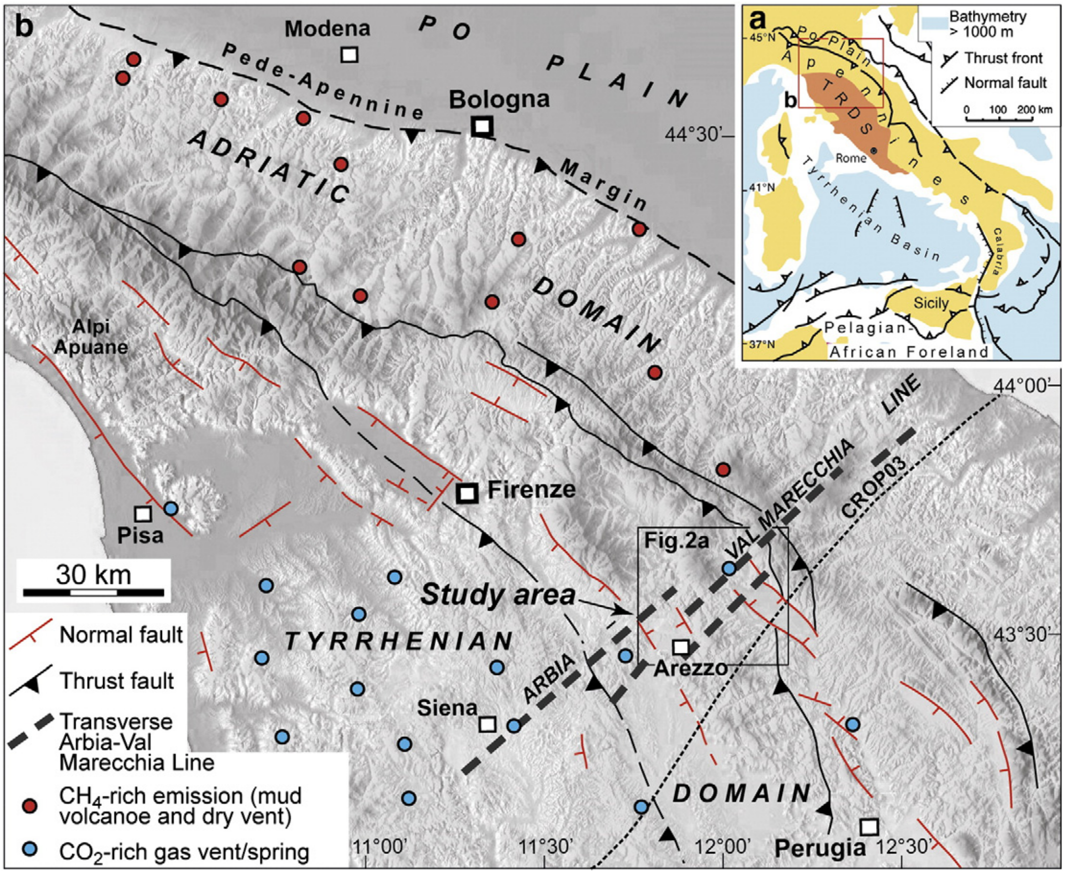

Fig. 1. (a) Schematic map of Italy. The location of the Tuscan Roman Degassing Structure (TRDS; Chiodini et al., 2004) is reported. (b) Location map of gas manifestations in the Northern Apennines from Minissale et al. (2000). Note that the study area is located around the boundary between the Adriatic CH_4-dominated and the Tyrrhenian CO_2-dominated provinces (e.g. Tassi et al., 2012a).

exploitation of the PSS1 CO_2-rich fluids for the production of industrial CO_2.

This paper is focused on the geochemistry of (i) fluids collected from the wellhead of the PSS1 borehole and the Mt. Fungaia gas discharges and (ii) fluid inclusions from the PSS1 drill-cores, the latter being sampled at the depth of 3864 to 3867 m. The comparison between fluid geochemistry of the Mt. Fungaia vents and Caprese Reservoir is aimed to investigate secondary processes that affect the chemical and isotopic compositions of reservoir fluids while uprising toward the surface. Seismic reflection profiles and paleo-fluids were analyzed to define the structural assessment of the studied area and to reconstruct the P–T–X conditions of fluid formation, respectively, in order to propose the evolution of the Caprese CO_2-rich Reservoir after its emplacement. Eventually, compositional data of fluids from Caprese Reservoir could be beneficial for Carbon Capture and Storage projects (CCS). Indeed, analytical data from “natural analogs” (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 (e.g. Pearce et al., 1996; Pearce, 2006; Voltattorni et al., 2009).

2. Geological background

2.1. Tectonic setting

The Northern Apennine is a NE-verging fold-and-thrust belt made up of stacked thrust units that can be referred to two main paleogeographic domains: (i) the oceanic Ligurian Basin and (ii) the continental margins of the Adria Plate. The Mesozoic Umbro–Tuscan sedimentary sequence was emplaced in the western margin of Adria and consists (from the bottom to the top) of a basal layer of Triassic evaporites (Burano Fm.), Mesozoic strata of carbonate platform and pelagic sediments. During the Apennine orogenesis, the horizontal shortening produced a thrust wedge that progressively incorporated the Umbro–Tuscan rocks, as well as the overlying siliciclastic turbidite sediments filling the foredeep basins, which formed ahead of the migrating chain (e.g. Principi and Treves, 1984; Ricci Lucchi, 1986). The Ligurian Units s.l. are the most elevated in the nappe pile and consist of Jurassic ophiolites (remnants of the Ligurian oceanic crust) and the associated Upper Cretaceous to Miocene sedimentary cover (e.g. Abbate et al., 1980; Abbate and Bortolotti, 1984; Bortolotti et al., 2001).

The PSS1 borehole occurs a few kilometers northwest of the Quaternary Upper Tiber Basin, which represents an important area of active subsidence and tectonic deformation (e.g. Boncio and Lavecchia, 2000; Sani et al., 2009; Fig. 2). The margins of this area are bounded by normal faults, which are considered potentially seismogenic on the basis of (i) the morphotectonic characteristics and high-resolution seismic reflection profiles (Delle Donne et al., 2007), and (ii) the hypocenter distribution (Ciaccio et al., 2006). The NE-dipping fault system delimiting the Anghiari hills is considered part of the Alto Tiberina Fault (ATF; Barchi et al., 1998; Boncio and Lavecchia, 2000; Heinicke et al., 2006; Fig. 2).

NE-trending steep faults pre-date and apparently delimit the Upper Tiber Basin to the northwest (Bonini, 2009a; Fig. 2). These faults are part of the regional transverse lineament known as Arbia-Val Marecchia Line (AVML; Liotta, 1991), which is one of the various tectonic elements crossing the whole Northern Apennines. Interestingly, CO_2 reservoirs and CO_2 natural manifestations are distributed along this lineament several kilometers southwest of the study area and along the southwestern segment of the Arbia-Val Marecchia Line near Rapolano (e.g. Santa