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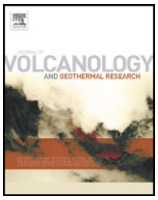

Fractionation processes affecting the stable carbon isotope signature of thermal waters from hydrothermal/volcanic systems: The examples of Campi Flegrei and Vulcano Island (southern Italy)

Stefania Venturi [a,b,*], Franco Tassi [a,b], Gabriele Bicocchi [a], Jacopo Cabassi [a,b], Francesco Capecchiacci [a,b], Giorgio Capasso [c], Orlando Vaselli [a,b], Andrea Ricci [d], Fausto Grassa [c]

[a] *Dipartimento di Scienze della Terra, Università di Firenze, Via G. La Pira 4, 50121 Firenze, Italy*
[b] *Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Via G. La Pira 4, 50121 Firenze, Italy*
[c] *Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione Palermo, Via Ugo La Malfa 153, 90146 Palermo, Italy*
[d] *Dipartimento di Scienze Biologiche, Geologiche ed Ambientali, Università di Bologna, Porta S. Donato 1, 40127 Bologna, Italy*

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ABSTRACT

The carbon isotopic composition of dissolved C-bearing species is a powerful tool to discriminate the origin of carbon in thermal waters from volcanic and hydrothermal systems. However, the $\delta^{13}C$ values of dissolved CO_2 and TDIC (Total Dissolved Inorganic Carbon) are often different with respect to the isotopic signature that characterizes the potential carbon primary sources, i.e. deep hydrothermal reservoirs, magmatic gases and organic activity. The most commonly invoked explanation for such isotopic values is related to mixing processes between deep and shallow end-members. Nevertheless, experimental and empirical investigations demonstrated that isotopic fractionation due to secondary processes acting on the uprising fluids from the hydrothermal reservoirs is able to reproduce the measured isotopic values. In this paper, we investigated the chemistry of thermal waters, collected at Campi Flegrei and Vulcano Island (southern Italy), whose origin is related to interaction processes among magmatic gases, meteoric water, seawater and hosting rocks. A special focus was dedicated to the $\delta^{13}C$ values of dissolved CO_2 ($\delta^{13}C_{CO2(aq)}$) and total dissolved inorganic carbon ($\delta^{13}C_{TDIC}$). The $\delta^{13}C_{CO2(aq)}$ and $\delta^{13}C_{TDIC}$ values in the water samples from both these systems ranged from (i) those measured in fumarolic gases, likely directly related to the deep hydrothermal-magmatic reservoir, and (ii) those typically characterizing biogenic CO_2, i.e. produced by microbially-driven degradation of organic matter. A simple mixing model of the two end-members, apparently explaining these intermediate carbon isotopic values, contrasts with the chemical composition of the dissolved gases. On the contrary, isotopic fractionation due to secondary processes, such as calcite precipitation, affecting hydrothermal fluids during their underground circulation, seems to exhaustively justify both the chemical and isotopic data. If not recognized, these processes, which frequently occur in volcanic and hydrothermal systems, may lead to an erroneous interpretation of the carbon source, causing an underestimation of the contribution of the hydrothermal/magmatic fluids to the dissolved carbon species. These results pose extreme caution in the interpretation of intermediate $\delta^{13}C_{CO2(aq)}$ and $\delta^{13}C_{TDIC}$ values for the assessment of the carbon budget of hydrothermal-volcanic systems.

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1. Introduction

Fluids from volcanic and hydrothermal systems significantly contribute to the global carbon cycle, since they discharge huge amounts of CO_2 to the atmosphere through active vents (open conduit craters and fumaroles) and diffuse soil degassing (e.g. Chiodini et al., 1998; Aiuppa et al., 2013; Burton et al., 2013; Conde et al., 2014). A significant portion of volcanic/hydrothermal CO_2 dissolves into subsurface waters as HCO_3^- and CO_3^{2-}, as a function of pH, and is discharged from springs and/or shallow wells (e.g. D'Alessandro et al., 1997; Inguaggiato et al., 2005; Chiodini et al., 2015a). The isotopic signature ($\delta^{13}C$) of dissolved CO_2 and total dissolved inorganic carbon (TDIC) are useful tools to discriminate the different sources of carbon in thermal waters, when a gas-free phase does not occur (e.g. Chiodini et al., 2000, 2004). Distinct $\delta^{13}C_{CO2(aq)}$ and $\delta^{13}C_{TDIC}$ values can indeed be recognized in C-bearing

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* Corresponding author at: Dipartimento di Scienze della Terra, Via G. La Pira 4, 50121 Firenze, Italy.
E-mail addresses: stefania.venturi@unifi.it (S. Venturi), franco.tassi@unifi.it (F. Tassi), gabriele.bicocchi@unifi.it (G. Bicocchi), jacopo.cabassi@igg.cnr.it (J. Cabassi), francesco.capecchiacci@unifi.it (F. Capecchiacci), giorgio.capasso@ingv.it (G. Capasso), orlando.vaselli@unifi.it (O. Vaselli), andrea.ricci34@unibo.it (A. Ricci), fausto.grassa@ingv.it (F. Grassa).

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dissolved species that derive from CO_2 generated by different processes, such as: 1) mantle/magmatic degassing, producing CO_2 typically showing $\delta^{13}C$ values around −6‰ vs. V-PDB (Rollinson, 1993; Sano and Marty, 1995; Hoefs, 2009), i.e. similar to the isotopic value of atmospheric CO_2 (ca. −8‰ vs. V-PDB; Scripps CO_2 Program); 2) degradation of organic matter, characterized by CO_2 with $\delta^{13}C < -20$‰ vs. V-PDB (Degens, 1969; Rollinson, 1993; Sano and Marty, 1995); 3) thermometamorphic reactions on carbonate rocks, producing isotopically heavy CO_2 ($\delta^{13}C = 0 \pm 5$‰ vs. V-PDB; Sano and Marty, 1995; Clark, 2015). Despite the isotopic fractionation of CO_2 to form $CO_{2(aq)}$ and (bi)carbonates species (e.g. Bottinga, 1968; Deines et al., 1974; Mook et al., 1974), this widely accepted classification is not consistent with the isotopic signature of a number of thermal waters from volcanic and hydrothermal areas, which show $\delta^{13}C_{CO2(aq)}$ values ranging from −18‰ to −9‰ vs. V-PDB (e.g. D'Alessandro et al., 1997; Caliro et al., 1999; Federico et al., 2002; Taran et al., 2002; Inguaggiato et al., 2005; Grassa et al., 2006; Yamada et al., 2011; Ruzié et al., 2013; Marrero-Diaz et al., 2015; Morikawa et al., 2016). In most cases, these isotopic values, which are intermediate with respect to those related to mantle/magmatic and biogenic CO_2, were interpreted as due to mixing processes between deep and shallow/marginal end-members (e.g. Italiano et al., 2009; Fourré et al., 2011; Ruzié et al., 2013). However, other studies demonstrated the strong influence of isotopic fractionation on the $\delta^{13}C_{CO2(aq)}$ and $\delta^{13}C_{TDIC}$ values, which were related to multi-step CO_2 dissolution (e.g. Weinlich, 2005; Gilfillan et al., 2009; Güleç and Hilton, 2016) and carbonate precipitation/dissolution (e.g. Ohwada et al., 2007; Gilfillan et al., 2009; Barry et al., 2014; Güleç and Hilton, 2016). These secondary chemical processes are considered to commonly affect thermal fluids from volcanic and hydrothermal areas (Simmons and Christenson, 1994 and references therein). Hence, they may represent a valuable alternative explanation for $\delta^{13}C_{CO2(aq)}$ and $\delta^{13}C_{TDIC}$ values not consistent with the primary CO_2 sources.

In the present study, we report a complete dataset, consisting of major ion chemistry, chemical composition of dissolved gases and carbon isotopes ($\delta^{13}C_{CO2(aq)}$ and $\delta^{13}C_{TDIC}$), measured in thermal waters from two volcanic systems in Italy: Campi Flegrei (Naples, southern Italy) and Vulcano Island (Aeolian Archipelago, southern Italy) (e.g. Boschetti et al., 2003 and references therein; Valentino and Stanzione, 2003 and references therein). The main aim is to investigate the mechanisms controlling the $\delta^{13}C_{CO2(aq)}$ and $\delta^{13}C_{TDIC}$ values in these fluids, in order to provide insights into the role played by the secondary chemical processes that may affect the estimation of hydrothermal/magmatic CO_2 contribution to the global carbon budget.

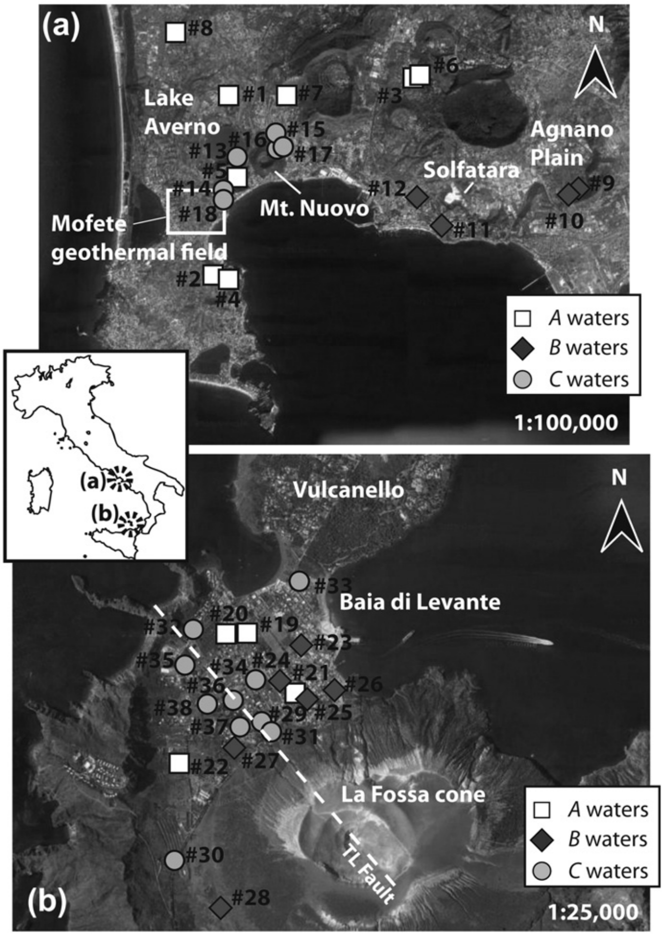

Fig. 1. Satellite photos of (a) Campi Flegrei caldera and (b) Vulcano Island. The sampling sites of thermal waters are reported. Symbols are according to the three groups of waters distinguished on the basis of the dissolved CO_2 isotopic composition, as follows: group *A* = white squares; group *B* = dark grey diamonds; group *C* = light grey circles (see the text for details). The Tindari-Letojanni (LT) Fault is shown in Fig. 1b (white dashed line).

2. Geological features and hydrothermal/magmatic systems of the study areas

2.1. Campi Flegrei

The Campi Flegrei caldera (Fig. 1a) is an active volcanic complex occupying ~100 km^2 of the Campanian Plain, NW of Naples (southern Italy). The caldera structure formed during two large eruptions, which produced (i) the Campanian Ignimbrite (39 ka; De Vivo et al., 2001) and (ii) the Neapolitan Yellow Tuff (14.9 ka; Deino et al., 2004). The volcanic system developed within the Campanian graben, where volcanic deposits (K-basalts, trachybasalts, latites, trachytes, alkali-trachytes and phonolites), marine and continental sediments overlie the Mesozoic carbonate basement located at 4 km depth. The last historical eruptive event occurred in 1538 CE (Di Vito et al., 1987), which originated the monogenic tuff cone of Monte Nuovo (Fig. 1a), after about 3000 years of quiescence.

The hydrothermal system of the Campi Flegrei caldera, which is related to fluids released from a magma chamber located at about 5 km below the town of Pozzuoli (e.g. Gottsmann et al., 2006), is responsible for frequent episodes of ground uplift and subsidence (*bradyseism*) accompanied by seismic activity (e.g. Bonafede and Mazzanti, 1998; Chiodini et al., 2003, 2012, 2015b; Gottsmann et al., 2006).

Two distinct hydrothermal reservoirs, located within the volcanic cover, were recognized in the area: (i) a seawater-contaminated shallow reservoir (depth < 2 km) diluted by meteoric waters, and (ii) a deep hydrothermal reservoir (>2 km) of hypersaline waters (Caprarelli et al., 1997; Valentino and Stanzione, 2003). The surficial expression of the hydrothermal activity within the caldera mostly consists of submarine and inland fumarolic vents, anomalous diffuse soil degassing (e.g. Chiodini et al., 2001; Todesco et al., 2003; Caliro et al., 2007; Vaselli et al., 2011; Passaro et al., 2016), and thermal water discharges and wells (e.g. Valentino and Stanzione, 2003, 2004).

2.2. Vulcano Island

Vulcano Island is the southernmost island of the Aeolian Archipelago (southern Italy), a subduction-related volcanic arc in the Southern Tyrrhenian Sea (Fig. 1b). It consists of a main edifice, mostly developed during the Pleistocene and Holocene through several stages of stratocone building and caldera collapse (Keller, 1980; De Astis et al., 1997), and a smaller island (Vulcanello), made of lavas and pyroclastic cones formed by nearly continuous activity between 1000 and 1250 CE (Arrighi et al., 2006). The last eruptive event occurred in 1888–1890 (Clocchiatti et al., 1994) from La Fossa, a 391 m high cone (Fig. 1b) having a base diameter of 1 km. La Fossa summit crater is

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