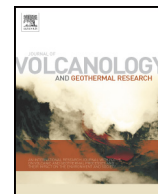




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Discrete monitoring of chemical parameters in ground waters of Mt. Etna volcano: 2000–2006

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ABSTRACT

Three sites of groundwater captation on Mt. Etna volcano (namely Currone, Ilice and Pavone) were sampled systematically for six years (from 2000 to 2006) for the determination of the major ionic composition of water. The monitored sites were chosen among those most representative of the geochemical characteristics of the groundwater systems of the volcano. The period studied was characterized by several strong eruptions of Mt. Etna, both at its summit craters and along its flanks. The overall composition of the waters sampled at Currone and Ilice falls in the group of bicarbonate-alkaline-earth compositions, whereas those from Pavone show a bicarbonate-alkaline composition. In all sites, however, some samples show input of chlorine-sulfate alkaline waters, likely due to interaction between fresh groundwater and either acidic waters from SO₂-polluted rainwater, (more evident at Pavone) or geothermal brines (more evident at Currone). Significant temporal variations affected, in a more or less marked way, all of the parameters measured at the three sites. Basic statistical correlations among the parameters at each site allowed to discover a general coherent temporal behavior of all major ions dissolved in Mt. Etna's ground waters. Factor Analysis allowed showing up to three main groups of parameters with similar temporal behavior, depending on the site. A first group was explained by interaction between volcanic ground waters and geothermal fluids; a second group was related with leaching of the host volcanic rocks by CO₂-rich volcanic water; a third group was explained as due to input of plume-SO₂-derived sulfate through water recharge. Using normal probability plots for each parameter at the three sites it was possible to reveal different geochemical populations explained as background, anomalous values and, possibly, outliers. Plotting the temporal patterns of all the monitored parameters versus the concurrent eruptive episodes at Mt. Etna, we discovered significant correlations that, although with different intensity and rate depending on the parameter and on the site, highlighted several geochemical processes induced by interaction between cold groundwater and magmatic/hydrothermal fluids, mostly following changes in the ground permeability of the volcanic pile. These processes seemed to be enhanced during periods of shallow magma accumulation inside of the volcano that preceded summit or flank eruptions occurred at Mt. Etna during the monitored period.

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1. Introduction

Mt. Etna volcano is among the best monitored volcanoes in the world, mainly because of its high frequency of eruptions, the easy access to most of its surface for any scientific purpose and the high potential impact of its eruptive activity both on the people living on its foot (about 900,000) and the civil infrastructures built in and around its area (pipelines, roads, railways, airports, etc.). A wealth of geophysical and geochemical parameters are being used for monitoring Mt. Etna's activity, leading to a remarkable improvement of our knowledge on

how this volcano works and stimulating the production of multidisciplinary models that attempt to explain its dynamics (e.g., Calvari et al., 2011; Patanè et al., 2013; Bonaccorso et al., 2014; Falsaperla et al., 2014; Mattia et al., 2015).

An important issue arising from the experience acquired on Mt. Etna in the last two decades is that geochemical parameters can provide useful information on the possible future eruptive behavior of this volcano on time spans ranging from months to days before eruptions, depending on the specific parameter being monitored. Attention, however, has been focused mainly on temporal monitoring (both discrete and continuous) of gas emissions from the summit craters, from fumaroles and from the soil (e.g., Bruno et al., 2001; Aiuppa et al., 2004; Caltabiano et al., 2004; Pecoraino and Giammanco, 2005; Neri et al., 2006; Shinohara et al., 2008; Giammanco and Bonfanti, 2009;

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Giammanco et al., 2013; Pering et al., 2013; De Gregorio et al., 2014). Despite the good level of knowledge on the hydrogeological (Ogniben, 1966; Aureli, 1973; Ferrara, 1975, 2011) and geochemical features of Mt. Etna aquifers (Giammanco et al., 1996, 1998; Aiuppa et al., 2000, 2003, 2004; Brusca et al., 2001; Parello et al., 2001; D'Alessandro and Vita, 2003; D'Alessandro et al., 2004, 2011; Bellia et al., 2015), the temporal monitoring of groundwater chemistry has not received a similar attention. There are at present only relatively few cases of studies focused on monitoring the temporal changes of groundwater temperature (Bonfanti et al., 1996a) or chemistry (Dongarrà et al., 1993; Bonfanti et al., 1996b; Quattrocchi et al., 2000; Giammanco et al., 2007; Federico et al., 2017) at Mt. Etna. Yet, this kind of research proved to be very useful for the detection of early signs of unrest at Mt. Etna, because significant changes in the abundances of many dissolved elements (major and minor ions, as well as trace elements) have been observed as a consequence of enhanced gas-water-rock interaction following strong input of magmatic/hydrothermal fluids in the local aquifers (e.g., Aiuppa et al., 2004; Giammanco et al., 2007; Federico et al., 2017).

Here, we present the results of about six years of discrete monitoring of the basic chemical features in the groundwater of Mt. Etna. Samplings were carried out periodically (several times per month) in a few selected sites for the determination on the major ionic species in solution, that are the easiest to analyze and those most sensitive to strong increases in the release of volcanic fluids that occur during magma ascent possibly leading to a new eruption.

2. Hydrogeological settings of Mt. Etna

Mt. Etna is a large volcanic edifice (highest altitude of 3320 m a.s.l. and total surface of about 1200 km²) that has grown up during the last 500,000 years on the eastern coast of Sicily (Southern Italy) with the alternate superimposition of lava flows and pyroclastic deposits (Branca et al., 2011). During the last 5000 years, Etna has been persistently active and erupted volcanic products essentially made of lavas, with a composition that ranges from alkali-basalt to hawaiite (Chester et al., 1985; Branca et al., 2011). Etna's volcanic products lie over a thick (>15 km) sedimentary substratum which is mostly composed of clays (Messinian age) to the East and South and of clay, marl and quartz-arenite units, aging from Triassic to upper Pliocene, to the West and North (Lentini, 1982; Branca and Ferrara, 2013).

The permeability of Etna's volcanics is generally high, ranging from 2.5×10^{-7} to 2.9×10^{-6} cm² (Aureli, 1973; Ferrara, 1975), while that of the sediments of Etna's basement is much lower (average value of 1×10^{-10} cm², according to Schilirò, 1988). Such a large permeability contrast, together with the remarkable amount of precipitations (from rain and snow) that characterize the area, imply that Mt. Etna volcano is also an important reservoir of groundwater (about 7×10^8 m³ of water available per year, according to Ogniben, 1966). This has allowed for a large availability of fresh water to the local population. Ground water has been extracted through an increasing number of water wells, drainage galleries and systems of spring water captation. However, in recent years uncontrolled and intense exploitation of the water resources of Mt. Etna caused a steady lowering of the water table (Ferrara, 1991; D'Alessandro et al., 2011).

The circulation of groundwater inside Mt. Etna is strongly influenced by the morphology of the sedimentary basement of the volcano (Ferrara, 2011; Branca and Ferrara, 2013). In fact, most of the waters falling on the ground surface as rain or snow percolate through the permeable volcanic rocks and, once the impermeable basement is reached, they move along radial directions towards the outer boundaries of the volcanic edifice. Besides, Mt. Etna's basement reaches its maximum height (about 1200 m a.s.l.) slightly NW of the summit of the volcano and it has a general slope towards SE. Therefore, ground waters tend to move and accumulate in the southern and eastern flanks of the volcanic edifice, where the number of springs and water-wells is the

highest (Ogniben, 1966; Ferrara and Pappalardo, 2008; Liotta et al., 2016, 2017). On the basis of the groundwater circulation, three main hydrogeological basins have been recognized on Etna (Ogniben, 1966; Ferrara, 1990): the first roughly corresponds to the Northern sector of the volcano, the second includes a great part of the Western and Southern flanks and the third, which is the largest one, includes almost all of the Eastern part of it (Fig. 1). Regardless of the hydrogeological basin considered, the seasonal variation of water discharge from all of the springs of Mt. Etna normally shows two maxima, from November to January and from May to June, respectively (Aureli, 1973). The first period of high water discharge follows the period of highest rainfall in the area, whereas the second period of high discharge is related to spring melting of the abundant snow cover of Mt. Etna, with consequent transitory increase in the recharge of water into the local aquifers (Ogniben, 1966).

3. Geochemical features of Mt. Etna groundwater

A meteoric origin of Etna's ground waters has been proposed by Anzà et al. (1989) based on the Deuterium/Hydrogen and ¹⁸O/¹⁶O isotopic ratios. According to the chemistry of major elements, groundwater samples of Mt. Etna typically display a bicarbonate type composition with only few samples showing a chloride-sulfate composition (Anzà et al., 1989; Giammanco et al., 1996, 1998; Aiuppa et al., 2000, 2004). The high HCO₃⁻ concentrations have been interpreted as due to: 1) water-rock interaction processes involving the basalts that constitute most of the volcanic rocks of Mt. Etna and 2) dissolution of magmatic CO₂ into the aquifers (Anzà et al., 1989; Allard et al., 1997; Aiuppa et al., 2004). The latter process is ubiquitous on Mt. Etna, but it is enhanced in the most fractured and seismically active zones of the volcano (i.e., the SW and the E flanks), where the leakage of magmatic gas is the highest, and it seems to mask any evolution of water chemistry from recharge to discharge areas (Aiuppa et al., 2004, and literature therein cited). Many processes have been invoked to interpret the source of the Cl-SO₄²⁻ waters: i) input of gases other than CO₂ (e.g., SO₂, HCl), mostly through plume-polluted rain that constitutes the local water recharge (Liotta et al., 2016; Federico et al., 2017); ii) interaction between groundwater and thermal brines rising from the sedimentary basement (Aiuppa et al., 2004; Giammanco et al., 2007); iii) interaction between groundwater and evaporitic deposits rich in gypsum and chlorides, which are present under Etna's volcanic products (Lentini, 1982); iv) pollution by NH₄-Ca-SO₄ wastewaters produced by agricultural activities, the latter process particularly apparent in the eastern flank of the volcano (Aiuppa et al., 2003, 2004). Lastly, it must be mentioned that due to overexploitation, in recent years Mt. Etna ground water displayed a general steady increase in its total dissolved solids content because of progressive extraction of water from deeper levels of the aquifer, characterized by slower circulation and higher salinity (D'Alessandro et al., 2011).

4. Eruptive activity of Mt. Etna during June 2000–December 2006

From January to August 2000 Mt. Etna was very active, producing 66 short-lived paroxysmal episodes from the South-East Crater (SEC; Lanzafame et al., 2003), that is the most active of the four summit craters of this volcano. Activity resumed in January 2001 with slow lava effusion at the NNE base of the SEC, which increased in rate until early May. From May 9 to July 13 the SEC produced again numerous short-lived paroxysmal episodes with lava fountaining (Behncke and Neri, 2003a, 2003b; Behncke et al., 2005). On July 17, 2001 a flank eruption began, erupting lava from two distinct magmatic feeder systems: one linked to the central conduit, and the other from an eccentric conduit (Behncke and Neri, 2003a; Acocella and Neri, 2003). Unusually strong explosive activity at the eccentric vents indicated particularly high volatile contents in the emitted magma (Andronico et al., 2005).

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