



Source and mobility of minor and trace elements in a volcanic aquifer system: Mt. Vulture (southern Italy)

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ABSTRACT

In this paper we provide a geochemical investigation on 34 groundwater samples in the Mt. Vulture volcanic aquifer representing one of the most important groundwater resources of the southern Italy pumped for drinking and irrigation supply. The present study includes the first data on the abundance and mobility of minor and trace elements and the thermodynamic considerations on water–rock interaction processes in order to evaluate the conditions of alkali basalt weathering by waters enriched in magma-derived CO₂. The results highlight the occurrence of two hydrofacies: bicarbonate alkaline–earth and alkaline waters deriving from low-temperature leaching of volcanic rocks of Mt. Vulture, and bicarbonate–sulfate–alkaline waters (high-salinity waters) related to prolonged water circulation in alkali and feldspathoids-rich pyroclastic layers interbedded with clay deposits. The Al-normalized relative mobility (RM) of metals in Vulture's aquifer varies over a wide range ($10^{-1} < RM < 10^4$), confirming that the basalt weathering is not a congruent and isochemical process. Chemical equilibrium studies show that the bicarbonate alkaline–earth and alkaline waters, having a short interaction with silicate minerals, plot very close to the kaolinite–smectite stability boundary, whereas the high-salinity waters fall in the stability field of smectite and muscovite because of prolonged interaction with alkali and feldspathoids-rich pyroclastic layers. Overall, for the bicarbonate alkaline–earth and alkaline waters, the release of toxic metals in solutions is related to the spatial variation of host-rock geochemistry, the high-salinity waters, collected near urban areas, show values higher than legal limits for Ni and As, likely as a consequence of anthropogenic contribution.

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1. Introduction

Trace elements are highly sensitive indices of human impact from local to global scale. Pollution impact studies require knowledge of the natural background concentrations and knowledge of pollutant behavior. Water quality investigations have clearly been a stimulus for measurement of toxic trace elements in order to understand their

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behavior in natural systems. From a more fundamental point of view, it is crucial to understand the behavior of trace elements in geological processes, in particular during chemical weathering and transport by waters. The presence of trace elements in groundwater is an important issue because it affects possible uses of water (e.g. Drever, 1997; Langmuir, 1996). It is known that groundwater flowing in unpolluted watersheds attains its salt content mainly from leaching of the host rocks. Therefore, the extent to which natural waters reproduce the composition of the dissolving rocks depends upon several factors, both physical (temperature, residence time, flow rate) and chemical (namely, the weathering of rock-forming minerals, the precipitation of sparingly soluble secondary minerals, the presence of reactive gas species, such as CO₂, and particular aquatic chemistry of the elements). Since the mobility of the trace elements is mainly governed by the physico-chemical condition (i.e., pH, temperature, redox conditions; Stumm and Morgan, 1996) and also by the interaction with others components (i.e., organic matter, pedogenic processes with podzolic soils formation; Angelone et al., 1990; Edmunds and Smedley, 1996), the wide concentration range for a given element can be explained by a variable extent of these factors within the studied aquifer system. As a consequence the transition from oxidant and/or neutral environments, characterizing the shallow part of the investigated aquifer where meteoric recharge occurs, to reducing environments, taking place at the deeper part of the aquifer, is related to the variability of the water–rock interaction processes and also to the greater dissolved gas species within the flowing groundwaters. Furthermore, the redox alteration can play locally an important role in determining the partition between the aqueous solution and solid phases, taking into account also that some elements can be found with different oxidation states. Among rocks of volcanic origin, basalts are particularly sensitive to chemical erosion (Berner and Berner, 1996). Different approaches have been developed to evaluate the geochemical mobility of elements during volcanic rock weathering. A first approach is to study the mineralogy and chemistry of weathering profiles (Carr et al., 1980; Chesworth et al., 1981; Nesbitt and Wilson, 1992; White, 1983), inferring an element mobility from a group of rocks characterized by an increasing degree of alteration. This approach is not easily generalized, since the primary minerals are characterized by different dissolution rates and the elements are partitioned between solution and secondary minerals in response to the aqueous chemistry. Therefore, immobile and mobile elements are commonly distinguished. An alternative approach is to study the aqueous fluid geochemistry. The relative mobility of the elements is computed from their water/rock concentration ratio, normalized to immobile element. This kind of approach was applied in several contexts such as in the French Massif Central (Meybeck, 1986), in basaltic volcanic islands (Berner and Berner, 1996; Gaillardet et al., 1995; Stallard, 1995) and in basalt weathering and groundwater transport at Mt. Etna volcano (Aiuppa et al., 2000a). In this context of volcanic activity, acidic and reduced gases are released to the surface and may produce extreme conditions in which weathering processes and the resulting geochemical mobility of major and trace elements are deeply modified. With the present study we report a detailed investigation of the geochemical processes controlling the major, minor and trace element distributions in the groundwaters hosted by Mt. Vulture volcanic aquifer. As the Mt. Vulture area represents one of the most important hydrogeological basin of southern Italy, the main purpose of this work is: (i) to report the chemical concentrations of many trace and minor elements that have never before been examined in Mt. Vulture groundwaters, (ii) to define the chemical–physical processes affecting the geochemical mobility of trace metals in such aqueous system, and (iii) to evaluate the water–rock interaction processes.

2. Geology and hydrology of the Mt. Vulture volcanic aquifer

Mt. Vulture is a Pleistocene composite volcano that is located to the easternmost border of the Apennine compressive front (Fig. 1), at the

western margin of the Apulia foreland about 100 km east of the Campanian Province. The origin of Mt. Vulture is related to the intersection between the NW–SE (Apenninic) and the NE–SW (Ofanto–Sele) fault systems. Radiometric dating indicates that volcanism occurred from 714 to 480 ka, with renewal of activity at 132 ka (Brocchini et al., 1994; Melluso et al., 1996; Serri et al., 2001). The older volcanic products are characterized by lavas and pyroclastics ranging in composition from basanites and foidites to phonolites, with several intermediate rock types (Beccaluva et al., 2002; De Fino et al., 1982; 1986). The most recent eruptions of Mt. Vulture produced several WNW–ESE aligned monogenic cones (Giannandrea et al., 2004). These volcanics have a carbonatitic–melilititic composition (Stoppa and Principe, 1997), although the primary origin for the carbonate fraction is widely debated by D’Orazio et al. (2007; 2008) and Stoppa et al. (2008). Some products erupted during this period contain ultramafic xenoliths and megacrysts of clinopyroxene, amphibole, olivine and phlogopite. The xenolith association includes residual spinel lherzolites and harzburgites, as well as cumulate wehrlites and dunites (Jones et al., 2000). Recently, Schiattarella et al. (2005) have grouped the whole volcanic units, previously studied by La Volpe and Principe (1991), in two distinct Supersynthems: 1) Monte Vulture, the oldest one and 2) Monticchio, the younger one. The basic volcanic rocks have been affected by hydrothermal alteration that has mobilized iron and enriched the rocks with volatile elements. The volcanic products lie over Pleistocene gravel and clay, in subhorizontal layers that cover the intensely deformed Flysch sediments of Miocene age. The hydrogeological basin of Mt. Vulture represents one of the most important groundwater resources of the southern Italy. The volcano hosts numerous springs and wells emerging from the highest to the lowest elevations around the cone. The volcanic aquifer is constituted of highly permeable units such as, coarse textured pyroclastic level fissured lava flows, fissured tuff, and low permeability units such as fine textured pyroclastic levels, compact tuff and paleosols. The more permeable units of these different lithological units constitute small aquifers which are partly interconnected but mainly separated by less permeable units. The porous and fractured lava flows show a hydraulic conductivity of about $k \sim 10^{-1}$ cm/s, while the tuff and the incoherent pyroclastic deposits, permeable only for porosity, is less than or equal to $k \sim 10^{-3}$ cm/s. In the fluvio-lacustrine gravel deposits have a value of about $k \sim 10^{-2}$ cm/s (Spilotro et al., 2005). Different conceptual hydrogeological models have been proposed for the Mt. Vulture aquifer. Celico and Summa (2004) hypothesize two independent hydrogeological basins: the first (Monticchio–Atella) that is located in the S–SE sector between the most important faults of the volcano (the Grigi Valley–Fosso del Corbo fault) to the north, and an unnamed fault in the south (Schiattarella et al., 2005); and the other (Melfi–Barile) that is situated in the northeast area, characterized by radial drainage. Recently, Spilotro et al. (2005; 2006) suggested a new conceptual hydrogeological model in which the surface drainage network constitutes the natural limits of the water catchments, where the pseudo-tectonic structure of Grigi Valley–Fosso del Corbo fault is the only drainage axis widely affecting preferential groundwater flow and no evidence for the presence of the southern fault as a subordinate drainage axis was observed. Finally, Parisi et al. (2011) showed an hydrogeochemical, hydraulic and integrated isotopic study that provides a better definition of the recharge and discharge patterns of the Mt. Vulture volcanic aquifer system. By means of this study, the W–NW area, at the highest elevations, was found to be the main recharge area close to the drainage axis (Grigi Valley–Fosso del Corbo fault), widely affecting the preferential groundwater flow, where several operating wells of companies and private owners are located. The flowing groundwater moves along radial flowpaths toward the lowest elevations in the S–SE and S–SE sectors but with differences in length and depth.

3. Water sampling and analytical methods

A total of 34 sampling sites from springs and operating wells of several companies and private individuals, used for irrigation and

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