

HYDROGEOCHEMICAL TRACING OF THE GROUNDWATER FLOW PATHWAYS IN THE MOUNT VULTURE VOLCANIC AQUIFER SYSTEM (BASILICATA, SOUTHERN ITALY)

SERENA PARISI

Dipartimento di Scienze Geologiche, Università della Basilicata, Via dell'Ateneo Lucano 10, 85100 Potenza

Stable isotope techniques, hydrogeochemical analysis and hydraulic data are employed to define the hydrogeochemical conditions and the main recharge processes occurring within the complex volcanic aquifer system of the Mount Vulture, representing one of the most important hydrogeological basin of southern Italy.

The present research given special emphasis of water geochemical mapping, statistical data analysis, water-rock interaction processes, geochemical modeling and water quality. Knowledge of the local hydrogeological setting (Celico & Summa, 2004; Spilotro *et al.*, 2006) and isotopic rain water composition (Paternoster *et al.*, 2008) were the starting point for a detailed hydrogeochemical and isotopic study. It has been demonstrate how natural tracers, such as $\delta^{18}\text{O}$, δD and $\delta^{34}\text{S}(\text{SO}_4)$, combined with hydrogeological (hydraulic properties of the aquifer host rocks) and hydrochemical data (groundwater physico-chemical parameters) can be used to get a refined understanding of groundwater flow pathways and to better understand the hydrogeochemical origin and evolution of the investigated groundwater.

The present methodology as demonstrated by the example of the Mount Vulture basin, constitutes a powerful tool to better define a conceptual hydrogeological model for complex hydrogeological systems. The improved understanding of groundwater flow patterns, especially within such complex volcanic and/or sedimentary environments is fundamental for the preservation and sustainable management of water resources.

The current knowledge obtained by hydrogeological studies indicates a very complex hydrogeological setting of the Mount Vulture basin. Mount Vulture is an isolated cone (1320 m a.s.l.) shaped strato-volcano of Quaternary age along the external edge of the Apennine Chain, close to the western portion of the *Bradanic foredeep* on the northeastern sector of the Basilicata region (Italy) (Fig. 1).

Volcanic activity took place from middle Pleistocene to the Upper Pleistocene, starting at about 0.73 Ma ago and ending at about 0.13 Ma ago (Buettner *et al.*, 2006). The Mount Vulture volcanic products consist of 700 m of dominantly undersaturated silica pyroclastic deposits and subordinate lava flows (Serri *et al.*, 2001; Giannandrea *et al.*, 2004). The peripheral sectors are characterized by the presence of the fluvio-lacustrine deposits from Pliocene to lower Pleistocene age, with intercalations of pyroclastic layers (Giannandrea *et al.*, 2006; Fig. 1). The oldest pre-Miocene bedrock units consist of deep-sea sediments belonging to units ranging from early Triassic to lower-middle Miocene (Boenzi *et al.*, 1987; Principe & Giannandrea 2002). Beneath the Meso-Cenozoic substratum units, radiolarians and limestones of the Apulian platform are found to a depth of about 5 km (La Volpe *et al.*, 1984).

The aquifer core is mainly constituted by pyroclastic and subordinated lava flows layers, with different permeable terms which locally give rise to distinct overlaid interconnected aquifers. Mount Vulture hydro-mineral basin shows an elevation difference of almost 1000 meters. These altitude

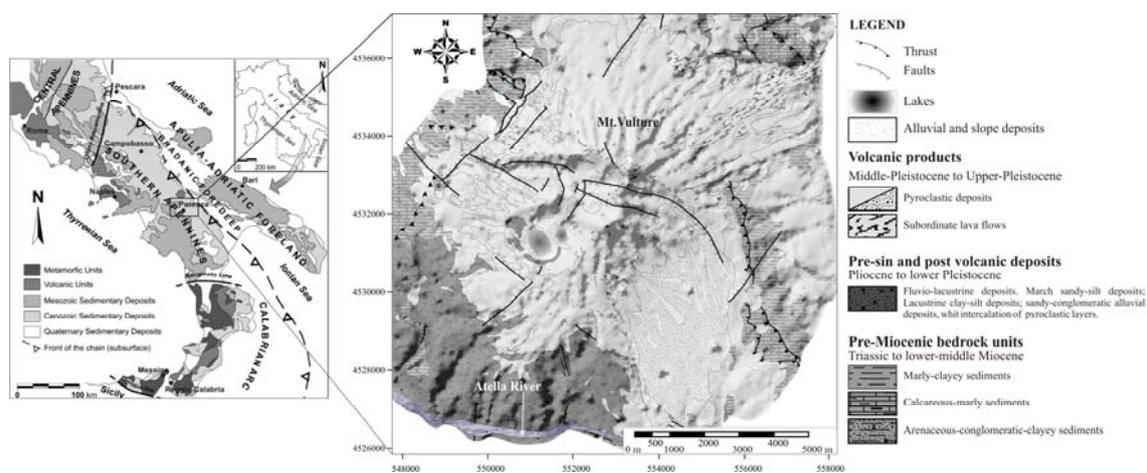


Fig. 1 - On the left, sketch geological map of the central-southern Italy (from Bonardi *et al.*, 2009). On the right geological setting of Mount Vulture area (base geological map by Giannandrea *et al.*, 2004, modified). The geological map is provided in Gauss-Boaga, Zone Est coordinates, using the Roma Datum of 1940.

gradients lead to significant temperature and precipitation gradients and provide excellent conditions for the application of water stable isotopes.

The research project reports analytical data for 48 groundwater samples taken at different altitudes ranging from 352 to 1000 m a.s.l., among springs and drilled wells used for irrigation and drinking water supply. Water samples were collected during three sampling campaigns, from June 2007 to June 2008, for stable isotope studies ($\delta^{18}\text{O}$, δD) major constituents (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^- and SiO_2), minor and trace elements (V, Al, As, B, Br, Cu, Fe, Mn, Ni, Pb, Rb, Se, Sn, Sr and Zn) analysis. To better constrain the origin of Mount Vulture groundwaters and water-rock interaction processes controlling their chemistry a total of 21 water samples were selected, during the first sampling, for investigation of sulfur isotopic composition of dissolved sulfate ($\delta^{34}\text{S}$ (SO_4)). Measurements for *pH*, temperature, electric conductivity, *Eh* and discharge value were determined while sampling by a high resolution multiparametric probe. Alkalinity was determined in the field by titration with HCl (0.1 M). Major ion determinations were carried out in the Gaudianello Spa laboratory on un-acidified (F^- , Cl^- , NO_3^- and SO_4^{2-}) and acidified (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) water samples with separate aliquots by ion chromatography (Dionex CX-100). All samples exhibited imbalances lower than 5%. Acidified and filtered water aliquots were analyzed for minor and trace elements by ICP-OES except for B and SiO_2 which were determined by molecular spectrophotometry Xion 500, at the Gaudianello Spa laboratories. Stable isotope (δD and $\delta^{18}\text{O}$) were measured at the Alfred Wegener Institute in Potsdam using a common equilibration techniques with a Finnigan MAT Delta-S mass spectrometer equipped with two equilibration units for the online determination of hydrogen and oxygen isotopic composition (Meyer *et al.*, 2000). The sulfur isotope composition in aqueous sulfate was performed at the Nevada Stable Isotope Laboratory.

Groundwater temperatures ranged from 10°C, cold water, to 19.8°C, slightly thermal waters. (Nathanson *et al.*, 2003). The analyzed groundwaters samples have variable *pH* values and redox state (*Eh*), which range from slightly acidic to neutral (*pH* 5.4 - 7.5) and from slightly reduced to oxidized ($-36 \text{ mV} < Eh < +185 \text{ mV}$), respectively; probably reflecting differences in circulation paths, water

discharge and in residence times within the aquifer. The increase in water acidity is principally due to the dissolution of CO₂, which is the principal gas of magmatic origin. The high dissolved CO₂ contents in the groundwater of the volcanic aquifer, are probably due to the ongoing active magmatic mantle outgassing (Caracausi *et al.*, 2009; Paternoster 2005). The mean electrical conductivity values vary between 0.19 mS cm⁻¹ and 17.97 mS cm⁻¹. The mean TDS values of the individual sites range from 208 to 18,000 mg L⁻¹. Vulture's groundwater generally displays a chemical composition from bicarbonate alkaline-earth to sulphate-bicarbonate alkaline. The principal dissolved anion bicarbonate resulting from the reaction of dissolved CO₂ to form HCO₃ (Stumm & Morgan, 1996). Contrary to soil CO₂ in the unsaturated zone, the deep CO₂ is directly injected in the saturated zone, with a high initial CO₂ content, and therefore a low initial pH value. The low-pH water is very aggressive towards the host volcanic rocks, leaching their more soluble components. As a consequence, major ion constituents are progressively brought into solution, pH increases to the typical values measured in Vulture groundwaters, and CO₂ is partially converted to bicarbonate. The dissolution of the host rocks depends on contact time between the rocks and water. Deep CO₂ produces a fast and extensive enlargement of the fracture systems in the host rocks principally in the saturated zone and it may create a specific organization of flow patterns in the saturated zone (Annunziatellis *et al.*, 2008, and references therein).

Most of the water samples show high concentrations of Na⁺, K⁺, and Ca²⁺. The Na-excess found in a few analyzed water samples may be due to the hydrolysis of Na-silicates and also to the exchange of Ca²⁺ for Na⁺, on the surfaces of clay-minerals (Na-smectite). This indicates an intensive water-rock interaction process, in agreement with results of Paternoster *et al.* (2009).

A few springs with highest TDS values and a sulphate-bicarbonate alkaline composition showed higher mineralization, with elevated contents of SO₄²⁻, Na⁺, Cl⁻, and dissolved CO₂. As reported by Paternoster *et al.* (2009), the δ³⁴S (SO₄²⁻) isotopic compositions of groundwaters with the highest concentration of SO₄²⁻, displays sulphur isotopic values similar to those measured by Marini *et al.* (1994) in the magmas, supporting a main origin from the leaching of mineral weathering products such as feldspathoids, belonging to the sodalite group found in the volcanic host rocks. This similarity of sulphur isotopic values is due to the longer residence times of groundwater within the host rocks, representing the local extension of the volcanic aquifer where fluvio-lacustrine sediments with intercalated pyroclastic layers could contain entrapped brackish groundwaters. Along the flow path, from the mountainous area to the lower altitudes, the groundwaters have highest content of dissolved ions. In the west-northwest sector the groundwaters are characterized by lower mineralization values showing a bicarbonate alkaline-earth composition as a consequence of the interaction between volcanic rocks and groundwaters of meteoric origin, flowing at high-mid altitudes, characterized by flowpaths with shorter residence times. At the lower altitudes in south-southeastern sectors, the springs near the base of the aquifer and occasionally in contact with the fluvio-lacustrine deposits, with intercalations of pyroclastic layers, are characterized as sulphate-bicarbonate alkaline composition with high salinity. This hydrogeochemistry variation is due to the deeper and lengthy flow pathways with longer groundwater residence time. The hydrogeochemical differences between waters at the highest altitudes, which probably are the main recharge areas, and the samples taken at the lowest altitudes are consistent with the conceptual hydrogeological model previously described, from the core to the boundaries of the aquifer, indicating an important role played by aquifer radial symmetry.

The average values of the isotopic content in groundwater during the present study ranged from -8‰ to -10.2 ‰ for δ¹⁸O and from -53‰ to -65‰ for δD. No significant seasonal variations in the

isotopic ratios are present. However, a few water points located in the west-northwest sector, shown an isotopic compositions, falling slightly outside of the analytical error. These springs show a high degassing rate (bubbling gases by Paternoster, 2005) which could results in a shift of the oxygen-18 isotopic composition towards negative values in the liquid phase. Under these conditions it is possible to assume that the hydrological features of the aquifer make the water bodies relatively homogeneous, which, as a consequence, are not influenced by the seasonal variation of the meteoric recharge. It was observed that most of the groundwater samples follow the LMWL, in particular fitting the WLMWL (Paternoster *et al.*, 2008) which defines more precisely the meteoric end-member in the local hydrological cycle, providing that the investigated groundwaters are meteoric in origin. Secondary processes that occur after the falling of rain, such as evaporation and evapotranspiration, do not appear to change the isotope values of groundwater significantly, so that isotope ratios can be used as tracers.

The recharge elevation was calculated using the equation relating altitudes and isotope ratios of precipitation with isotopic gradients of Mount Vulture area (-0.17‰ and -0.84‰ for $\delta^{18}\text{O}/100$ and $\delta\text{D}/100\text{m}$, respectively) reported by Paternoster *et al.* (2008). Recharge altitudes of sampling points were calculated resolving “equation’s Paternoster: $\delta^{18}\text{O}\text{‰} = -0.0017 \text{ H} - 7.28$ ”, for altitudes (H) defining the corresponding $\delta^{18}\text{O}$ values of the sampling points. The real elevations represent to the spring altitudes and the water table elevations above sea level of the shallow and deep wells.

The integrated study of the rainwater isotopic composition and groundwater hydrogeochemical and isotopic characteristics over one complete hydrological cycle, highlights the following points:

- the groundwater geochemical characteristics found in the investigated aquifer, shown heterogeneity among different sectors. The two identified hydrogeochemical water types reflect the water-interaction processes taking place within the host aquifer rocks. The water-rock interaction process is mainly affected from uprising of CO_2 -rich gases which cause an increase of the water acidity promoting basalt weathering with an enrichment in certain chemical species (*i.e.*, Na^+ , Ca^{2+} , SO_4^{2-}) and a high total carbon content.

- the hydrogeochemical data and the $\delta^{34}\text{S}$ (SO_4^{2-}) isotope analysis shown the occurrence of two distinct water types. The first water is Na-rich and derived from low-temperature leaching of volcanic rocks of Mount Vulture. The second water type, including the high-salinity waters, displays a bicarbonate-sulfate-alkaline composition and high values of dissolved CO_2 (Paternoster, 2005) possibly related to their circulation in fluvio-lacustrine sandy-clayey conglomerate deposits, with intercalations of feldspathoid-rich pyroclastic layers. These volcanic deposits are confined by impermeable layers, and may contain entrapped ancient saline waters. This could explain the very high content of sulfate, sodium, chlorine and other minor chemical species in these waters. The sulfate- $\delta^{34}\text{S}$ values from +4.0‰ to +8.6‰ are similar to those measured by Marini *et al.* (1994) in the local magmas (+4.0‰ to +8.5‰), supporting a dominant origin from leaching of the volcanic rocks. The highest sulfate- $\delta^{34}\text{S}$ values (+9.3‰ to +10.4‰) are due either to the interaction with pyroclastic layers principally rich in feldspathoids belonging to the sodalite group or slight modification of groundwater sulfate $\delta^{34}\text{S}$ by sulfate reduction in parts of the aquifer contaminated by agriculture activity. Finally, the study of sulfur isotopic composition highlighted that an evaporite source, such as Upper Triassic and/or Messinian evaporite deposits, is not required to explain the high TDS of some Mount Vulture groundwaters, as suggested by Barbieri *et al.* (2005).

Using the isotopic gradient (0.17‰ for $\delta^{18}\text{O}/100\text{m}$) three main sectors within the Mount Vulture hydrogeological system can be distinguished: the west-northwestern sector, which constitutes the main

recharge area of the studied aquifer, showing an isotopic signature similar to rain water. The slightly seasonal fluctuations of few water points, characterized by the occurrence of high degassing rate (bubbling gases), could result in a shift of the oxygen-18 isotopic composition towards negative values in the liquid phase. These slightly seasonal fluctuations in the $\delta^{18}\text{O}$ values are probably due also to the shorter groundwater flowpath of the west-northwest sector confirming the hydrogeological setting of the considered areas. The recharge contributing to groundwater appears to be derived from a mean elevation ranging from 700 m a.s.l. to 1100 m a.s.l., close to the real elevation of the springs and well water tables; the second and third sectors represent the main discharge areas toward the south-southeast and north-northeast areas respectively. No evidence for seasonal variation of the groundwater isotopic composition was observed. The mean elevation of the recharge area of the deeper groundwater is about 1100 m a.s.l. which is a hydrologically reasonable value for the Mount Vulture area. This implies that the deeper waters that are recharged at higher elevations have longer flowpaths. This confirms that, in the Mount Vulture region most flow in the region conforms to the radial pattern, but the highest to the lowest altitudes there are some irregularities in the flow. Based on this study, the south-southeast and north-northeast sectors represent the principal outflowing areas where the deeper groundwater discharge derives from about 5 km far away.

This investigation improved the previously conceptual hydrogeological model proposed by Spilotro *et al.* (2006), whereby, at large scale, was defined the radial streamlines of the groundwater flowpath. The present hydrogeochemical, hydraulic and integrated isotopic study allowed to better define the recharge and discharge patterns of the Mount Vulture volcanic aquifer system. By means of this study the west-northwest area, at the highest altitudes, was found to be the main recharge area close to drainage axis (Grigi Valley - Fosso del Corbo fault) widely affecting the preferential groundwater flow. The flowing groundwater moves along radial flowpaths toward the lowest altitudes, at the south-southeastern and north-northeastern sectors but with differences in length and depth. This fact is supported also by the groundwater hydrogeochemical differences from the highest to the lowest altitudes of the volcanic aquifer.

The complex hydrogeochemical characteristics of groundwater at a volcanic site has resulted in the development of stable isotopes and chemical tracers tools for investigating recharge processes and groundwater flow pathways of these hydrogeological systems. Given the importance of the studied area, the present investigation can be useful to the studies of volcanic aquifer comparable to the Mount Vulture one. The results of the present investigation are an example of how the environmental isotope tracers can be used to get recharge and discharge patterns in a complicated hydrogeological context like the volcanic aquifer ones. The presented work allows us to refine knowledge that can contribute to policies of conservation and management, also with time based criteria, of the sensitive recharge area that should be protected for drinking water supply and water quality. Therefore, this study may be used as an aid in regional planning to establish groundwater management rules.

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