

Geochemical model of the phreatic system of Vulcano (Aeolian Islands, Italy)

G.Cortecci

Dipartimento di Scienze della Terra e Geologico-Ambientali, Università di Bologna, Italy

T.Boschetti

Dipartimento di Scienze della Terra, Università di Parma, Italy

ABSTRACT: Most thermal and cold waters from shallow wells in the Vulcano Porto plain were sampled in June 1995, June 1996 and January-February 1997, and analysed chemically for major ions and isotopically for $\delta^{18}\text{O}$, $\delta^2\text{H}$ of water and $\delta^{34}\text{S}$ of dissolved sulfate. A few water samples were also analysed for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. When combined with relevant chemical and isotopic data on rocks, mineralizations and fumarolic gases, the hydrogeochemical features from this study lead to a conceptual model by which the groundwaters at Vulcano are ultimately mixtures, in quite variable proportions, of a meteoric component and a hydrothermal-magmatic component. Minor contributions of seawater may be restricted to wells close to shoreline.

1 INTRODUCTION

Vulcano Island (Aeolian archipelago in the southern Tyrrhenian Sea) is the site of an active volcano, its cone being situated at a very short distance from the Vulcano Porto plain where the studied groundwaters come from (Fig. 1). Present-day activity is manifested by fumaroles at the La Fossa crater (high temperature gases, with CO_2 , SO_2 , H_2S and HCl as the major components in the dry fraction) and at the Baia di Levante beach (low temperature gases, with CO_2 and H_2S as the major components in the dry fraction). The last eruption took place in 1888-1890. Volcanic rock deposits range from leucitic tephrites to highly potassic trachytes, with some occurrences of alkali-rhyolitic obsidian.

Many studies on the chemical and isotopic compositions of the phreatic system of Vulcano were carried out during the 1980s and 1990s, and several genetic models were proposed. Controversial is the involvement of seawater in feeding the hydrologic system. In the present work, the chemical and isotopic data acquired from water samples collected during 1995 to 1997 from most of the existing wells in the Vulcano Porto plain are presented and a genetic model drawn out. The data include the sulfur isotopic composition of sulfate in solution. This parameter is of particular relevance for assessing the role of seawater, its value in seawater sulfate being largely different from those of sulfur species in both fumarolic gases and volcanic

rocks at Vulcano (Cortecci et al. 1996). Preliminary results from the 1995 sampling were published in Cortecci et al. (2001).



Figure 1. Map of Vulcano Porto area and location of studied well waters. The latter are subdivided in three groups as defined later on in the text. The dashed lines represent main structural lineaments (Gabbianelli et al. 1991).

2 SAMPLING AND ANALYSES

Water from twenty-two to thirty-seven wells was sampled in June 1995, June 1996 and January-February 1997, and analysed for the major chemical composition and the hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) isotopic composition of water and the sulfur isotopic composition ($\delta^{34}\text{S}$) of dissolved sulfate. Some water samples were also analysed for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Sampling and analytical procedures and accuracies of measurements are reported in Cortecchi et al. (2001).

3 RESULTS AND DISCUSSION

3.1 Chemical results

Most of the studied groundwaters are rich in alkalis (especially sodium) and low in magnesium and calcium. The major anions ratio is shown in Figure 2, where all samples lie outside the field expected for mature (equilibrated) geothermal waters as defined by Giggenbach (1988).

In the diagram, the majority of samples fall within a ternary mixing triangle, with endmembers represented by bicarbonate-meteoric water (W19; Scrivio well) and local volcanic (hydrothermal-magmatic) water, the latter with extreme sulfate to chloride ratios as calculated from the chemical data reported by Chiodini et al. (1995) for hydrothermal and magmatic components of crater fumaroles.

In the calculation, sulfate in volcanic waters is assumed to be derived exclusively from complete disproportionation of the fumarolic SO_2 . Named phreatic-volcanic waters (14 to 41°C) are distinct with respect to the sulfate-chloride waters which are

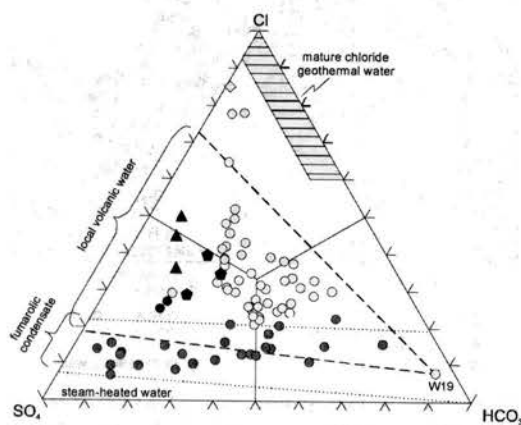


Figure 2. Triangular diagram for major anions (in ppm). For explanation of depicted fields, see text. Symbols as in Figure 1.

low in bicarbonate and have higher temperatures in the range 44 to 74°C. Steam-heated waters (21 to 57°C) are depleted in chloride, and fall within the mixing polygon delimited by bicarbonate-rich meteoric-phreatic waters and crater-type fumarolic sulfate-rich condensates, the sulfate in these latter deriving from complete oxidation of fumarolic SO_2 and H_2S . Seawater inputs may be concluded for water samples close to the seawater point. These samples refer to the Scarcella W20 well (June 1996) and the Camping Togo-Togo W34 well (June 1996), both situated close to the shoreline.

The relative concentrations of major cations are shown in Figure 3. Most samples plot close to the isochemical rock dissolution line relevant for Vulcano, thus supporting the importance of this process in determining the chemical composition of groundwaters. Waters appear to be immature, with W19 and W0 samples being the most immature and the most mature, respectively. The application of the Giggenbach's (1988) K-Mg thermometer to the W0 water samples provides an equilibrium temperature of $190 \pm 4^\circ\text{C}$. The Na-K-Mg composition of the geothermal water may lie on the intersection between the K-Mg isothermal line at 190°C , provided by the W0 well, and the K-Na isothermal line at 250°C estimated for the geothermal reservoir that probably exists beneath Vulcano (Cortecchi et al. 2001 and reference therein).

In the diagram of Figure 4, main features are: (1) steam-heated waters are shifted towards higher K to Na ratios and lower Mg to Ca ratios, as expected from dissolution of advanced argillic alteration facies depleted in Mg relative to Ca, coupled with

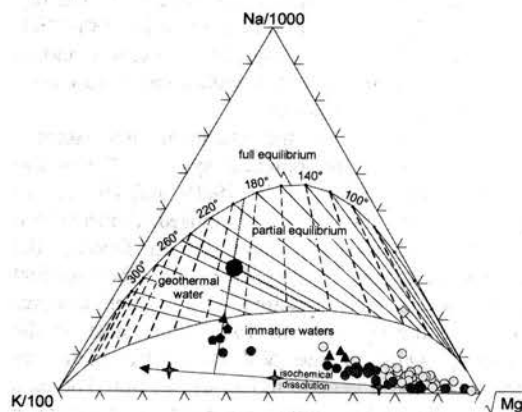


Figure 3. Trilinear diagram for cations (in ppm). Their relative concentration values are compared with the nonequilibrium to equilibrium fields as discussed by Giggenbach (1988). Stars identify the amount of dissolved volcanic rock from Vulcano. Other symbols as Figure 1.

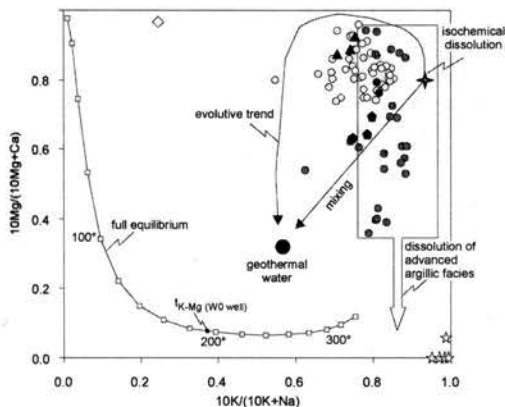


Figure 4. Mg-Ca-K-Na plot for studied waters. Symbols as in Figure 1. Average composition of volcanic rocks from the La Fossa cone and the Lentia complex (big star) is from De Astis et al. (1997). Small stars refer to advanced argillic alteration products from the volcanic cone (Fulignati et al. 1999).

leaching and/or cation exchange involving Na-minerals, and (2) water W0 may be a mixture of geothermal water with a groundwater chemically evolved after isochemical dissolution of volcanic rocks. This interpretation may be also applied to W2 and W4 waters.

3.2 Isotopic results

Inspection of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data in Figure 5 shows that most waters can be interpreted as almost purely meteoric. Exceptions are some steam-heated waters enriched in heavy isotopes probably by steam separation at 140°C (e.g. Bolognesi & D'Amore 1993), and the sulfate-chloride waters, which arrange along a mixing line between a meteoric component and a geothermal component. Interestingly, well water W2 may be interpreted as geothermal water mixed with a hypothetical largely shifted steam-heated water.

Strontium isotope analyses were performed on the hot waters W0 and W2, and the cold waters W20, W21 and W34. Following the approach of Pennisi et al. (2000), the $^{87}\text{Sr}/^{86}\text{Sr}$ signature was used in combination with the $\delta^{18}\text{O}$ signature, in order to evaluate the isotopic effects on water due to interaction with rocks at 250°C (Fig. 6). The main results are (1) the geothermal reservoir at depth is actually fed by fumarolic condensate after interaction with rocks, rather than exchanged meteoric water, and (2) seawater may be appreciably present in well waters W20 and W34.

The sulfur isotopic composition of well waters are shown in Figure 7, along with relevant data on S-bearing sources at Vulcano. The water $\delta^{34}\text{S}$ values

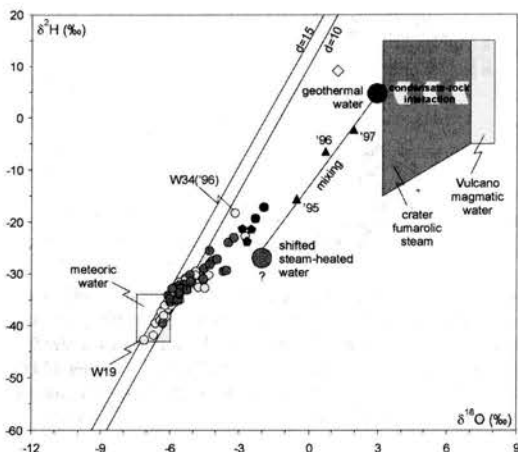


Figure 5. $\delta^2\text{H}$ vs $\delta^{18}\text{O}$ plot for well waters, compared to the isotopic fields of other relevant water types at Vulcano. Data sources are: Bolognesi & D'Amore (1993) for magmatic water, Capasso et al. (1999) for fumaroles, Cortecchi et al. (2001), and references therein) for geothermal water, and meteoric precipitation. Symbols as in Figure 1, with the exception of open square relative to local rainwaters.

are within the range observed for gaseous species in the crater fumaroles, thus suggesting a mostly volcanic origin of sulfur via hydrolysis of $\text{SO}_2 \pm$ oxidation of H_2S . Waters W20 and W34 may be ternary mixtures, composed by groundwater, seawater and occasionally diluting meteoric water.

4 CONCLUSIONS

The chemical and isotopic data series acquired on the shallow groundwaters of Vulcano during 1995 to 1997 highlight a conceptual genetic model by which

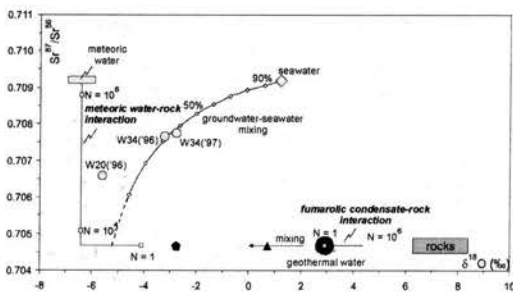


Figure 6. The strontium and oxygen isotopic composition of selected well waters, compared to the isotopic effects related to water-rock interaction at 250°C and for different water to rock ratios (N; by volume). Symbols as in Figure 1. Data on La Fossa and Lentia rocks are from De Astis et al. (1997). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70918 in seawater and rainwater was used in the computation.

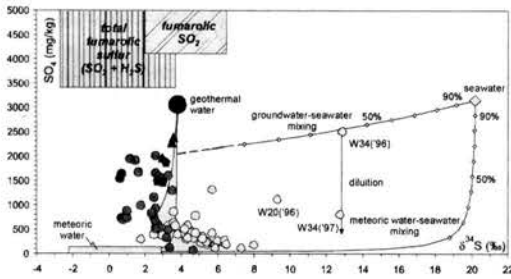


Figure 7. Chemical and sulfur isotopic compositions of sulfate ions, compared with a number of mixing models involving geothermal water, steam-heated water, local meteoric water (on average 25 mg/l SO_4^{2-} and $\delta^{34}\text{S} = +0.2\text{‰}$) and seawater (3050 mg/l SO_4^{2-} and $\delta^{34}\text{S} = +20.2\text{‰}$). Data on geothermal water are from Cortecchi et al. (2001).

waters are ultimately mixtures, in quite variable proportions, of a meteoric component and an hydrothermal-magmatic component. The latter is largely prevailing in the hottest groundwaters of sulfate-chloride type. The contributions of seawater are very minor and restricted to wells close to the shoreline.

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