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Isotopic ratio and concentration of sulfur in the undersaturated alkaline magmas of Vulture Volcano (Italy)

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Abstract Both the $\delta^{34}S$ value and the total S content of products from Vulture Volcano, Italy are mainly controlled by the separation of S gases, predominantly SO_2, from high f_{O_2} magmas containing S predominantly as SO_4^{2-}. The addition of evaporites to such magmas appears to be a relatively uncommon and limited phenomenon. The total S content of the most primitive product of Vulture Volcano (5600 mg/kg) is very high. The high $\delta^{34}S$ value of 4‰ indicates an origin through the partial melting of a mantle containing high S, enriched in ^{34}S of unknown origin.

Key words Sulphur isotopes · alkaline magmas magma degassing · magma contamination · Vulture Volcano, Italy

Introduction

Vulture is the most southern of the Quaternary potassic volcanoes of Italy (Fig. 1).

One of the peculiarities of Vulture volcanic rocks is the enrichment in some volatile elements, in particular S, which reflects the ubiquity and abundance of haüyne. Based on the hypothesis of Rittmann (1933), Hieke Merlin (1967) proposed that not only the high contents of volatile elements in Vulture volcanic rocks, but also the evolution from trachytes to foidites, could be explained through the massive assimilation of carbonate–evaporite rocks of Late Triassic age, present underneath Vulture and neighbouring areas. The thickness of this sequence exceeds 1.7 km, as testified by the findings of the Foresta Umbra-1 deep well (Martinis and Pieri 1964), sited in the nearby Gargano peninsula (FU in Fig. 1). However, as pointed out by Marinelli (1975), the massive assimilation of carbonate–evaporite rocks cannot explain the evolution from trachytes to leucite-bearing rocks because 'it seems difficult to imagine that a similar [quite viscous] magma may blend perfectly together the products of an assimilation reac-

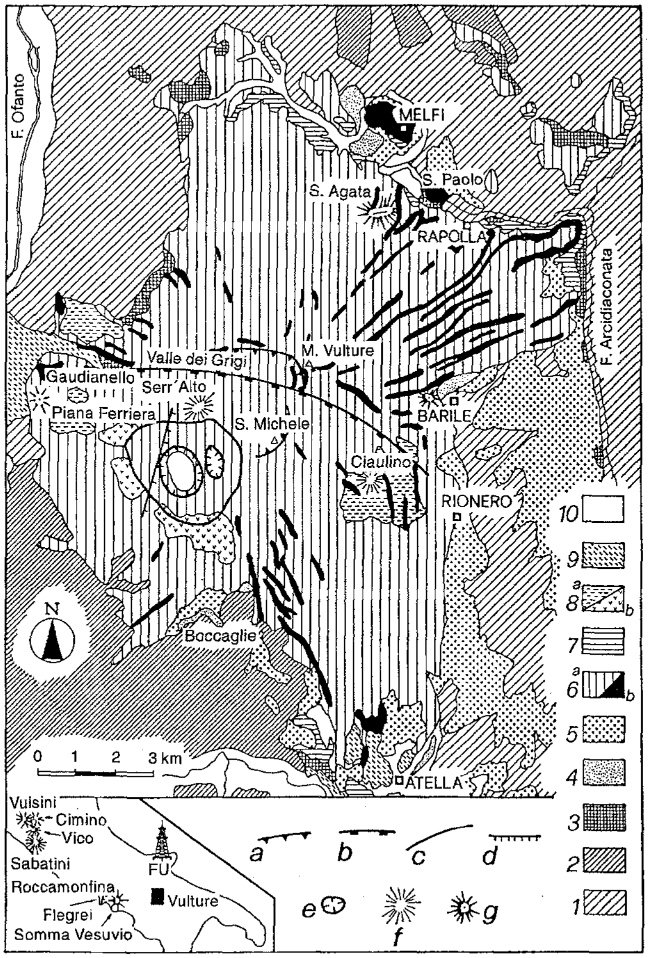

Fig. 1 Simplified geological map of area around Vulture Volcano

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tion, in short periods of time and in a restricted space'. The occurrence of assimilation processes was also ruled out by Vollmer (1975) because it should have caused significant changes in the $^{87}Sr/^{86}Sr$ ratio of Vulture volcanic rocks, which are not seen. Nevertheless, simple mixing models between Vulture magmas and Triassic carbonate–evaporite rocks indicate that the $^{87}Sr/^{86}Sr$ ratio does not allow us to detect assimilation processes if the fraction of assimilated sedimentary rocks is lower than 0.10–0.15. In fact, Sr isotopes are poor indicators of this process, as both the Sr content and Sr isotope ratio of volcanic rocks (Sr from 1000 to 3000 mg/kg; $^{87}Sr/^{86}Sr$ from 0.7056 to 0.7063; Vollmer 1975, 1976; Hawkesworth and Vollmer 1979; Paiotti 1993) are comparable with those of Triassic evaporites (Sr 2860 ± 699 mg/kg; average $^{87}Sr/^{86}Sr$ 0.7080; Barbieri et al. 1976; Paiotti 1993; Barbieri, personal communication), as already pointed out by Marinelli (1975).

To clarify this matter, we analyzed the isotope ratio and concentration of S in Vulture products which were representative of the whole volcanic history. Sulfur isotope ratios of several anhydrite samples from the Foresta Umbra-1 deep well were also analyzed to identify the presumed contaminant.

Sample preparation and analysis

Volcanic rocks and anhydrite samples were prepared for chemical and isotope analyses by two different procedures.

Each ground sample of volcanic products was mixed with an alkaline mixture (Na_2CO_3 plus KNO_3; Na_2CO_3/KNO_3 ratio 8:1) and fused in a Pt crucible at 950° C. After cooling, the sample was transferred into a china cup, treated with 1 M HCl and dried. The residue was moistened with concentrated HCl and dried again. After cooling, 50 ml of 1 M HCl were added to the residue to dissolve all the chemical species, except silica. After filtration, part of the filtrate was used to determine total S, as SO_4^{2-}, by ion chromatography. Ammonia was added to another part of the filtrate, after heating to 60° C, to precipitate iron as $Fe(OH)_3$. Elimination of iron by filtration was needed to preclude the formation of $Fe–SO_4$ ion pairs and loss of SO_4^{2-}. Barium chloride was added to the new filtrate, after acidification with HCl and heating, to precipitate SO_4^{2-} ions as $BaSO_4$. This was filtered, washed and heated in a Pt crucible.

A few samples of haüyna were also prepared for isotopic analysis, following the same procedure as that for volcanic rocks.

Ground samples of anhydrite were dissolved in deionized water at room temperature. The insoluble residue was eliminated through filtration, whereas the filtrate was acidified with HCl and heated. Sulfate ions were precipitated as $BaSO_4$.

Samples of $BaSO_4$ were analyzed for $\delta^{34}S$ relative to CDT, following standard procedures (not detailed here), by the Institute of Geological and Nuclear Sciences, New Zealand and Krueger Enterprises, USA.

Results are given in Table 1. The overall reproducibility of the isotope data is close to 0.2‰, as indicated by the replicate preparation and analysis of two samples.

Table 1 Analytical data

Sample No.*	Sample location	$\delta^{34}S$ (hauyna) (‰ vs CDT)	$\delta^{34}S$ (whole rock) (‰ vs CDT)	S (mg/kg)	Nb (mg/kg)
Vulture volcanic rocks					
VUT251	Monticchio Lakes		+ 4.0	5626	49
VUT235	Gaudianello	+ 8.7	+ 4.3	2195	71
VU1936	M. SS. Constantinopoli	+10.6	+ 6.1	2257	71
VU1907	NATO Base	+ 8.9	+ 7.8	1251	77
VUT215	Molara	+ 9.2	+ 6.6	2167	87
VUT252	C. Sportivo di Rionero		+ 6.8	1908	99
VUT253	Piano di Croce		+ 8.5	5667	112
VUT69	Prete della Scimmia		+ 4.6	2163	119
VU1680/b	Masseria Boccaglie		+ 4.7	4598	153
VU1523	Melfi		+ 7.6	9021	157
Upper Triassic anhydrites					
FU3323	Foresta Umbra 1 well		+15.3		
FU3491-2	Foresta Umbra 1 well		+14.8		
FU4232	Foresta Umbra 1 well		+14.6		
FU4315	Foresta Umbra 1 well		+14.2		
FU4536-7	Foresta Umbra 1 well		+15.1		
FU4720-1	Foresta Umbra 1 well		+13.7		
FU4831	Foresta Umbra 1 well		+13.5		

* Numbers of FU samples refer to the depth below ground level

Discussion of results

The $\delta^{34}S$ values of anhydrite samples range from +13.5 to +15.3‰, with an average of +14.4‰. These results are slightly lower than the $\delta^{34}S$ values previously obtained for Upper Triassic evaporites (Burano Formation) of the Italian Adriatic area (range from +15 to +17.4‰, average +16.1‰; Cortecci et al. 1981), but within the range for Europe, from +10.6 to +18.4‰, and in good agreement with the European average of +14.6‰ (Nielsen et al. 1991).

The isotope composition of S in haüyna of the Vulture volcanic rocks is systematically higher than in corresponding whole rock samples. Therefore, haüyne does not seem to be a valuable indicator of the sulfur isotopic characteristics in the melt, at least as far as Vulture is concerned. The S in haüyne could represent the composition of SO_4^{2-} in the melt and the lower $\delta^{34}S$ of the whole rock indicates the presence of another, isotopically lighter, S species, such as a sulfide (Giggenbach, personal communication). However, this cannot be clarified on the basis of the available data. Only whole rock data will be considered in the following discussion. To interpret these data it is necessary to consider the redox conditions of Vulture magmas.

Redox conditions and distribution of S species in Vulture magmas

The redox conditions of magmatic systems are conventionally described by f_{O_2}, although oxygen is not involved in the oxidation–reduction reactions occurring in magmatic environments (Giggenbach 1987) and the actual redox buffer is generally the Fe^{2+}–Fe^{3+} couple. In this paper, f_{O_2} will be used to describe the redox conditions for conventional reasons.

Sulfur is present in magmas both as 'ionic' species, S^{2-} and SO_4^{2-}, and as gaseous species, H_2S and SO_2 (e.g. Sakai et al. 1982). Both the SO_4^{2-}/S^{2-} ratio and the H_2S/SO_2 ratio are essentially controlled by redox conditions, whereas temperature, pressure and melt composition have only minor effects on S speciation (Wallace and Carmichael 1992). Owing to the lack of thermodynamic data on 'ionic' S species, it is not possible to build a comprehensive thermodynamic model involving S^{2-}, SO_4^{2-}, H_2S and SO_2 together. The SO_4^{2-}/S^{2-} and H_2S/SO_2 ratios are, therefore, evaluated separately as a function of f_{O_2}.

The composition of the magnetite–ulvöspinel solid solutions in Vulture volcanic rocks (Dell'Anna and Di Pierro 1974) represents a possible method of estimating their redox conditions, referring to the calibration data of Buddington and Lindsley (1964). On the basis of the composition of all magnetite–ulvöspinel solid solutions from Vulture volcanic rocks, the following relationship is obtained:

$$\log f_{O_2} = 15.063 - 29953/T \qquad (1)$$

where T is the temperature in K. Compositional variations of magnetite–ulvöspinel solid solutions imply deviations in f_{O_2} lower by 0.6 log units.

Based on the available data on S^{2-}–SO_4^{2-} equilibrium, Wallace and Carmichael (1992) proposed that a log linear relationship links the sulfate fraction in total 'ionic' S, $SO_4^{2-}/\Sigma S^{\pm}$, and the relative f_{O_2}, choosing the Ni–NiO couple as reference buffer (NNO; Huebner and Sato 1970). Replacing the NNO buffer, this expression can be rewritten as follows:

$$\log[SO_4^{2-}/\Sigma S^{\pm}] = 0.48 \log f_{O_2} - 5.20 + 11986/T \qquad (2)$$

Substituting Equation (1) in Equation (2), the following relationship is obtained:

$$\log[SO_4^{2-}/\Sigma S^{\pm}] = 2.03 - 2391/T \qquad (3)$$

This expression, which describes the $SO_4^{2-}/\Sigma S^{\pm}$ ratio of Vulture volcanic rocks as a function of temperature, is valid for temperatures below 905° C. Above this threshold the $SO_4^{2-}/\Sigma S^{\pm}$ ratio obviously approaches unity. Although the $SO_4^{2-}/\Sigma S^{\pm}$ ratio decreases to 0.80 at 850° C and 0.63 at 800° C, it is evident that SO_4^{2-} is by far the dominant 'ionic' S species in Vulture magmas. This conclusion is consistent with the presence of haüyne in Vulture volcanic rocks, which indicates that f_{O_2} is very high and that all S is oxidized (Carmichael and Ghiorso 1986).

The $X_{SO_2}/(X_{SO_2}+X_{H_2S})$ ratio of Vulture magmas can be evaluated referring to the reaction

$$H_2S + \tfrac{3}{2}O_2 = SO_2 + H_2O \qquad (4)$$

Its equilibrium constant depends on temperature according to the following equation:

$$\log(X_{SO_2}/X_{H_2S}) = 18.609 - \log P_{H_2O} - 17553/T \qquad (5)$$

This is obtained using the thermodynamic data reported by Giggenbach (1987) and assuming that f_{O_2} is defined by Equation (1). With $P_{H_2O} = P_{tot}$, values of the $X_{SO_2}/(X_{SO_2}+X_{H_2S})$ ratio of Vulture magmas at different T, P conditions can be calculated (Table 2). Table 2 shows that SO_2 is by far the prevailing gaseous species in Vulture magmas over a wide range of temperature and pressure, whereas H_2S may be present only at $T < 900°$ C and high pressure, conditions inconsistent

Table 2 Calculated values of the $X_{SO_2}/(X_{SO_2}+X_{H_2S})$ratio of Vulture magmas at different temperature/depth conditions

Pressure (bar)	Temperature (° C)					
	800	900	1000	1100	1200	1300
30	0.856	0.993	1.000	1.000	1.000	1.000
100	0.642	0.978	0.998	1.000	1.000	1.000
300	0.374	0.937	0.996	1.000	1.000	1.000
1000	0.152	0.816	0.985	0.999	0.999	1.000
3000	0.056	0.597	0.957	0.996	0.999	1.000

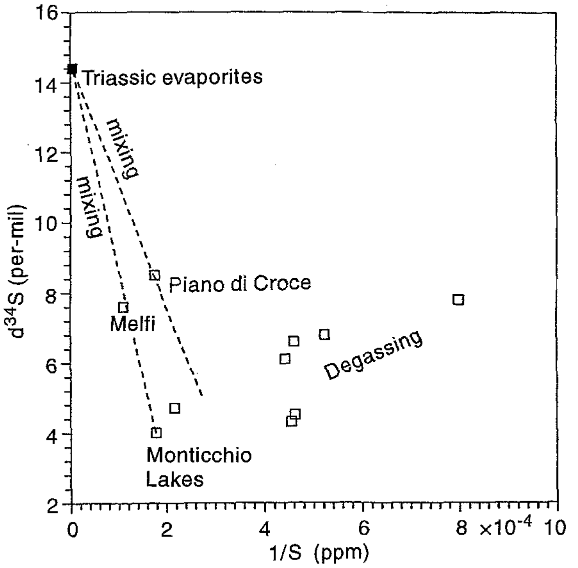

Fig. 2 $\delta^{34}S$ versus 1/S plot. The open squares indicate Vulture volcanic rocks

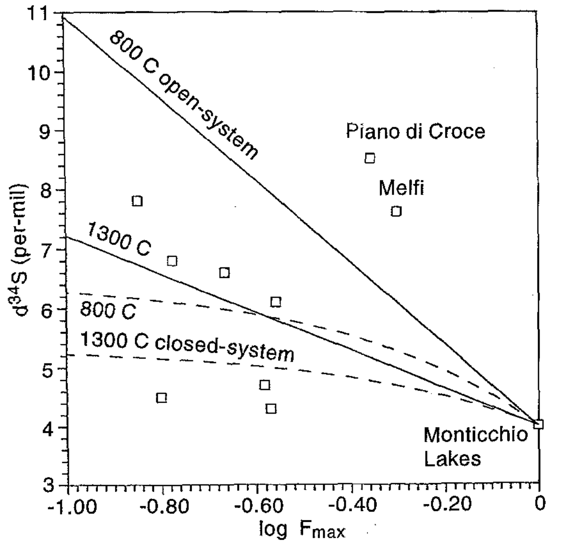

Fig. 3 Plot of $\delta^{34}S$ versus log F_{max}, where F_{max} represents the maximum fraction of S remaining in the magma, under the hypothesis of minimum degassing. The straight lines and curves represent the effect of theoretical isothermal degassing according to the open and closed system models, respectively. The open squares indicate Vulture volcanic rocks

with the chemical and mineralogical characteristics of such magmas.

Influence of degassing on the isotopic ratio and concentration of total S in Vulture magmas

Inspection of the $\delta^{34}S$ versus 1/S plot for Vulture volcanic rocks (Fig. 2) shows that: (i) most samples make up a trend characterized by increasing $\delta^{34}S$ values and decreasing S content; (ii) the most primitive products, the hydromagmatic surges of Monticchio lakes, occupy an end-member position; and (iii) only the Melfi haüynophyre and the Piano di Croce haüynitite lava plot far from it.

As shown earlier, because of the high f_{O_2} of Vulture magmas, SO_2 and SO_4^{2-} are the main gaseous and 'ionic' species, respectively. In such a system, the trend in $\delta^{34}S$ versus 1/S plot (Fig. 2) is likely to be due largely to the separation of SO_2 from its parent magma, as expected by Sakai et al. (1982) and observed by Faure et al. (1984).

To substantiate this interpretation, the theoretical changes in the $\delta^{34}S$ value of Vulture magmas, caused by isothermal degassing at temperatures of 800–1300° C, have been calculated (Valley 1986), for open and closed system degassing, according to

$$\delta^{34}S_f = \delta^{34}S_i + 1000(F^{\alpha-1} - 1) \qquad (6)$$

$$\delta^{34}S_f = \delta^{34}S_i + (F - 1)\,1000 \ln \alpha \qquad (7)$$

The indices f and i indicate the final and initial states, respectively, F is the fraction of S remaining in the magma and α is the equilibrium isotope fractionation factor between SO_2 and SO_4^{2-} in the magma. The temperature dependence of α is described by Taylor (1986)

$$1000 \ln \alpha = -0.42(10^3/T)^3 - 1.933(10^3/T)^2 - 0.105(10^3/T) - 0.41 \qquad (8)$$

where T is the temperature in K. Although this equation holds in the 600–1000° C range, it has been extrapolated up to 1300° C. Because there is no such thing as an undegassed, subaerially erupted volcanic product, there is no way to know the true S content and $\delta^{34}S_i$ of the parent magma. However, assuming the most primitive Vulture sample, hydromagmatic surges of Monticchio lakes, to be representative of the 'initial' state, we can calculate the maximum fraction of S remaining in the magma, F_{max}, under the hypothesis of minimum degassing, by means of

$$F_{max} = (S_s Nb_i)/(S_i Nb_s) \qquad (9)$$

The symbols S_s and Nb_s indicate the concentrations of total S and Nb in each sample, whereas S_i and Nb_i refer to the contents in the most primitive product. This equation accounts for the increase in S content due to fractional crystallization, based on the hypothesis that no S-bearing solid phase is precipitated. Niobium is used as a reference element owing to its incompatible behaviour in Vulture magmas, as shown by De Fino et al. (1986).

In Fig. 3, $\delta^{34}S$ values are plotted versus log F_{max}, together with theoretical lines of isothermal degassing, for both open and closed systems. Although natural processes are obviously more complex than this simple model, Fig. 3 shows that most samples are consistent with the occurrence of minimum SO_2 degassing, excluding the Melfi haüynophyre and the Piano di Croce haüynititic lava.

Influence of contamination by evaporites on the isotopic ratio and concentration of total S in Vulture magmas

As shown in the preceding sections, both the peculiar $\delta^{34}S$ value and high S content of the Melfi haüynophyre and the Piano di Croce haüynititic lava are not explained by minimum SO_2 degassing. Assuming these two magmas to be contaminated by Late Triassic anhydrites, their S content before contamination is constrained, in Fig. 2, by the intersection of each mixing line (which are straight lines in this plot, e.g. Faure 1986) with the degassing trend. The S content in the uncontaminated magmas is about 6160 mg/kg for Melfi and 3580 mg/kg for Piano di Croce. The fraction of anhydrite, f_a, involved in this mixing process is given by the following relationship:

$$f_a = (S_c - S_u)/(S_a - S_u) \qquad (10)$$

where S_a, S_u and S_c are the concentrations of S in the anhydrite (235000 mg/kg) and in the uncontaminated and contaminated magma, respectively. The value of f_a is 0.0125 for Melfi and 0.009 for Piano di Croce.

These have to be considered as maximum values. In fact, accepting the magma of Monticchio lakes to already be considerably degassed, true F values could be substantially lower than F_{max} (Fig. 3) . If so, the chemical and isotopic characteristics of the Melfi haüynophyre and the Piano di Croce haüynititic lava could also be explained by the loss of SO_2, at comparatively low temperatures, without any addition of anhydrite.

Comparison with other volcanic areas

The most primitive product of Vulture volcano exhibits a $\delta^{34}S$ value (+4.0‰) much higher than primordial mantle (about 0‰; e.g. Faure 1986; Nielsen et al. 1991). Although the high $\delta^{34}S$ values of primitive Vulture magmas may be explained in terms of the partial melting of a mantle enriched in ^{34}S, it is impossible, at present, to establish with certainty the cause(s) of such an enrichment.

The S content of the most primitive product of Vulture volcano (5600 mg/kg) is comparable with that shown by: (1) the high f_{O_2} trachyandesitic magma of the 1982 eruptions of El Chichón volcano, Mexico, which contained an estimated pre-eruptive S content of 10400 mg/kg (Varekamp et al. 1984) or perhaps lower (2000–4000 mg/kg; Carmichael and Ghiorso 1986); and (2) the high f_{O_2} undersaturated alkaline magmas of the Eifel, Germany (up to 2000 mg/kg; Bogaard et al. 1990).

It is very unlikely that the magma of Monticchio lakes assimilated evaporitic S during its ascent. In fact, the presence of pyrope-rich garnet and forsteritic olivine indicates a direct mantle provenance, and some depositional textures (such as the cored pelletal lapilli) suggest that this magma ascended in a very short time (Principe and Stoppa, unpublished data). The high S content of this magma probably reflects the presence of high f_{O_2} conditions – that is, a high Fe^{3+}–Fe^{2+} ratio in the liquid generated through partial melting. In fact, the available data on basic magmas indicate that, under strongly oxidizing conditions, S^{2-} is suppressed and S solubility is not limited by saturation with respect to a solid sulfide phase or by the separation of an immiscibile Fe–S–O liquid phase. Furthermore, the absence of SO_4^{2-}-bearing phases in the most primitive Vulture magmas suggests that S solubility is not limited by saturation with respect to such phases. These magmas become saturated with respect to haüyne (rather than anhydrite, probably due to silica deficiency) only on cooling and fractional crystallization.

Conclusions

Both the isotopic ratio and concentration of total S in Vulture volcanic rocks reflect mainly the separation of gases, whose prevailing S species is SO_2, from high f_{O_2} magmas, whose dominant S species is SO_4^{2-}. The addition of evaporites to such magmas is a relatively uncommon and limited process. In fact, it possibly affected only the Melfi haüynophyre and the Piano di Croce haüynitite lava, among the 10 samples considered here, and the fraction of admixed evaporites is <0.01 for both.

The high $\delta^{34}S$ value of the most primitive product of Vulture magmas suggests that it originated through partial melting of a mantle enriched in ^{34}S. It is not possible, at present, to establish with certainty the cause(s) of such an enrichment.

The high S content of primary Vulture melts implies a high Fe^{3+}–Fe^{2+} ratio in the liquid generated by partial melting in the upper mantle.

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