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COMPOSITION OF BULK PRECIPITATION
ON ISLAND OF VULCANO
(AEOLIAN I. ITALY)

SUMMARY

The chemistry of rainwaters collected monthly, over two-year period (1987-1989), in two rain-gauges installed at Vulcano Porto (0 m a.s.l.) and Vulcano Piano (400 m a.s.l.) is discussed. Total contents (TDS) and type of dissolved salts in precipitation on Vulcano vary significantly during the year.

The average isotope composition of rainfall on Vulcano is: $\delta D = -32\text{‰}$ and $\delta^{18}O = -6.4\text{‰}$. Rainfall on Vulcano is essentially influenced by sea-salts and particulate material of continental origin. The result is a chemism sometimes typical of chloride-sulphate alkaline waters and sometimes of bicarbonate-earth alkaline waters. However, sulphate ions are important components of rainfall. Although a significant quantity of sulphate comes from sea-salt aerosol, part of this ion is probably of volcanic origin.

RIASSUNTO

Composizione delle precipitazioni nell'Isola di Vulcano (Eolie, Italia). Nel presente lavoro viene discusso il chimismo dei campioni di acqua piovana, prelevati mensilmente in un periodo di due anni (1987-1989), da due pluviometri posti a Vulcano Porto (0 m s.l.m.) and Vulcano Piano (400 m s.l.m.). Il contenuto totale ed il tipo di sali disciolti (TDS) nelle precipitazioni dell'isola di Vulcano variano in maniera significativa durante l'anno. La composizione isotopica media delle piogge sull'isola di Vulcano risulta: $\delta D = -32\text{‰}$ and $\delta^{18}O = -6.4\text{‰}$. Le precipitazioni atmosferiche a Vulcano risentono essenzialmente del contributo di sali marini e del materiale particolato di origine continentale. Si osserva così un chimismo a volte tipico di acque cloro-solfato alcaline e a volte tipico di acque bicarbonato alcalino-terrose. Lo ione solfato è comunque un importante componente delle precipitazioni. Sebbene sia stato osservato che una significativa quantità di solfato provenga dal contributo dei sali marini, parte di essa è di probabile origine vulcanica.

INTRODUCTION

The potential impact of volcanic gases on the land has become a topic of considerable interest. Most scientific works regarding the island of Vulcano have generally dealt with its past and recent volcanic activity, mainly aiming at acquiring information useful for volcanic surveillance. However, if research on the risk of toxic gas emissions are excluded (BADALAMENTI *et al.*, 1984, 1988, 1991; BRONDI & DALL'AGLIO 1991), it turns out that there are very few works regarding the influence of an active volcano on some environmental aspects. Information on both isotopes and composition of rainfall of Vulcano may resolve some questions on the origin and chemistry of the groundwaters and fumarole vapor of the island. Isotope composition of precipitations at Vulcano has already been discussed in CAPASSO *et al.* (1992). This report tries to fill partly the void, at least as regards the chemical composition of rainfall on the island, on the possible influence of gas emissions on rain chemistry. The chemistry of rainwater samples, collected monthly in two rain-gauges installed at Vulcano Porto (0 m a.s.l.) and Vulcano Piano (400 m a.s.l.) is here discussed. For comparisons, a third rain-gauge was installed at Castoreale Terme on the tyrrhenian coast of Sicily, in front of Vulcano island, at an altitude of 400 m. Since the gauges were constantly uncovered to the air, the type of atmospheric deposition collected turned out to have two main components: wet and dry precipitations. Data on single rainfalls were not recorded, since initially samples were collected for the sole purpose of determining their isotope compositions. For the same reason pH at the moment of sampling was not measured either. Single samples, therefore, refer to monthly precipitation on the island and represent a composite sample of both wet and dry precipitations.

METHODS

Precipitation was measured monthly over the two-year period 1987-1989, using a bulk sampler equipped with a funnel, both in polyethylene. To avoid evaporation and consequent isotope fractionation, paraffin oil was added to the sampler. Sampler for chemical analyses were first filtered to separate them from the paraffin oil and solid residues. Laboratory determinations were carried out by means of atomic absorption spectrophotometry and ion chromatography. Bicarbonate ions were determined by titration with HCl, with double checking of the equivalence point using methyl orange and potentiometric methods. Table 1 shows the analytical data.

Tab. 1

Chemical composition of the analyzed water samples. Ion concentrations are expressed in meq/l; millimeters of rain are reported under the mill column.

NAME	DATE	Na	K	Ca	Mg	HCO ₃	Cl	SO ₄	F	NO ₃	mill	
CASTROREALE	Mar. 87	0.195	0.016	0.270	0.107	0.240	0.208	0.121	n.d.	0.005	159	
	May. 87	0.282	0.048	0.362	0.135	0.370	0.264	0.230	0.009	0.003	35	
	Jun. 87	0.126	0.052	0.506	0.104	0.230	0.195	0.348	0.015	n.d.	21	
	Jul. 87	0.190	0.065	0.815	0.328	0.740	0.166	0.334	0.010	0.004	14	
	Sep. 87	0.112	0.048	0.432	0.058	0.400	0.110	0.172	0.006	0.003	45	
	Oct. 87	0.039	0.006	0.160	0.048	0.048	0.180	0.043	0.066	0.005	0.003	116
	Nov. 87	0.214	0.038	0.201	0.109	0.270	0.212	0.092	0.010	0.006	0.006	122
	Dec. 87	0.360	0.033	0.219	0.116	0.200	0.384	0.121	0.022	0.004	0.004	155
	Jan. 88	0.151	0.013	0.101	0.048	0.120	0.126	0.064	n.d.	0.014	0.014	155
	Feb. 88	0.443	0.026	0.197	0.129	0.180	0.522	0.114	0.003	0.022	0.022	174
	Mar. 88	0.356	0.017	0.149	0.098	0.160	0.391	0.116	n.d.	0.029	0.029	126
	Apr. 88	0.258	0.038	0.417	0.153	0.360	0.263	0.265	0.014	0.004	0.004	35
	Sep. 88	0.112	0.016	0.241	0.078	0.300	0.104	0.066	n.d.	0.003	0.003	90
	Oct. 88	0.131	0.031	0.223	0.084	0.260	0.148	0.088	0.005	0.004	0.004	90
	Nov. 88	0.116	0.021	0.182	0.073	0.210	0.124	0.066	n.d.	0.002	0.002	116
	Dec. 88	0.282	0.042	0.175	0.111	0.260	0.314	0.102	n.d.	n.d.	n.d.	133
	Jan. 89	0.136	0.029	0.204	0.106	0.250	0.136	0.088	0.005	0.045	0.045	60
	Mar. 89	0.219	0.030	0.678	0.266	0.580	0.257	0.304	0.012	n.d.	n.d.	33
	PORTO	Mar. 87	0.751	0.028	0.330	0.219	0.200	0.952	0.183	0.021	0.004	78
		Apr. 87	0.518	0.045	0.236	0.167	0.200	0.584	0.208	0.019	0.068	36
May. 87		0.774	0.047	0.316	0.205	0.190	0.763	0.290	0.024	0.066	22	
Jun. 87		0.288	0.028	0.316	0.138	0.120	0.335	0.250	0.028	0.042	27	
Jul. 87		0.681	0.042	0.503	0.229	0.150	0.824	0.523	0.031	0.004	12	
Sep. 87		0.518	0.051	0.572	0.031	0.270	0.966	0.391	0.014	0.052	38	
Oct. 87		0.252	0.018	0.130	0.202	0.100	0.333	0.151	0.016	0.010	0.010	79
Nov. 87		0.448	0.028	0.264	0.139	0.240	0.473	0.170	0.009	0.016	0.016	44
Dec. 87		0.914	0.040	0.305	0.234	0.220	1.060	0.238	0.012	0.015	0.015	133
Jan. 88		0.312	0.021	0.919	0.046	0.850	0.299	0.118	0.011	0.014	0.014	85
Feb. 88		2.190	0.053	0.257	0.501	0.180	2.660	0.337	0.010	0.032	0.032	83
Mar. 88		1.660	0.038	0.184	0.304	0.140	1.550	0.287	n.d.	0.053	0.053	99
Apr. 88		1.100	0.045	0.712	0.445	0.100	1.690	0.722	0.033	0.015	0.015	30
May. 88		0.395	0.021	0.345	0.143	0.190	0.452	0.248	0.011	0.040	0.040	56
Sep. 88		0.658	0.032	0.532	0.190	0.200	0.745	0.517	0.016	n.d.	n.d.	62
Oct. 88		0.205	0.021	0.169	0.100	0.160	0.198	0.119	n.d.	0.020	0.020	70
Nov. 88		0.371	0.027	0.206	0.143	0.260	0.500	0.169	n.d.	0.029	0.029	105
Dec. 88		0.728	0.026	0.195	0.190	0.200	0.845	0.171	n.d.	0.042	0.042	115
Jan. 89		0.335	0.250	0.180	0.128	0.100	0.412	0.210	0.014	0.068	0.068	21
Mar. 89		2.220	0.084	0.594	0.602	0.200	2.720	0.687	0.022	n.d.	n.d.	25
PIANO	Mar. 87	0.434	0.048	0.174	0.112	0.100	0.504	0.130	0.070	0.030	94	
	Apr. 87	0.376	0.031	0.168	0.112	0.120	0.367	0.166	0.028	0.051	40	
	May. 87	0.446	0.051	0.276	0.156	0.450	0.469	0.181	0.110	0.065	34	
	Jun. 87	0.249	0.028	0.305	0.080	0.100	0.274	0.204	0.020	0.061	32	
	Jul. 87	0.399	0.032	0.339	0.183	0.290	0.469	0.297	0.029	0.005	13	
	Sep. 87	0.214	0.035	0.679	0.199	0.690	0.285	0.183	0.230	0.005	0.005	52
	Oct. 87	0.279	0.017	0.131	0.072	0.280	0.183	0.083	0.007	0.015	0.015	132
	Nov. 87	0.283	0.021	0.160	0.090	0.150	0.290	0.103	0.008	0.002	0.002	76
	Dec. 87	0.457	0.028	0.203	0.139	0.220	0.484	0.124	0.007	0.011	0.011	150
	Jan. 88	0.214	0.016	0.105	0.074	0.100	0.251	0.080	0.007	0.024	0.024	93
	Feb. 88	0.897	0.023	0.149	0.200	0.100	0.933	0.164	n.d.	0.034	0.034	96
	Mar. 88	0.700	0.025	0.138	0.167	0.170	0.738	0.176	n.d.	0.045	0.045	140
	Apr. 88	0.750	0.032	0.486	0.240	0.580	0.660	0.284	0.002	0.002	0.002	37
	May. 88	0.318	0.015	0.251	0.092	0.220	0.263	0.150	0.004	0.038	0.038	74
Sep. 88	0.376	0.021	0.432	0.132	0.190	0.456	0.285	0.023	0.070	0.070	89	

PLUVIOMETRY AND SEASONAL VARIATIONS

Fig. 1 compares the millimeters of rain collected monthly in the three gauges. Total rainfalls were 724 mm (1987) and 666 mm (1988) on Vulcano, and 996 and 681 mm at Castoreale. The average values observed at Vulcano result greater than the 522 mm reported by CICALA (1987).

Rainfall on Vulcano is greatly influenced by season. The rainiest months were March, October and December in 1987, and March, November and December in 1988.

Total contents (TDS) and type of dissolved salts in precipitation vary significantly during the year. Average weighted values were 100, 55 and 41 mg/l for the gauges at Vulcano Porto, Vulcano Piano and Castoreale respectively. Sodium and chloride are the more abundant constituents of rainfall, with a cation sequence $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$ and an anion sequence in which sulphates prevail over bicarbonates at Vulcano Porto, while the opposite occurs at Vulcano Piano. Na and Cl concentrations decrease as a function of distance from the sea. Concentrations of sulphate and nitrate ions are higher in the less abundant precipitations which occur in summer. From the isotope viewpoint, the waters examined showed typical seasonal variations (Fig. 2), values ranging from a minimum of -65‰ to a maximum of 0.0‰ on hydrogen and from a minimum of -9.3‰ to a maximum of -10‰ on oxygen. Average weighted values in the two-year observation period were: $\delta\text{D} = -34\text{‰}$ and $\delta^{18}\text{O} = -6\text{‰}$ for Vulcano Porto and $\delta\text{D} = -30\text{‰}$ and $\delta^{18}\text{O} = -6.8\text{‰}$ for Vulcano Piano.

DISCUSSION

The average weighted chemical composition of the Vulcano and Castoreale rainfall is shown in Fig. 3. The average weighted value of the concentration of each single ion (C_j) was calculated by means of the equation:

$$C_j = \frac{\sum_i C_{ji} Q_i}{\sum_i Q_i} \quad i = 1, 2, 4$$

where C_j is the concentration of the j -th ion in the i -th sample and Q_i is the rainfall in millimetres. Geochemical analyses of water samples can be examined using the Langelier diagram which shows relationships between the principal anions and cations expressed as percentages of the total of each in meq/l. From a classificative viewpoint (Fig. 4), almost all precipitations on Vulcano plot in the field of chloride-sulphate alkaline waters. There are only three exceptions, falling in the bicarbonate-earth alkaline field and referring to samples from Vulcano Piano (September 1987) and Vulcano Porto (October 1987

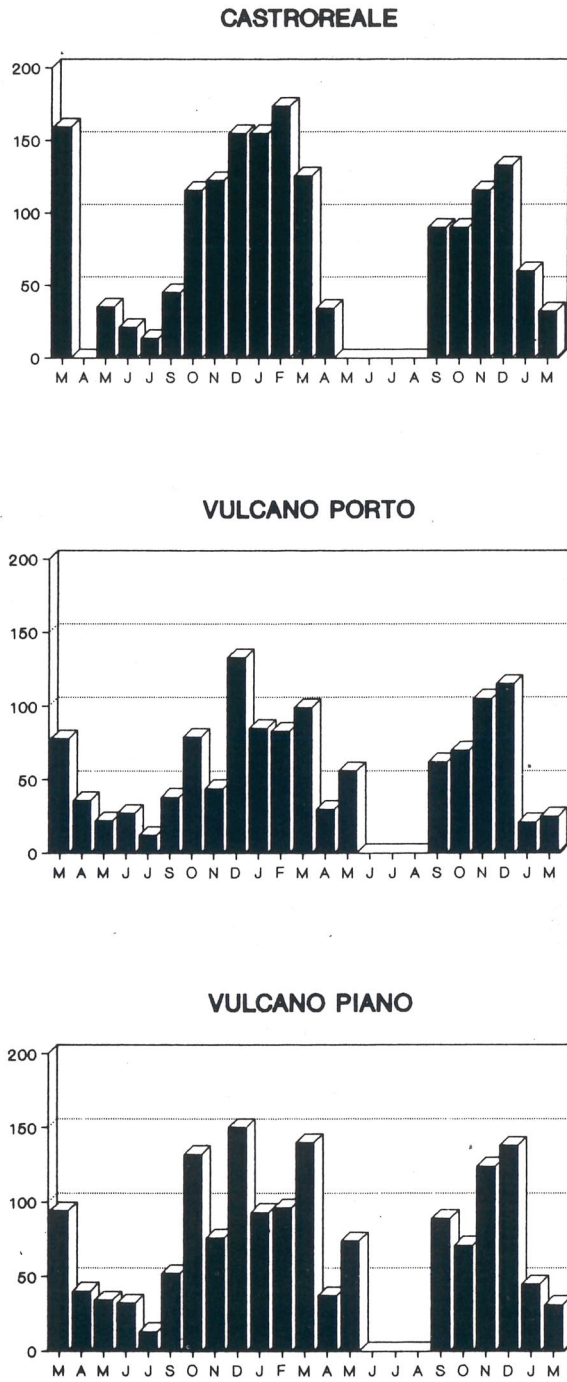


Fig. 1 — Millimeters of rain water collected monthly in the three samplig sites (Mar.87-Mar.89).

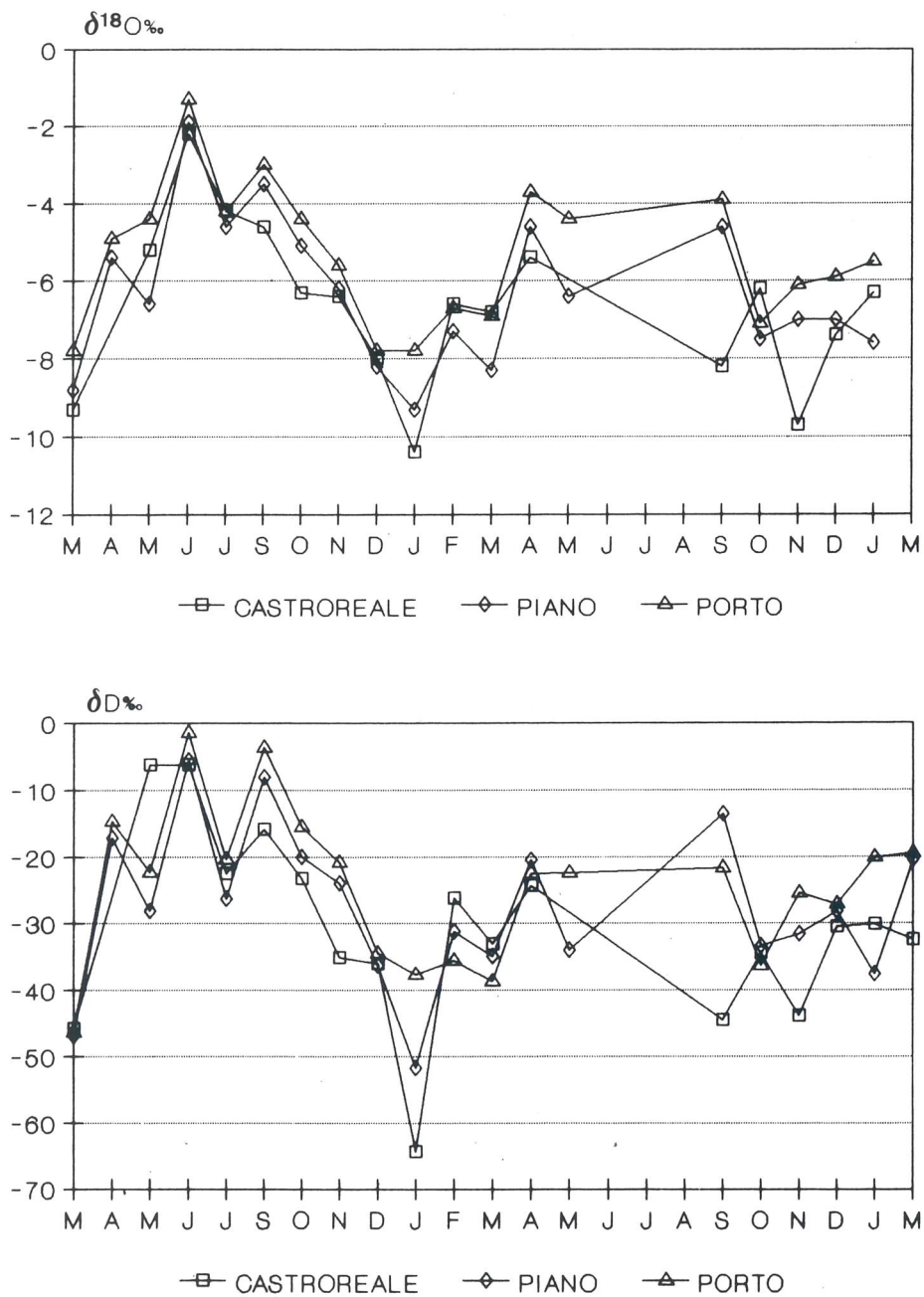


Fig. 2 — Isotopic composition of bulk precipitations. (Data from Capasso et al. 1992). Isotope ratios of oxygen and hydrogen are reported as ‰ units, referring to the international V-SMOW standard (Gonfiantini, 1978).

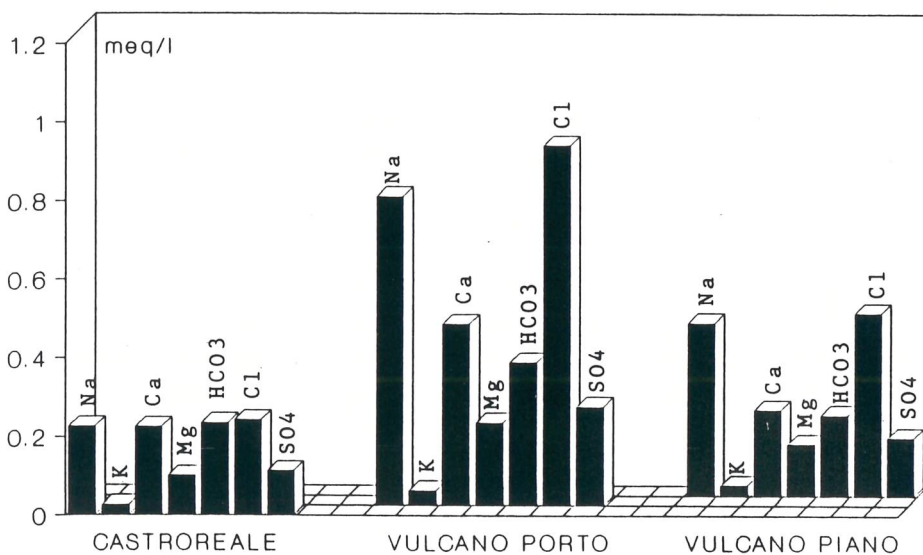


Fig. 3 — Monthly volume-weighted average chemical composition (meq/l) of bulk precipitation at Vulcano island and Castroreale.

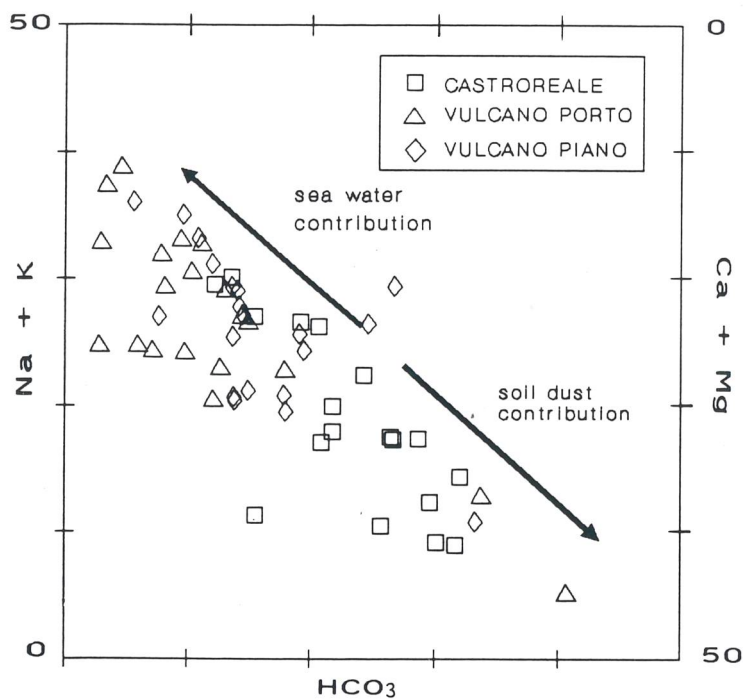


Fig. 4 — Langelier-Ludwig diagram; different symbols show the position of sample of three sites.

and January 1988). The data set defines samples which may be derived from two end members: bicarbonate-earth alkaline waters, and waters with compositional ratios similar to seawater. Moreover, the two terms correspond to two different processes: alteration of lithospheric material transported by winds into the rain-gauges, and mixing of rainwater with minute droplets of seawater. In the latter case, salts may also occur by leaching of sea-salt residues produced by the evaporation of nebulized droplets of seawater in the atmosphere in the immediate environs of the coast. The position of intermediate samples has to be considered as different contributions of the end-members.

Sodium and chlorine have high correlation coefficient (0.97). Concentrations of these ions in the Vulcano precipitations differ from those at Castoreale. The fact that the contents of sodium and chloride ions are higher in the rain nearer the sea confirms their common, marine, origin. Our data do not allow us to establish exactly if these ions reach the sampler in form of solid particles of NaCl or as a sea droplets.

If we assume that the chloride ion is completely of marine origin the sulphate/chloride ratio (Fig. 5) clearly shows that hardly any of the samples reflect the typical ratio for this pair of ions in sea water. In fact we observe an excess of sulphate ions, definitely indicating a different origin. Thus, if the sulphate comes only partly from marine aerosol, its origin must be sought in the gaseous sulfur compounds produced by volcanic emanations and those of the industrial area only a few kilometres from the island of Vulcano, or from continental solid material.

A simple calculation will help to clarify its origin. If from the total content of sulphate ions is subtracted the sea water contribution the total sulphate load at Vulcano Porto is still greater than those at either Vulcano Piano or Castoreale (Fig. 6). Thus, the excess of sulphate ions on Vulcano with respect to the contribution of sea-salt, is of local origin as there is no evident reason why the island should receive more sulphate than Castoreale, although the latter locality is near an active oil refining industrial area. It has been estimated in tens of tons/day the release of SO₂ and H₂S from the crater and Porto area (BARBERI *et. al.*, 1991). It should be remind that ionic loads in bulk precipitation are functions of both dry deposition and rainfall. Dry fallout deposition is independent of rainfall, while ionic contents due to washout generally increase with the amount of rainfall. Fig. 7, therefore, confirms that sulphate ions belong to wet precipitation and are transported to the ground after interaction of the water with sulfur compounds present in the atmosphere. The greatest quantities of annual sulphate load observed at Vulcano Porto, confirm this hypothesis.

Rainwaters were also analyzed for their contents of nitrate and fluoride ions. The total load of nitrogen species amounted to 216 and 252 mg/year

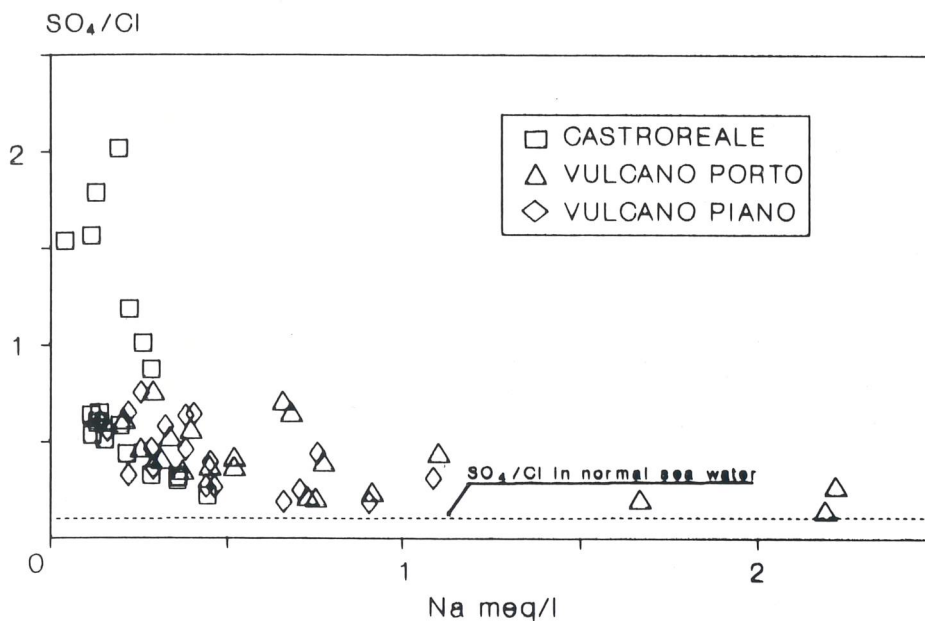


Fig. 5 — Relationship between sodium ions and the SO₄/Cl ratio. The SO₄/Cl ratio in the precipitations shows that sulphate ordinarily exceeds that available from sea-salt.

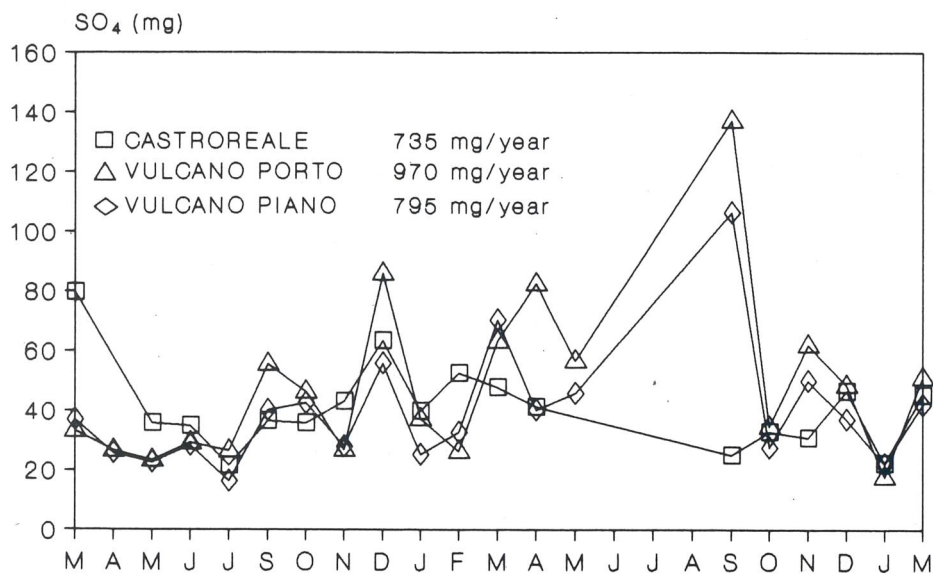


Fig. 6 — Sulphate loads (mg/month) in the three different sampling sites corrected for sea water contribution. The annual loads of sulphate for the three sites are also reported.

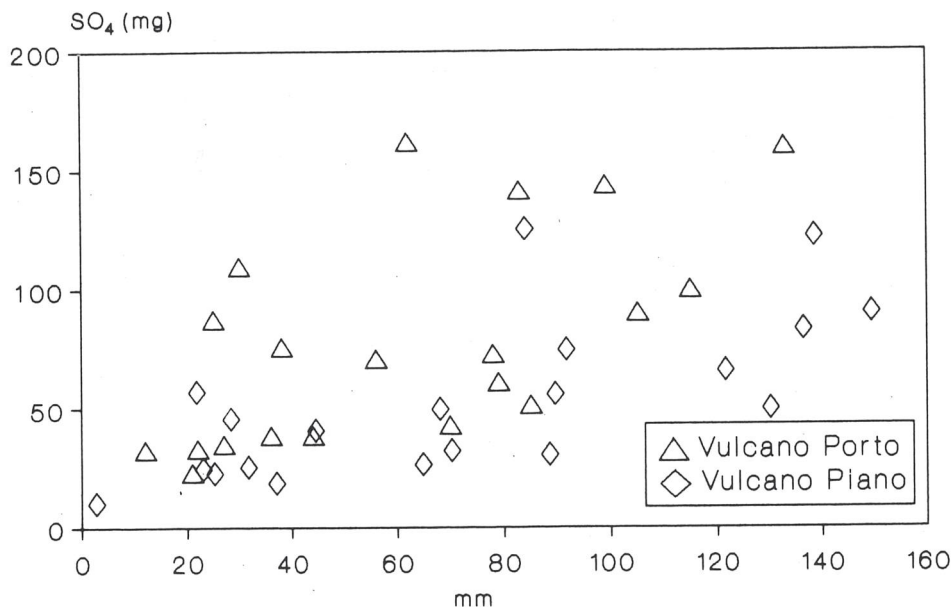


Fig. 7 — Relationship between sulphate load and amount of precipitations.

respectively at Vulcano Porto and Vulcano Piano, and 104 mg/year at Castoreale. As samples were taken monthly, the NO_3 concentrations actually reflects total nitrogen, i.e., the sum of nitrate ions present in the atmosphere and those produced by the reaction:



No significant correlation was observed between sulphate and nitrate ions.

As regards fluoride ions, a greater total load was observed at Vulcano Piano (44 mg/year) than at Vulcano Porto (25 mg/year) and Castoreale (16 mg/year).

CONCLUSIONS

On the basis of the results obtained and the considerations proposed here, some conclusions on the chemistry of the rainfall on Vulcano can be drawn:

- rainfall on Vulcano is essentially influenced by sea-salt. The result is a chemism sometimes typical of chloride-sulphate alkaline waters and sometimes bicarbonate-earth alkaline waters;
- sulphate ion is an important component of rainfall. Although a signi-

ficant quantity of sulphate comes from sea-salt aerosol, an excess of this ion, probably of local origin, i.e., volcanic, is also observed. The excess is more marked at Vulcano Porto than at Vulcano Piano or Castoreale, although the latter site is near a highly industrialized area;

— the emission of volcanic gases influences rain chemistry and thus the ecosystem of the island, even at sea level. Episodes of low pH rains may easily be expected.

— Additional researches are needed to better define the impact of volcanic emissions into the atmosphere of Vulcano.

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