

GIOVANNI PICCARDI *, MARINO MARTINI **, PAOLA CELLINI LEGITTIMO *

ON THE PRESENCE OF Cu, Zn, Cd, Sb, Bi AND Pb
IN THE FUMAROLIC GASES OF VULCANO
(AEOLIAN ISLANDS) ***

ABSTRACT. — Concentrations of Cu, Zn, Cd, Sb, Bi, Pb in the condensates of fumaroles of Vulcano were determined.

The correlation coefficients among their abundances and the main constituents of the fluid phase seem to point out that processes at shallow depth can play an important role in determining the observed situation.

The enrichment of metals in fluids seems mainly due to dissolution of dispersed metal sulphides; the presence of water vapour and a sufficient H^+ concentration act as positive factors for such a process.

Both these conditions are achieved when deep emanations are cooled down by mixing with percolating surface waters.

Metal content of fluids depends also on their abundances in country rocks, while their presence in fumarolic gases appears related to volatility of their chloride compounds.

RIASSUNTO. — È stata determinata la concentrazione di Cu, Zn, Cd, Sb, Bi, Pb nei condensati dei gas fumarolici di Vulcano.

Lo studio della loro correlazione con i costituenti più abbondanti delle emanazioni, sembra indicare un ruolo non secondario di processi relativamente superficiali nel determinare la situazione verificata. Appare probabile infatti l'esistenza di un processo di arricchimento nei fluidi sostanzialmente dovuto a dissoluzione di solfuri metallici contenuti allo stato disperso nelle rocce, e che tale processo sia facilitato dalla presenza di vapor d'acqua e dalla maggiore dissociazione di HCl; queste condizioni risultano soddisfatte quando emanazioni di origine profonda vengono in contatto con acque di percolazione in zone a relativamente piccola profondità con conseguente abbassamento della temperatura ambientale.

Il contenuto in metalli dei fluidi è condizionato dalla loro abbondanza nelle rocce, mentre la loro venuta in superficie come costituenti di gas fumarolici dipende invece dalla volatilità dei relativi composti clorurati.

Introduction

The presence of heavy metals, in trace form and proper minerals, among the volcanic incrustations has long been acknowledged (ZAMBONINI, 1912; PANICHI, 1914; ZAMBONINI et al., 1924; DI FRANCO, 1942), while information on the content of such elements in fumarolic gases was more recently acquired (DELSEMMÉ,

* Istituto di Chimica Analitica. ** Istituto di Mineralogia, Petrografia e Geochimica.

*** Centro di Studio per la Mineralogia e la Geochimica dei Sedimenti (C.N.R.), Firenze. Pubblicazione n. 220 del Progetto Finalizzato Geodinamica.

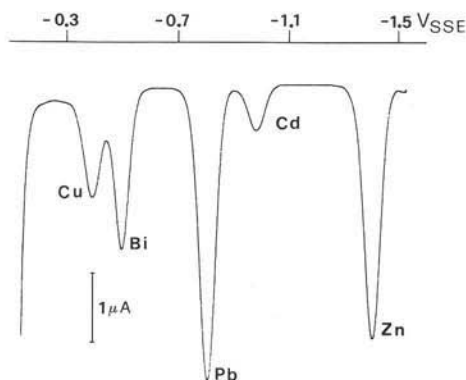


Fig. 1. — Voltammogram of a sample containing zinc, cadmium, lead, bismuth, copper.

1960; MURATA, 1960; OANA, 1960; MIZUTANI, 1970; OZEROVA et al., 1974; NIKITINA and MENYAILOV, 1976; NAUGHTON et al., 1976).

The transport of metals as volatile compounds has also been considered an important factor in ore genesis (KRAUSKOPF, 1957, 1964), but sufficient information is not yet available for a correct definition of such a process and the identification of its most significant parameters.

Therefore, this kind of investigation on Vulcano's fumaroles seemed apt to provide useful informations for a better understanding of this phenomenon.

Experimental methods

The fumarole vapours were conveyed to the surface by means of steel pipes placed in the ground, then condensed in polyethylene bottles. The condenser was made up of a series of pyrex pipes with ball-and-socket joints. Each pipe was lined with a layer of gauze kept wet during the sampling operation by a continuous dripping of water.

Concentrations of Zn, Cd, Pb, Bi and Cu were obtained through the technique of differential pulse anodic stripping voltammetry in an acetic buffer at pH 4.7. The interfering substances had been previously oxidized through digestion with concentrated $\text{HNO}_3 + \text{HClO}_4$.

A typical voltammogram of a sample containing all the above mentioned elements is given in fig. 1.

The determination of Sb was carried out by means of alternating current anodic stripping voltammetry; samples were previously oxidized with H_2O_2 in order to eliminate the interfering substances and subsequently reduced with ascorbic acid to bring antimony to +3 oxidation level (PICCARDI and UDISTI, 1979).

Analysis of results

The observation of table 1 allows us to verify that concentrations of the determined metal fluctuate within rather wide limits. The correlation factor amongst the considered variables (table 2) shows the positive role played by the chloride ions in assessing the entity of such concentrations, while a negative contribution of temperature can also be observed.

TABLE 1
Concentrations of the considered metals in condensates

sample number	date of collection	Zn	Cd	Pb	Cu	Bi	Sb
F 5 C 2	VI.77	997	132	670	486	121	2990
C 5		7661	-	339	167	62	998
F 8 C 2	VI.77	5277	-	103	222	-	1153
C 3		22600	140	172	305	-	973
F 5 C 1	XII.77	315	-	74	88	25	324
C 3		567	12	51	389	31	340
F 8 C 1	XII.77	211	10	58	89	-	653
C 3		110	-	46	22	-	848
F 9 C 2	XII.77	148	-	60	82	-	521
C 4		264	-	52	60	35	240
F 5 C 1	II.78	111	-	57	30	59	1019
C 3		75	-	31	75	70	1312
F 8 C 2	II.78	80	-	52	55	35	270
C 3		129	-	49	17	31	369
F 9 C 2	II.78	241	-	59	93	-	330
C 3		118	17	47	127	31	517
F 5 C 1	V.78	319	-	31	39	97	678
C 3		237	34	47	245	90	510
F 9 C 2	V.78	416	-	60	18	-	260
C 3		366	24	80	58	78	274
F 10 C 1	V.78	308	17	21	122	63	169
C 2		295	9	207	38	45	107
F 2	IX.78	32	-	-	-	-	148
F 5	IX.78	384	-	108	156	20	119
F 9	IX.78	45	13	41	31	-	205
F 11	IX.78	115	-	801	229	20	443
F 2	III.79	68	15	22	28	60	74
F 5	III.79	422	20	51	51	-	248
F 9	III.79	383	32	96	50	60	81
F 11	III.79	316	11	23	11	96	1076

Values are in ppb. Dashes mean concentrations below the detection limit (3 ppb).

TABLE 2
Correlation coefficients among temperature, acid constituents and metal content of condensates. Since Cd and Bi concentration is often below the detection limit, these metals were not taken into account

	Temp	Cl	F	S _{cond}	Cu	Zn	Sb	Pb
Temp.	1.00	-0.30	0.77	0.51	-0.24	-0.39	-0.16	-0.14
Cl		1.00	-0.37	-0.48	0.58	0.20	0.65	0.72
F			1.00	0.26	-0.22	-0.37	-0.13	-0.35
S _{cond}				1.00	-0.53	-0.36	-0.42	-0.35
Cu					1.00	0.37	0.55	0.63
Zn						1.00	0.14	0.23
Sb							1.00	0.78
Pb								1.00

The values of temperature, Cl, F, S_{cond}, are taken from MARTINI et al. (1979).

In other words, the concentration of metals in the condensates of the studied fumaroles is higher with the raising of the chloride content and with the lowering of the temperature.

If the first factor brings us back to the gas emanations of deep origin, which are in fact characterized by a high concentration of hydrochloric acid, the second factor seems to indicate that an important part of the process of metal enrichment in the fumaroles of Vulcano takes place in a low temperature environment, which can be identified with the uppermost portion of the volcanic system.

We do not know the actual distribution of the investigated metals between sulphide and silicate minerals at Vulcano, and by comparison with rocks of the same kind we can only suppose that Zn, Cd, Sb and Bi are present in the form of sulphides, while partially Cu and mainly Pb are concentrated in silicate minerals.

The presence of metals in the fluid phase can be attributed to reactions between rocks and the fluid itself, which are more efficient the higher is the acidity of the fluids, and also the longer the contact between the reagents.

In the examined system the acidity is practically due to the dissociation of HCl, and the relative constant pK_a assumes the value of +1.24 at 300° C, -0.06 at 200° C and -2.9 at 100° C (HELGESON, 1969); there follows that concentration of H^+ is higher at lower temperatures.

Water vapour, allowing a better contact between the reacting species, acts also as a positive factor in facilitating the considered reaction. Percolation waters, due both to rain and nocturnal condensation, by mixing with exhalations of deep origin in relatively shallow zones of the volcanic system, can give rise to fluids very high in water vapour and at a rather low temperature, thus obtaining both of the above mentioned conditions.

Through the value of the thermodynamic data, KRAUSKOPF (1957) calculated that for all the most common metals, and therefore also the ones here taken in consideration, the chloride compounds are the most volatile. Later on (1964) the same scientist defined more accurately the characteristics of the transport of metallic compounds in the fluid stage, by elaborating diagrams at various temperatures and fugacities of HCl and ΣS , and pointing out the relative volatilities of the metallic chlorides. Introducing into the calculation outlined by KRAUSKOPF the values of the variables of the order of the ones observed at Vulcano, we obtain the following order of volatilization:



positively influenced by temperature.

However, as we already saw before, the rising temperature, by reducing the dissociation degree of HCl, has a negative influence on the process of dissolution of metal compounds of the rocks.

The factors considered as producing the enrichment of metal compounds in fluid phases and their volatilization, do not work at the same time; most volatile

compounds can thus be detected in fumarolic gases for a wide range of temperature and composition, while it is rather difficult to obtain sufficient conditions which allow the presence of less volatile compounds.

TABLE 3
Metal content in rocks

	acid rocks	Vulcano
Cu	20 ppm	93 ppm
Zn	60 ppm	46 ppm
Cd	250 ppb	<20 ppm
Sb	200 ppb	<20 ppm
Bi	100 ppb	<20 ppm
Pb	20 ppm	28 ppm

Mean values for acid rocks are taken from Handbook of Geochemistry, those for Vulcano from Valette (1977).

in spite of the lower volatilization degree, can be justified by their greater content in the country rocks.

On the other hand, the concentration of the elements in the emanations also depends on their concentration in the rocks with which fluids come in contact. Therefore, keeping also in mind the data of table 3, we think the higher concentration of Pb and Cu with respect to Bi and Cd in the studied condensates,

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