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MOBILITY OF ZINC, CADMIUM, LEAD AND COPPER IN NATURAL WATERS OF VOLCANIC AREAS

ABSTRACT. — Samples of natural waters collected in different volcanic areas (Azores, Greece, The Philippines, New Zeland) have been investigated with reference to their content of some heavy metals.

The analyses were carried out by differential pulse anodic stripping voltammetry.

Following the general chemical composition of the studied solutions, the possible main forms of metal species have been evaluated.

The concentrations of the considered elements appear to depend both on the extent of rock alteration and the saturation with respect to sparingly soluble compounds.

In spite of different origins of samples no significant difference was observed, the behaviour of metals being determined by the actual values of the chemical-physical variables.

RIASSUNTO. — È stato studiato il contenuto di alcuni metalli pesanti in campioni di acque naturali raccolte in differenti aree vulcaniche (Azzorre, Grecia, Filippine, Nuova Zelanda).

Le analisi sono state eseguite mediante voltammetria anodica in impulso differenziale. Sono state valutate le principali specie metalliche possibilmente presenti, in relazione

alla composizione chimica fondamentale delle soluzioni. La concentrazione degli elementi considerati appare dipendere sia dal grado di altera-

zione delle rocce sia dalla saturazione delle soluzioni rispetto a composti poco solubili. Nonostante le origini diverse non sono state osservate differenze significative nei campioni

studiati; il comportamento delle specie metalliche è determinato dal valore delle variabili chimico-fisiche.

The concentration of heavy metals in natural waters is normally related to their content in rocks and to the extent of alteration processes.

Areas interested by volcanic phenomena show a higher degree of present or past alteration of rocks, and an investigation on the metal content of natural waters pertaining to these areas seemed apt to provide useful information about the behaviour of such elements and the possible influence of the actual stage of volcanic activity.

Copper, zinc, cadmium and lead were determined in spring waters from different areas of recent volcanism interested by fumarolic manifestations (Azores, The Philippines, New Zealand, Greece) along with the main physical-chemical constituents.

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TABLE 1

Locations of the studied samples

lo.	sample	Name	Location		
	1	Lagoa das Furnas	S.Miguel	Azores	
	2	Caldeira de Esguicho	S.Miguel	Azores	
	3	Agua Prata	S.Miguel	Azores	
	4	Agua Miguel Enrique	S.Miguel	Azores	
	5	Agua Santa	S.Miguel	Azores	
	6	Agua de Caldeirão	S.Miguel	Azores	
	7	Aqua azeda de Rebentão	S.Miguel	Azores	
	8	Caldeira de Esquicho	S.Miguel	Azores	
	9	Ribeira Quente	S.Miguel	Azores	
	10	Ribeira Grande	S.Miguel	Azores	
	11	Ribeira Grande	S.Miguel	Azores	
	12	Caldeira Velha	S.Miguel	Azores	
	13	Thermal water	Miranda	New Zealand	
	14	Whakarewarewa	Rotorua	New Zealand	
	15	Champagne pool	Waiotapu	New Zealand	
	16	Ohaki pool	Braodlands	New Zealand	
	17 -	Thermal water	Wairakei	New Zealand	
	18	Vlikhada	Thira	Greece	
	19	Explosion crater	Nysiros	Greece	
	20	Pali	Nysiros	Greece	
	21	Mandraki	Nysiros	Greece	
	22	Vromotopo	Kos	Greece	
	23	Agios Focas	Kos	Greece	
	24	Mahallo	Leyte	The Philippines	
	25	Anahawan	Leyte	The Philippines	
	26	Tongonan	Leyte	The Philippines	
	27	Daklan	Luzon	The Philippines	
	28	Daklan	Luzon	The Philippines	
	29	Daklan	Luzon	The Philippines	
	30	Montelago	Mindoro	The Philippines	
	31	Montelago	Mindoro	The Philippines	

Experimental

Table 1 shows the locations of the investigated samples, while in table 2 the analytical results are given.

The metal contents have been determined by the technique of differential pulse anodic stripping voltammetry, using an acetic buffer at pH 4.7; samples have been previously oxidized with concentrated $HNO_3 + HClO_4$ to eliminate the interferring substances (PICCARDI and CELLINI LEGITTIMO, 1974).

Analysis of the results

Previous results of investigations of this kind, pertaining to thermal waters of New Zealand, are reported by WEISSBERG (1969) and show Pb and Zn concentrations, determined by emission spectrography, similar to those obtained in the present work.

With regard to metal distribution in volcanic rocks, not many data are available, and it is difficult to obtain a representative average for the concentrations of the studied elements; a comparison with the known data about standard reference igneous rocks is thus preferred (table 3).

It is possible to verify that the abundance order of the elements in the solutions

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			A	nalyt	ical 1	esult.	5			
No.	sample	Temp.	PH	HCO3	cı ⁻	so_4^{2-}	Cu	Zn	Cđ	Pb
	1	78	2.81		0.16	23	11	320	2.1	13
	2	63	6.65	5.0	4.5	6.2	8.4	46	0.2	8.8
	3	32	5.57	2.8	0.40	0.47	7.4	38		5.9
	4	16	5.42	2.2	0.46	0.51	11	42	-	16
	5	88	7.57	6.7	1.4	0.38	14	90	3.1	29
	6	70	6.15	4.0	1.1	0.51	2.2	597	8.3	57
	7	15	5.24	1.8	0.48	0.35	3.3	26		
	8	99	7.86	9.6	6.3	1.3	3.9	28		11
	9	38	6.21	7.8	6.2	1.4	18	27		21
	10	87	2.19		0.60	16	17	1820	270	73
	11	17	6.05	0.86	0.52	0.01	82	121	3.8	16
	12	87	2.68		0.24	6.1	12	66		1.4
	13	56	8.65	1.6	5.9	0.32	15	8.4		10
	14	93	9.20	2.8	16	2.0	27	22	67	10
	15	74	6.30	1.4	53	0.80	11	34	110	8.1
	16	84	7.50	12	29	3.0	7.1	38	1.5	6.4
	17	95	5.30		0.20	4.2	14	60	3.1	7.7
	18	31	6.90	3.3	53	7.6	22	41		29
	19	95	2.00		1.5	86	27	68	4.6	91
	20	27	6.90	2.9	231	16	13	15		8.5
	21	49	6.70	4.5	582	32	11	33		105
	22	20	3.10		4.8	10	13	59		5.5
	23	45	6.45	23	620	70	15	105		7.1
	24	46	6.00	9.6	22	5.6	15	14		9.3
	25	62	6.30	12	56	11	8.8	39		17
	26	96	6.50	0.75	102	1.7	6.3	14		4.8
	27	80	2.40		3.6	7.6	307	369		
	28	60	6.30	9.0	98	22	4.9			0.6
	29	21	2.30		0.50	8.2	5.7	173		
	30	62	6.80	1.1	63	7.0	4.7	25		2.3
	31	76	6 50	0.91	80	11	7 2	5 6		11

TABLE 2 Analytical results

 HCO_8^- , Cl⁻ and SO_4^{2-} are expressed as millequivalents per liter; Cu, Zn, Cd and Pb are given in parts per billion (ppb).

TABLE 3

Mean values of Cu, Zn, Cd, Pb in standard reference igneous rocks

	acid	intermediate	basic	ultrabasic
Cu	12	50	70	9
Zn	70	90	100	50
Cđ	0.03	0.05	0.13	0.04
Pb	36	30	13	14

Values are given in parts per million (ppm).

is almost always the same as in the rocks, thus providing an evidence that the concentrations of metals in waters are mainly depending on their content in country rocks.

The possibility of forming complexes is another important factor for the persistence of metals in natural solutions, since the single ions are easily adsorbed by colloids, clay minerals and organic material.

Metal complexes with inorganic ligands like HCO₃, CO₃²⁻, SO₄²⁻, Cl⁻, are here



Fig. 1. - Saturation curve with respect to ZnCO₃.



Fig. 2. - Saturation curves with respect to Cu2(OH)2CO3 for different pH values.

taken into account; the possible influence of soluble organic complexing agents should also be considered, at least for Cu^{2+} , but its extent appears exceedingly difficult to determine (SYLVA, 1976).

By the values of the constants for complex-ion formation it appears that in the investigated solutions metals are mainly present as ion pairs with SO_4^{2-} at pH below 4, while for higher pH values hydrogencarbonate and carbonate complexes



Fig. 3. - Saturation curve with respect to PbCO_a.



Fig. 4. — Saturation curve with respect to CdCO₈.

are formed; for pH > 8 copper and zinc can form an hydroxide complex. The stability of chloride complexes is only depending on Cl⁻ concentrations.

In most of the considered samples the metal contents follow the mobility order calculated for Pb, Cu and Zn at different pH values, in aqueous solutions containing Cl⁻, SO_4^{2-} and CO_3^{2-} (MANN and DEUTSCHER, 1977, 1980).

In natural waters associated to a low temperature fumarolic stage of volcanic

activity, the low pH values are mainly due to the surface oxidization to H₂SO₄ of gaseous sulphur species escaping from confined aquifers; carbon dioxide pressure, temperature and the chemical nature of the contact rocks are instead the factors determining the pH conditions in springs outflowing from unconfined aquifers.

Strong acid conditions can be kept by a deep gaseous contribution only; otherwise a progressive neutralization by the country rocks takes place, with gradual change of the environment chemical character.

Sulphuric solutions can produce a rather strong alteration of rocks, but their metal concentrations can rarely reach saturation values of sulphate compounds, because of either their general high solubility, or, as in the case of the sparingly soluble lead sulphate, the insufficient availability of metal in rocks.

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Saturation with respect to carbonate compounds can instead be observed in solutions of neutral character.

Figg. 1-5 show the saturation curves for ZnCO₃, Cu₂(OH)₂CO₃, PbCO₃, CdCO₃, PbSO₄, and the points representing the studied samples. Mean solubility data for the observed temperature range are used for Pb and Zn compounds, and for Cu and Cd carbonates valuet at 25° C only are available; these limitations



Fig. 5. - Saturation curve with respect to PbSO4.



activities of carbonate ions.

do not seem to affect significantly the general meaning of the observed situation.

Activity values are reported; activity coefficients have been calculated by the extended Debye-Hückel equation (LINDSAY, 1979). One sample only appears over-saturated with respect to cadmium carbonate, while no saturation is observed for zinc carbonate and lead sulphate; all this is well justified by the solubility of those compounds, and does not need any further consideration.

It is instead rather interesting to observe that several samples contain quantities of metals of the same order, and that the concentration of carbonates represent the determinant factor in producing conditions of saturation with respect to the corresponding lead and copper compounds. If we take into account the samples 2-8, from Caldeiras das Furnas (Azores) (BENCINI et al., 1980) which include some of the here investigated solutions and pertain to a narrow area, the activities of carbonate ions appear strictly depending on temperature (fig. 6).

A dilution effect consequent to mixing of deep solutions with surface waters is obviously involved in the observed situation, but the low pH values of the coolest samples seem to point out a major role of carbon dioxide activities.

A decrease in solution temperature, by increasing carbon dioxide solubility, produces lower pH values and, referring to the saturation diagrams, is sufficient to shift the position of a sample from the saturation to the undersaturation field.

If the dilution process were a deep one, the higher aggressiveness of the resulting cooler and more acidic solutions could produce a higher extent of rock leaching to restore saturation conditions, while with a simple near surface mixing undersaturation only should be observed.

If this is a correct interpretation, a general original saturation with respect to the less soluble compounds (malachite, cerussite) can be inferred for most of the investigated thermal waters in spite of the different areas; any of the contact rocks involved in alteration processes can provide a sufficient quantity both of lead and of copper, and any of the ground waters could reach a carbonate concentration sufficient to fulfil the saturation requirements.

Generally speaking, when no surface or near surface dilution occurs spring waters will be saturated with respect to the above mentioned compounds, while undersaturation concentrations will be observed when a certain degree of permeability will allow shallow mixing processes.

The change from one to the other situation should imply alterations in the permeability pattern, which could be due to small local changes or even related to variations of major extent in the volcanic system.

We do not want to overestimate the meaning of the metal concentration in natural waters of volcanic areas, but nevertheless it seems that a periodical survey of these minor chemical characters could provide an additional rather sensitive chemical indicator in the frame of long term programs of surveillance of active volcanoes.

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