MINERALOGICAL MAGAZINE, MARCH 1976, VOL. 40, PP. 481–6

Base metal enrichment in volcanic sublimates and secondary alteration products from Vesuvius and Vulcano

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SUMMARY. A wide range of volcanic sublimates and alteration products from the Johnston-Lavis collection[2] has been analysed for major elements plus copper, lead, and zinc. 'Aphthitalite' and 'natrikalite' from Mount Vesuvius and an 'alum' from the island of Vulcano all proved to be enriched in copper and selected analyses are tabulated. The process leading to copper and lead enrichment of the Vesuvian material may be vapour phase transport as chloride followed by sulphation on sublimation. It is suggested that the source of the copper found in the alum sample from Vulcano could be of interest to economic geologists.

SOME copper deposits show close spatial and temporal relationships to basic volcanic or calc-alkaline sub-volcanic rocks and it may be significant that many volcanic 'sublimates' and alteration products are enriched in copper and other base metals. Sillitoe (1972) has assigned considerable significance to certain of these occurrences by suggesting that covelline and native sulphur in crater deposits of active Andean volcanoes may be visible volcanic byproducts of an active subvolcanic porphyry copper system.

As part of an investigation of metal segregation processes in the volcanic environment we analysed a wide range of 'sublimates' and alteration products contained in the Johnston-Lavis collection, which is housed at University College (London). These samples were collected from the Aeolian Islands and Mt. Vesuvius by the late Professor Johnston-Lavis over the period 1880–1910.

This note represents selected chemical analyses of material from Vesuvius and the island of Vulcano (Aeolian Islands), which was notable for its strong copper enrichment. Metal analyses were carried out by atomic absorption spectrophotometry, sulphate analyses by barium sulphate precipitation, and chloride analyses using a chloride-ion selective electrode.

'Sublimates' from Mount Vesuvius

The 'sublimates' and alteration products of Mount Vesuvius have long been known to include a wide range of copper-bearing minerals such as atacamite, vesbine, chalcanthite, tenorite, and covelline (Phillips, 1869; Lacroix, 1907; Zambonini, 1921).

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Our chemical analyses of 'aphthitalite' and 'natrikalite' collected and identified by Johnston-Lavis from around high-temperature crater fumaroles in 1892 and 1880 respectively, show that these products are strongly enriched in copper (see Table I).

'*Aphthitalite*' (Samples 1 to 4, Table I). There is some doubt about the exact identity of this mineral. Although its chemistry and habit are similar to those of aphthitalites described by Dana (1951) and Winchell and Winchell (1964) it is biaxial with $2V_\gamma = 20°$, the acute bisectrix being perpendicular to the surface of the platelets. Its X-ray diffraction spectrum is very similar to that reported for Vesuvian aphthitalite by Winchell and Benoit (1951) except that the *d* spacings are approximately 0·5 % smaller.

TABLE I. *Partial chemical analyses* (*wt.* %)

Assignment*	'Aphthitalite'				'Natrikalite'		'Alum'	
Sample Colour	1 Pale blue	2 Creamy green-blue	3 Mid-grey	4 Deep blue	5 Pale green	6	7 Pale blue	8 Pale green
Al	0·05	0·08	0·06	0·07	0·03	0·08	5·41	5·18
Ca	0·01	0·01	0·09	0·01	0·01	0·09	0·64	<0·00$_5$
Mg	0·01	0·07	0·07	0·06	0·04	0·00$_1$	0·26	1·00
Fe	0·07	0·10	0·04	0·07	0·04	0·13	0·56	0·49
Mn	0·01	0·02	0·01	0·00$_4$	0·00$_2$	0·01	0·01	0·06
Na	7·80	6·73	7·56	7·88	7·33	14·20	3·37	3·83
K	32·18	32·23	32·09	28·86	33·96	25·40	0·68	0·15
Cu	0·65	0·78	0·59	2·22	0·10	0·10	3·11	0·32
Pb	1·20	1·60	1·29	3·80	0·07	0·05	0·00$_5$	0·00$_1$
Zn	0·05	0·09	0·07	0·19	0·01	0·00$_1$	0·00$_3$	0·01$_6$
Cl	<0·01	<0·01	<0·01	0·06	53·10	54·50	<0·01	<0·01
SO_4	57·40	52·80	56·80	47·60	0·00	0·00	49·60	39·60
H_2O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	37·2	48·90
Total	99·40	94·52	98·67	90·82	94·69	94·56	100·80	99·55

* Johnston-Lavis's assignment.
n.d. not determined.

The samples occur as dendritic to platy layered aggregates, which vary in colour from pale cream to deep grey or turquoise. The platelets vary from hexagonal to prismatic in form and the aggregates radiate from the point of surface to which they were originally attached. They have the appearance of growth in open space, perhaps from a vapour phase rather than from an aerosol suspension.

The molar ratio of potassium to sodium in these samples varies from 2·2:1 up to 2·8:1. All four samples are notably enriched in copper (up to 2·2 wt. %) and lead (up to 4 wt. %), and moderately enriched in zinc (up to 0·2 wt. %). These copper and lead values are very similar to those reported by Zambonini (1921) in sky-blue aphthitalites from Vesuvius. The exact mode of incorporation of the base metals is not known. However, no inclusions of copper or lead minerals were identified in thin section and X-ray diffraction powder photographs showed no evidence of such inclusions.

There is an over-all decrease of 0·5 per cent in *d* spacings from sample 2 to sample 4, which may possibly be due to the increasing Na : K ratio and in part to the incorporation of copper and lead into the lattice. The biaxial character of the mineral also suggests possible incorporation of these metals into the lattice as Winchell (1927) reports that 'with about 30 % $CuSO_4$ in crystal solution(?) the substance is orthorhombic (?) with(−) 2V= large'.

Samples 2 and 4 contain small (< 50 μm) opaque inclusions insoluble in aqua-regia and these together with metals not analysed may explain the low 'totals' reported in Table I and the poor cation–anion balance for the analyses. In contrast samples 1 and 3 are free of these inclusions and the almost perfect ion balance deduced from the analyses suggests that non-sulphate inclusions are absent.

Although a detailed discussion of the processes that may have led to this base metal enrichment is beyond the scope of this communication the following points may be relevant: We know of no conclusive evidence for the vapour transport of volatile metal sulphate or sulphite species in high-temperature volcanic gases. However, the transport of gaseous cuprous chloride in high temperature volcanic gases has been demonstrated by Tazieff (1960) and Delsemme (1960), who identified CuCl lines in the emission spectra of volcanic gases and Naboko (1959) who reported the distillation of cuprous chloride gas from lava and its direct sublimation to form atacamite. Below 900 °C the cuprous chloride trimer (Cu_3Cl_3) is stable and vapour-phase transport of this species forms the basis of the metallurgical 'copper segregation' process (Sale, 1971). Lead and zinc can also be extracted from sulphide and silicate ores below 900 °C as volatile chloride compounds and this suggests that these metals might also be transported as chlorides in high-temperature volcanic gases. The vapour pressure of zinc metal is 724 mm at 900 °C, which suggests that zinc could be transported as a metallic species in high-temperature volcanic gases. The ratio of zinc metal to zinc chloride in any volcanic gas depends on the product of the HCl and O_2 fugacities and the temperature of the gas. A simple calculation using the thermodynamic data of Kubaschewski *et al.* (1951) indicates that at 900 °C f_{Zn° and f_{ZnCl_2} would be equal if f_{HCl} and f_{O_2} were 3×10^{-3} atm. and 10^{-12} atm. respectively (i.e. $f_{O_2}\times f_{HCl} = 3\times 10^{-15}$). If $f_{O_2}\times f_{HCl}$ exceeds 3×10^{-15} at 900 °C or for the same fugacities of O_2 and HCl the temperature is lower, $ZnCl_2$ will be the dominant zinc species in the gas stream.

A report that the copper and zinc contents of fumarolic gases of Showashinzan volcano (Japan) increases sympathetically with the chloride content of these gases provides some circumstantial evidence of the vapour transport of zinc as well as copper by volatile chloride species (Mizutani, 1970). Although it may not be significant it is interesting to note that the most metal-rich aphthitalite sample is also the most chloride rich.

Palmieri (1873) describes the direct sublimation of tenorite and 'lead oxides' together with halite from high-temperature gases escaping from fissures in the 1872 Vesuvian lava, and it seems possible that the copper and lead were transported as volatile chlorides, which decomposed with increasing oxygen fugacity to deposit oxides.

Although aphthitalite is a sulphate the base metals and alkali metals contained in these particular specimens may also have been transported as volatile chlorides in an SO_2/SO_3-rich gas stream. In this case SO_3 plus water vapour could have displaced HCl from the chlorides at the time of sublimation to form base-metal-enriched aphthitalite. Evidence for the simultaneous gas-phase transport of copper and sodium in this way was obtained by Murata (1960), who measured the intensity ratio of CuCl to NaCl emission in the volcanic flames of Kilaue. The ratio of Na to Cu in the gas deduced in this way was 25:1 by weight.

The suggested role of SO_2 in the displacement of HCl from the transported chlorides seems reasonable in view of Johnston-Lavis's comment (1908) that natrikalite deposition was associated with steady emission of HCl-rich gases while aphthitalite deposition occurred simultaneously with abundant emission of 'sulphurous acids' during 'eruptive paroxysms'.

The *natrikalite* (Samples 5 and 6) occurs as a pale green, coarsely fibrous, 2 cm thick encrustation with atacamite, hematite, and realgar adhering to its upper surface. Chemical analysis (Table I) shows that the molar ratio of sylvine to halite is approximately 1 : 1 and that although copper and lead enrichment is pronounced there is no enrichment in zinc. The low totals and the imperfect cation–anion balance may be due to water and non-chloride impurities such as haematite and realgar, which are dispersed throughout the samples.

Johnston-Lavis (1908) reported that at the time this sample was collected (1880) halite and tenorite were continually depositing around high-temperature lava vents, while Palmieri (1873) described the simultaneous deposition of tenorite, lead oxides, and halite around vents in the earlier 1872 lava. If it is assumed (from these observations) that the copper, lead, and alkali metals were transported as volatile chlorides then the copper and lead contents in the natrikalite described here cannot be considered surprising.

Perhaps the most notable feature of these analyses is the very low zinc content compared with that of the aphthitalite samples. Analyses of other 'sublimates' in the Johnston-Lavis collection (not reported here) indicates that sulphate sublimates are consistently richer in zinc and have lower copper-zinc ratios than chloride sublimates. A similar feature has been noted by Naboko (1959) in describing sublimates formed during the eruption of basaltic lavas in Kamchatka and the Kuriles. He reports that sulphate 'sublimates' (whether true sublimates or precipitated from aerosol suspension) are always richer in zinc than chloride sublimates.

Our discussion of the formation of the 'sublimates' has not been detailed and we realize that volatilization as a chloride species is not the only way in which metals may be transported in volcanic gases. For example Naboko (1959) has described the transport of alkali metal salts in aerosol suspension over quite long distances from eruptive centres. A process that (to our knowledge) does not appear to have been suggested is the transport of metals such as vanadium, molybdenum, manganese, and iron as volatile carbonyl compounds, even though this process is of considerable metallurgical importance (Sale, 1971).

'*Alum*' from the Island of Vulcano (Samples 7 and 8). These alteration products were collected from Isolo Fariglioni (Island of Vulcano) around 1890 and were identified as 'alum' by Professor Johnston-Lavis. Sample 7 is a pale-blue earthy mass containing discrete crystals of chalcanthite. X-ray diffraction shows it to consist of tamarugite, $NaAl(SO_4).nH_2O$ (approximately 50 wt. %), alunogen (approximately 30 wt. %), chalcanthite (approximately 10 wt. %), and traces of gypsum. Sample 8 is apple green in colour and has a similar earthy texture. The only minerals identified by X-ray diffraction were tamarugite and alunogen. In addition to the high copper contents (3·1 and 0·72 wt. % respectively) the low levels of zinc and lead are notable.

Unfortunately, Johnston-Lavis's field notes are not available and we have been unable to find any reference in the literature to the collection of this material. However, minor copper mineralization associated with alum and voltaite in the Grotto de Faraglione (alum caves) has been described by Bergeat (1899). The precipitation of these materials from acid sulphate waters that had percolated through the surrounding pyroclastics had been described by Judd (1875).

Recent seismic and petrochemical studies suggest that Vulcano may lie above an active subduction zone that strikes parallel to a line running through the islands of Vulcano and Stromboli and dips towards the west-north west (Barberi *et al.*, 1973). It might be rewarding therefore to investigate the source of the copper carried by these acid ground waters as high-level low-grade copper mineralization would not be unexpected in an environment such as this.

The main purpose of this contribution is to add to the rather limited data on the chemistry of volcanic byproducts. A justification for presenting analysis of material collected last century is that the nature of the sublimates and alteration products formed may have varied with time. In the case of the 'alum' from Vulcano a more important justification is that it was collected when the volcano was more active than at present and before a great deal of the alum had been removed by small-scale mining activities.

Acknowledgements. We thank Dr. M. K. Wells and Professor Donovan of University College, London, for their kindness in making material in the Johnston-Lavis Collection available to us and Dr. A. T. Huntingdon for his helpful advice during preparation of the manuscript. This was undertaken as part of a project supported by a NERC research grant.

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[*Manuscript received 31 July 1974; revised 24 February 1975*]