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A CHEMICAL STUDY OF THE YELLOW INCRUSTATIONS ON THE VESUVIAN LAVA OF 1631¹

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INTRODUCTION

In 1879 Arcangelo Scacchi² described yellow crusts that coat the walls of crevices in the massive lava flows of 1631 at Vesuvius. He suggested that there was present a possibly new element, much like vanadium, which he provisionally named *vesbium*, after an ancient name of Vesuvius. To the substance forming the crusts, which he thought to be a vesbate of aluminum, he gave the name *vesbine* (*vesbina*). Most of the chemical reactions on which he based the distinction between vesbium and vanadium are not decisive, and others are explained by the presence of various elements that have been revealed by more recent study. Indeed, Scacchi himself was later convinced of the identity of vesbium with vanadium.

For many years no further study of vesbine was made, the chief reasons being the rarity and the small quantity of the material and the difficulty of obtaining it in a state of purity. In 1910 Zambonini,³ from study of a very minute quantity of material, not sufficient for complete analysis, showed definitely that vesbine is a vanadate. He thought that the base was probably uranium and that the mineral was allied to carnotite, this conclusion being based on certain chemical reactions and on the radioactivity of the specimen.

Some years later De Luise⁴ published an analysis of vesbine with the following results: V₂O₅ 11.83, Cl 7.16, PbO 5.77, CuO

¹ This résumé and, in part, literal translation, of a somewhat lengthy and detailed paper by the two authors, (to be published in the Memoirs of the Academy of Naples), has been made at the request of Professor Zambonini. It is published in the American Mineralogist, in accordance with his desire, as a mark of his esteem for the Society. (H. S. W.)

² A. Scacchi: *Atti Accad. Sci. Napoli*, 13 December, 1879.

³ Zambonini: *MINERALOGIA VESUVIANA, Napoli*, 1910, p. 315.

⁴ L. De Luise: *Notizie sulla Eruzione Vesuviana del 1906, Portici*, 1914, p. 17.

38.36, H₂O 28.87, loss and undetermined 7.16, sum 99.15. He interpreted these figures to indicate that vesbine is a mixture of vanadate of lead ("descloizite") and vanadate of copper ("volborthite"), with probably an oxychloride of copper.

As De Luise's analysis and his interpretation of the constitution of vesbine were open to criticism a new study of the material was made. The greatest difficulty in the study of vesbine is that of obtaining pure material. The yellow vesbine is almost always mixed with green, blue, and brown substances (to be investigated later), and even the purest is tenaciously attached, as a very thin film, to the surface of the lava. Separation by means of heavy solutions presents many difficulties. A very small quantity of the mineral in solution was obtained by treatment with very dilute nitric acid.

SPECTROSCOPIC STUDY

The presence of vanadium and of lead and copper, as the main constituents, was determined by qualitative chemical tests; but lead was found to be present in much larger amount than copper, contrary to De Luise's results. As there was not material sufficient for a complete analysis, for the determination of the elements present in small amounts, a spectroscopic study was undertaken. For this purpose a Hilger spectroscope was used, the region of the spectrum that was examined being from 4900 Å to 3200 Å.⁵

The spectroscopic examination demonstrated the presence in vesbine of the following elements: V, Mo, Ti, W, Cr, Cb(?), Ta(?), Pb, Cu, Al, Mn, Co(?), Zn, La, Ce, Nd, Y, Dy(?), and Er. The presence of the rare earths and of tungsten are of special interest, as these elements had not hitherto been detected at Vesuvius.

Vanadium was definitely established to be present by the identification of 76 lines, among them the two "ultimate" lines, 4408.5 and 4379.2. Molybdenum, which had previously been detected at the volcano in a Vesuvian sodalite,⁶ was identified by many lines, including the "ultimate" one 3903.0. The presence of tungsten was determined by the "ultimate" lines 4302.4 and

⁵ A long list of the spectral lines observed is given in the original paper, which it is not necessary to reproduce here. (H. S. W.).

⁶ Freda: *Rend. Accad. Sci. Napoli*, 1878, pp. 88, 136; Zambonini: *MINERALOGIA VESUVIANA*, 1910, p. 214.

3215.6. The presence of titanium in fumarolic salts had already been shown.⁷ The presence of chromium was indicated by the two "ultimate" lines 3605.3 and 3593.4, and some others. The spectroscopic determination of columbium and tantalum is somewhat doubtful. The presence of columbium and tantalum have been noted by Prior⁸ in guarinite of Monte Somma, and that of columbium in dysanalyte of Monte Somma by Zambonini.⁹

Of special interest is the very probable presence of cobalt and zinc in spectroscopic traces, two elements that have been detected only rarely and in very small quantity in the fumarolic deposits of Vesuvius. The presence of cobalt was indicated especially by the "ultimate" line 3405.1; while that of zinc is shown by the two "ultimate" lines 4722.2 and 4810.5.

The detection of some of the elements of the rare earths in vesbine is of particular interest, inasmuch as none of these seem to have been observed previously in the exhalation products of Vesuvius. That they are present is not surprising, because one of us¹⁰ has shown that the rare earth elements are isomorphogenic with the metals of the alkaline earths and with bivalent lead, while the other author¹¹ has prepared synthetically pyromorphite, vanadinite, and mimetite, in which lead is partially replaced by lanthanum, and has shown the presence of some of the rare earths in natural pyromorphite. Inasmuch as vesbine contains much lead, it is clear that this may be partially replaced by rare earth metals, which have been found only in traces.

Lanthanum is certainly present, as we have identified the "ultimate" line 3949.1, and another persistent line, 3988.5, as well as others. Of cerium there were observed the two "ultimate" lines 4012.4 and 4040.8, as well as the persistent line 4186.6. The three persistent lines of neodymium, 4303.6, 4177.3, and 3951.2, were present in the spectrogram. Yttrium was identified by the "ultimate" line 3710.3, and also by the lines 3774.3 and 3600.7. The two persistent lines of erbium, 3692.4 and 3906.3, as well as others, were seen. There are also indications of the presence of lines of dysprosium and of thorium.

⁷ Coniglio: *Ann. Osserv. Vesuv.*, (3), 1, 37, 1924; Zambonini and Coniglio: *Rend. Accad. Lincei*, (6), 3, 521, 1926; and unpublished researches by Carobbi.

⁸ Prior: *Min. Mag.*, 15, 257, 1909.

⁹ Zambonini: *Rend. Accad. Sci. Napoli*, 4 April, 1918.

¹⁰ Zambonini: *Riv. Min. Crist. Ital.*, 45, 1915; *Zeit. Kryst.*, 58, 226, 1923.

¹¹ Carobbi and Restaino: *Gazz. Chim. Ital.*, 56, 59, 1926; *Rend. Accad. Sci. Napoli*, 6 and 13 Feb., 1926.

Certain lines shown in the table, such as those of potassium, calcium, strontium, and zirconium, are attributed to particles of contaminating silicates, not to vesbine, and the spectroscopic indications of silicon and of phosphorus were very faint. Pentavalent phosphorus and arsenic were discovered later, in the course of a chemical analysis, their presence being not surprising, as vesbine is a vanadate. This is the first time that arsenic has been detected at Vesuvius.

CHEMICAL ANALYSIS

It is very difficult to isolate vesbine in a state of purity and in quantity sufficient for accurate chemical analysis. The mineral forms very thin films, so firmly adherent to the walls of crevices in the lava that they can be detached only along with particles of the lava or of the pneumatolytic minerals that cover it: the thicker crusts, which are more readily loosened, are usually much mixed with other substances.

Thanks to the friendly kindness of Prof. Eugenio Scacchi, who put at our disposition the rich collection of lavas of 1631 with vesbine, (collected by A. Scacchi), we were able, by scraping and scratching, to collect a couple of decigrams of very impure vesbine. Many treatments with heavy solutions yielded scarcely 6 centigrams and a half of material, which, under the microscope, was seen to be somewhat contaminated with silicates, especially feldspars and sodalite; so much so that the quantitative analysis showed the presence of 10.4 per cent of SiO_2 . Professor E. Scacchi made another sacrifice: he gave us about one gram and a half of vesbine mixed with fragments of lava and silicates (essentially sodalite), which represent the last residuum of the material collected with so much care by A. Scacchi. This was for us particularly precious because it consisted of typical vesbine.

The analysis was carried out as follows. The pulverized material was treated with very dilute nitric acid, first in the cold and then slightly warmed for a few minutes. The vesbine dissolved entirely. The insoluble residue (particles of lava and small crystals of pneumatolytic silicates) was weighed.

The solution was evaporated to dryness, thus separating the silica. Then, successively, the lead was precipitated as sulphate, the copper was determined electrolytically, and the molybdenum and arsenic were precipitated by hydrogen sulphide under pressure,

and alumina with a little iron were precipitated in the filtrate by ammonium hydroxide. As the aluminum hydroxide was contaminated by vanadium, (as has been noted by others), even after several reprecipitations, this trace of vanadium was determined colorimetrically. Phosphoric pentoxide was determined in the ammonia precipitate, Treadwell's procedure being used.

After the separation of aluminum and iron the vanadium was determined by the use of cupferron, according to the method of Turner.¹² Manganese, cobalt, etc., were precipitated by an excess of ammonium sulphide, and the filtrate was evaporated to dryness. The ammonium salts were driven off and a small amount of vanadium was determined colorimetrically in the acid solution. Calcium and magnesium were searched for, but with negative results.

Water, chlorine, and arsenic were determined in three separate portions, the last colorimetrically.

The final results were as follows.

ANALYSIS OF VESBINE				
CuO	12.90	0.162	} 0.296	4.01*
MnO	0.22	0.003		
PbO	29.31	0.131		
V ₂ O ₅	12.90	0.071	} 0.073	1.00
P ₂ O ₅	0.19	0.001		
As ₂ O ₃	0.20	0.001		
MoO ₃	0.47	0.003		
H ₂ O (over CaCl ₂)	2.13	0.118	} 0.550	7.53
H ₂ O (110°)	1.80	0.100		
H ₂ O (110°+)	5.98	0.332		
SiO ₂	4.68			
Al ₂ O ₃	4.89			
Fe ₂ O ₃	0.24			
Mn ₃ O ₄	0.45			
CaO	none			
MgO	none			
Cl	0.82			
Insoluble	20.07			
	97.25			
O for Cl ₂	0.18			
	97.07			
Na ₂ O (by dif)	2.93			
	100.00			

* CuO+MnO+PbO=0.293; 0.003 being assumed to form with MoO₃ a compound R''MoO₄.

Reducing to 100 per cent the constituents referable to vesbine, this mineral would have the following composition:

¹² W. A. Turner: *Am. Jour. Sci.*, (4), 41, 339, 1916.

CuO	19.52
MnO	0.33
PbO	44.34
V ₂ O ₅	19.52
P ₂ O ₅	0.28
As ₂ O ₅	0.30
MoO ₃	0.71
H ₂ O (total)	15.00
	<hr/>
	100.00

According to the analysis, SiO₂, Al₂O₃, Na₂O, and Cl are present in relative amounts scarcely different from those needed to form sodalite. The percentages, referred to the amount of SiO₂ and based on the formula of sodalite, are calculated to be: Al₂O₃ 4.0, Na₂O 3.2, Cl 0.9—figures which show that the silicates that contaminate the vesbine are essentially sodalite. Vesbine is, therefore, definitely not a silico-vanadate, as one might suppose, but a simple vanadate. The absence of silica was also shown by microchemical tests on carefully selected particles of vesbine, and the absence of alumina was also proved microchemically.

Vesbine is, thus, certainly a vanadate of lead and copper; lead being replaced in very small amount by elements of the rare earths, while some of the manganese and cobalt are regarded as vicarious with copper. The greater part of the manganese shown in the complete analysis is regarded as derived from hausmannite, which forms brown or blackish crusts contaminating the vesbine, the presence of which is shown by the evolution of chlorine on treatment with hydrochloric acid, the approximate relative amount of Mn₃O₄ having been thus determined.

Some of the total water of vesbine is so very weakly bound that it is rapidly taken up by calcium chloride; another portion is eliminated at 110°; while the remainder (5.98 per cent) is driven off only at a higher temperature. It was impossible to study the course of dehydration because of the lack of sufficient material. The ready elimination of water is in harmony with the apparently amorphous character of vesbine. The mineral is, clearly, one of those the water content of which varies with the water-vapor pressure of the ambient.¹³

¹³ The term "*ambient*" (Italian *ambiente*) is here used instead of "surrounding medium" or "atmosphere," as being shorter, self-explanatory, and etymologically correct. The word is given in the Century and in the Standard dictionaries. It is suggested that "*ambient*" might well replace the other two terms. "Surrounding medium" is somewhat jargonesque, and the "atmosphere" may not be the air in certain cases. (H. S. W.)

If sufficient $\text{CuO} + \text{PbO}$ is subtracted to form with the MoO_3 a normal molybdate, $\text{R}''\text{MoO}_4$, the ratios of the constituents of vesbine are as follows: $\text{R}''\text{O} : (\text{V}, \text{P}, \text{As})_2\text{O}_5 : \text{H}_2\text{O} = 4.01 : 1 : 4.55$, or $4 : 1 : 4.5$ if only the water driven off above 110° be considered; or $4 : 1 : 7.5$ if the total water be considered.

The formula for vesbine, in equilibrium with air at 25° , is, therefore; $(\text{Pb}, \text{Cu})_3\text{V}_2\text{O}_8 \cdot (\text{Pb}, \text{Cu}) (\text{OH})_2 \cdot 6.5\text{H}_2\text{O}$. This becomes $(\text{Pb}, \text{Cu})_3\text{V}_2\text{O}_8 \cdot (\text{Pb}, \text{Cu}) (\text{OH})_2 \cdot 5\text{H}_2\text{O}$ for vesbine dried over calcium chloride at 25° : and $(\text{Pb}, \text{Cu})_3\text{V}_2\text{O}_8 \cdot (\text{Pb}, \text{Cu}) (\text{OH})_2 \cdot 3.5\text{H}_2\text{O}$ for vesbine partially dehydrated at 110° .

Since the water-content of vesbine varies with the aqueous pressure of the ambient and with the temperature, the values for the molecules of water are of slight importance. It would appear that the most acceptable formula for vesbine is that of the material dried over calcium chloride, namely: $(\text{Pb}, \text{Cu})_3\text{V}_2\text{O}_8 \cdot (\text{Pb}, \text{Cu}) (\text{OH})_2 \cdot 5\text{H}_2\text{O}$.

Vesbine is, thus, a hydrated cuprodescloizite, using this name in the sense proposed by Wells;¹⁴ that is to say, a descloizite in which zinc is wholly, or almost wholly, replaced by copper.

Our analysis differs much from that by De Luise. It appears to be probable, from the large amount of chlorine found by him, that De Luise examined a mixture of vesbine with much atacamite (?), this name being given provisionally, following A. Scacchi, to the green incrustations on the lava of 1631.

That our analysis is approximately exact, and that the pure vesbine has a fairly constant composition, is indicated by a study of a small quantity of vesbine detached "by him"¹⁵ from the rock with a stiff brush, which we tried to purify with heavy liquids. Only 0.0655 of a gram of material was thus obtained. This was fused with carbonate and nitrate of sodium, and the mass lixiviated with water, CuO and PbO being determined in the residue. The results were: CuO 12.4 and PbO 25.3 per cent; so that these two oxides show the ratio 1.37 (CuO) : 1.0 (PbO), while the ratio in the principal analysis is 1.24 : 1.00. The agreement may be regarded as satisfactory, when the small amount of material used is considered.

Vesbine, heated in the closed tube, gives off water and becomes brown. Before the blowpipe, mixed with sodium carbonate on

¹⁴ H. G. Wells: *Am. Jour. Sci.*, (4), 36, 636, 1913.

¹⁵ De Luise (?). (H. S. W.)

charcoal, the mass becomes blue, and finally one obtains small scales of metallic copper and globules of lead. The salt of phosphorus bead is green in the reducing flame. Vesbine dissolves in dilute nitric acid, yielding a characteristic bluish green solution. Under the microscope it appears to be amorphous.

ORIGIN

Vesbine was found by A. Scacchi, as has been said, in the lava of 1631, as very thin coatings on the walls of crevices, and De Luise reports having found it in the lava of 1868, but very rarely.¹⁶ It would not be surprising to find it in the lavas of other Vesuvian eruptions, inasmuch as the composition of the lavas of Vesuvius does not appear to have changed much since the eruption of 79 A. D.

Vanadium, however, exists in very small amounts in the lavas of Vesuvius, so that one can understand how vesbine, a vanadate, is found in the lavas of 1631. These, given their great mass, have been able to concentrate, in the exhalations during their cooling, the vanadium needed for the formation of the observed vesbine. One might also assume that the lavas of 1631 were richer in vanadium than later lavas, because the eruption of 1631 took place after a long period of repose, during which the upper part of the magma column, which formed the flows of that eruption, were enriched in volatile exhalations from the lower portions. Indeed, autopenumatolytic minerals are notably much more abundant in the lavas of 1631 than in those of other eruptions. On the other hand, the exhalations from the Vesuvian magma, which are fairly uniform on the whole, sometimes give evidence of the presence of elements that are not usually found or which occur only in very small amount. Such is the case, for example, with caesium, which has been recently observed by one of us, with Dr. L. Coniglio, in considerable quantity.

It might be thought, in view of its occurrence only on the walls of crevices in the lava, that vesbine is a direct product of autopenumatolysis, such as are some silicates (sodalite, feldspars, mica, etc.) and oxides (hematite, magnetite, and cuprite), which likewise coat the same walls. Vesbine appears, in every case, to be clearly of later formation than these minerals, since it covers and incrusts

¹⁶ I have observed the films, as a great rarity, in lavas of 1631. (H. S. W.)

them cleanly. There are specimens which might lead one to think that the vesbine is a pneumatolytic product, especially those in which the vesbine itself adheres closely to the rock, forming on it thin films, impossible to dislodge. In some cases these are not uniform, but constitute small rosettes, more or less elongated, or they are closely appressed; so that one might think them to be lichens.

On the examination of many specimens, however, as, indeed, is obvious from the presence of water easily driven off at a low temperature, it is clear that vesbine was not formed by gas reactions at a high temperature, but that it is to be considered, on the contrary, as the product of solutions that began after the cooling of the mass of lava, which would, thus, in some respects, correspond to the formation of zeolites in other eruptive rocks. Many of the specimens preserved in the Mineralogical Museum of Naples are very instructive in this respect, and they show clearly that the vesbine and the material of the other colored incrustations of the lava of 1631 formed a sort of mud, which ran over the walls of the crevices of this lava.¹⁷

According to our observations, we think that vesbine has been formed thus. Among the products of the exhalations of the lava of the eruption of 1631 there were alkaline vanadates. Water, which was certainly present during the cooling and solidification of the lava, dissolved these and thus made them capable of reacting with the [traces of] lead and copper present in the magma. Thus there came about the existence of vesbine, which in one place was immediately deposited, and elsewhere was carried to varying distances, to form on the walls of the crevices the crusts that have been described.

CONCLUSIONS

1. The identity of vesbium with vanadium has been definitively shown, by spectroscopic and chemical methods.
2. Vesbine has a composition corresponding to that of a hydrated cuprodescloizite, which is best represented by the formula $(\text{Pb, Cu})_3\text{V}_2\text{O}_8 \cdot (\text{Pb, Cu})(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. The amount of water, however, varies with the water-vapor pressure of the ambient.

¹⁷ In the original paper several photographs are given, which show various modes of occurrence of vesbine, but which it is not necessary to reproduce here. (H. S. W.)

3. It has been established, by spectroscopic methods, that in vesbine lead is replaced, to a very small extent, by metals of the rare earths, among which have been certainly recognized La, Ce, Nd, Y, and Er, and Dy doubtfully. This is the first time that the rare earth elements have been detected in Vesuvian lavas. The same may be said of tungsten, which was also noted spectroscopically; it probably replaces molybdenum. There are doubtful spectroscopic indications of the presence of columbium and of tantalum, neither of which have heretofore been noted at Vesuvius. Arsenic, also found by us as the orthoarsenate in vesbine, is new for the Vesuvian fumaroles.

4. It is shown that vesbine is not an autoneumatolytic product, but that it was formed at a period after the solidification of the lava, through the agency of water.

NOTES ON THE TRICLINIC PYROXENES

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The standard treatises on mineralogy all refer rhodonite, bustamite, fowlerite and babingtonite to the triclinic pyroxenes, but show no agreement at all regarding the other members of the group. Dana¹ includes hiortdahlite in the group, but it is excluded by others because it is not a metasilicate; Hintze² includes jadeite as a triclinic pyroxene, but other authors agree that it is monoclinic; Groth³ adds schizolite and margarosanite to the triclinic pyroxenes, but their crystallographic angles and constants differ decidedly from those of any pyroxenes. Washington and Merwin⁴ add sobralite, pyroxmangite and vogtite to this triclinic group of minerals, but suggest that the group should not be regarded as pyroxenes.

Every mineralogist understands that mineral formulas are practically always simplified too much to represent accurately the real composition. Such simplification is highly desirable so long as no elements which are necessary to the mineral are excluded from the formula. For example, it is proper to consider that ZnS is the formula of sphalerite since the iron, usually present, is entirely unnecessary and merely proxies for part of the zinc. Similarly, it

¹ *System of Mineralogy*, 1892, p. 344.

² *Handbuch der Mineralogie*, II, 1897, p. 960.

³ *Mineralogische Tabellen*, 1921, p. 88 and 108.

⁴ *Am. Mineral.*, VIII, 1923, p. 215.