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Onoratoite,¹ a new antimony oxychloride from Cetine di Cotorniano, Rosia (Siena, Italy)

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Summary. Onoratoite, a new antimony oxychloride $Sb_3O_{11}Cl_2$ from the antimony mines of Cetine di Cotorniano, Rosia (Siena, Italy), is triclinic with lattice constants a 18.92, b 4.03, c 10.31 Å, $\alpha \simeq \gamma \simeq 90^\circ$, β 110°. Density 5.3 meas., 5.49 calc. The needle-like crystals are elongated on [010] and show as prominent form {001}. Other forms present are {100}, {201}, {401}, {412}.

The new mineral is optically biaxial negative, extinction angle small and variable from 0° to 14°. Orientation β : [100] ca. 8°; α : [001] ca. 12°; γ : [010] 0 to 14°. Refractive indices are $2.26 > \gamma > 2.23$, $2.23 > \beta > 2.18$. Birefringence $\gamma - \beta$ 0.024 (meas.).

The stability field of onoratoite has been investigated by systematic thermogravimetric and differential thermal analysis of antimony oxychlorides and by a direct study of equilibrium relationships in the system $SbCl_3$ - Sb_2O_3 - HCl - H_2O . The probable mechanism of formation of onoratoite is discussed.

Onoratoite is named in honour of the Italian mineralogist Ettore Onorato.

AMONG the oxidation products of the antimonite of Cetine di Cotorniano near Rosia, Siena, Tuscany, some specimens had been collected by the late Professor Pelloux before the Second World War showing very fine white needles grown on the antimonite crystals (fig. 1). These specimens have been regarded and identified in some collections as cervantite and sometimes as valentinite.

A previous study by Fornaseri (1947) had shown the presence of chlorine in the mineral, which was thus to be considered as an antimony oxychloride. A first chemical analysis of the material, which proved to be different from all antimony oxychlorides known in the chemical literature, was attempted by Fornaseri (1947), leading to the formula

¹ This new mineral has been approved by the Commission on New Minerals and New Mineral Names of the International Mineralogical Association. Some members of the Commission suggested that the name should be onoratoite instead of onorite and this suggestion has been accepted by the authors of this paper.

$\text{Sb}_3\text{O}_4\text{Cl}$. As very little material was available at that time, the above formula was a tentative one and further research work was necessary in order to determine the composition of the new antimony oxychloride.



FIG. 1. Needles of onoratoite grown on stibnite. Cetine di Cotorniano, Rosia, Siena (Italy). $\times 4$.

Recently more material was available and on the other hand an extensive research work by Belluomini, Fornaseri, and Nicoletti (1967) on the SbCl_3 - Sb_2O_3 - HCl - H_2O system showed the existence of a well-defined antimony oxychloride $\text{Sb}_8\text{O}_{11}\text{Cl}_2$ the composition of which has been never clearly stated in the chemical literature (Cooke, 1877; Lea and Wood, 1922; Edstrand, 1955b).

Now it has been shown that the natural antimony oxychloride of Cetine di Cotorniano and $\text{Sb}_8\text{O}_{11}\text{Cl}_2$ oxychloride are identical from the chemical and the structural standpoint as well.

Chemical analyses of the natural and synthetic materials gave:

	Sb_2O_3	SbCl_3	H_2O	Sum
Natural mineral ¹	87.90	12.10	Nil	100.00
Synthetic ² $\text{Sb}_8\text{O}_{11}\text{Cl}_2$	88.32	11.80	Nil	100.12
Theory for $\text{Sb}_8\text{O}_{11}\text{Cl}_2$	87.55	12.45	Nil	100.00

¹ Based on a thermogravimetric analysis.

² Average of eight analyses of different samples.

The chemical composition of the natural and synthetic compounds is thus consistent with the formula of the anhydrous antimony oxychloride $\text{Sb}_8\text{O}_{11}\text{Cl}_2$.

TABLE I. X-ray powder diffraction data for onoratoite and artificial $\text{Sb}_8\text{O}_{11}\text{Cl}_2$.
Cu-K α , Ni filter; camera diameter 57.3 mm; intensity: visual estimate

<i>Onoratoite</i>		$\text{Sb}_8\text{O}_{11}\text{Cl}_2$ <i>artificial</i>		<i>Onoratoite</i>		$\text{Sb}_8\text{O}_{11}\text{Cl}_2$ <i>artificial</i>	
<i>d</i>	<i>I/I</i> ₀	<i>d</i>	<i>I/I</i> ₀	<i>d</i>	<i>I/I</i> ₀	<i>d</i>	<i>I/I</i> ₀
4.394	5	4.394	5	1.854	15	1.856	15
4.056	10	4.038	10	1.807	30	1.803	30
3.741	20	3.765	10	1.715	20	1.719	20
3.406	5	3.406	5	1.694	15	1.694	15
3.190	100	3.176	100	1.657	10	1.654	10
3.041	50	3.036	50	—	—	1.617	10
2.822	50	2.811	50	1.591	20	1.589	20
2.677	60	2.681	40	1.574	20	1.578	20
2.598	30	2.595	30	—	—	1.520	5
2.544	30	2.534	30	1.434	15	1.431	15
2.403	5	2.379	5	1.419	15	1.416	15
2.252	5	2.241	5	1.376	20	1.371	20
2.111	20	2.100	20	1.303	5	1.296	5
2.030	20	2.029	20	—	—	1.254	5
—	—	1.927	5	—	—	1.247	5

The crystals are needle-like and show triclinic, pseudomonoclinic symmetry. Lattice constants, as determined by Professor Sgarlata of the Institute of Mineralogy of the University of Rome with a single-crystal diffractometer are: a 18.92 Å, b 4.03 Å, c 10.31 Å, $\alpha \approx \gamma \approx 90^\circ$, β 110°, V 738.7 Å³; space group $P\bar{1}$. X-ray powder data are given in Table I. Density: calculated 5.49, measured¹ 5.3.

The needle-like crystals are elongated [010] and flattened {001}; other present forms are {100}, {201}, {401}, and {412}. The crystals are biaxial negative, the extinction angle on (001) is small and variable from 0° to 14°. Orientation α : [001] *ca.* 12°; β : [100] *ca.* 8°; γ : [010] 0–14°. Observed on (001) the crystals show a rather excentric emergence of the acute bisectrix. The refractive indexes, estimated by the immersion method making use of S–Se melts calibrated by the prism method are: $2.26 > \gamma > 2.23$, $2.23 > \beta > 2.18$. Birefringence (from retardation measurement) $\gamma - \beta$ 0.024.

The antimony oxychloride found at Cetine di Cotorniano (Rosia, Siena) is thus to be considered a new mineral species and the name of

¹ By loss of weight in benzene.

onoratoite is proposed in honour of the Italian mineralogist Ettore Onorato.

Onoratoite is insoluble in water, completely soluble in 6*N* hydrochloric acid. With nitric acid it yields a white antimony pentoxide residue and the solution reacts for Cl^- ions. It is also soluble in strong sodium

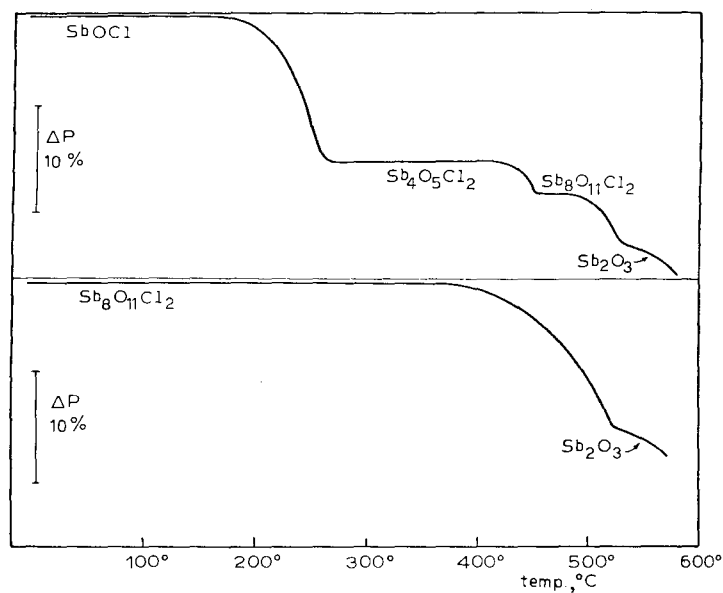


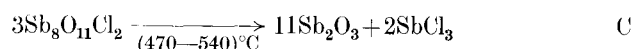
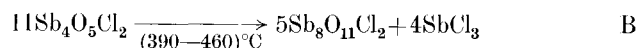
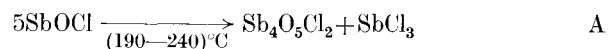
FIG. 2. Thermogravimetric curves for SbOCl and $\text{Sb}_8\text{O}_{11}\text{Cl}_2$.

hydroxide and in concentrated tartaric acid solution. Heated in a closed tube onoratoite gives off SbCl_3 vapours, which condense on the walls of the tube in the form of oily drops, and leaves a residue of antimony oxides.

As shown by the TGA (fig. 2) the onoratoite starts to decompose at 380°C giving off SbCl_3 . At $510\text{--}50^\circ\text{C}$ the distillation of SbCl_3 is finished and the residue has the composition of Sb_2O_3 and the crystal structure of valentinite. At higher temperature the sublimation of Sb_2O_3 occurs when operating in nitrogen atmosphere and oxidation to higher oxides in the presence of oxygen.

In order to investigate the stability relationship of $\text{Sb}_8\text{O}_{11}\text{Cl}_2$ TGA, DTA, and equilibrium methods in aqueous solution have been employed.

The thermal decomposition of the higher antimony oxychlorides SbOCl and $\text{Sb}_4\text{O}_5\text{Cl}_2$ has been investigated by TGA (Belluomini, Fornaseri, and Nicoletti, 1967). It has been shown that with rising temperature the following reactions take place:



This is shown in the TGA diagram of fig. 2, where the different steps of the decomposition of SbOCl are exhibited.

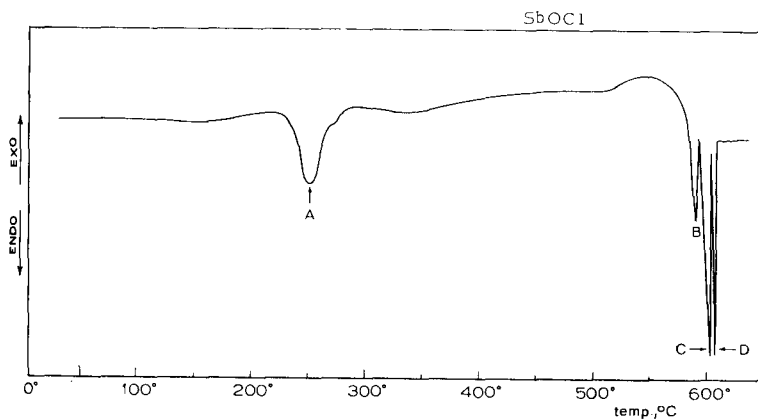
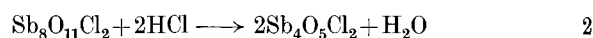
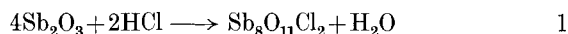


FIG. 3. Differential thermal analyses curves for SbOCl .

The thermal effects corresponding to the reactions A, B, and C are displayed in the DTA diagram of fig. 3. A first endothermic effect occurs at 230 °C, corresponding to the reaction A; a second endothermic effect, corresponding to the reaction B, occurs at 580 °C; the endothermic peak corresponding to the reaction C occurs at 600 °C, followed by the endothermic D peak due to the melting of Sb_2O_3 . The transformation temperatures as indicated by the DTA are somewhat higher than those indicated by the TGA for the reactions A, B, and C. This shift has been fully discussed in Belluomini *et al.* (1967).

An investigation of the system SbCl_3 - Sb_2O_3 - HCl - H_2O has been carried out by studying the hydrolysis of SbCl_3 at different dilutions and temperatures and by equilibrating Sb_2O_3 with HCl at different

concentrations at 100 °C. By both methods the existence of the $\text{Sb}_8\text{O}_{11}\text{Cl}_2$ oxychloride has been confirmed, although its stability range is very narrow. This is particularly shown in the diagram of fig. 4 where on the abscissa the chlorine content in the solid phases and on the ordinate the Cl^- normality in the liquid phase are reported. The reactions taking place in aqueous solution are:



Since the only chemical parameter effective in conditioning the above equilibrium is the HCl concentration, the equilibrium constants are $K_1 = 1/a_{\text{HCl}}^2$; $K_2 = 1/a_{\text{HCl}}^2$ at 100 °C for reactions 1 and 2 respectively. From the concentration measurements we get $K_1 = 905$ and $K_2 = 155$ assuming as activity coefficients at 100 °C for HCl concentrations of 0.04 *N* and 0.105 *N* the values of 0.798 and 0.764 respectively; the activity coefficients were obtained by extrapolation to 100 °C of values based on the data of H. S. Harned and R. W. Ehlers as reported by Harned and Owen (1943). From the above values $\Delta G_0^{100^\circ\text{C}}$ values are obtainable: for reaction 1 $\Delta G_0^{100^\circ\text{C}} = -5.0$ kcal and for reaction 2 -3.7 kcal.

In spite of its narrow range of stability onoratoite, $\text{Sb}_8\text{O}_{11}\text{Cl}_2$, can be easily obtained artificially by one of the following procedures: by boiling for 50 hours 1 g commercial Sb_2O_3 with 1100 ml of 0.76 *N* hydrochloric acid; by hydrolysis of SbCl_3 with water (1 part of SbCl_3 to 40 parts of water) in a sealed tube at 300–5 °C; by hydrolysis of SbCl_3 with water in the ratio of 1 part of SbCl_3 to 150 parts of water at boiling temperature for 50 hours; by reaction of hydrochloric acid solutions (0.1 *N*) on Sb_2S_3 in a sealed tube at 200 °C; by pyrolysis of $\text{Sb}_4\text{O}_5\text{Cl}_2$ at atmospheric pressure in a temperature range from 320 to 400 °C (at higher temperatures the reaction is too rapid); or by pyrolysis of $\text{Sb}_4\text{O}_5\text{Cl}_2$ from 410 to 430 °C in a vacuum-sealed tube (in this case well-developed crystals are formed from a gas phase). Onoratoite occurs as an oxidation product of stibnite in the quaternary antimony deposits of Tuscany and has been found in the old antimony mines of Cetine di Cotorniano near Rosia, Siena. The needle-like crystals grow directly on the stibnite crystals, or sometimes over a thin intermediate layer of stibiconite. Quartz deposition was active during the alteration process of the stibnite and the quartz seems to have formed later than stibiconite and onoratoite, although the latter appears sometimes to be later than quartz. Onoratoite seems thus to have been formed in different generations.

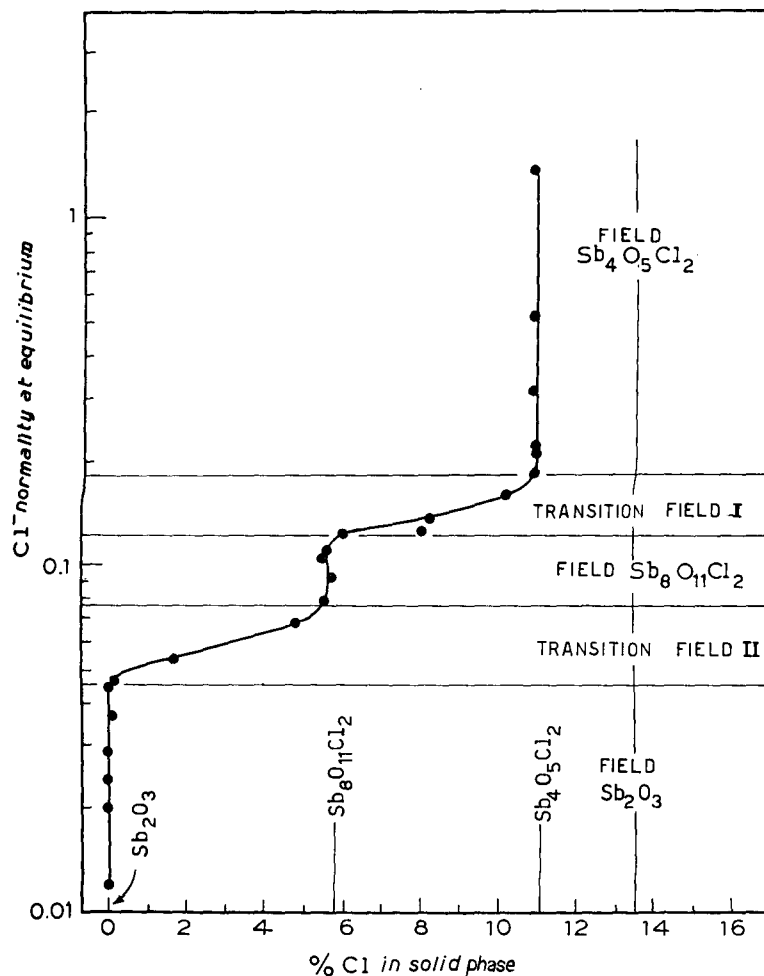


FIG. 4. Diagram showing the stability fields of various antimony oxychlorides as a function of Cl⁻ normality.

The lower temperature limit of formation of onoratoite can be estimated at 60 °C, since below this temperature a hydrated antimony oxychloride (γ -phases according to Edstrand, 1955*a*) would have been formed (Belluomini *et al.*, 1967). The higher temperature limit cannot easily be established; the temperature obviously could not have been higher than the melting temperature of stibnite (540 °C). At atmospheric

pressure a more defined upper limit is established by the decomposition temperature of onoratoite (380 °C).

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