

## Hetaerolite from the Rodna Base Metal Ore Deposit: A New Occurrence

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### Abstract

A new occurrence of hetaerolite from Rodna/Rumania is described and detailed mineralogical and chemical investigations undertaken.

### Introduction

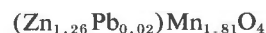
The mineral hetaerolite ( $\text{ZnMn}_2\text{O}_4$ ) which is chemically similar to the mineral hausmannite, was first described from the Sterling Hill deposit, New Jersey, by Moore (1877) and later studied in detail by Palache (1910). Other localities where hetaerolite is known to occur include the Franklin Mine, New Jersey, and Leadville, Colorado (Frondele and Heinrich, 1942). Recently Hewett and Fleischer (1960) have reported hetaerolite from the Contact Mine, Grant County, New Mexico, and the Lucky Cuss Mine, Tombstone, Arizona. They as well as Ramdohr and Frenzel (1956) before them, expressed the opinion that hetaerolite—as a product of weathering of Mn-bearing zinc ores—is much more abundant than previously thought. Now hetaerolite has also been found in the Pb–Zn-deposit at Rodna, Rumania, probably the first locality in Europe. The Rodna deposit belongs to the neogene metallogenetic province of the Carpathian Mountains (Giusca, Cioflica, and Udubasa, 1969) and consists of metasomatic ore-bodies in metasomatic limestones and of injections in andesitic explosion-breccias. The ores consist predominantly of pyrite, sphalerite, pyrrhotite, and galena (Udubasa, 1970). The hetaerolite discussed here was found in cavities within the crystalline limestones where it occurs in a matrix of limonitic ochre together with broken-off fragments of galena crystals, which have been partially coated by cerussite.

Macroscopically the hetaerolite is usually stalactitic but occasionally botryoidal in appearance (Fig. 1). Under reflected light it is gray, and similar to magnetite. Its reflectivity measured with a Leitz-microphotometer is 17–19 percent (see Nichol and

Phillips, 1965) and decreases considerably under oil immersion. The mineral is weakly pleochroic, even under oil immersion; reflection pleochroism can be observed only along zone or grain-boundaries. Changes in color and reflectivity were nevertheless observed frequently; they were attributed, however, to differences in grain-size and porosity. As a rule homogeneous, coarse grained zones tend to be enclosed by fine-layered ones (Fig. 2), which points to rhythmic separation from a gel. Hetaerolite is clearly anisotropic, but without colorplay. Of interest are the “pyramidal” microstructures observed under crossed nicols (Fig. 3), which are interspersed with fine-grained layers. This feature leads to an increase in anisotropy. Internal reflections were not observed.

### Experimental Results

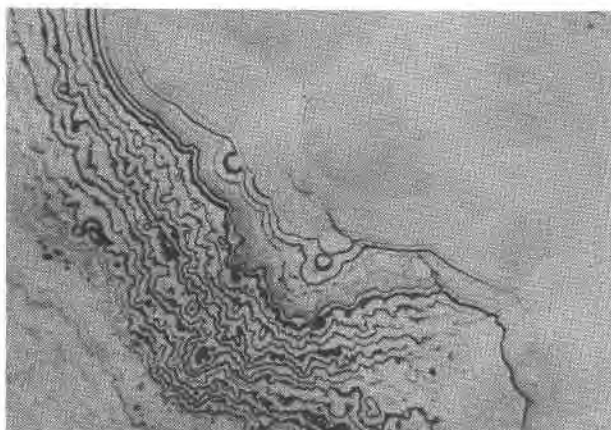
The hetaerolite was analyzed for Mn, Zn, and Pb with the electron microprobe (Table 1). Spectrally pure metallic manganese, synthesized zinc-oxide, and stoichiometric galena were used as standards. The corrections were carried out using the X-ray absorption coefficients of Heinrich (1966). Infrared-spectrometric study showed only 1.0 percent OH. Disregarding this small quantity of OH, the chemical formula for hetaerolite from Rodna may be reduced to:



Hetaerolite coexists locally with a mineral which, based on microprobe analysis ( $\text{MnO}_2$ , 59.69 percent;  $\text{PbO}$ , 32.34 percent;  $\text{ZnO}$ , 5.33 percent), appears related to either coronadite or cesarolite. Its small quantities prevented its study by means of



FIG. 1. Hetaerolite from Rodna. Scale in cm.



(a)



(b)

FIG. 2. Fine-layered hetaerolite encrusted with a weakly recrystallized zone of the same mineral. Polished section, oil immersion, magnification 930  $\times$ . (a) parallel nicols (b) crossed nicols.

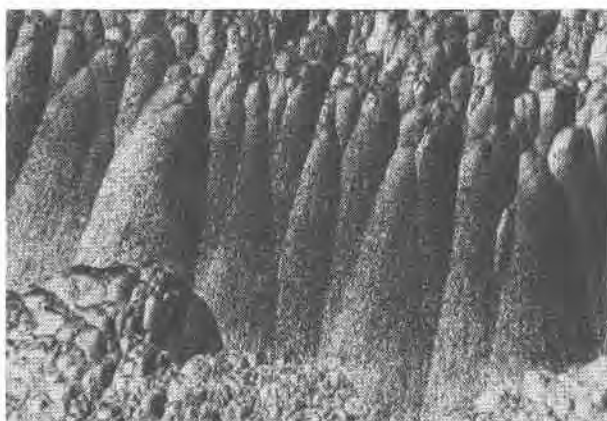


FIG. 3. "Pyramidal" textured hetaerolite overgrowing a fine-grained zone. Polished section, crossed nicols, oil immersion, magnification 550  $\times$ .

X-ray analysis. Its optical properties could not be determined with exactness. Its reflectivity is greater than of hetaerolite ( $R = 22\text{--}23$  percent) and its hardness less. The mineral appears to be weakly anisotropic.

The thermal behavior of hetaerolite was studied with a Mettler DTA-analyzer using a heating-rate of  $10^\circ\text{C}/\text{min}$  in flowing air. DTA and TGA measurements were obtained simultaneously with this instrument. Hetaerolite shows a double reversible exothermic reaction at  $460$  and  $480^\circ\text{C}$  (Fig. 4). Both peaks possibly point to the oxidation of the manganese in the hetaerolite. The small (irreversible) peak (reaction) at  $882^\circ\text{C}$  is similar to the phase-change of hausmannite from the  $\alpha$ -form to the  $\beta$ -form (Agiorgitis, 1969). From this it may be assumed that the structure of hetaerolite already shows a certain amount of order prior to attaining the double peak, *i.e.*, at about  $480^\circ\text{C}$ . A subsequent X-ray study of the heating end-product showed only hetaerolite (Table 2). Whether a phase-change from  $\alpha$ -hetaerolite to  $\beta$ -hetaerolite takes place at  $882^\circ\text{C}$ , as with hausmannite, is uncertain. However, the

TABLE 1. Electron Microprobe Analysis of Hetaerolite from Rodna

	Wt %		Wt %	At. %
ZnO	40.48	Zn	32.51	17.76
Mn <sub>2</sub> O <sub>3</sub>	56.44	Mn	39.28	25.53
PbO	1.94	Pb	1.80	0.31
		O	25.27	56.40
		Sum	98.86	100.00

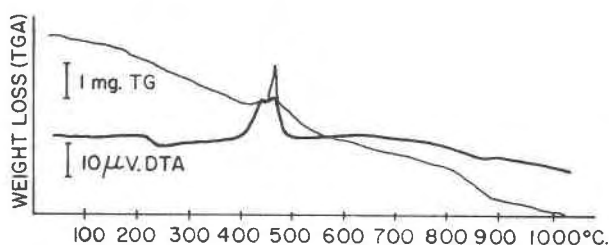


FIG. 4. Thermogram of DTA and TGA for hetaerolite. The curves were carried out using the same analyzer in an atmosphere of flowing air 5.7 l/h at a heating rate of 10°C/min.

thermogravimetric curve permits us to assume a phase-change based on the continuous decrease in weight. The X-ray data for the starting material (I) and the tempered material (II) clearly show (Table 2) a difference in the intensity of the lines as well as a shift in the  $d$ -values between the non-tempered and tempered material. The differences in the intensity of the lines are not only the product of a difference in the crystallinity of both substances but possibly also a difference in  $a_0$ .

The infrared spectra for substances I and II show similarities in the 700  $\text{cm}^{-1}$  range (Fig. 5). The reduction in the width of the peak at half maximum for heat-tempered substances points to improved crystallinity. The four bands measured correspond to the vibrations  $\nu_1$  (636  $\text{cm}^{-1}$ ),  $\nu_2$  (540  $\text{cm}^{-1}$ ),  $\nu_3$  (405  $\text{cm}^{-1}$ , 350  $\text{cm}^{-1}$ ), and  $\nu_4$  (below 200  $\text{cm}^{-1}$ ). The bands occurring in the frequency range around

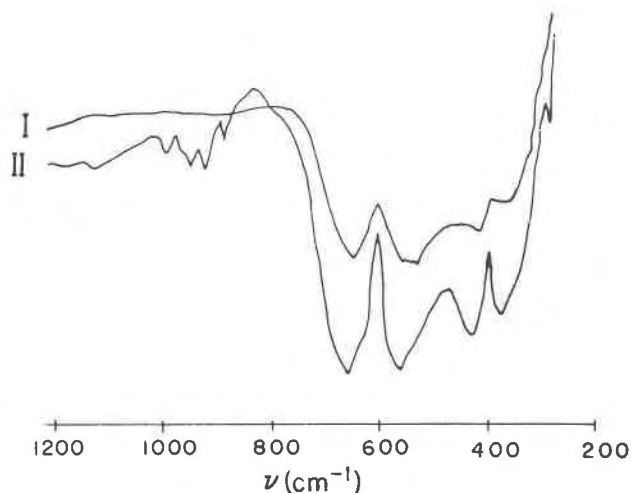


FIG. 5. IR-spectra of non-tempered (I) and tempered (II) hetaerolite. The spectra were obtained for both substances using a Perkin Elmer IR-624 spectrophotometer, with KBr as the matrix material. Spectra were recorded over the range 200–4000  $\text{cm}^{-1}$ .

900  $\text{cm}^{-1}$  could not be identified with certainty. The fact that other Mn-compounds—for example  $\text{KMnO}_4$ —show absorption bands in the 930–900  $\text{cm}^{-1}$  range would tend to indicate that a small fraction of the octahedrally coordinated  $\text{Mn}^{3+}$  was oxidized to  $\text{Mn}^{5+}$  or  $\text{Mn}^{7+}$ . This assumption is supported by the observed continuous reduction in weight during thermogravimetric analysis.

Changes in the crystal structure after heating are also indicated by a split in the  $\nu_3$ -vibrations. This split possibly points to a substitution of the octahedrally coordinated  $\text{Mn}^{3+}$  by  $\text{Mn}^{5+}$ , whereas in the case of a substitution of the tetrahedrally coordinated  $\text{Mn}^{2+}$  by  $\text{Mn}^{3+}$ , a separation in the  $\nu_4$ -vibrations would be expected. According to Preudhomme and Tarte (1971) only  $\nu_3$  can be split. Therefore, it is possible that the Pb-fraction of hetaerolite from Rodna occupies the octahedral Mn-positions in the crystal structure. The distribution of cations is dependent on temperature and hence can influence changes in the crystallographic axes.

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TABLE 2. Hetaerolite X-ray Data, before Heating (I) and after Heating (II)\*

I			II			ASTM	
Int.	$d(\text{Å})$	$hkl$	Int.	$d(\text{Å})$	$hkl$	Int.	$d(\text{Å})$
4	4.79	101	8	4.81	101	10	4.87
54	3.00	112	60	3.02	112	70	3.04
15	2.84	200	39	2.85	200	40	2.85
20	2.65	103	76	2.68	103	90	2.69
60	2.45	211	100	2.46	211	100	2.46
96	2.32	004	38	2.32	004	30	2.30
42	2.01	220	30	2.01	220	30	2.01
--	--	204	15	1.78	204	30	1.79
8	1.74	105	28	1.74	105	50	1.75
10	1.67	312	25	1.67	312	40	1.68
--	--	303	15	1.61	303	30	1.61
20	1.56	321	28	1.55	321	50	1.56
17	1.50	224	55	1.51	224	80	1.51
20	1.42	400	26	1.42	400	40	1.43

\*I  $a_0 = 5.70$ ; II  $a_0 = 5.71$ ; ASTM  $a_0 = 5.721$ .  
 Diffractometer, Cu-K $\alpha_1$  radiation, Ni-filter, 1°2 $\theta$ /min.  
 by 40 kV and 20 mA.

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