

## Polytypism of heterogenite

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**SUMMARY.** A new variety of heterogenite was found in samples from Mindigi, Shaba,<sup>1</sup> Zaïre.<sup>2</sup> Photometric reflectance varies from 0.235 to 0.165 at  $\lambda$  5890 Å in air. The bireflectance is 0.070, the degree of anisotropy is 0.7 and the main index in air is 2.7. A thermal weight-loss curve and a microprobe analysis are given and discussed, indicating the formula (Co,Ni) O.OH.

The new variety, referred to as heterogenite-H, is hexagonal with cell dimensions  $a$  2.85,  $c$  8.80, space group  $P6_3/mmc$  and cell-content 2 [(Co, Ni)O.OH]. Indexed X-ray powder data are given. A crystal structure is suggested based on CoO.OH octahedra layers and indicating a polytypic relation between heterogenite-H, the 2H form, and normal heterogenite, the 3R form.

THE term heterogenite (Frenzel, 1872) has priority to design hydrated cobalt oxides with formula CoO.OH (Hey, 1962). The minerals of the heterogenite group occur in many different forms (crystalline masses, reniform, encrustations, porous aggregates, stalactites); their composition and physical properties differ considerably from one variety to another. They all are nevertheless defined by a close resemblance of their X-ray diffraction patterns (table I). The unit cell has been determined by Kondrashev and Fedorova (1954). It is trigonal with probable space group  $R\bar{3}m$ , cell dimensions  $a = 4.676$  kX,  $\alpha = 35^\circ 28'$  and unit-cell contents [CoO.OH]; hexagonal unit-cell dimensions:  $a = 2.855$  Å and  $c = 13.157$  Å.

In fact one can define two extreme types in this mineral group: one is crystalline with a sharp unique X-ray diffraction pattern, the other is pseudo-crystalline, showing only broad lines corresponding to the strongest ones of the crystalline type, and between them there is a whole series of intermediate varieties.

The crystalline heterogenites are black and display a metallic lustre. The density is variable: 4.32 (Schoep and Cuvelier, 1939), 4.37 (De Leenheer, 1950), 4.72 (Kondrashev and Fedorova, 1954), 4.50 (Deliens, 1972). The hardness varies from 4 to 5. Vickers microhardness ranges from 420 up to 560 kg/mm<sup>2</sup> for a 100 g load (Deliens, 1972). Microscopic examination of heterogenites with reflected light shows strong reflection pleochroism and anisotropy. The maximum bireflectance measured in air with yellow light gives values from 0.065 (De Leenheer, 1950) to 0.086 (Deliens, 1972) and with green light 0.070 (Ramdohr, 1969).

<sup>1</sup> Shaba: new name since 1971 for Katanga.

<sup>2</sup> Zaïre: new name since 1971 for République Démocratique du Congo.

Chemical analysis of Shaba minerals (Deliens, 1972) indicates that Co exists mainly as  $\text{Co}^{3+}$ . Nickel substitutes up to 2 per cent and copper only to a small extent. The mineral fits the formula  $\text{CoO}\cdot\text{OH}$  with less than 1.5 per cent molecular water.

The pseudo-crystalline heterogenites occur as coal-black botryoidal masses with conchoidal fracture. The density varies around 3 (De Leenheer, 1950; Deliens, 1972). The hardness ranges from 3 to 4. Microscopic examination usually shows isotropic masses, although these heterogenites can display a weak anisotropy of 'aggregate in layers' (De Leenheer, 1950). Vickers microhardness varies from 60 to 170  $\text{kg}/\text{mm}^2$  for a 100 g load. Chemical analysis of Shaba minerals proved the presence of  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$ , with a ratio 1/1 in the least crystalline specimen (RGM 10817), together with a high copper content (nearly 20 %  $\text{CuO}$ ). Therefore we assume the formula  $(\text{Co}_2\text{O}_3, \text{CoO}, \text{CuO}) \text{H}_2\text{O} + n$  per cent molecular water.

X-ray powder patterns of crystalline heterogenites from Shaba showed a set of reflections that were not characteristic of heterogenite. The crystalline zones are composed of two mineral species in juxtaposition of which one is heterogenite *sensu stricto*. The other was isolated from sample RGM 10800 of the collection of the 'Musée royal de l'Afrique Centrale' (heterogenite from Mindigi).

#### *Examination of the new mineral*

*Microscopic description.* The crystal habit is hexagonal prismatic with well developed  $\{0001\}$ . The size ranges from 0.1 to 1 mm; intergrowths or twinning were commonly observed. The colour is black to grey with a strong metallic lustre, that resembles the lustre of specularite.<sup>1</sup> The mineral has a good cleavage parallel to  $\{0001\}$ , as does molybdenite, and it seems to be malleable.

*Optical properties.* Examination with reflected light shows the mineral as twinned pleochroic plates varying from white to grey (fig. 1). Under crossed nicols they are strongly anisotropic. The reflectivity measured in air with monochromatic yellow light ( $\lambda = 5890 \text{ \AA}$ ) is  $R_{\text{max}} = 0.235$  and  $R_{\text{min}} = 0.165$  for the strongly anisotropic sections. The bireflectance is 0.070. The degree of anisotropy  $\rho$  is 0.7 and the main index in air is 2.7. The maximum value for the Vickers microhardness with a 100 g load is 640  $\text{kg}/\text{mm}^2$ .

*Electron microprobe analysis.* An electron microprobe analysis was carried out with an AMX-apparatus. Profiles were taken for cobalt and nickel (fig. 2) and show a homogeneous distribution of cobalt in all the grains examined. The nickel curve fluctuates, but this is partly due to the increased sensitivity, which was 10 times higher than for cobalt, nickel only being present in small amounts. A spectral analysis

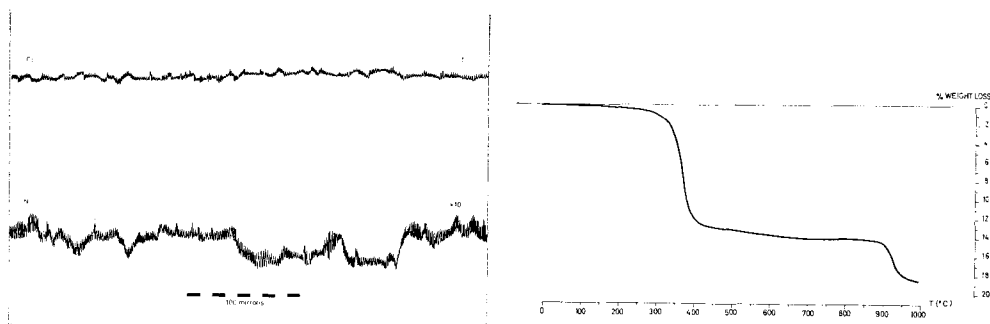


FIG. 1. Photomicrograph of sample RGM 10800. Crossed polars.  $\times 83$ .

<sup>1</sup> Specularite is a hematite variety.

indicated the exclusive presence of these two elements, disregarding the structural water content, which was determined by thermal dehydration.

*Thermal dehydration.* The water content of the mineral was determined with a thermobalance. The curve (fig. 3) shows two steps: the first between 200° and 450 °C with a maximum gradient between 300° and 375 °C, the second between 900° and 975 °C; they correspond to the transformation from oxy-hydroxide to spinel ( $\text{Co}_3\text{O}_4$ ) and to the reduction of  $\text{Co}_3\text{O}_4$  to  $\text{CoO}$ , respectively, according to the reactions:



FIGS. 2 and 3: FIG. 2 (left). Electron microprobe analysis: section for Co and Ni across sample R.G.M. 10800. FIG. 3 (right). Thermal dehydration: weight-loss curve of sample R.G.M. 10800.

$6(\text{Co,Ni})\text{O.OH} \rightarrow 2(\text{Co,Ni})_3\text{O}_4 + 3\text{H}_2\text{O} + 1/2 \text{O}_2$  and  $\text{Co}_3\text{O}_4 \rightarrow 3\text{CoO} + 1/2 \text{O}_2$ . The weight loss caused by the first reaction represents 12.8% of the initial weight, which is in good agreement with the theoretical value of 12.7% for  $\text{CoO.OH}$ . The mineral has lost 19.4% of the initial weight at 1000 °C and is devoid of molecular water.

*Chemical formula.* The results of the electron-microprobe point analysis of specimen RGM 10800 were converted to 100% using the water content from the thermal dehydration results:  $\text{Co}_2\text{O}_3$  88.1, NiO 2.0,  $\text{H}_2\text{O}^+$  9.9. The formula corresponds to  $(\text{Co,Ni})\text{O.OH}$ .

*Conclusion.* The chemical analysis indicates that the mineral has the same composition as heterogenite.

#### *X-ray diffraction analysis*

*Powder patterns.* X-ray powder diffraction analysis was performed on a Guinier-De Wolff Multiple-Focussing-II camera with  $\text{Fe-K}\alpha$  and on a Debye-Scherrer camera, 114.6 diameter, with  $\text{Fe-K}\alpha$  and Ni-filter. The results are given in table I and compared with those of normal heterogenite. The indexing was done using the data of the monocrystal analysis. The relative intensities could not be measured since the diffraction lines were spotty, owing to the impossibility of preparing fine powder, because of the good basal cleavage and the apparent malleability of the mineral.

*Determination of cell dimensions and space group.* The new mineral is hexagonal; the cell dimensions as determined from oscillation and Weissenberg photographs were refined for film shrinkage and camera errors by the least squares method of Cohen. They are  $a$   $2.855 \pm 0.005$  Å and  $c$   $8.805 \pm 0.005$  Å.

While it was not possible to determine the density of the mineral we supposed that the density was approximately the same as that of normal heterogenite, 4.72 g/cm<sup>3</sup> (Kondrashev and Fedorova, 1954). There are thus 2[CoO.OH] units in the cell.

TABLE I. X-ray powder data for heterogenite-2H, from sample 10800 obtained from a 114.6 mm diameter Debye-Scherrer camera taken with filtered Fe-K $\alpha$  radiation. Comparison with normal heterogenite-3R as given by Hey (1962)

Heterogenite-2H				Heterogenite-3R			
$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{obs}}$	$hkil$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{obs}}$	$hkil$
4.39	4.403	vvs	0002	4.40	4.377	vvs	0003
2.472	2.476	ms	11 $\bar{1}$ 0	2.428	2.425	m	1011
2.381	2.384	mw	10 $\bar{1}$ 1	2.315	2.310	vs	10 $\bar{1}$ 2
2.195	2.201	vvw	0004	2.208	2.188	vw	0006
2.158	2.159	s	10 $\bar{1}$ 2	1.979	1.972	mw	1014
1.892	1.893	vw	10 $\bar{1}$ 3	1.804	1.798	s	10 $\bar{1}$ 5
1.644	1.645	s	10 $\bar{1}$ 4	1.501	1.493	mw	1017
1.429	1.430	mw	11 $\bar{2}$ 0	1.427	1.424	ms	11 $\bar{2}$ 0
1.358	1.360	mw	11 $\bar{2}$ 2	1.374	1.366	vw	10 $\bar{1}$ 8
1.262	1.263	ms	10 $\bar{1}$ 6	1.356	1.354	m	11 $\bar{2}$ 3
1.236	1.238	vs	20 $\bar{2}$ 0	1.230	1.229	vw	20 $\bar{2}$ 1
1.199	1.199	vvw	11 $\bar{2}$ 4	1.216	1.212	mw	20 $\bar{2}$ 2
1.191	1.192	w	20 $\bar{2}$ 2	1.199	1.194	vw	11 $\bar{2}$ 6
				1.163	1.159	wb	1.0.1.10
					1.155		20 $\bar{2}$ 4
				1.120	1.116	mw	20 $\bar{2}$ 5
1.100	1.101	vw	0008	1.036	1.031	vw	20 $\bar{2}$ 7
1.079	1.079	mw	20 $\bar{2}$ 4	1.024	1.019	vvw	11 $\bar{2}$ 9
1.024	1.024	vvw	11 $\bar{2}$ 6				
1.006	1.006	w	10 $\bar{1}$ 8				

Oscillation about  $c$  shows a symmetry plane perpendicular to the sixfold rotation axis that is evident from Weissenberg photographs. The systematic absences are  $hh\bar{2}hl$  for  $l = 2n + 1$  and  $hkil$  when  $h - k = 3n$  and  $l = 2n + 1$ , characteristic of the space groups  $P\bar{6}2c$  and  $P6_3/mmc$  with atoms in special positions. The unit cell contains four oxygen and two cobalt ions as well as the two hydrogens. So only the twofold and fourfold special positions are possible. These positions are common to both space groups so the correct space group is  $P6_3/mmc$ .

*Polytypism and proposed structure.* Comparison between the cell dimensions of normal heterogenite and the new mineral indicates an interesting relation: heterogenite has  $a$  2.855 Å and  $c$  13.157 Å while the new mineral has the same value of  $a$  and  $c$  8.805 Å, which is  $\frac{2}{3}$  of  $c$  of heterogenite.

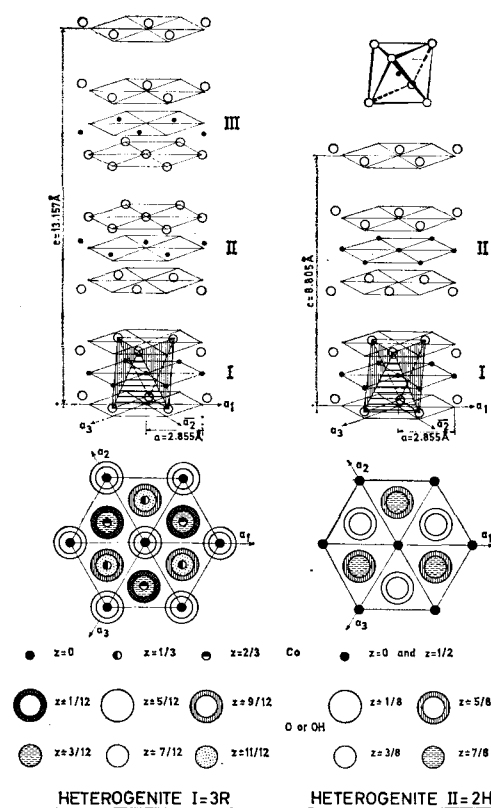


FIG. 4. Top left: Front view of heterogenite-3R as proposed by Kondrashev and Federova (1954). Bottom left: Projection along  $c_{\text{Hex}}$  of heterogenite-3R. Top right: Structural Unit: the  $\text{CoO.OH}$  (or  $\text{Co(O.OH)}_6$ ) octahedron. Middle right: Front view of the suggested structure for heterogenite-2H. Bottom right: Projection along  $c$  of heterogenite-2H.

The layer structure of heterogenite, as proposed by Kondrashev and Federova can explain this relation. Each layer is composed of two sheets of O or OH in hexagonal close packing with Co in octahedral coordination between the sheets (fig. 4) and is in fact a layer of  $\text{Co(O.OH)}_6$  octahedra. The 'unit-cell' of the layer has  $a = 2.855 \text{ \AA}$  and  $c \approx 4.4 \text{ \AA}$ . The layers are stacked parallel to one another with a periodicity 3. The parameter relation suggests for the new mineral a stacking of the same layers but with a periodicity 2 (fig. 4).

Although we have not been able to carry out a structure analysis we have tried to check this polytypic relation. Using the indications of the space group's special positions and the atom positions of the heterogenite structure, we place the Co-ions in position 2a (0,0,0 and 0,0,1/2) and the oxygens in the 4f position ( $1/3, 2/3, z$ ;  $2/3, 1/3, z$ ;  $2/3, 1/3, 1/2+z$ ;  $1/3, 2/3, 1/2-z$  with  $z \approx 1/8$ ) (fig. 4). Just as for heterogenite we accept the existence of hydrogen bonds between the oxygens of adjacent layers, although we have no evidence for this.

To check the suggested structure for the new mineral we have calculated the relative intensities, based on the above coordinates and a value of  $B = 1.4 \text{ \AA}^2$  for the temperature factor as for heterogenite.

A preliminary visual estimation of the observed intensities showed very good agreement with the calculated ones for filtered Mo- $K\alpha$  zero level Weissenberg photographs. In spite of strong absorption in the higher levels, taken with filtered Cu- $K\alpha$  radiation, there is a rough but obvious correspondence between calculated and observed intensities.

#### Conclusion

The new mineral has about the same optical and physical properties and about the same chemical composition as heterogenite. We therefore assume it to be a variety of

heterogenite. X-ray analysis suggests a polytypic relation, the new mineral being heterogenite-2H, while the normal mineral is heterogenite-3R.

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## REFERENCES

- DE LEENHEER (L.), 1950. *Ann. Serv. Mines, Com. Spéc. Katanga*, **15**, 1.  
DELIENS (M.), 1972. Thèse de doctorat.  
FRENZEL (A.), 1872. *Journ. prakt. Chem.*, new ser. **5**, 404.  
HEY (M. H.), 1962. *Min. Mag.* **33**, 253-9 [M.A. **16-173**].  
[KONDRASHEV (Yu. D.), and FEDOROVA (N. N.)] Кондрашев (Ю. Д.) и Федорова (Н. Н.), 1954. Докл. акад. наук СССР (*Compt. Rend. Acad. Sci. URSS*) **94**, (2) 229-31.  
RAMDOHR (P.), 1969. *The ore minerals and their intergrowths*. Oxford (Pergamon Press).  
SCHOEP (A.) and CUVELIER (V.), 1929. *Bull. Soc. belge Géol.* **39**, 74 [M.A. **4-347**].

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