

Cobaltic hydroxide in nature.

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[Read 7 June 1962.]

Summary. Natural cobalt hydroxide is CoO.OH , not Co(OH)_2 as has recently been asserted; for this mineral the name heterogenite has priority. Copper, frequently present, may be in solid solution as $(\text{Co,Cu})(\text{O,OH})\text{OH}$, or may be as finely divided malachite; for cuprian heterogenite, the name schulzenite has priority.

COBALTIC hydroxide was first reported as a mineral by A. Frenzel (1872) from Schneeberg, Saxony, and by A. Breithaupt (1872) from Oria, Motril, Sierra Almahilla, Spain, and from Rothenburg, Saalfeld. Frenzel's mineral, to which he gave the name heterogenite,¹ was essentially CoO.OH , with only minor impurities but, according to Frenzel's available-oxygen determination made by Bunsen's method, with some 15 % Co(OH)_2 and about 10 % excess water. Breithaupt's was admittedly a gross mixture, interpreted as consisting of cobaltic hydroxide, a basic cobaltous carbonate, malachite, and pharmacolite; he gave the name winklerite, apparently to the mixture (which only contained 10 % Co_2O_3), but A. Weisbach (1882), who cited three new analyses of material from Motril, applied this name to the cobaltic hydroxide. Frenzel's name has a few months' priority over Breithaupt's, and his material was purer and better described.

Weisbach's material was nickeliferous, with Co:Ni from 4 to 2. Nickelian heterogenite had already been described as a distinct species by F. Sandberger (1876*b*) from St. Anton, Heubachtal, Wittichen, Baden,² and from the Eberhard mine, Alpirsbach, Schwarzwald, and named heubachite, the formula being given as $3(\text{Co,Ni})_2\text{O}_3.4\text{H}_2\text{O}$. Cuprian heterogenite, from an uncertain locality, probably northern

¹ This name has no reference to heterogeneous in its current English meaning of a mixture, 'composed of diverse elements'; Frenzel derives it from 'ἑτερογενής, d.i. von anderer Art', to emphasize that, although outwardly like the black manganese oxides, the mineral is of quite another kind.

² Sandberger had earlier reported this material as asbolane (1868) or as heterogenite (1876*a*).

Chile, was described by P. Martens (1895) under the name schulzenite (Co:Cu about 4). A further occurrence of impure heterogenite, near Middleburg, Transvaal, was described as a new mineral, transvaalite, by T. B. McGhie and J. Clark (1890).

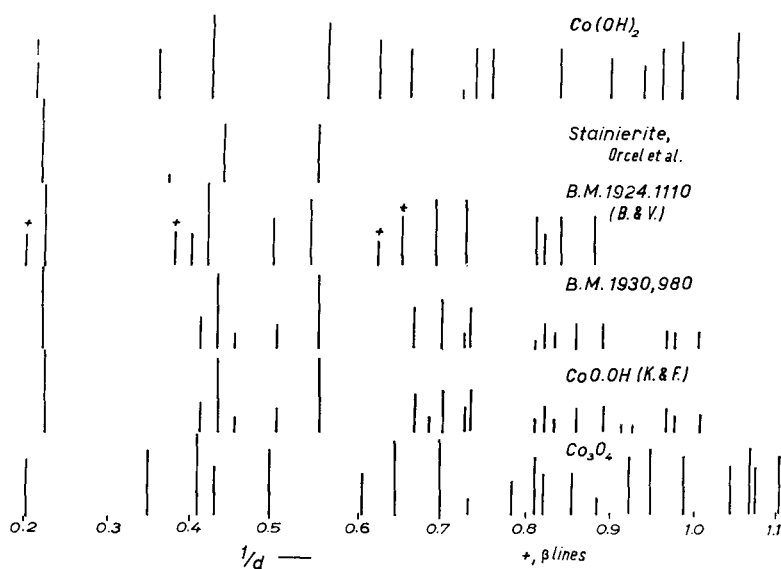


FIG. 1. X-ray powder patterns of artificial and natural cobalt oxides: $\text{Co}(\text{OH})_2$, data of G. Natta and A. Reina (1926); CoO.OH , data of Yu. D. Kondrashev and N. N. Fedorova (1954); Co_3O_4 , prepared from $\text{Co}(\text{NO}_3)_2$ by ignition at 850°C , taken with $\text{Co-K}\alpha$ radiation; Stainierite, Orcel *et al.*, data of J. Orcel, S. Hénin, and S. Caillère for material from the Congo; B.M. 1934,1110 (B. and V.), data of V. Billiet and A. Vandendriessche (1940a), on a British Museum specimen from Good-springs, Nevada; B.M. 1930,980, analysed material (A, table I) from Katanga, taken with $\text{Co-K}\alpha$ radiation.

Heterogenite was reported from Katanga by A. Schoep (1921); this material was thought by A. Schoep and V. Cuvelier (1929) to be amorphous, and though they did not examine heterogenite from the type locality, nor any of the other natural cobaltic hydroxides, they did not hesitate to say of them: 'il semble que tous ceux qui furent décrits jusqu'à présent sont de nature colloïdale'.

Schoep and Cuvelier also examined material from Mindigi, Katanga, which proved to be compact but crystalline and anisotropic with strong bireflectance and pleochroism; this they regarded as the crystalline

equivalent of the colloidal heterogenite, and named it stainierite; in this they have been followed by C. Palache, H. Berman, and C. Frondel (1944), although V. Billiet and A. Vandendriessche (1940 *a, b*) had proved that the 'colloidal' heterogenite is in fact microcrystalline 'stainierite', though of very fine grain, giving diffuse X-ray powder photographs. Billiet and Vandendriessche showed that the numerous species distinguished by L. de Leenheer (1929; 1930; 1934, mindigit; 1935*a*; 1935*b*, trieuite; 1936, boodtite; 1939), are all simply varieties of one species $(\text{Co}_2\text{O}_3, \text{CuO}) \cdot \text{H}_2\text{O}$, varying somewhat in Co:Cu ratio; the variations in optical properties, water content, density, hardness, and appearance under the ore-microscope are due to variations in crystal size. They also showed that the American material (from Goodsprings, Nevada: D. F. Hewett, 1931; S. R. B. Cooke, and D. J. Doan, 1935) belongs to the same species.

Billiet and Vandendriessche's work appeared to have cleared up the position except that they adopted the name stainierite in place of heterogenite, which has sixty years' priority and was based on a perfectly adequate description and analysis. But in 1957 H. Strunz gave the formula of the natural hydrated cobalt oxide (for which he adopts the name transvaalite, without giving any reasons for this choice) as $\text{Co}(\text{OH})_2$, assigned it to the brucite family, and gave cell-dimensions measured on artificial $\text{Co}(\text{OH})_2$ by G. Natta and A. Reina (1926); he adds: 'Zu Transvaalite gehören wahrscheinlich: Heterogenit, Stainierit, Mindigit, Trieuit, Winklerit, Heubachit und Schulzenit'; boodtite he indexes as 'Mindigit, inhomogen'.

J. Orcel, S. Hénin, and S. Caillère (1958), who adopt the name stainierite and describe a further occurrence at Bou Azzer, Morocco, also state that the natural mineral is cobaltous hydroxide, $\text{Co}(\text{OH})_2$, with or without some replacement of Co by Cu. In support of this conclusion they cite: the close resemblance of X-ray powder photographs of the natural mineral and of an artificial preparation¹ to those of brucite; the fact that thermal dehydration gave losses of 13.35 % (Bou Azzer) or 13.80 % (Congo), the product having a magnetite structure, while the calculated losses are, for $\text{Co}(\text{OH})_2 \rightarrow \text{Co}_3\text{O}_4$ 13.60 %, and for $\text{CoOOH} \rightarrow \text{Co}_3\text{O}_4$ 12.70 %; and the fact that solutions of the mineral (Bou Azzer) and of the artificial hydroxide, prepared by the action of

¹ Obtained by precipitation of cobaltous chloride with soda (presumably NaOH); no precautions against air oxidation are mentioned, nor is the colour of the preparation stated. L. J. Thénard (Ann. Chim., 1804, vol. 50, p. 124) and many later authors record that cobaltous hydroxide (pink or blue) oxidizes readily in air; the air-oxidation leads to black $\text{CoO} \cdot \text{OH}$ or to mixtures containing it.

boiling strong sulphuric acid, contained the cobalt wholly in the divalent state.¹

This conclusion is completely at variance with the evidence of Frenzel, Breithaupt, Sandberger, Weisbach, McGhie and Clark, Martens, Schoep and Cuvelier, Benrath (in Schneiderhöhn and Ramdohr, 1931), and de Leenheer, all of whom report the evolution of chlorine when the mineral is warmed with hydrochloric acid, and several of whom made direct available-oxygen determinations. Moreover, the evidence is quite inconclusive: the very broad similarity between the X-ray powder patterns of brucite and heterogenite (only four lines were reported and compared) does not imply isomorphism; the difference in the thermal dehydration losses could well be due to adsorbed water, which can be held very tenaciously; and the procedure of dissolving the mineral in hot strong sulphuric acid could be reasonably expected to reduce any cobaltic oxide present, with evolution of oxygen. Indeed, the X-ray powder data reported by S. R. B. Cooke and D. J. Doan (1935), by V. Billiet and A. Vandendriessche (1940), and by J. OrceI, S. Hénin, and S. Caillère (1958) all agree better² with the published diagrams of G. F. Hüttig and R. Kassler (1929) and of Yu. D. Kondrashev and N. N. Fedorova (1954) for artificial CoO.OH than with the published data for Co(OH)_2 (G. Natta and A. Reina, 1926; G. F. Hüttig and R. Kassler, 1930; W. Lotmar and W. Feitknecht, 1936).

We have therefore undertaken an examination of four specimens of natural cobalt hydroxide (heterogenite). All the specimens were analysed (table I), and X-ray powder photographs were taken; two (*A* and *B* in table I) give sharp powder patterns in excellent agreement with Kondrashev and Fedorova's, in which no sign of impurity can be detected; one (*C*) gives a moderately diffuse pattern, but no lines due to a second phase are detectable and it is clear that the high copper content of this material is essential; the fourth specimen (*D*), apparently homogeneous, was received from Professor Schoep in 1930 as stainierite, but it gave an X-ray photograph on which the lines of malachite are clearly visible, and this specimen can reasonably be interpreted as a mixture of about 20 % malachite and 80 % heterogenite. Malachite is certainly not present in quantity in the analysed material of specimen *C*.

¹ The evidence is that titration of the solution with ceric sulphate in presence of ethylenediamine tetracetic acid gives 54.2 % Co in the Bou Azzer mineral and 61.2 % in the artificial preparation, as against 55.0 % total Co in the Bou Azzer mineral and 63.40 % calculated for Co(OH)_2 (CoO.OH contains 64.10 % Co).

² In comparing these powder data allowance has to be made for the presence of β lines in Cooke and Doan's and in Billiet and Vandendriessche's patterns.

TABLE I. New chemical analyses of heterogenite with a recalculation as hydroxides (in the case of *D*, after subtraction of an estimated 20 % of malachite). Water determined by difference.

	A.	B.	C.	D.
Co ₂ O ₃	74.7	74.0	72.3	59.4
Fe ₂ O ₃	0.5	1.9	1.4	3.5
Al ₂ O ₃	0.2	2.0	0.4	0.1
CuO	3.6	3.7	14.5	17.3
NiO	0.3	6.4	1.1	0.6
CoO	nil	nil	nil	3.4
H ₂ O	[20.7]	[12.0]	[10.3]	[15.7]*
CoO.OH	82.8	82.1	80.1	82
FeO.OH	0.6	2.2	1.6	5
AlO.OH	0.2	2.3	0.4	0
Cu(OH) ₂	4.4	4.5	10.4	6
Ni(OH) ₂	0.3	7.9	1.4	1
Co(OH) ₂	nil	nil	nil	5
H ₂ O	[11.7]	[1.0]	—	—
CuO	—	—	6.1	—

* H₂O + CO₂.

A. 'Stainierite', Katanga (B.M. 1930,980).

B. 'Heterogenite', Shinkolobwe, Katanga (B.M. 1957,582).

C. Schulzenite, Chile (B.M. 87097).

D. 'Stainierite', Mindigi, Katanga (B.M. 1930,902). Original material from Professor Schoep, but containing admixed malachite.

The unit cell of heterogenite, as determined by Yu. D. Kondrashev and N. N. Fedorova (1954) on artificial material, is rhombohedral (space-group $R\bar{3}m = D_3^2d$) with a 4.676 Å, α 35° 28', and contains one formula unit CoO.OH (hexagonal unit a 2.849, c 13.130 Å); the mineral is isostructural with NaHF₂, and not with goethite, lepidocrocite, manganese, or groutite. Density calculated, 4.92; observed 3.07 (de Leenheer, mindigite), 3.43 (Breithaupt, winklerite), 3.44 (Frenzel, heterogenite), 3.75 (Sandberger, heubachite), 3.85 (McGhie and Clark, transvaalite), 4.32 (Schoep and Cuvelier, stainierite), 4.72 (Kondrashev and Fedorova, artificial). The low observed densities are clearly due to the fine state of subdivision of most of the natural material.

The chemical analyses were directed primarily to ascertaining the state of oxidation of the minerals. They were made on samples of 4 to 20 mg, which were dissolved in a M/5 solution of iodine monochloride in strong HCl, to which a small weighed excess of M/20 KI had been added. Under these conditions Ni⁺⁺, Co⁺⁺, Fe⁺⁺⁺, and Cu⁺⁺ would remain unaltered, while Co⁺⁺⁺ would oxidize to ICl some of the iodine liberated by the reaction $I' + ICl \rightarrow I_2 + Cl'$; the remaining free iodine was titrated with M/200 KIO₃, and the Co⁺⁺⁺ content calculated as

Co₂O₃ or CoO.OH. In the titrated solution, Fe, Al, Ni, and Cu were determined colorimetrically, and total cobalt colorimetrically or gravimetrically on suitable aliquots.

TABLE II. X-ray powder data for heterogenite from Katanga, Congo (B.M. 1930,980; Filtered Co-*K*α radiation, 11.46 cm diameter camera). The other specimens examined gave identical patterns.* The calculated spacings are based on the unit-cell of Yu. D. Kondrashev and N. N. Fedorova (1954), and the column *I*_{KF} is derived from their *F*²*p*_{calc} (ibid., p. 230, table 1, last column) by multiplying their figures by the Lorentz-polarization factor, taking the square root of the product, and scaling to *I*₀₀₀₃ = 10. This quantity should be comparable with our visually observed intensities: vvs ≡ 10; vs ≡ 9; s ≡ 8; ms ≡ 7; m ≡ 6; mw ≡ 5; w ≡ 4; vw ≡ 3 or 2; vvw ≡ 2 or 1.

<i>hkl</i>	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>I</i>	<i>I</i> _{KF}	<i>hkl</i>	<i>d</i> _{obs.}	<i>d</i> _{calc.}	<i>I</i>	<i>I</i> _{KF}
0003	4.40 Å	4.377 Å	vvs	10.0	11 $\bar{2}$ 6	1.199 Å	1.194 Å	vw	1.7
$\bar{1}$ 011	2.428	2.425	m	3.5	$\bar{1}$ 0.1.10	1.163	{1.159}	wb	{2.9
10 $\bar{1}$ 2	2.315	2.310	vs	9.0	20 $\bar{2}$ 4				
0006	2.208	2.188	vw	1.5	2025	1.120	1.116	mw	2.9
$\bar{1}$ 014	1.979	1.972	mw	3.3	0.0.0.12	—	1.094	—	1.6
10 $\bar{1}$ 5	1.804	1.798	s	7.0	1.0. $\bar{1}$.11	—	1.074	—	1.0
$\bar{1}$ 017	1.501	1.493	mw	4.4	20 $\bar{2}$ 7	1.036	1.031	vw	2.5
0009	—	1.459	—	1.4	11 $\bar{2}$ 9	1.024	1.019	vw	2.2
11 $\bar{2}$ 0	1.427	1.424	ms	4.5	2028	0.990	0.9862	vw	1.7
10 $\bar{1}$ 8	1.374	1.366	vw	2.5	$\bar{1}$ 0.1.13	0.933	0.9347	vw	1.6
11 $\bar{2}$ 3	1.356	1.354	m	4.0	12 $\bar{3}$ 1	0.927	{0.9302}	mw	{1.8
20 $\bar{2}$ 1	1.230	1.229	vw	1.3	$\bar{1}$ 232				
20 $\bar{2}$ 2	1.216	1.212	mw	2.7					

* The photograph of B.M. 1930,980 also showed, very faintly, the strongest line of quartz (*d* 3.334 Å), and three extremely faint lines at *d* 2.977, 2.254, and 1.538 Å that cannot be indexed on Kondrashev and Fedorova's cell; these lines were not observed on photographs of any of the other specimens, and are probably due to small amounts of unidentified impurities.

The analytical results confirm quite clearly the older interpretation of heterogenite as essentially CoO.OH.

Of the many names proposed for natural cobaltic hydroxide, heterogenite has a clear priority over transvaalite, stainierite, mindigite, trienite, and boodtite. Heubachite is a nickelian¹ and schulzenite a cuprian heterogenite, while winklerite was clearly a gross mixture.

Acknowledgements. The author wishes to thank Dr. R. J. Davis and Miss E. Fejer for the preparation and measurement of the X-ray photographs.

¹ Sandberger (1876*b*) reported the nickel as Ni₂O₃, but the analytical methods used by Zeitschel are not stated. The available oxygen in B.M. 1957,582 (*B*, table I) corresponds exactly to its cobalt content, and there is no evidence that nickel can be oxidized to the trivalent state in alkaline solutions by air, whether alone or in the presence of cobalt. We believe the nickel in heubachite was in fact divalent.

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