

FERROCARPHOLITE, THE HITHERTO UNKNOWN FERROUS IRON ANALOGUE OF CARPHOLITE PROPER

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ABSTRACT

Ferrocapholite, the hitherto unknown ferrous iron analogue of carpholite proper, was found as a magnesian variety with the formula $H_4(Fe, Mg)Al_2Si_2O_{10}$. It builds dark green prismatic crystals in a cobble of vein-quartz collected West of Tomata, eastern Central Celebes, by the late Dr. Ir. W. H. Hetzel (Celebes expedition of 1929 of the Netherlands Indies Geological Survey under the leadership of Prof. Dr. H. A. Brouwer). It is orthorhombic dipyramidal with $a_0=13.77 \text{ \AA}$, $b_0=20.18 \text{ \AA}$, $c_0=5.11 \text{ \AA}$; $a_0:b_0:c_0=0.682:1:0.253$, and the space-group is *Ccca*. The unit-cell contains $8H_4(Fe, Mg)Al_2Si_2O_{10}$. Observed crystal faces: {010}, {100} and {110}; cleavage {010} perfect, {110} indistinct. Twinning was not observed. Hardness $5\frac{1}{2}$; fusibility $3\frac{1}{2}$; sp. gr. 3.04; $\gamma=1.647$, $\beta=1.644$, $\alpha=1.628$, $2V_\alpha=49^\circ$, dispersion weak $r>v$, with reference to α ; $c=\gamma$, $b=\alpha$, $a=\beta$. Pleochroism in thin section varies from yellow-green (α and β) to very light blue-green (γ). The optical characteristics of ferrocapholite correspond almost entirely to those of carpholite proper, $H_4MnAl_2Si_2O_{10}$.

Comparable practically manganese-free carpholite-like material, probably magnesian ferrocapholite with a larger content of magnesium, was found in situ at two other localities in eastern Central Celebes.

INTRODUCTION

During the latter part of the last world war the author studied a collection of igneous and metamorphic rocks from eastern Central Celebes, collected by the 1929 expedition of the Netherlands Indies Geological Survey under the leadership of Prof. Dr. H. A. Brouwer. Four of the investigated samples were found to contain minerals with the optical characteristics of carpholite, $H_4MnAl_2Si_2O_{10}$. One of these, a blastosammitic schistose carpholite-quartzite, appeared on qualitative chemical investigation to show a considerable content of manganese, which checked the optical determination as carpholite. The content of manganese of the carpholite-like material in the three other samples, however, appeared to be negligible in comparison to that of carpholite from Wippra, one of the main localities of this comparatively rare mineral. One of these three samples (No. 15-161^x) was found to contain a large quantity of the carpholite-like material; this sample, which consists of vein-quartz with the said mineral, was found by the late Dr. Ir. W. H. Hetzel as a cobble west of Tomata.¹ In the two other samples the mineral is of subordinate or local occurrence. More detailed chemical investigations

¹ For the exact position of the locality mentioned the reader is referred to the author's paper on the igneous and metamorphic rocks from eastern Central Celebes, page 72.

were performed on the material from the vicinity of Tomata. Since it was not possible to have quantitative chemical analyses made during the latter part of the war, only the results of a spectrochemical analysis by Dr. R. Schmidt could be given in the author's paper on the rocks from eastern Central Celebes. According to this analysis by Dr. Schmidt the mineral from the vicinity of Tomata contained mainly magnesium, iron, aluminum and silicon; the concentration of magnesium was estimated to be at least twenty times as large as the concentration of manganese. Since Jakob and Hesemann (1927) had described a magnesian carpholite with predominant manganese from Hettstedt (Harz), which could be optically distinguished only with difficulty from the more manganese-rich varieties of this mineral, the material from Celebes was first thought to represent the still unknown magnesium analogue of carpholite proper; the material, however, remained unnamed pending a quantitative chemical analysis.

According to a second spectrochemical analysis by Dr. Schmidt, the results of which were not included in the paper on the rocks from eastern Central Celebes, the content of iron appeared to be much larger than that of magnesium. This was confirmed by a quantitative chemical analysis performed in the year 1949. The material from the vicinity of Tomata, therefore, appeared to represent the hitherto unknown ferrous iron analogue of carpholite proper, for which the name *ferrocarpholite* is proposed. Besides the optic data already published in 1947, this paper contains mainly new chemical and x-ray data.

The author is indebted to Prof. Dr. H. A. Brouwer for affording him the opportunity to study this interesting mineral.

CHEMICAL PROPERTIES

A quantitative chemical analysis was performed on material from the sample that was found west of Tomata (No. 15-161^x). Quartz and heavy minerals from some parts of the sample, in which no ore was observed, were separated with the aid of bromoform. During the drying process, which was not performed by the author himself, a small amount of water may have been lost. After further purifying by means of a magnetic treatment and hand-picking, the concentrate appeared to be practically pure.

The average of duplicate analyses of this material is given in Table 1, together with the deviations of the separate analyses. For some of the minor constituents no duplicate data are available owing to lack of material. For H₂O+ a lower percentage was obtained during the first determination; the percentage given in Table 1 was obtained after prolonged heating at the request of the author. The difficulties encoun-

TABLE 1. CHEMICAL ANALYSIS, RATIOS, AND EMPIRICAL UNIT-CELL CONTENTS OF FERROCAPHOLITE

	1	2	3		4	
SiO ₂	37.38 (± 0.04)	37.59	0.6259	Si	16.27	8 \times 2.03
Al ₂ O ₃	29.23 (± 0.01)	29.39	0.2883	Al	14.99	
Fe ₂ O ₃	2.06 ($\pm 0.02^5$)	2.07	0.0130	Fe'''	0.68	
TiO ₂	0.22 ($\pm 0.00^5$)	0.22	0.0028	Ti	0.07	15.81 8 \times 1.98
MgO	2.51 ($\pm 0.05^5$)	2.52	0.0625	Mg	0.07	
MnO	0.14 ($\pm 0.00^5$)	0.14	0.0020	Mg	1.63 { 1.56	
FeO	17.88 ($\pm 0.01^5$)	17.98	0.2502	Mn	0.05	8.12 8 \times 1.01
CaO	0.13 (± 0.03)	—		Fe''	6.51	
Na ₂ O	0.14 (± 0.03)	—		H	29.09	8 \times 3.64
K ₂ O	0.09 ($\pm 0.00^5$)	—		O	78.92	8 \times 9.87
H ₂ O ⁻	0.34 (± 0.02)	—				
H ₂ O ⁺	10.02	10.08	0.5595			
P ₂ O ₅	—					
SO ₃	0.12	—				
F	tr. ¹					
V ₂ O ₅	tr. ²					
Total	100.26	99.99				

1. Ferrocapholite from cobble west of Tomata: average of duplicate analyses with deviations of separate analyses. Anal. Laboratorium voor Delfstoffenonderzoek van de Dienst van de Mijnbouw, Bandoeng (1949).
2. Analysis 1 recalculated to 100% after subtraction of CaO, Na₂O, K₂O, H₂O⁻ and SO₃.
3. Ratios of 2.
4. Empirical unit-cell contents.

¹ Less than 0.02%.

² 0.011%.

tered in the determination of H₂O⁺ indicate that the water-content may be even higher than 10.02%.

According to the second spectrochemical analysis by Dr. Schmidt the main constituents are accompanied by traces of vanadium (more) and germanium (less).

Of the minor percentages recorded in the analysis, those which would require more or less unusual substitutions are within the limits of error to be expected for a normal chemical analysis (cf. Hillebrand and Lundell), and therefore have been omitted in the recalculated analysis. TiO₂ and MnO, which are commonly determined with greater accuracy, and which do not require unusual substitutions, have been retained.

The molecular weight of the unit-cell of ferrocapholite was calculated from the volume of the unit-cell and the density, both given in a later

part of this paper, and appeared to be 2600. The empirical unit-cell contents were found by multiplying the ratios for the recalculated analysis with 2600 and 0.01. According to its ionic radius Ti has been grouped together with Al and Fe^{'''}, accompanied by an equal amount of Mg (cf. Hallimond, page 70). Except for hydrogen, the empirical unit-cell contents thus obtained show good integral ratios. There are, however,

TABLE 2. ANALYSIS OF FERROCARPHOLITE COMPARED WITH THEORETICAL COMPOSITION AND WITH MODERN ANALYSES OF CARPHOLITE PROPER

	1	2	3	4	5	6
SiO ₂	37.38	36.79	38.68	35.73	36.07	42.14
TiO ₂	0.22	0.23	0.13	0.18	0.20	0.35
Al ₂ O ₃	29.23	29.60	28.98	26.71	29.84	26.72
Fe ₂ O ₃	2.06	2.09	3.02	2.02	1.36	2.71
Mn ₂ O ₃	—	—	—	—	22.00	10.35
FeO	17.88	17.65	4.12	2.31	1.86	2.00
MnO	0.14	0.14	11.92	19.88	—	1.90
MgO	2.51	2.48	—	—	—	3.24
CaO	0.13	—	0.79	0.23	—	—
Na ₂ O	0.14	—	0.30	—	—	0.22
K ₂ O	0.09	—	—	—	—	0.16
H ₂ O ⁺	10.02	11.03	12.14	12.66	8.14	10.06
H ₂ O ⁻	0.34	—	—	—	—	0.15
SO ₃	0.12	—	—	—	—	—
F ₂	tr.	—	—	0.44	0.97	—
V ₂ O ₅	tr.	—	—	—	—	—
	100.26	100.01	100.08	100.16	100.44	100.00
F ₂ =O					0.41	
					100.03	

1. Ferrocapholite from cobble west of Tomata: results of analysis.
2. Theoretical composition of ferrocapholite with similar replacement ratios.
3. Carpholite, Wippra. Anal. H. Otto.
4. Carpholite, Schlaggenwald. Anal. H. Otto.
5. Carpholite, Schlaggenwald. Anal. J. Jakob.
6. Carpholite, Hettstedt. Anal. J. Jakob.

several arguments which indicate that the H-content of the unit-cell is 32 instead of 29. First, the difficulties encountered during the determination of H₂O⁺ indicate that the water-content may be higher, as mentioned above. A comparison with the analyses of carpholite proper by Otto and Jakob (see Table 2) indicates that Jakob encountered similar difficulties in the determination of the water-content; the deficient totals of his analyses, however, were attributed by Jakob to the presence of

Mn₂O₃, an assumption which was later criticized by Otto, who obtained much higher figures for H₂O, i.e. 12.66% and 12.14%. Secondly, some water may have been lost during the drying in making the mineral separation. And lastly, the symmetry relations of the space-group *Ccca* indicate that the hydrogen-content of the unit-cell may be 28 or 32, with a much greater probability for the latter figure. Therefore, the water-content given in the analysis is assumed to be about 1% low (see Table 2) corresponding to 32 H atoms per unit-cell.

Thus, the formula obtained for ferrocapholite may be written as H₄(Fe,Mg)Al₂Si₂O₁₀, the unit-cell containing 8 H₄(Fe,Mg)Al₂Si₂O₁₀. The material from the vicinity of Tomata may be more exactly described as magnesian ferrocapholite.

The density calculated from the cell-volume and the above formula, with minor replacements as given in the recalculated analysis, is 3.05, which is in good agreement with the measured value 3.04.

CRYSTALLOGRAPHIC PROPERTIES

The ferrocapholite of the analyzed sample forms separate prismatic crystals and aggregates of parallel fibres with a length up to about 1 cm. The crystals are always elongated in the direction of the *c*-axis. In thin section the crystals do not show regular terminations.

According to the *x*-ray data given in a later part of this paper ferrocapholite is orthorhombic dipyramidal, with $a_0:b_0:c_0=0.682:1:0.253$. During the investigation with the aid of the goniometer almost all crystals appeared to be very poorly developed or bent and almost all signals were very vague. In this respect ferrocapholite corresponds to carpholite proper, on which almost no crystallographic measurements have been made. Observed crystal faces are: {010}, {100} and {110}. The results of measurements on the best developed crystals observed are still unsatisfactory. They are given in Table 3.

TABLE 3. CRYSTALLOGRAPHIC MEASUREMENTS ON FERROCAPHOLITE

	(010)∧(110)	(100)∧(110)	(010)∧(100)
First crystal	56° 9'	33°53'	90° 2'
Second crystal	55°39'	33°35'	89°33'
	56°11'	33°47'	89°47'
	56°11'	33°54'	89°59'
	56°14'	34°28'	90°42'
Average	56° 5'	33°55'	

The deviations from 90° of the values obtained for (010)∧(100) illustrate the great inaccuracy of the results of the measurements. According to the *x*-ray data, the angles of (110) with (010) and (100) are 55° 42'

and $34^{\circ} 18'$; the deviations of the values found by the author are supposed to be mainly due to the unsatisfactory development of the crystals. The values calculated from the *x*-ray data correspond very well with the values measured one hundred years ago by Kenngott for the prism angles of carpholite proper from Schlaggenwald: $111^{\circ} 27'$ and $68^{\circ} 33'$.

The cross-sections of the prisms of the analyzed ferrocarpholite often have the shape of rhombs with a truncation (100) of the obtuse angle (see de Roever 1947, Plate III, Fig. 2).

Twinning was not observed.

PHYSICAL PROPERTIES

The ferrocarpholite from the vicinity of Tomata shows a dark green colour.

The crystals show a perfect cleavage according to {010}, while there is also an indistinct cleavage parallel to {110}. Furthermore the prisms may show a cross-parting.

Before the blowpipe the mineral melts more easily than actinolite and less easily than almandite. The fusibility is $3\frac{1}{2}$.

The mineral scratches fluorite and apatite but not orthoclase; therefore $H = 5\frac{1}{2}$.

With the aid of the suspension method the specific gravity was found to be 3.04; the specific gravity of the heavy solution was determined by means of a Westphal balance, and checked with the aid of a pycnometer.

OPTICAL PROPERTIES

The refringence of the analyzed ferrocarpholite is moderate; with the aid of the immersion method¹ a value of 1.647 ± 0.001 was found for γ in sodium-light. The negative birefringence is rather strong; for γ - α values of 0.019–0.020 were found with the aid of the Berek compensator and the universal stage, by comparison with quartz in thin section. For the partial birefringence γ - β values of 0.0033–0.0034 were found in two sections; for β - α a value of 0.016 was measured in one section. From the determination of γ , of the birefringence and of the partial birefringences we find as approximate values for the other indices: $\beta = 1.644$ and $\alpha = 1.628$. In one of the sections with the strongest birefringence some irregular cross-veins were observed with a slightly lighter color and with a birefringence that is 0.002 more than that of the main body of the crystal.

¹ With the aid of mixtures of α -monochloronaphthalene and α -monobromnaphthalene. The temperature could not be controlled; practically contemporaneous observations with microscope and refractometer were made at the same distance from the same sodium-flame.

For the optic axial angle $2V_\alpha$ values of 49° were found in two sections with the aid of the universal stage. The same value was calculated from the above-mentioned figures for the refringence and the partial birefringences. The dispersion is weak, $r > v$ with regard to α .

The mineral shows parallel extinction in sections perpendicular to the optic bisectrices and the optic normal; γ is in the longitudinal direction of the crystals and α in the longitudinal direction of the cross sections, i.e. perpendicular to the cleavage {010}. Consequently, the elongation is positive, (100) is the optic axial plane, and $c = \gamma$, $b = \alpha$ and $a = \beta$ (see Fig. 1). In thin section the analyzed ferrocapholite shows a

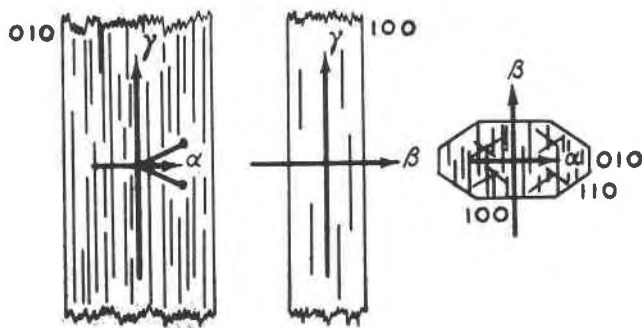


FIG. 1. Optic orientation of ferrocapholite.

distinct pleochroism from yellow-green (α and β) to very light blue-green (γ); α and β show a very slight difference in color. The blue-green color of γ is distinctly observable in a slide with a thickness of about 0.035 mm.

Except for the colors in the sample and in thin section the optic characteristics of ferrocapholite (see also Table 5) correspond almost entirely with those reported for carpholite proper. Some recent optic data on carpholite proper are given for comparison in Table 4. In the literature the γ of carpholite proper is described as being colorless,¹ but carpholite from Wippra in the collection of the Geological Institute, Amsterdam, appeared in thicker sections to be of an extremely light bluish green color parallel to the c -axis.

X-RAY DATA

The cell-dimensions and the space-group of ferrocapholite were kindly determined in the laboratory of Prof. Dr. Carolina H. Mac Gil-

¹ According to Mügge, who also gives details on crystal faces and cleavage for carpholite proper, the absorption in the longitudinal direction is almost imperceptible in a thin section.

TABLE 4. OPTIC CHARACTERISTICS OF FERROCARPHOLITE COMPARED WITH THOSE OF CARPHOLITE PROPER ACCORDING TO MODERN DETERMINATIONS

	Ferrocapholite, west of Tomata	Carpholite, Schlaggenwald (Jakob and) Heseemann	Carpholite, Schlaggenwald Larsen and Berman	Carpholite, Schlaggenwald Otto	Carpholite, Wippra Otto	Carpholite, Hettstedt (Jakob and) Heseemann
Color in sample	dark green	straw-yellow	straw-yellow			greenish yellow
Pleochroism	very light blue-green to yellow-green	colorless to pistachio-green	colorless to pale yellow			colorless to golden yellow
Indices						
γ	1.647	1.639	1.630	1.632	1.637	1.638
β	1.644	1.632	1.628	1.630		1.631
α	1.628	1.617	1.611	1.613	1.619	1.612
Birefringence	0.019-0.020	0.0215	0.019	0.019	0.018	0.028
$2V_{\alpha}$	49°	70°	50°			62°

lavy, Amsterdam, to whom the author expresses his sincere thanks.

For the cell-dimensions the following results were obtained: $a_0=13.77$ Å, $b_0=20.18$ Å, $c_0=5.11$ Å. For carpholite proper the only value known is that of $c_0=5.3$ according to a preliminary determination by Strunz, who concluded that carpholite belongs to his group of inosilicates with endless chain structures. The same may hold true for ferrocapholite.

Weissenberg diagrams of the zero and first layer line around the c -axis, and of the zero layer line around the a -axis, show the space-group to be $Ccca = D_{2h}^{22}$.

From a fibrous specimen of carpholite proper from Wippra a rotation diagram was made. A comparison of this diagram with a rotation diagram of a single crystal of ferrocapholite shows that the two structures are isomorphous.

A full structure determination is in progress in Prof. Mac Gillavry's laboratory.

OCCURRENCE

The analyzed ferrocapholite, which was found in a cobble of vein-quartz west of Tomata, is further accompanied by red ore-material and by very small quantities of rutile, leucoxene, zircon and tourmaline.

In two other samples from eastern Central Celebes investigated by the author practically manganese-free carpholite-like minerals are of subordinate or local occurrence. These are a blastopsammitic schistose biotite- and chlorite-bearing sericite-quartzite with quartz veins containing the said mineral (No. 17-47^x), and a blastosephitic sericite-quartzite (No. 17-42), both collected in situ by Prof. Dr. H. A. Brouwer, east of Tamondjengi, north of the trail to Majoemba, and SW. of Peleroe on the trail to Majoemba.¹

TABLE 5. OPTIC CHARACTERISTICS OF FERROCAPHOLITE COMPARED WITH THOSE OF OTHER PRACTICALLY MANGANESE-FREE CARPHOLITE-LIKE MINERALS FROM EASTERN CENTRAL CELEBES

	Ferrocapholite, west of Tomata, 15-161 ^x	SW. of Peleroe, 17-42	East of Tamondjengi, 17-47 ^x
Color in sample	dark green	gray-green to green	gray-green to green
Pleochroism			
γ	very light blue-green	extremely light bluish green	extremely light bluish green
β	yellow-green	light yellow-green or light green-yellow	green-yellow
α	yellow-green	light green or light yellow-green	green-yellow
Indices			
γ	1.647	1.640	1.638
β	1.644	1.636	1.633
α	1.628	1.621	1.617
Birefringence	0.019-0.020	0.019	0.020-0.021
$2V_{\alpha}$	49°	55°-57°	60°-61°
Orientation	$c = \gamma$ $b = \alpha$ $a = \beta$	$c = \gamma$ $b = \alpha$ $a = \beta$	$c = \gamma$ $b = \alpha$ $a = \beta$

¹ For the exact position of the localities mentioned the reader is referred for the author's paper on the igneous and metamorphic rocks from eastern Central Celebes, page 72.

Since the refringence and other optical characteristics of the minerals in these samples are close to those of ferrocapholite (see Table 5), while the content of manganese is negligible in comparison with that of carpholite from Wippra, we may also be dealing here with magnesian ferrocapholite, which in view of its lower refringence may have a larger content of magnesium. The minerals are associated with quartz, sericite, biotite, chlorite, hematite, leucocoxene, tourmaline, rutile and zircon. In one of these rocks some crystals of zircon were found as inclusions in the carpholite-like mineral; around the crystals of zircon no diverging optical characteristics of the carpholite-like mineral were observed.

In all localities mentioned the mineral occurs in veins in or as a constituent of low grade metamorphic phyllitic and quartzitic rocks, among which some original sandstones and conglomerates could be recognized. The metamorphism of these rocks is of alpine age and may belong to the greenschist facies, which in other parts of Celebes was found to be younger than the wide-spread glaucophanitic metamorphism of the eastern part of this island. It is not impossible, however, that these low grade metamorphic rocks belong to a facies characterized by the stability of pumpellyite, or to the glaucophane-schist facies itself.

For further details the reader is referred to the author's paper on the igneous and metamorphic rocks from eastern Central Celebes.

REFERENCES

- HALLIMOND, A. F., On the graphical representation of the calciferous amphiboles: *Am. Mineral.*, **28**, 65-89 (1943).
- HILLEBRAND, W. F., AND LUNDELL, G. E. F., Applied inorganic analysis (New York, London, 1929).
- JAKOB, J., AND HESEMANN, J., Karpholith, seine chemischen und optischen Eigenschaften: *Schweiz. Min. Petr. Mitt.*, **7**, 134-137 (1927).
- KENNGOTT, A., Ueber Antrimolith, Poonalith, Harringtonit, Karpholith, Berzelin, Gismondin, Zeagonit, Zirkon: *Berichte über die Mittheilungen von Freunden der Naturwissenschaften in Wien*: gesammelt und herausgegeben von Wilhelm Haidinger, **7**, 189-194 (1851).
- LARSEN, E. S., AND BERMAN, H., The microscopic determination of the nonopaque minerals: *U.S.G.S., Bull.* **848** (1934).
- MÜGGE, O., Ottrelith- und Karpholithschiefer aus dem Harz: *Neues Jahrb. f. Min.*, etc. **1918**, 75-98.
- OTTO, H., Die Rolle des Mangans in den Mineralien: *Min. Petr. Mitt.*, *N.F.* **47**, 89-140 (1936).
- ROEVER, W. P. DE, Igneous and metamorphic rocks in eastern Central Celebes: *Geological explorations in the island of Celebes under the leadership of H. A. Brouwer*, 65-173 (Amsterdam, 1947).
- STRUNZ, H., Systematik und Struktur der Silikate: *Zeits. Krist.*, **98**, 60-83 (1938).

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