

CONTRIBUTIONS TO THE MINERALOGY OF NORWAY

No. 12. Hisingerite in "Dark" Larvikite.

By

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Abstract. Magnesium- and calcium-bearing hisingerite, typically with extremely fine magnetite inclusions, occurs spatially associated with pyroxene (and very possibly as an alteration of olivine) in "dark" larvikite. It has a specific gravity of ca. 1.80, a waxy to subvitreous luster, is black to dark brown in reflected light and golden- to wine-brown by transmitted light, and has a greenish brown to olive green streak. Optical studies indicate the presence of intimately intermixed amorphous and crystalline phases. The amorphous phase has an index of refraction that ranges from 1.480 to 1.486. The crystalline phase has a beta index that ranges from 1.470 to 1.478, is biaxial negative, has a $2V$ of 60° to 70° , and has oblique extinction. X-ray diffraction patterns consist of three broad reflections with d values of their central portions of ca. 4.44, 2.575, and 1.535. Differential thermal analyses show the following reactions: large endothermic with peak at ca. 125° C., medium-sized exothermic with peak at ca. 450° C., and small exothermic at ca. 970° C. Chemical analyses, all of which have necessarily been made on contaminated material, are consistent with previously published analyses.

This study has pointed up the fact that relationships among materials called hisingerite, chloropal, nontronite, natural iron oxide gel., *etc.* need much further investigation and clarification. It is suggested that for a start the name hisingerite could be restricted to either the amorphous or the crystalline phase with the listed characteristics.

Introduction

Hisingerite was named by Berzelius (HISINGER, 1828) after W. Hisinger, his coworker during the early electrolysis experiments which led to Berzelius' famous electro-chemical theory. The type material came from Riddarhyttan in Vestmanland, Sweden.

Although it has been noted, by way of reference, that hisingerite was reported to occur at Solberg, Norway (DANA, 1892, p. 702), none was truly recorded from any Norwegian locality until the recent listing of two localities by NEUMANN (1959, p. 233)¹.

The hisingerite reported upon herein was discovered during the separation of minerals from each of the chief intrusive phases of the Oslo Series rocks in conjunction with the writer's current investigation of the possible utilization of K-feldspar obliquities as geological condition(s) indicators.

With these rocks, typically the lightest fraction consists chiefly of K-feldspar. However, the "dark" larvikite used proved exceptional. After the K-feldspar fraction was removed, a lighter-weight, nearly black, apparently magnetic fraction remained.

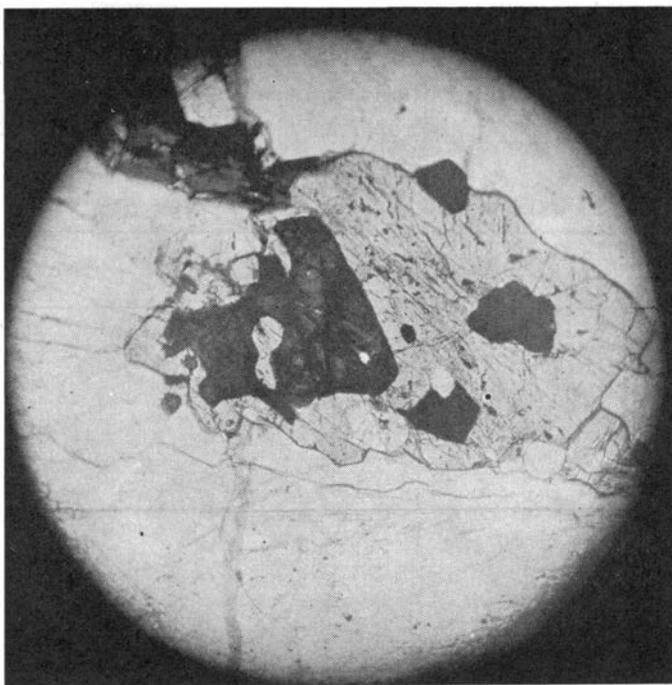
After numerous investigations it has been decided that the obtained data best support the conclusion that most of this material is hisingerite. This is a report of the determined data plus a discussion of certain aspects of them and their bearing on the use of the designation hisingerite.

Localities and host rock

The investigated material was first found to occur in one of the "dark" larvikites from the Mineralogisk Museum collection. This larvikite was collected by S. Bergstøl from the Klåstad Steinbrudd, Tjølling, in 1960. Subsequently, the material has been found also to occur in the only other "dark" larvikite checked — one collected by the writer, in 1959, at a quarry north of Viksfjord and 2–4 km east of Larvik (Valby).

Larvikite has been described petrographically by many workers (*e.g.*, BARTH, 1944) so will not be described in detail in this paper. Suffice it to say, the type in which the hisingerite was found to occur is the typically beautiful "dark" type. In thin sections of the Tjølling material this type can be seen to consist chiefly of oligoclase and alkali feldspar plus small amounts of varietal biotite, barkevikitic hornblende, and titanite and lesser amounts of accessory apatite, magnetite

¹ Apparently "i Nerike" was interpreted as "in Norway". The original report (Cleve and Nordenskiöld, 1866, p. 170) reads: "från Solberggrufvan i Nerike". Nerike is an old provincial designation for the area around Örebro in southcentral Sweden.



1 mm

Figure 1. Hisingerite within titanite of Tjölling "dark" larvikite. Notice how shape is possibly suggestive of partially resorbed olivine.

and sphene plus traces (found to be about 0.01 per cent by weight) of the hisingerite.

The hisingerite has thus far been found to occur chiefly as subhedral to anhedral grains (probably pseudomorphous after olivine — see Figure 1) within pyroxene grains.

Previous work on hisingerite

As noted in the introduction, hisingerite was named by Berzelius. Subsequently, hisingerite has been described from numerous world-widespread localities. Attention is called especially to the numerous references given by DANA (1892, p. 72), SUSTCHINSKY (1910), and HEWETT and SCHALLER (1925). Since the report of Hewett and Schaller, two papers concerning the mineral are particularly noteworthy — those of GORDON (1944) and SUDO and NAKAMURA (1952).

Actually, there is little agreement today as to either the definition or the place within the general mineral classification scheme for hisingerite. Commonly, identification has been based on chemical composition even though optical properties are inconsistent (see Table I).

Table 1.
Diverse optical data reported for hisingerite.

Locality:	Isotropy:	Index(es):	2V, sign, etc.	Reference:
Bellvue King, Idaho	iso-	1.44		Hewett & Schaller;
Wilmington, Delaware	iso-	1.45 —1.47		Schaller Hawkins & Shannon
Tjølling, Norway	aniso-	1.470—1.478	60°—70°,(-)	this paper
Tjølling, Norway	iso-	1.480—1.486		this paper
Riddarhyttan, Swed.	iso-	1.49 —1.53		Hewett & Schaller
not reported	iso-	1.49 —1.51, 1.59 & 1.66		Larsen
Parry Sound, Ontario	amorph. & crystalline	1.50 —1.56		Schwartz
Llallagua, Bolivia	iso-	1.52		Gordon
Various localities, e.g., Långban & Orijarvi, Sweden	aniso- (cryptocrystalline)	> 1.535	uniaxial (-) ??	Sustchinsky
Chognacota, Bolivia	iso-	1.57		Gordon
Wilmington, Delaware	aniso-	α —1.562 β —1.580 γ —1.582 β ranges — 1.552—1.595	small (-); parallel ext. (this is "canbyite")	Hawkins & Shannon
Minnie Moore, Idaho	aniso- & iso-	1.66	small (nearly uniaxial) (-) ?	Hewett & Schaller
Llallagua, Bolivia	aniso-	1.715—1.730	(-) elong.	Gordon
Edna May Deeps Mine, West Australia	aniso- & iso-	none given		Simpson
Kawayama, Japan	aniso- & iso-	none given		Sudô & Nakamura

Some workers have suggested tentatively that it is the iron-equivalent of allophane; others have suggested that it should be placed in the nontronite (and, thus, the montmorillonite) clan; *etc.*; *etc.* WINCHELL and WINCHELL (1951), without any stated basis, have classified it as a phyllosilicate, *i.e.*, made up of sheets of SiO_4 tetrahedra.

Origins suggested for the mineral are also diverse. Many occurrences appear to favor formation as the result of some weathering process(es). Relationships at other occurrences appear to preclude such an origin and to favor, instead, for example, formation as a hypogene mineral. The only consistency is that each suggested mode of formation makes the hisingerite secondary. On the basis of data thus far presented, all suggested origins appear to be quite tenable.

As mentioned, the only authentic report of hisingerite occurrences in Norway are those given by NEUMANN. He has recorded (1959, p. 233) the fact that there are specimens in the collection of the Mineralogisk Museum from "pegmatite dykes at Hyttåsen, Mjærum farm in the county of Östfold and at Drag, Tysfjord in the county of Nordland". Therefore, this paper presents the first descriptive material concerning hisingerite from Norway.

Physical properties

The chief physical properties of the mineral separated from the larvikite may be listed:

Color: dark brown to black in reflected light;
golden- to wine-brown by transmitted light.

Streak: olive green to greenish brown.

Luster: waxy to subvitreous.

Breakage: conchoidal fracture; one imperfect cleavage or parting (possibly inherited).

Diaphaneity: transparent in thin pieces.

Hardness: 3—3.5.

Specific Gravity: ca. 1.786.

Magnetism: Non-magnetic?

The low specific gravity is a noteworthy character of this hisingerite. As noted, it was because of this characteristic that the mineral

was discovered. The given value was determined by Westphal-balance checking of the specific gravity of a fluid within which grains (-90 mesh) remained at any level at which they were placed. It is considered approximate because the fluid used contained much acetone which may have evaporated during the process of the measurements (thus making the liquid become heavier) and also because nearly all grains are contaminated by magnetite (S. G. — ca. 5.0). Nonetheless, this specific gravity is lower than the 2.5–3.0 range given for previously reported hisingerite. In fact, it is more nearly that generally reported for chloropal, *i.e.*, 1.727–2.105 (DANA, 1892, p. 701).

The “*Non-magnetic?*” needs explanation. It was discovered early in this investigation that a simple way to separate the mineral was by magnetic and heavyliquid methods. The mineral appeared to be magnetic. Actually, it now appears that it is not magnetic itself but reacts to a magnetic field because nearly all grains of it contain finely divided grains of magnetite. However, this is still subject to some question because a few grains with no microscopically (highest power with a petrographic microscope) visible inclusions of magnetite are slightly magnetic. It is thought that probably even these grains contain submicroscopic magnetite and that the apparent magnetic properties depend on this because a few similarly “pure-appearing” grains are *not* attracted by the same intensity magnetic field.

Optical properties

The following optical properties were determined on separated grains:

Crystalline and amorphous phases occur together in many individual grains.

Crystalline parts show: $\beta = 1.470 - 1.478$

Biaxial (—)

$2V = 60^\circ - 70^\circ$ (variable)

Δ — low to moderate

Oblique extinction

Elongation (+)?

Color — golden- to wine-brown

Pleochroism — none

Amorphous phase shows: $n = 1.480 - 1.486$

Because the optical properties can be determined for the above designated crystalline part and because they are essentially the same for all of those parts checked, it would appear that this is a distinct crystalline phase and not merely a gel material with some parts made birefringent because of tension polarization as suggested by SUDÔ and NAKAMURA (*op. cit.*, p. 619). X-ray data are corroborative.

Thermal data

A tracing of the Differential Thermal Analysis curve for the hisingerite from the "dark" larvikite plus the curve for hisingerite contaminated by pyrite, as given by SUDO and NAKAMURA (*op. cit.*, p. 620), and a typical "diluted" pyrite curve comprise Figure 2.

The setup used in this investigation was an FH305 furnace in vertical position heated at the rate of 12.5° C/min.; Leeds and Northrup x-y recorder; Pt + Pt+ 10Rh thermocouple; three point system; scale multiplication of 2. The hisingerite was comprised by both the crystalline- and amorphous-appearing phases and was diluted approximately 1:1 with Al₂O₃ (curve A). Sudô and Nakamura also used a mixture — 1:3 = hisingerite:alumina and used a heating rate of 10° C/min. (curve B). The pyrite was also diluted (<20 per cent); its curve is taken from McLAUGHLIN (1957, p. 366) (curve C).

The exothermic reaction at ca. 465° C on curve B was attributed by Sudô and Nakamura to pyrite contamination. Curve A for the hisingerite from the "dark" larvikite is similar to their curve even to the point of also having an exothermic reaction at ca. 450° C. This Norwegian hisingerite has *no* pyrite contamination! Further, its only possible contaminants — feldspar and magnetite have no exothermic reactions near 450° C. (see, for example, data given by KÖHLER and WIEDEN, 1954 and MACKENZIE, 1957, pp. 305—306). It is true that pyrite may have an exothermic reaction at ca. 450° C. (see curve C). Possibly the double-hump on the exothermic "peak" of curve B is real and one of the "humps" belongs to pyrite whereas the other belongs to hisingerite. However, it appears more likely that the reported "less than 1%" pyrite contamination might not have given any recordable reaction and that the double hump "peak" is completely attributable to a hisingerite reaction.

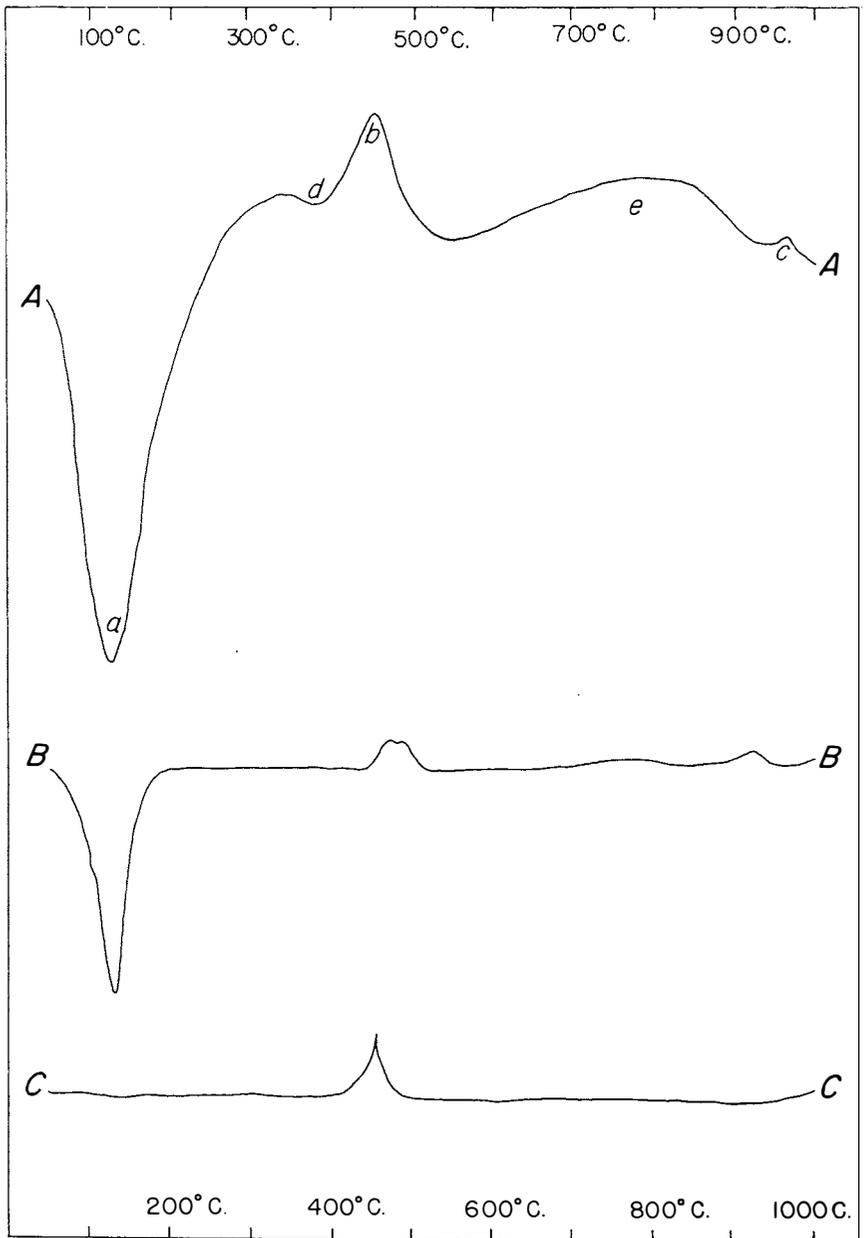


Figure 2. Differential Thermal Analyses Curves for A. Norwegian Hisingerite, B. Japanese Hisingerite, and C. Diluted pyrite. See text for full explanation.

If this is the case, the curve may be interpreted tentatively as follows: endothermic reaction (a) — loss of water; exothermic reaction at ca. 450° C. (b) — some structural adjustment, *e.g.*, (re)crystallization of all or part of dewatered (and amorphous ??) material; exothermic reaction at ca. 970° C. (c) — formation of something, *e.g.*, one of the high temperature modifications of SiO₂ or perhaps some spinel; the small endothermic reaction (d), if it actually is such, may, for example, represent loss of traces of water that were retained after the major endothermic reaction or perhaps some structural change such as breakdown of any retained crystallinity; the broad, more or less exothermic bulge (e) between the two better defined exothermic peaks may also be of little or no real significance — on the other hand, it may represent lag (re)crystallization of material not or not fully changed during the reaction manifest by the ca. 450° C. peak and/or some change in oxidation state or other reaction that occurs over a relatively wide temperature range.

The D. T. A. curve for hisingerite and the curve for a hydrated ferric oxide gel prepared by adding 9*N* alkali to 0.2*N* ferric chloride solution to pH 8.5 at 90° C. and washed free from salts after standing for two hours as given by MACKENZIE (1957, p. 308) are also somewhat similar. However, this is the only ferric oxide gel, about which data are available, which has a D.T.A. curve with temperatures of reaction similar to those of hisingerite and, there is one marked difference — the lack of the exothermic peak at ca. 970° C. on the ferric oxide gel curve and its presence on the hisingerite curve.

X-Ray investigations

The hisingerite has been subjected to numerous *x*-ray diffraction setups. In each case, a powder was used. The following setups were employed: General Electric XRD-3 and XRD-5 diffraction units with spectrogoniometers and CoK α radiation with iron filter and CuK α radiation with nickel filter, respectively, were used at scanning rates of 1 degree 2 θ /0.5 min. and 1 degree 2 θ /5.0 min.; a Westinghouse unit with a 114.6 mm. camera and CuK α radiation with nickel filter was used with exposure times of 4–8 hours; and, a Norelco unit with a 6 mm camera and CrK α radiation with vanadium filter was used

with exposure times of 6–24 hours on both untreated and glycolated hisingerite.

Only the CrK α radiation over 18 or more hours exposure times yielded patterns for anything other than the contaminants.

Three broad lines not attributable to any of the possible contaminants appear on all films exposed for 18 hours or more with the CrK α — vanadium filter setup. The d values for these broad reflections are given as Table II.

Also presented on Table II are the d values given by SUDÔ and NAKAMURA (*op. cit.*) and d values of highest intensity reflections for one of the nontronites investigated by GRUNER (1935). The last-listed is presented to show that whereas all of the lines possibly "fit" nontronite, many of the strong nontronite lines are lacking in the pattern of the material from the larvikite.

Table 2.
X-ray data (numbers are d values in Å units).

Hisingerite in larvikite:			Hisingerite, Kawayama Mine, Japan (Sudô & Nakamura, <i>op. dit.</i>):	Nontronite, Faratsiho, Madagascar Gruner, 1935):*
edge (in):	edge (out):	ca. ave.:		
				13.9
				7.1
4.6668	4.2110	4.44	4.44	4.44
				3.54
2.6422	2.5109	2.575	2.61	2.588
				2.507
				1.72
				1.678
1.5430	1.5280	1.535	1.50	1.519
				1.481
				1.23

* Only relatively high-intensity reflections are given here.

Because there was such a partial "fit", however, the hisingerite was subjected to glycolation to see if it would exhibit any tendency to expand like nontronite (as a member of the montmorillonite clan) does. No change was evident in subsequently taken x-ray patterns.

Chemical analysis

The chemical analysis given as Table III represents the hisingerite from Valby *plus* contamination by magnetite. This magnetite contamination plus the fact that all iron is reported as Fe_2O_3 means that the reported Fe_2O_3 is too high. The silica value also must be at least slightly incorrect — it was determined optically that the "silica skeleton" which remained after solution by HCl (HEWETT and SCHALLER also refer to this — *op. cit.*, p. 33) was accompanied by about 20 per cent feldspar; this was taken into account, strictly on the basis of feldspar:silica ratios found to obtain as the result of grain counts made under the microscope, so far as establishing the value given in the analysis.

Table 3.

Approximate chemical analysis of hisingerite

SiO_2	36.67
Fe_2O_3	42.21
MgO	4.48
CaO	1.18
H_2O ($> 110^\circ \text{C}$)	4.67
H_2O ($< 110^\circ \text{C}$)	8.86
<i>total</i>	<u>98.07</u>

analysts: P.S. Dear & R.V. Dietrich

Spectrochemical analyses of the material show that it (again, *plus* magnetite contamination) contains, in addition to the reported major constituents, the following elements (with figures reported to the nearest numbers in the series .03, .015, .007, *etc.*): Be-.00015, Na-.03, Al-.3, Ti-.007, V-.0007, Cr-.0003, Mn-.7, Co-.007, Ni-.003, Cu-.007, Zn-.03, Sr-.0015, Ag-.000015, and Ba-.0007 (analyst: H.W. Worthing, U.S. Geol. Surv.).

General discussion and conclusions

It is quite evident that (at least on the basis of some previously published data) some of the reported characteristics of this hisingerite fit chloropal better than they do hisingerite (*e.g.*, the Specific Gravity). It is equally evident that published optical data for materials iden-

tified as hisingerite are inconsistent — especially the reported indices of refraction but even more particularly, so far as theoretical considerations are concerned, the admission of amorphous *and* crystalline materials as constituents of a single mineral species. Heretofore, only Sudô and Nakamura have published any x -ray or D.T.A. data for hisingerite. They noted that the D.T.A. data were identical for the two phases. Both their D.T.A. and x -ray data and those found to be characteristic of the material from Norway are in remarkable agreement.

Nonetheless, there is considerable confusion!

The present writer believes that much of this may be removed if hisingerite is defined strictly as either amorphous or crystalline. Although the former would appear to have priority, on the basis of the original description, the latter might be the better choice — optical, x -ray, and D.T.A. data which are coordinated and correlated to at least some of the material(s) called hisingerite are available for the crystalline phase. Thence, if this suggestion were followed, the so called amorphous phase, in particular, should receive further study (perhaps it is not “amorphous”, for example, to electron diffraction) and perhaps be redefined as a separate species.

Until this is done, it seems best merely to call the material, the investigation of which is reported herein, simply hisingerite.

If this hisingerite is pseudomorphic after olivine, it is of replacement or alteration — *i.e.*, secondary — origin. If the Mg-content of the hisingerite reflects that of a preexisting olivine, that olivine would appear to have been a fayalite, probably near ferrohortonolite, in composition. Actually, however, BARTH (*op. cit.*, p. 78) has found the olivine in larvikite from “opposite Håö” to be a relatively Mg-rich olivine (Fo₇₀). This introduces the question — what was the composition of the olivine, if present, in the “dark” larvikite in which the hisingerite now occurs? Two alternatives and likely dependent resolutions of the problem of hisingerite genesis are: 1. If the olivine was of composition similar to that determined by Barth for the Håö larvikite, it would appear that ferric iron must have replaced most of the magnesium (which, of course, would have to have been taken away). As Professor Barth (personal communication, 1961) has noted with respect to this alternative “much more ‘unlikely’ replacement processes take place in pseudomorphism”. Further, if the active

solutions were high in ferric iron and low in magnesium, the hisingerite could have been precipitated (perhaps even with the accompaniment of magnetite formation) and magnesium could have been dissolved thus precluding serpentinization. *or* 2. If the olivine was an Fe-rich variety, unlike that found to occur in the Håö rock, the high Fe:Mg ratio might, in itself, account for formation of hisingerite in lieu of serpentinization plus formation of magnetite, (generally the process of alteration of the more common Mg-rich olivines). In any case, either of these alternatives appears more likely than any simple conditional control because of the presence of magnetite intimately intermixed with the hisingerite just as it typically is with serpentine after olivine. So far as these considerations are concerned, it will be most interesting to see if Fe-rich olivines from any localities have been altered to hisingerite.

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