ON THE CRYSTAL CHEMISTRY OF HISINGERITE

BENGT LINDQVIST AND SVEN JANSSON, *Mineralogical-Geological Inst., University of Uppsala, Uppsala, Sweden., Division of Chemical Technology, The Royal Institute of Technology, Stockholm, Sweden.*

ABSTRACT

In place of the current conception of hisingerite belonging to the montmorillonite group, a tentative proposal is offered that it is principally a mica mineral with extensive substitutions of Fe for Si (the reason for the cryptocrystalline character) and with inter-layer hydronium ions.

INTRODUCTION

Referring to the new data for hisingerite and neotocite newly published by Whelan and Goldich (1961), the writers would like to comment on this subject. This paper will deal with the *x*-ray and electron diffraction data of hisingerite and associated chlorite, but new aspects of the crystal structure of hisingerite will also be presented. The results are based upon an investigation of nine hisingerite samples—most of them being manganese varieties (neotocites)—from different localities in Sweden. With a few exceptions the samples are characterized macroscopically by a more or less platy appearance (Fig. 1). For those specimens mentioned in the text, the following notations have been used.
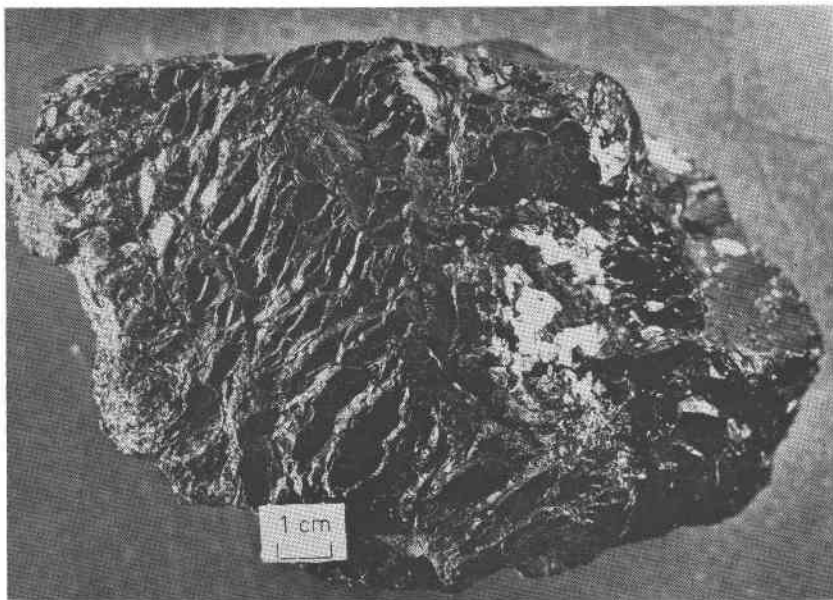

FIG. 1. Platy neotocite (Spec. K8) Photo: G. Andersson.

(MGIU = Mineralogical-Geological Inst., University of Uppsala)

(RMA = Dept. of Mineralogy, Swedish Museum of Natural History, Stockholm)

Spec. H1: ferrous hisingerite (on pyroxene skarn) from the Sjöström Mine, Hofors, Gästrikland.

Spec. S4: ferric hisingerite from the Solberg Mine, Elvestorp, Västmanland (coll. MGIU 400/2).

Spec. G5: neotocite from the Gillinge Mine, Svärta, Södermanland (coll. MGIU 400/4).

Spec. K8: neotocite from Klapperud, Dalsland (coll. RMA g26307).

Spec. E9: neotocite from the Erik-Ers Mine, Torsåker, Gästrikland (coll. RMA g26285).

All the specimens exhibit a very weak birefringence and the range of refractive indices in a fresh powder is 1.62–1.64. The determinations of the specific gravity, which were not very reproducible, gave an approximate value of 2.7 ± 0.1.

X-RAY DIFFRACTION DATA

Compilations of available x-ray data for hisingerite show that the general features are in good agreement, in spite of their vagueness. In the present case, four broad and diffuse bands were recognized in the powder diagrams of all the samples. Their interplanar spacing as measured to the centres of the bands varied within the following limits: 1) 4.3 to 4.6 Å, 2) 3.55 to 3.63 Å, 3) 2.57 to 2.63 Å, and 4) 1.54 to 1.60 Å. These values are more or less in accordance with previous data except that the last figure is somewhat too high.

In some cases, additional lines were also found, *i.a.* at about 7.3 Å. This line is also reported by Whelan and Goldich and is attributed by them to the formation of an "incipient chlorite structure." This is certainly an adequate explanation. It will be shown, however, that the 3.6 Å band is also a "false" one and depends on the presence of chlorite.

The occurrence of a chlorite phase in the hisingerite material has been positively established for many of the present samples. By mounting specially chosen mineral fragments large enough to furnish a usable plane surface, x-ray diffractometer traces typical for chlorite have been obtained. Owing to the enhanced preferred orientation, the basal reflections are well recorded. All of the x-ray diffractometer traces follow the scheme of Fig. 2, in which the weakness of the first and third order basal reflections is most prominent, indicating a high-iron or high-manganese chlorite. The peaks are generally more or less broadened but from the position of 002 reflections recorded at up to 7.28 Å the chlorites often seem to be of a rather "wide-spaced" variety, maybe approaching gonyerite, the manganese chlorite from Långban (Frondel, 1955). However, no significant variations between chlorites of Mn-rich and Mn-poor hisingerites were reproducible.

It should be emphasized that the chlorite, giving no impression of being a secondary coating, seems to be related to the hisingerite in a most intimate way. The broadness of the 3.6 Å line on the x-ray powder photographs also suggests a cryptocrystalline character of most of the chlorite.

ELECTRON DIFFRACTION DATA

As it was felt that the x-ray data are too few to permit any unequivocal interpretation, the attempt has been made to obtain electron diffraction patterns in the hope that additional information could be won. A piece of hisingerite (Spec. S4) was ground to a fine powder which was pressed into a reflection specimen holder or collected on a copper
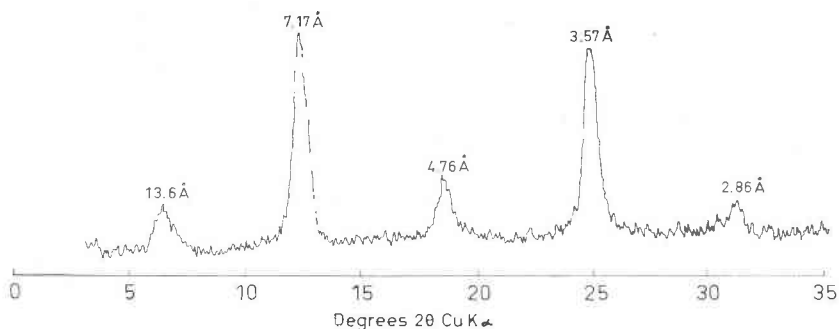

FIG. 2. X-ray diffractometer curve from a plane surface of Spec. S4.

electron-microscopy grid. Placed in the electron beam of a Trüb, Täuber & Co. electron diffraction apparatus, the specimen turned out to be highly insulating, which caused considerable trouble. With the help of a charge neutralising device it was possible to obtain at least one good pattern characteristic for hisingerite. A pattern of silver was taken as standard for the measurements. As might be expected there is some sharpening of the lines as compared to the x-ray powder photograms. For further comparisons Table 1 is to be consulted. The 3.6 Å band is evidently proved to be alien to hisingerite and must be attributed to chlorite. Moreover, the resemblance to the hectorite data is unmistakable. For the hectorite Nagelschmidt (1938) has stated the lengths of a and b axes to be 5.24 and 9.16 Å. Thus, the same approximate values are applicable to the hisingerite specimen.

CRYSTAL STRUCTURE

The similarity to montmorillonite where x-ray data are concerned led Gruner (1935) to introduce hisingerite as a nontronite species. This similarity is strengthened here, as already stated. In the absence of basal

TABLE 1. DIFFRACTION DATA

(1)	(2)	(3)	*hk*
4.45 (m)	4.53 (s)	4.57 (vs)	11, 02
3.63 (m)	—	—	—
2.57 (m)	2.58 (s)	2.65 (s)	13, 20
—	—	2.285 (vw)	22, 04
—	1.73 (w)	1.748⎫ (m)	24, 31
		1.689⎭	15
1.54 (m)	1.53 (m)	1.527 (vs)	33, 06
1.38 (vw)	1.34 (w)	1.320 (s)	26, 40
—	—	1.267 (vvw)	35, 17, 42
—	0.98 (vw)	0.990 (w)	19, 46, 53
—	0.89 (vw)	0.878 (w)	39, 60

(1) *X*-ray diffraction data of Spec. S4.

(2) Electron diffraction data of Spec. S4.

(3) Non-basal *X*-ray reflections of Mg-beidellite (hectorite), Hector, San Bernardino Co., California (Nagelschmidt, 1938).

reflections, however, the related series of *hk* bands cannot actually be used as a criterion for montmorillonite in particular but reveals only a layer lattice with analogous dimensions within the layers. Besides montmorillonite, the data could, for example, fit mica as well as chlorite. Furthermore, the absence of basal reflections renders the glycolation technique unsuitable for diagnostic purposes (Dietrich, 1961).

When considering the structure, the main question arises as to why the stacking of the hisingerite layers is so extremely poor that basal reflections cannot be recognized by any means. According to the writers a restricted crystallite growth of hisingerite (in the direction of the *c*-axis) can possibly be dependent on a rather extensive substitution of Fe for Si. On a small scale this could be realized in montmorillonite, but attention should also be paid to the mica alternative with its increased possibilities of tetrahedral substitutions. In the latter case the lower charge of the tetrahedral layers must be balanced by the supply of interlayer hydronium ions as neither potassium, sodium, nor calcium are present in sufficient amounts.

In order to study the compositional variations, the chemical analyses of twelve hisingerites have been recalculated. In Table 2 they are presented as incomplete structural formulas (interlayer ions and oxygen omitted). The calculations are based upon the hypothetical assumption that the intralayer cations, as in true mica, constitute 21 valences per basic formula. Higher charge will accordingly raise all the figures and at the same time raise the ratio of octahedral to tetrahedral ions.

In no case is a Si-index typical of montmorillonite attained (even after

TABLE 2. DISTRIBUTION OF INTRALAYER CATIONS IN HISINGERITES AS BASED UPON A MICA MODEL

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
Tetrahedral												
Si	3.09	3.03	2.91	3.05	3.07	3.09	3.11	3.20	3.25	3.28	3.30	3.32
Al	0.29	0.20	0.14	0.04	0.12	—	0.05	—	—	—	0.34	0.39
Fe^{2+}	0.62	0.77	0.95	0.91	0.81	0.91	0.84	0.80	0.75	0.72	0.36	0.29
Octahedral												
Fe^{3+}	0.75	1.53	1.55	1.62	1.79	1.93	1.47	1.27	0.52	1.65	1.01	1.13
Fe^{2+}	0.94	0.17	0.11	0.34	0.16	0.05	0.32	0.32	1.75	0.06	0.36	0.42
Mg	0.86	0.48	0.60	0.20	0.10	0.00	0.35	0.68	0.30	0.31	0.96	0.66
Mn	0.03	0.02	—	—	—	—	0.05	0.01	0.05	—	0.03	0.07
Sum of octahedral ions	2.58	2.20	2.26	2.16	2.05	1.98	2.19	2.28	2.62	2.02	2.36	2.28

(1) Spec. H1 (incomplete analysis)

(2) Spec. S4 (SiO_2 35.24, TiO_2 0.00, Al_2O_3 2.00, Fe_2O_3 35.51, FeO 2.40, MnO 0.34, MgO 3.77, CaO 1.99, Na_2O 0.00, K_2O 0.04, H_2O^+ 10.42, H_2O^- 9.03, CO_2 0.00, Sum 100.74) (B. Almqvist and B. Lindqvist, analysts)

(3) Nicholson Mine, Saskatchewan, Canada (Bowie, 1955)

(4) Parry Sound, Ontario, Canada (Schwartz, 1924)

(5) Riddarhyttan, Sweden (Cleve and Nordenskiöld, 1866)

(6) Kawayama Mine, Japan (Sudo and Nakamura, 1952)

(7) Montauban-les-Mines, Québec, Canada (Osborne and Archambault, 1950)

(8) Saksagan, Krivoi Rog, Russia (Nikolsky, 1953)

(9) East Mesabi, Minnesota, USA (Whelan and Goldich, 1961)

(10) Blaine Co., Idaho, USA (Hewitt and Schaller, 1925)

(11) and (12) Beaver Bay, Minnesota, USA (Whelan and Goldich, 1961)

correction for higher charge). A structural formula of montmorillonite can only be derived by equating trivalent iron to divalent as done by Whelan and Goldich. If, however, the main component is montmorillonite, it could occur more likely interstratified with chlorite. To fit the chemical data the ratio of montmorillonite to chlorite in that case should be about 2:1 as a rough estimate.

The main reason to present the chemical data in the way demonstrated in Table 2 is to illustrate the possible fit to the mica structure. The Si-index generally coincides with, or approaches the values of muscovite (Si 3.0) or "illite" (Si 3.3–3.4). Under the given assumptions it is seen from the last row of Table 2 that dioctahedral varieties would dominate but there would also be examples of pronouncedly trioctahedral character.

In Table 2, manganese specimens are not included because of the analytical difficulties involved in determining the valence states of manganese. It can be mentioned that application of the same calculation method upon the neotocite sample analyzed by D. Thaemlitz and C. O. Ingamells and cited by Whelan and Goldich would give a Si-index distinctly below the range of Table 2.

Finally, it must be admitted that no major conclusions can be drawn from the chemical analyses. It seems, however, as if the range of chemical

variations are more likely ascribed to isomorphism of a poorly crystallized silicate than to the occurrence of (non-silicate) impurities.

Thermal Data

Several DTA curves have been published, but the reactions recorded have been interpreted in somewhat different ways, and the data are not particularly illustrative. The writers have preferred to follow the thermal behavior by means of weight loss curves and x-ray phase analyses. In this way it has been shown that the thermal stability of hisingerite is remarkably lower than what is to be expected for a montmorillonite.

As to the dehydration stage it appears that almost all water (inclusive of hydroxyl) is driven off already on heating to 500° C. Contemporaneously the crystalline structure is completely destroyed as witnessed by the vanished hk bands. Thus, the destruction temperature is considerably lower than of any known montmorillonite or mica, which might be correlated to the exceptional conditions of substitution.

The recrystallization process starts at about 800° C., principally with the formation of ferrites (and braunite).

Cation Exchange Capacity

As far as is known, the exchange capacity of hisingerite has never been investigated. Some preliminary tests of this pertinent property will therefore be presented here. The powdered samples were Ca-saturated by treating with calcium acetate solution (pH 8) and the amount of calcium subsequently replaced by NH_4^+ ions was determined. By electrometric titration the number of hydrogen ions replaced during the first process also was determined. Perhaps there are some objections to the method used, but the following results will reasonably indicate the right magnitude. The figures refer to the total cation exchange capacity and to released hydrogen (within parentheses), both expressed in meq/100 g.

Spec. E9:	20	(10)
Spec. K8:	25	(5)
Spec. S4:	25	(25)
Spec. G5:	50	(15)

Apparently the values lie within the range typical for illite and chlorite. The very high cation exchange capacity of montmorillonite, considered to be one of its most unique properties, has not been encountered in any case.

Concluding Remarks

Even if there are great difficulties in obtaining pure hisingerite samples, the amount of uncontrollable, amorphous impurities which may be

present does not seem to be large enough to affect the chemical pattern. The fact that hisingerite represents a layer silicate cannot be doubted, but there are no unequivocal indications of it being a montmorillonite mineral, either from structural or thermal data, or from the study of infrared absorption spectra performed by Whelan and Goldich (1961). There are, on the contrary, some features which are incompatible with the montmorillonite theory, as for example, the low cation exchange capacity.

It is implied above and here tentatively proposed that hisingerite is built principally upon a mica model. This would require that there are Fe proxying for Si and hydronium for interlayer alkali ions. The rather extensive incorporation of iron in the tetrahedral layer must create a strained lattice which could be the explanation for the extremely poor crystallinity of hisingerite.

It is not claimed here that this hypothesis is necessarily the correct one, but the aim has been merely to accentuate the fact that hisingerite definitely warrants further study.

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