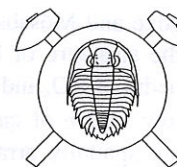# Minerals of the hisingerite-neotocite series from Chvaletice, Železné hory Mts., eastern Bohemia, Czech Republic*

Minerály hisingerit-neotokitové řady ze Chvaletic v Železných horách, východní Čechy (Czech summary)

(2 text-figs., 4 photos)

PAVEL POVONDRA

Department of Mineralogy, Charles University, Albertov 6, Praha 2, 128 43, Czech Republic

The hydrous ferri-manganese silicates from the Fe-Mn Chvaletice deposit correspond compositionally to $[R_3Si_3O_{10}]$. n H_2O, i.e. to the hisingerite-neotocite series. Both Fe and at least part of Mn in these mineral phases are trivalent, R : Si typically equals to unity, water content is highly variable and contents of magnesium, aluminium and alkali metals are low. Trace elements (e.g. Cu, Ni, Co, V) do not show any geochemical affinities to the major components. All physical parameters (optical properties, specific gravity, thermal properties, X-ray and IR absorption spectra) correspond well to those previously described for this mineral series. The minerals of the hisingerite - neotocite series have a gel-like structure (i.e. they are physically isotropic) but often contain anisotropic domains with incipient crystal structure. Most of the water present (up to 70 %) is free, probably occupying large open pores and it is released at temperatures less than 200 °C. The rest (30 % of water) is present in fine pores, probably bound via hydrogen bonds to the oxygen atoms of the co-ordination polyhedra and it is released at temperatures 200-400 °C. Minerals of the hisingerite-neotocite series in Chvaletice are likely to have originated through two different processes: (1) hypogeneous dissolution of primary Mn-silicates, e.g. knebelite and (2) reaction of cool silica-saturated solutions with solutions containing Fe and Mn. Product of such reaction - $SiO_2 \cdot FeO[OH]$ - has formed under slightly alkaline and oxidizing conditions.

Key words: hisingerite, neotocite, optical properties, chemical analysis, trace elements, densities, IR-spectrometry, thermal analysis

Introduction

Amorphous natural mineral phases with gel-like structure and composition corresponding to $[R_3Si_3O_{10}]nH_2O$ are known as the hisingerite-neotocite series. Their chemical composition is not constant: R-position is often occupied by iron and manganese but phases with magnesium and alkali metal contents up to 10 and 12.5 wt %, respectively have also been described (Wheelan - Goldich 1961, Dorfman - Soklakov 1964). The R : Si ratio and water content vary within the range of 0.7-1.7 and 15-30 wt %, respectively. Due to their chemical variability and amorphous state these phases have been previously described under different names: stratopeite, sturtite, penwithite, cambite, tschinglusuite (Chukhrov 1992). Finally, it has been found that these phases were not part of sheet silicate mineral group but form a separate Fe-Mn mixing series hisingerite-neotocite (Clark - Easton 1978) and that hisingerite corresponds to the original sturtite from Broken Hill, New South Wales, Australia (Eggleton et al. 1983, Dunn et al. 1984). XRD study of hisingerite and ferrihydrites (Farmer 1992) has pointed out a possible confusion of the two groups. Lack of any crystal arrangement is reflected in variations of physical properties even within individual samples: despite being optically isotropic, the samples contain highly anisotropic domains.

* This paper is dedicated to Professor Lubor Žák on the occasion of his 70th birth anniversary.

Refraction index varies within the range of n = 1.42-1.72, specific gravity ranges from 2.0 to 3.3 g·cm⁻³, hardness and microhardness vary from 3 to 3.5 and 440 to 450 kg·mm⁻², respectively. IR spectra show strong absorbancies in three regions: 450-440 cm⁻¹ (Si-O-R stretching vibrations), 1030-1015 cm⁻¹ (Si-O tetrahedra valence vibrations), 1650-1640 cm⁻¹ (H_2O deformation vibrations). In addition to the IR absorption and Fourier transmission infrared (FTIR) spectrometry, also magnetic resonance, Mössbauer spectrometry and radial distribution function analysis studies of hisingerites have been previously carried out. As the hisingerites either do not show any diffraction patterns or the diffusion lines can only point to a weakly pronounced layered structure, X-ray and electron diffraction techniques have not provided any additional information. Similarly, all previous thermal studies of hisingerite have not contributed to the recognition of its structure.

On the basis of differential thermal analysis (DTA), X-ray diffraction, IR and Mössbauer spectrometry data, hisingerites were defined as semi-amorphous (poorly crystallized) Fe^{3+} silicates containing structural elements similar to those of Fe^{3+}-rich dioctahedral smectites (Mackenzie - Berezowski 1980). Similar definition has been used for distinguishing hisingerite from an interstratified halloysite (Quantin et al. 1984). Data from high-resolution transmission electron microscopy (HRTEM), X-ray radial distribution function analysis, chemical analysis, X-ray absorption

edge and Mössbauer spectrometry have indicated that the structure of hisingerite contains networked poly-hedra of RO_6 and SiO_4 which form the surface of a hollow sphere of ca 50-100 Å in diameter. The spheres are spatially arranged in a physically isotropic solid matrix with more than 10 % of pores being interconnected. Outer surface (10-20) of the sphere shows a rudimental structure of initial partitioning of layers rich in Si and Fe (Mn). This structure may indicate formation of structural domains similar to layered silicates (Eggleton et al. 1983, Eggleton 1987). Similarly, the structural analysis of hisingerite from Krivoy Rog, Ukraine (Valter et al. 1988) based upon specific surface, porosity, pore size and distribution measurements and other physical criteria suggests a formula $\{R'_x \quad R_y^{2+}\}(M^{3+}_{4-(x+2y)} \quad M^{2+}_{(x+2y)})[Si_4O_{10}](OH)_4O_2 \; nH_2O$ (R stands for exchangeable cations, M for octahedral cations, n = 2-3 and H_2O is water present in the fine pores). Both the efficient leaching of Fe using dilute HCl and the physical properties of the solid residue (silicagel) suggest the solid matrix of this mineral consists of two phases: $FeO(OH)$ and SiO_2.

Minerals of the hisingerite-neotocite series are often present in alteration zones around Mn deposits (Andrushenko et al. 1985, Pires 1983, Vasileva 1986), adjacent to Fe deposits (Chukhrov et al. 1987, Valter et al. 1988) and associated with polymetallic ores (Kovalenko et al. 1988). They are also present in hydrothermal assemblage in alkaline rocks of the Khibiny Massif, Kola Peninsula, Russia (Semenov - Khomyakov 1986), on joint planes of basalts (Shayan 1984) and associated with the youngest phase of pegmatite-formation process (White 1987). Minerals of the hisingerite-neotocite series are also present in argillitized pyroclastic rocks of a submarine volcano in Japanese Sea (Srebrodolskii et al. 1982). In all these occurrences formation of the minerals of the hisingeri-te - neotocite series is associated with low temperature water activity and rock alteration during exogenous processes. However, they can also originate through coagulation processes from colloidal solutions. Temperature of hisingerite formation at a massive Cu-Ni ore deposit in Talnakh, Siberia, Russia has been established at 120-140 °C using decrepitation techniques (Aplomov and Sereda 1983). Hisingerite has been synthetized by a homogeneous coagulation from H_2SiO_3, Fe^{3+} and chelate solutions, with variable composition depending on temperature, pH and coexisting cations (Kaji - Tarutani 1988). Crystal chemistry data on hisingerite are summarized in Brigatti (1982) and Chukhrov (1992).

Neotocite from the abandoned iron and manganese deposit in Chvaletice has been previously described by Slavík (1928) and Kvaček - Hoffman (1965). The aim of this paper is to present new mineralogical data on the hisingerite-neotocite phases from various genetic host rock types of this locality using material obta-

ined from the extensive mining activity during 1960-1970.

Sample occurrence and description

Fe-Mn ore deposit in Chvaletice is located in northern part of the Železné hory Upper Proterozoic complex, between Sovolusky and Chvaletice. It forms a part of re-folded recumbent syncline. By tradition the host-rocks of the deposit are subdivided into three stratigraphic horizons: (1) underlying the deposit are graphitic pyrite-bearing shales (pre-ore formation), followed by (2) Mn-Fe carbonate rocks of the deposit (ore formation) which are overlaid by (3) graphitic shales containing massive sulphidic mineralization (post-ore formation; cf. Cháb et al. 1982). Six samples of hisingerite-neotocite mineral series, which were collected from various places in the Chvaletice super-quarry for the present study, form either up to 1 cm thick joint filling in the host-rock or they are present as part of the matrix in mylonitic host-rock.

N-1: Chvaletice East, 3rd level of the superquarry. Quartz vein in a fine-grained hornfels underlying Mn-rich horizon. Neotocite is present along the contact of quartz and hornfels, associated with pyrite and accessory rhodochrosite.

N-2: Chvaletice West. Vein containing neotocite, euhedral pyrite and rare rhodochrosite within neotocite grains.

N-3: Chvaletice East, southern face of the quarry, 100 m W of the road Chvaletice-Zdechovice. Hornfels with vein containing rhodochrosite (kutnohorite?), pyrite and neotocite.

N-4: Chvaletice East, western part of 3rd level of the superquarry. Quartz vein from the central part of Mn-rich horizon with abundant pyrite, accessory rhodochrosite and neotocite.

N-5: Chvaletice East. Neotocite-rich vein containing rhodochrosite, Mn-asbestos and accessory pyrite.

N-6: Chvaletice East, 2nd level of the superquarry. Joint filling in hornfels formed by neotocite, accessory pyrite and rhodochrozite.

Experimental techniques and results

0.5-1 mm size fraction was used for hand-picking the hisingerite-neotocite mineral phases and the resulting mineral separates contain only trace amount of pyrite and rhodochrosite. To prevent any alterations of the active gel surface the heavy liquid separation was avoided, and due to only weak paramagnetic properties of the hisingerite-neotocite phases the magnetic separation was not efficient.

Small chips of the mineral are dark-brown to black in colour, mineral has brown streak, resinous lustre, conchoidal fracture and it is brittle. Incomplete electron microprobe analyses (in wt %) of three grains from the sample N-1 point to the following variability

in their chemical composi-
tions: SiO_2 63.9-35.6-43.9,
FeO_T 8.7-6.9-6.1, MnO
24.0-57.7-49.2. Four grains
from sample N-6 yielded
the following data: SiO_2
48.2-3.6-49.6-16.5, FeO_T
40.2-3.4-35.4-10.2 and
MnO 9.7-88.0-12.3-69.5.
On the other hand, linear
traverses across individual
grains have shown only litt-
le variability. Values cor-
responding to an 18-points
traverse across a 0.5 mm
grain from sample N-1 are
(average and standard devi-
ation in wt %): SiO_2 38.76
(2.50), FeO_T 39.09 (1.09),
MnO 1.58 (0.23). Data for
a similar grain from sample

Photo 1. Sample N-1, untreated, magnification x3000

N-6 are: SiO_2 42.22 (1.85), FeO_T 5.99 (1.62), MnO
35.65 (2.56). However, up to 100 % differences in
composition were found between cores and rims of in-
dividual grains.

Optical microscopy: In thin section the mineral is
transparent to translucent, often reddish-brown and
mostly optically isotropic. Domains of fine network
fracturing and mosaic disintegration of the original gel
show a strong optical anisotropy and higher refraction
index. Such inhomogeneities are often associated with
colour changes from brown in the core to clear in the
rim. Refraction indices (immersion method) vary both
within individual samples and in the whole suite of
samples in the range
1.546(3)-1.638(3) and inc-
rease with increasing Fe-
content.

Electron microscopy:
Mineral phases were studi-
ed using a scanning elec-
tron microscope REM
BS340. Samples N-1 and
N-6 are shown before and
after a 15 min leaching by
dilute cold HCl on photos
1, 2 and 3, 4, respectively.
While before the acid lea-
ching the mineral surface
in both cases is compact,
only with irregular margins
along the cracks, after the
acid leaching the samples
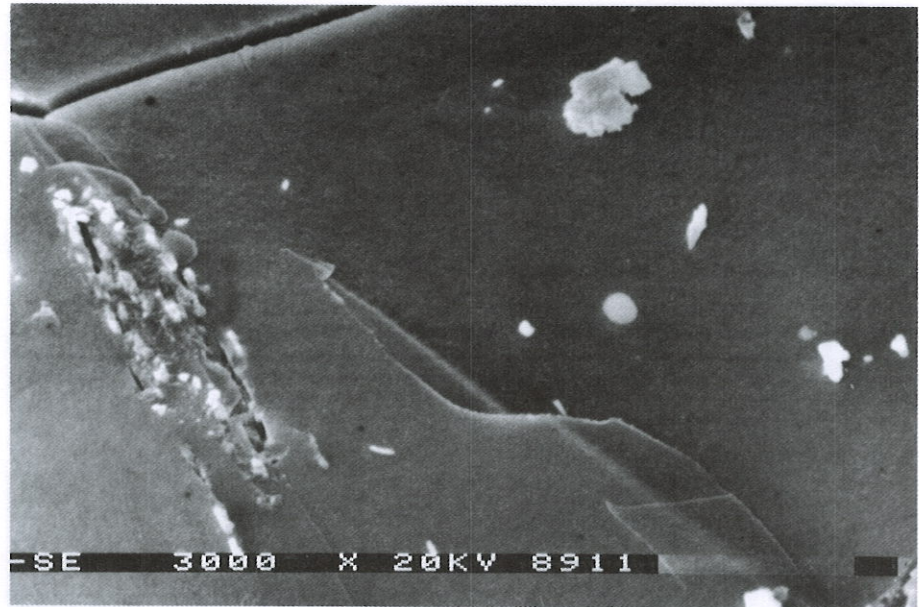show lamellar fracturing of
the residual silicagel. As a

result of acid leaching hisingerite completely looses
cations but its silicate framework remains compact.
Oblique lamellae which are ca 200 nm thick are likely
to form as a result of outer layer pressure during the
process of gel solidification. It is only at high magnifi-
cation (15 000x) when it becomes apparent that the
layers consist of small regular lamellae (ca 10 nm
thick) which stick to the basal face at 20-30° angle.
Formation of the lamellae is rather a result of mecha-
nical than of a structural process (i.e. incipient phyllo-
silicate crystallization). Unfortunately, the photos
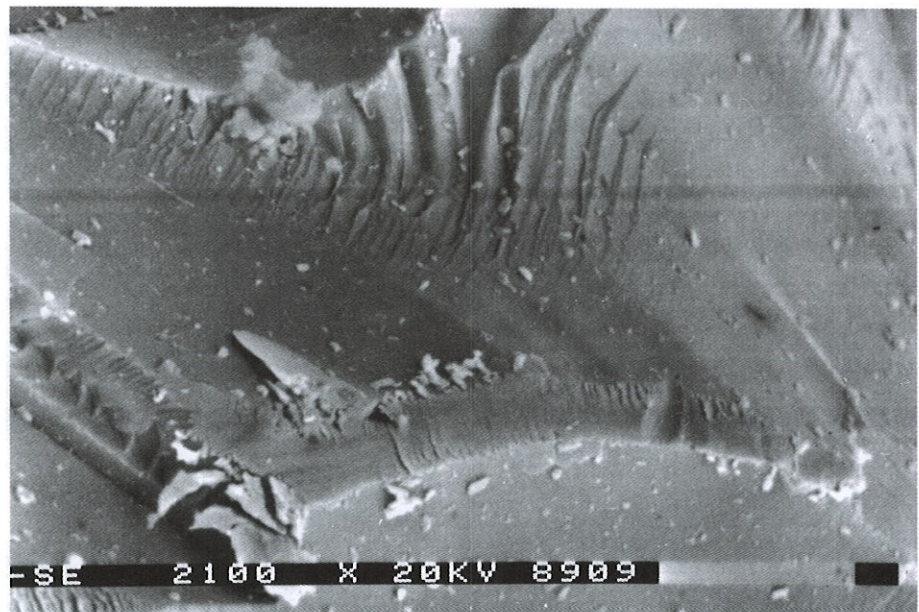obtained are not reproducible.

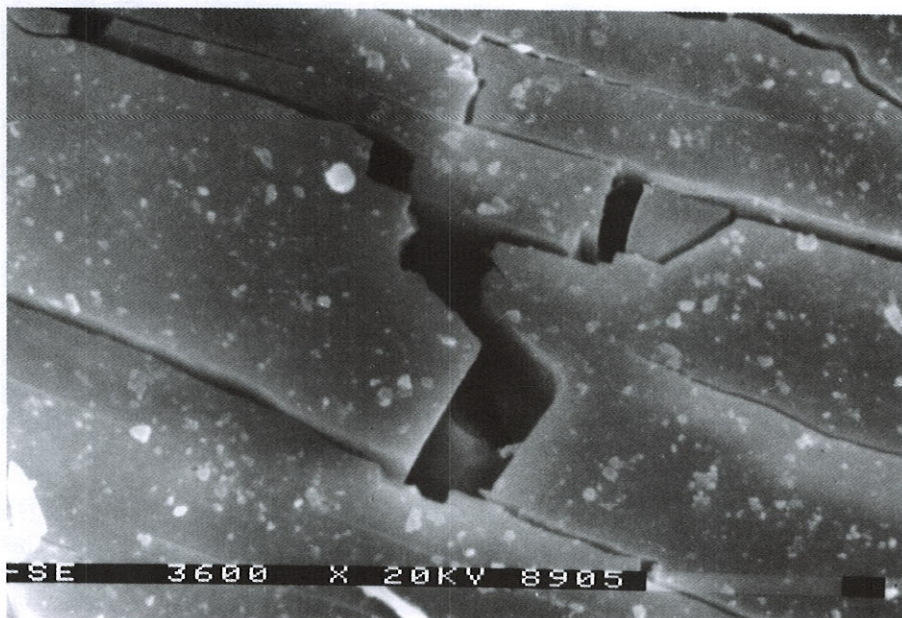Photo 2. Sample N-1, etched with dil. HCl, magnification x2100

Photo 3. Sample N-6, untreated, magnification x3600

Wet chemical analyses: Homogenized mineral separates were used for wet chemical analyses after being stored in desiccator containing sulphuric acid. Prior to the analysis mineral separates were dissolved in HCl. Trace elements, C, S and P were analyzed from separate powder, their concentrations were recalculated to pyrite, rhodochrosite (destinezite) and a corresponding amount of cations has been subtracted from the total concentrations. Exchangeable ions were analyzed using AAS technique after being leached from mineral powder with a cold 1M ammonium chloride solution for 100 hours. Average mineral chemical compositions and analyses calculated on the basis of 10 oxygen atoms 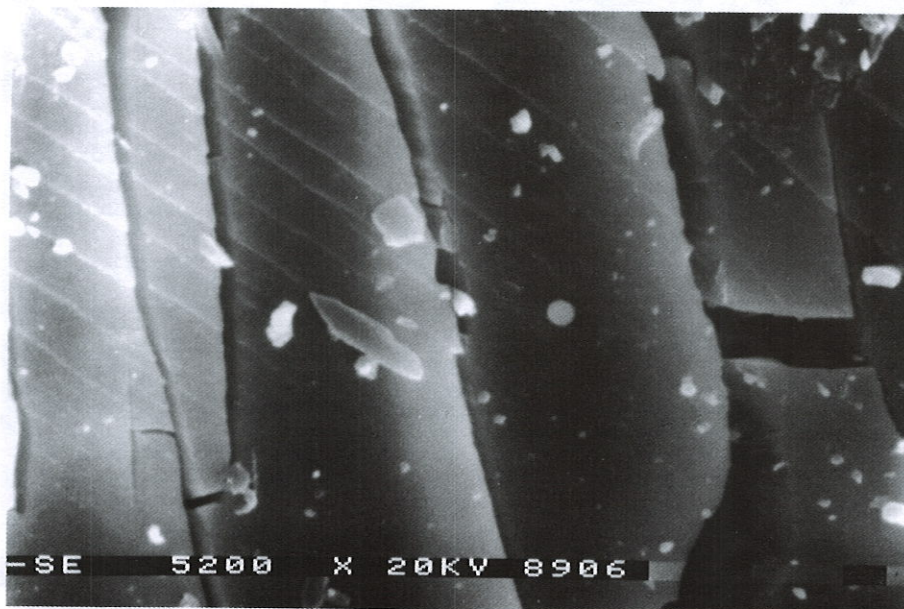are given in Table 1. The data suggest that even a random sampling is probably representative of the whole hisingerite-neotocite series in the Chvaletice deposit. Figure 1 gives references to 30 literature data for hisingerite-neotocite mineral phases which were used for comparison with the new mineral compositions from the Chvaletice deposit, well corresponding to $(R_3Si_3O_{10})$ $\cdot nH_2O$ formula. Triangular plot on Fig. 1 shows the ratios of Si, Fe and Mn atomic quotients. The values of individual analyses plot close to $(Mn_3Si_3O_{10})\cdot nH_2O$ - $(Fe_3Si_3O_{10})\cdot nH_2O$ joint which corresponds to solid solution composition of the neotocite-hisingerite end-members. Samples from the Chvaletice deposit contain no titanium, all iron is present as Fe^{3+} as well as part of manganese which is, however, also present as Mn^{4+}. Average cation : Si ratio per formula unit equals to 1.00 (standard deviation 0.06). Aluminium and magnesium contents are low, average values from 36 neotocites are 0.115 (st. dev. 0.113) and 0.095 (st. dev. 0.068) per formula unit for Al and Mg, respectively, and correspond well to those from neotocites from the Chvaletice deposit. Mg contents in mineral phases show no strong correlations with contents of other elements ($r_{Mn/Mg}$ = -0.224, $r_{Mg/Fe}$ = -0.095, n = 36). While the amount of exchangeable cations sorbed on the gel surface is only small (cf. Table 2), large number of water molecules is present in the gel (4.2-5.7 molecules of water per 1 gel molecule).

The studied phases are very poor in trace elements (see Table 2). No relations have been found between Co and Ni contents: both these elements were expected to be associated with Mn. Contrasting Co and Ni contents in samples N-5 and N-6 (which both have similar Mn contents) suggest the Co and Ni distribution is random. These samples have also low con-

Photo 4. Sample N-6, etched with dil. HCl, magnification x5200

Table 1. Chemical analyses of hisingerites-neotocites from Chvaletice and their recalculation on the basis of 10 oxygens

Sample	N-1	N-2	N-3	N-4	N-5	N-6
SiO_2	37.89	39.10	35.12	33.94	34.80	34.00
Al_2O_3	0.29	1.89	0.23	0.04	-	-
Fe_2O_3	6.64	10.79	17.75	16.11	37.03	34.79
MnO_2	5.71	2.91	2.08	3.60	0.71	0.68
MnO	31.01	25.84	20.64	24.80	6.78	7.26
MgO	0.46	1.10	0.62	0.49	1.34	1.44
CaO	0.22	0.40	0.33	0.29	0.24	0.24
Na_2O	0.09	0.09	0.09	0.06	0.07	0.07
K_2O	0.02	0.03	0.03	0.02	0.03	0.02
H_2Otot	16.06	17.98	19.62	19.15	17.63	15.37
$MnCO_3$	0.33		0.42		0.16	4.18
FeS_2	0.09		1.88		1.25	1.95
Total	98.81	100.13	98.81	98.50	100.04	100.00
Si^{4+}	3.185	3.210	3.100	2.997	2.887	2.909
Al^{3+}	0.028	0.183	0.024	0.004		
Fe^{3+}	0.421	0.667	1.180	1.071	2.315	2.224
Mn^{3+}	0.332	0.165	0.127	0.220	0.041	0.040
Mn^{2+}	2.200	1.797	1.543	1.855	0.477	0.526
Mg^{2+}	0.058	0.135	0.082	0.065	0.166	0.184
Ca^{2+}	0.020	0.035	0.031	0.028	0.021	0.022
Na^+	0.015	0.014	0.015	0.010	0.011	0.012
K^+	0.002	0.003	0.003	0.002	0.003	0.002
SR	3.075	2.999	3.005	3.255	3.034	3.010
Si/R	1.036	1.070	1.032	0.921	0.952	0.966

tents of exchangeable cations: Ca > Mg > Na (in average Ca = 36 %, Mg = 17 % and Na = 11 % from the total). Such results are not compatible with layered structure of at least part of neotocites (Fe-montmorillonite).

Specific gravity: Pycnometric and double-weighing methods were carried out to measure the specific gravity of both the fine-grained mineral powder and the mineral separate (size fraction 0.5-1 mm). The results from the two techniques are not consistent (cf.

Table 2. Trace and exchangeable elements (p.p.m.)

Sample	Co	Cr	Cu	Ni	Zn	V	P
N-1	310	14	62	360	6	5	32
N-2	25	12	14	21	16	5	147
N-3	165	12	114	160	251	5	1725
N-5	36	17	2	48	15	5	5
N-6	189	10	29	154	20	5	5

Sample	Na_2O	%[+]	K_2O	%[+]	CaO	%[+]	MgO	%[+]
N-1	99	11	tr.	-	77	35	91	20
N-3	62	7	13	5	41	12	52	9
N-5	78	11	tr.	-	127	53	252	19
N-6	90	13	tr.	-	108	45	251	18
Mean		11		5		36		17

+ % of the original contents

Table 3) despite sample degassing, storing in a reference liquid (both hot and cold) and centrifuging. The differences are not due to sample inhomogeneity but they rather reflect the role of pore quantity, size and distribution in the hisingerite phase: the mechanical properties of pores can prevent the liquid entering the gel structure.

Thermal behaviour: Mineral dehydration experiments have been carried out using open-air step-heating (48 hours) of mineral powder from 75 to 200 °C. Similar dehydration curves for all samples suggest the following water loss sequence (in cummulative %): 30-53 % / 75 °C, 45-57 % / 100 °C, 51-63 % / 125 °C, 54-66 % / 150 °C, 56-70 % / 175 °C and 58-72 % / 200 °C; all water is lost by 600 °C.

DTA has been carried out in a thermal interval of 20-1000 °C at a heating speed of 10 °C/min. A strong endothermic reaction at 200 °C followed by 300-500 °C minimum corresponds to a complete loss of water. Variable speed of water diffusion through the fine pores inside the gel structure is reflected in two different

Fig. 1. Number of Si, Fe and Mn atoms per formula unit in hisingerites and neotocites from the Chvaletice deposit (*full circles*); previously published data are plotted for comparison: *open squares* - Clark and Easton (1978); *diamonds* - Whelan and Goldich (1961); *V-triangles* - Kvaček and Hoffman (1965); *triangles* - Eggleton et al. (1983); *open circles* - Alexiev (1960), Dorfman (1964), Lindqvist and Jansson (1962), Kazachenko et al. (1981), Valter et al. (1988), Lazarenko et al. (1977)
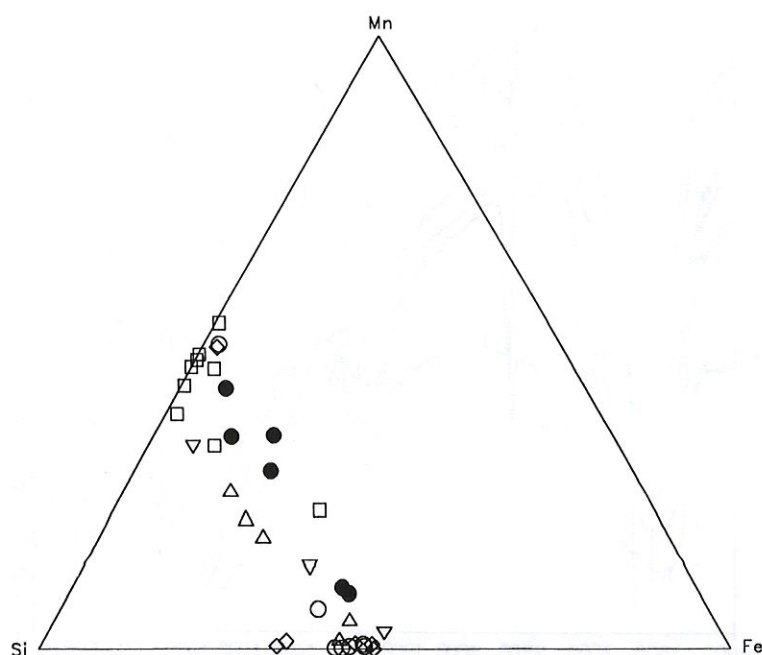
Table 3. Densities of the Chvaletice hisingerites (g.cm⁻³)

Sample	N-1	N-2	N-3	N-4	N-5	N-6
i	2.50-2.61	2.16-2.56	2.60-2.70	2.80-2.95	2.41-2.56	2.69-2.90
ii	2.85	2.79	2.82	3.10	3.38	3.14
iii	2.64	2.49	2.74	3.08	2.58	2.60
iv	2.60	2.43	2.60	2.95	2.45	2.70

Expl.: i) pycnometer - water, 0.25-1 mm size fraction; ii) pycnometer - water, sample dried at 110 °C per 1 day; iii) powdered sample - water, double weighing; iv) powdered sample - xylene, double weighing

velocity intervals for water loss from the mineral. Exothermic maximum at 450-700 °C corresponds to the crystallization of a solid solution of disordered braunite. As the original gel structure has a strong influence on this maximum, there are large differences in the corresponding temperatures between individual samples: chemically similar samples N-5 and N-6 have their maxima at 470 and 610 °C, respectively. The shift in temperature reflects different porosities (and reactivities) of the respective starting materials. Breakdown of silicate and formation of Fe^{3+} and Mn^{3+} combined oxides causes exothermic maximum at ca 950 °C. X-ray diffraction patterns after 5 hours of annealing (700 °C, open air) of hisingerite-neotocite yield d-values similar to the most intensive d-values of braunite. The increasing Fe content is accompanied by disappearance of reflections 313 and 220 (d = 4.49 and 2.35, respectively) and increasing intensity of reflection 116 (2.97).

X-ray diffraction: Low intensity diffusion peaks were obtained using a Dron 2.0 instrument (CuKa, 0.5°/min). Such X-ray diffraction patterns are similar to that of glass rather than to a fine-grained crystalline material. Values of d = 4.6, 4.4, 2.6 and 1.5 well correspond to the previously published data for the hisin-

gerite-neotocite series (cf. Lindqvist - Jannson 1962, Eggleton et al. 1983, Farmer 1992). As a result of progressive heating the diffraction peak at 2.6 shifts to higher d-values and at temperatures above 600 °C it forms the strongest braunite reflection (d = 2.75).

IR spectroscopy: A technique of FTIR-KBr tablets using a Perkin Elmer instrument has been employed to obtain IR transmission spectra of studied mineral phases. IR spectra of the six hisingerite-neotocite samples from Chvaletice (Fig. 2) are similar and correspond well to those previously published (Mackenzie - Berezowski 1980). IR patterns of all studied samples have narrow absorption peak at 3460 cm⁻¹ (valence vibration H-O-H), 1640 cm⁻¹ (H_2O deformation vibration), 1023 cm⁻¹ (Si-O valence vibration) and 450 cm⁻¹ (Si-O deformation vibration). Split of absorption bands in the range 3500-3450 cm⁻¹ corresponds to H-O-H bonds (3542, 3481, 3388 and 3233 cm⁻¹) and may reflect vibrations related to four oxygens in SiO_4 tetrahedras: intensities of these absorbancies decrease with increasing Fe/Mn substitution. Variable intensity of absorption bands at 2360 cm⁻¹ may correspond to free CO_2 dissolved in water which is adsorbed on colloidal surface of the mineral. Similarly to IR spectra of Fe-rich chlorite, a weak absorbancy in the range 940-400
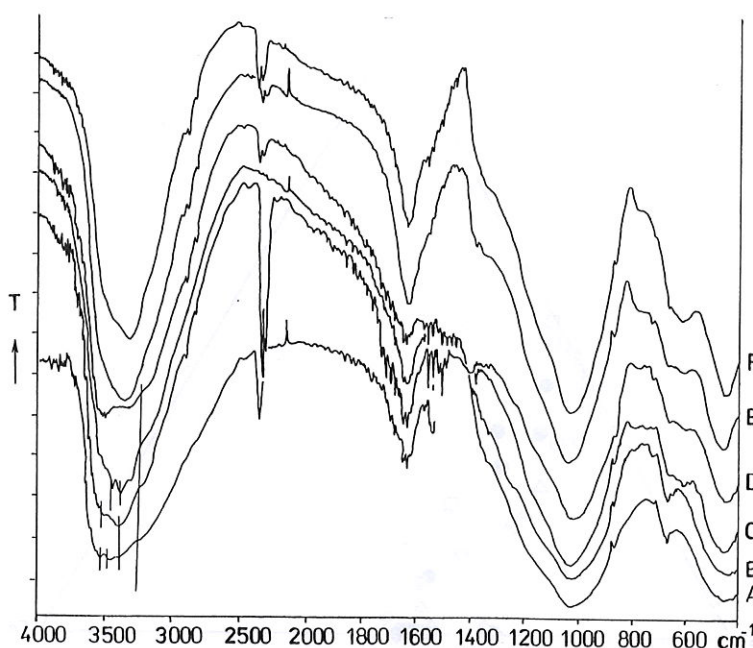

Fig. 2. IR absorption spectra (KBr tablets) in the range 4000-400 cm⁻¹ of hisingerites and neotocites from the Chvaletice deposit; A = N-5, B = N-6, C = N-3, D = N-4, E = N-2, F = N-1

cm^{-1} may reflect Si-O-Fe vibrations (870 and 670 cm^{-1}) or OH vibrations in several layered silicates at 840, 750 and 560 cm^{-1} (Mackenzie - Berezowski 1980). However, a more detailed dehydration study in the 70-600 °C temperature range, together with more detailed X-ray diffraction and IR absorption data are needed to shed more light on this problem.

Conclusions

Evidence from both the chemical study and study of physical properties suggest there is a common occurrence of hydrous Fe-Mn silicates of the hisingerite-neotocite series at the pyrite-manganese deposit in Chvaletice. These mineral phases have R : Si ratio constantly equal to unity and a variable water content. All iron and part of manganese are present as trivalent. All studied mineral phases have a typical gel-like structure and are physically isotropic. However, an incipient crystal structure formed by spatially networked chains of SiO$_4$ and RO$_6$ polyhedra (like that of layered silicates) is also present. Up to 70 % of water is present in large pores (channels) fixed to the surface of solid phase by van der Waals bonds. The remaining 30 % of water are present in fine pores, probably hydrogen-bound to the oxygen atoms. Both types of water bonding can be distinguished using DTA and IR absorption spectrometry. Trace element contents are very low and the trace elements do not show any geochemical affinities to the major chemical components. Low exchangeable capacities of studied phases suggest the trace elements are not adsorbed on the surface of the solid phase but bound in co-ordination polyhedra.

In Chvaletice the minerals of hisingerite-neotocite series have originated through two different processes. Partly they have formed in situ as a result of hypogenous dissolution of primary Mn-silicates (pyroxmangite, rhodonite, knebelite) due to activity of post-volcanic and, or, post-metamorphic fluids. A direct evidence for such processes are pseudomorphoses of neotocite after knebelite present in the rocks. Hisingerite-neotocite phases present in a form of joint fillings, or forming part of younger quartz-carbonate veins, have formed by direct precipitation and mixing of silica-saturated solutions (alkali silicate) with solutions containing Fe and Mn ions. Product of this reaction corresponds to SiO$_2$. FeO(OH) and the reaction progress is rapid even under normal conditions. As the hisingerite-neotocite minerals represent the youngest phase of the mineral association (younger than both the pyrite and carbonates), and consistent with their low trace element contents, it is likely that their parent solutions were cold and cation-poor. Lack of Fe^{2+} suggests that the precipitation reaction took place under slightly alkaline to neutral conditions, while oxidation of manganese can be attributed to activity of air oxygen dissolved in water which was in contact with the solid phase.

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Minerály hisingerit-neotokitové řady z Chvaletic v Železných horách, východní Čechy, Česká republika

Vodnaté železito-manganaté křemičitany chvaletického ložiska Fe-Mn odpovídají teoretickému vzorci $(R_3Si_3O_{10}).n\ H_2O$ a variabilním poměrem Fe/Mn dobře pokrývají řadu neotokit-hisingeritovou. Železo v nich vystupuje jako trojmocné, mangan převážně jako dvojmocný, ale jeho část je oxidována do valenčního stupně 3+ (4+). Pro tyto minerály je charakteristický konstantní poměr R/Si blízký 1. Obsah vody silně kolísá. Charakteristické jsou i nízké obsahy hliníku, hořčíku a kovů alkalických. Poměrně nízké jsou i obsahy stopových prvků (Cu, Ni, Co, V), jejichž vstup do pevných fází se neřídí žádným geochemickým vztahem k obsahu hlavních komponent. Fyzikální vlastnosti (optické chování, hustota, termické chování, rtg.-difrakce, IR-absorpční spektra) dobře odpovídají již dříve popsaným. Zkoumané minerály mají typickou gelovou stavbu, jsou fyzikálně izotropní, ale lze v nich nalézt zárodečnou krystalovou stavbu a náznaky anizotropie. Byla potvrzena dvojí pozice vody, jejíž větší část (70 %), volněji vázaná a těkající do 200 °C, je patrně vodou uloženou ve velkých dutinách. Zbylá voda unikající mezi 200-400 °C, vázaná patrně přes kyslíky koordinačních polyedrů vodíkovými můstky, je vodou jemných pórů. Chvaletické hisingerity-neotokity vznikly dvojím způsobem: (i) hypogenním rozkladem primárních křemičitanů manganu, hlavně knebelitu a (ii) přímým srážením z roztoků nasycených kyselinou křemičitou a roztoků obsahujících ionty železa (manganu). Srážecí reakce proběhla v mírně zásaditém prostředí, nasyceném vzdušným kyslíkem, a její produkt odpovídá hmotě $SiO_2.FeO(OH)$.