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FERRIERITE FROM THE DRILLHOLE KR-1, KREMNICKÉ VRCHY MTS. (CENTRAL SLOVAKIA)

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Abstract: The zeolite ferrierite was found in tectonic zones of andesite in the drillhole KR-1 near Kremnica (Central Slovakia). Ferrierite occurs in paragenesis with opal and chalcedony, occasionally in assemblage with mordenite. Powder diffraction pattern of ferrierite is identical with reference data, its lattice parameters are a = 19.201(4), b = 14.124(4), c = 7.501(2) Å. Chemical composition is characterised by Si/Al ratio ranging between 4.331 and 4.963 respectively, predominant exchangeable cations are Mg > Ca > K, and unusual high Ba-contents (0.192 - 0.298 per fromula unit).

Key words: Kremnica, ferrierite, X-ray powder diffraction, electron microprobe.

Introduction

The drillhole KR-1 is situated in Kremnica ore district, 2 km west of the town Kremnica and approximately 100 m W of the summit of the Jarabica Hill (937.9 m above the sea level). The drillhole, having a final depth of 373 m, penetrated a complex of Badenian andesites, which belongs, according to Konečný et al. (1983) to the Zlatá Studňa Formation. The hole was drilled to define more precisely, on the basis of manifestations of hydrothermal activity connected with the formation of quartz-goldbearing veins, the geological-depositional conditions at the northern marginal belt of the ore district. A detailed petrographical-geochemical characterization of rocks from drillhole has been presented in the manuscript of Böhmer & Mecháček (1964). During mineralogical studies of several thin veinlets (up to 2 mm), from a depth of 350 m, white radial aggregates of crystals were found, accompanied by opal at the rims of the veinlets. Preliminary identification, based on powder diffraction data and semi-quantitative spectral analysis, indicated the zeolite-group mineral ferrierite, which had not previously been found in the territory of Slovakia.

Ferrierite is a relatively rare mineral, and from its discovery in the year 1918 until the end of the sixties it was only known from the Canadian locality Kamloops (Graham 1918 in Gottardi & Galli 1985). Further published findings of fissure ferrierite were made in Bulgaria (Kirov & Filizova 1965), Yugoslavia (Barič 1965), Italy (Alietti et al. 1967), California (Wise et al. 1969), Japan (Yajima et al. 1971) and Austria (Zirkl 1973). As a rock-forming volcanogenic - sedimentary mineral in assemblage with mordenite, it forms in rhyolite tuffites a deposit near Lovelock, Nevada (Regis 1970). In Japan it occurs as an alteration product of tuffs (Hayakava & Suzuki 1969).

Ferrierite is an Si-rich orthorombic zeolite with space-group symmetry *Immm* and idealized formula unit according to Gottardi & Galli (1985)

$$(Na,K)\,Mg_2Ca_{0.5}\,[Al_6Si_{30}O_{72}]\cdot 20\,H_2O.$$

As one of the zeolites that forms suitable crystals, it was an object of several crystallographic studies on the ordering of atoms in the Si-Al skeleton (Smith 1986).

According to the results of Gramlich-Meier et al. (1985) some ferrierites are monoclinic (space group symmetry $P2_1/n$).

Experimental

Powder diffraction patterns were obtained with a DRON-3 diffractometer using Ni-filtered Cu radiation and a scanning speed 1°/min and on the Philips authomatic powder diffractometer in the Institute of Mineralogy and Crystallography, University of Vienna. Reference JCPDS (1990) data are a part of the instrumental software.

SEM studies were done at the Dionýz Štúr Geological Institute, Bratislava (analyst Stankovič) on the JEOL JSM-840 instrument. For a study using secondary electrons, chips of samples were gold-coated; for backscattered electron images we used polished carbon-coated thin sections. Further experimental details are given in figure captions.

Electron-probe microanalyses have been carried out on JEOL JSM 840 microprobe (Central Laboratory of Electron-optic Methods, Comenius University, analyst Krištín). Operating conditions were as follows: accelerating voltage 15 KV to reduce the volatilization of the weakly bonded water and lighter elements (without succes in the case of Na), wavelenght-dispersion system, phi-ro-z corrections of experimental data.

Thermal studies (DTA and TGA) were made on a derivatograph Mettler, wieght of sample 50 mg, heating rate 10 °/min, upper limit of experiments 1000 °C.

Results of experimental work

Optical study

Under the microscope the radial aggregates of ferrierite are colourless. All the information obtained from microscopic studies was limited because of the small size of the crystals. Parallel extinction indicated either orthorombic or monoclinic symmetry. The refractive indices determined by the immersion method are n_{max}= 1.482, n_{min} = 1.478 and correspond to the values found for ferrierite by Graham (1918) in Winchell & Winchell (1951).

X-ray data

Powder diffraction pattern as well as reference data (JCPDS, 1993, card No. 39-1382) are listed in Tab. 1. The match between the sample and standard is evident.

Lattice parameters were calculated and least-squares refined using the program CELREF (Appleman & Evans 1972). The mineral was indexed in the space group *Immm*. The values thus obtained are: a = 19.201(4), b = 14.124(4), c = 7.501(2) Å (numbers in parentheses are the standard deviations referring to the last digit).

SEM study

Crystal morphology presented in Fig. 1 a-c was studied using secondary electrons. As follows from the study in backscattered electrons, our ferrierite consists of two phases with different equivalent atomic number (on the photograph as a darker and lighter part,

Table 1: Powder diffraction data, values d in 10^{-10} m. Reference data taken from JCPDS (1990), record No. 39-1382.

d_{obs}	I_{obs}	d_{tab}	I_{tab}	*hkd*	d_{obs}	I_{obs}	d_{tab}	I_{tab}	*hkl*
11.31	2	11.38	3	110	3.071	5	3.076	12	521
9.56	100	9.60	100	200	2.973	14	2.977	13	530
7.03	2	6.98	5	101	-		2.955	4	402
6.62	1	6.63	3	011	2.913	2	2.901	4	132
5.82	19	5.84	18	310	2.842	1	2.846	1	440
-		4.97	2	121	2.723	2	2.726	5	422
4.79	4	4.80	5	400	2.691	4	2.696	6	710
4.56	1	4.58	2	130	2.639	2	2.643	3	051
-		4.01	21	321	2.584	3	2.581	4	350, 701
3.964	43	3.974	38	420	2.565	1	2.572	3	042
3.883	5	3.888	14	411	2.431	2	2.432	4	602
3.788	17	3.797	20	330	2.368	8	2.372	9	730
3.701	30	3.708	31	510	-		2.319	1	451
3.561	3	3.562	14	112	2.238	1	2.255	2	811
3.527	22	3.535	26	040	-		2.212	2	323
3.489	5	3.493	22	202	-		2.190	2	712
3.409	4	3.416	8	501	2.148	1	2.115	4	460
-		3.318	7	420	2.111	4	2.109	3	910
3.311	6	3.310	6	022	2.052	1	2.051	3	901
3.197	7	3.199	9	600	-		2.021	3	802
3.149	3	3.151	10	141	2.005	2	2.006	3	523, 642
3.127	3	3.130	4	222	-		1.969	4	921

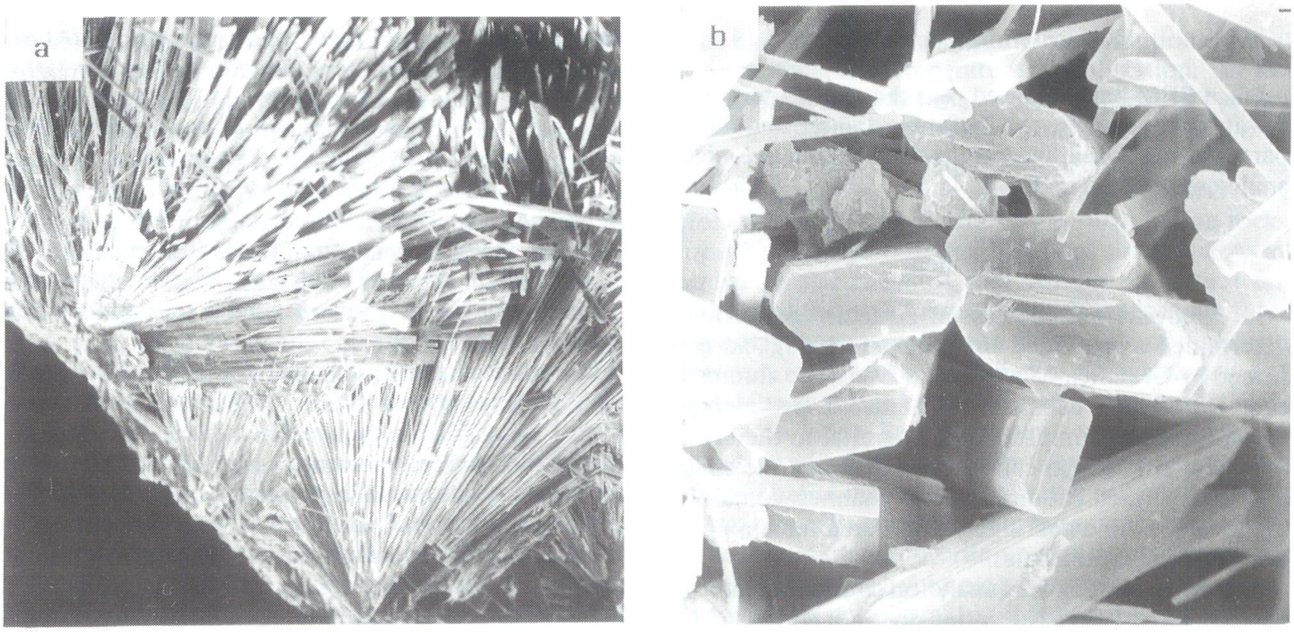

Fig. 1a-b. SEM micrographs of ferrierite crystals. Secondary electrons: **a** - aggregate of radiating blades of ferrierite (magnification 400 x); **b** - cross-sections of crystals perpendicular to Z axis. Orthorhombic mm2 symmetry is evident. Fibres are probably mordenite (magn. 1000 x).

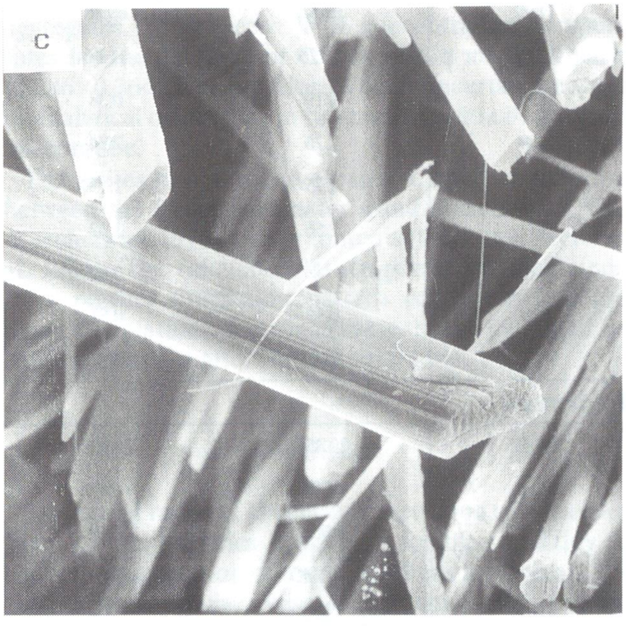

Fig. 1c. SEM micrograph of ferrierite crystals. Detail of a ferrierite crystal showing perfect cleavage parallel to (010) (magn. 1000 x).

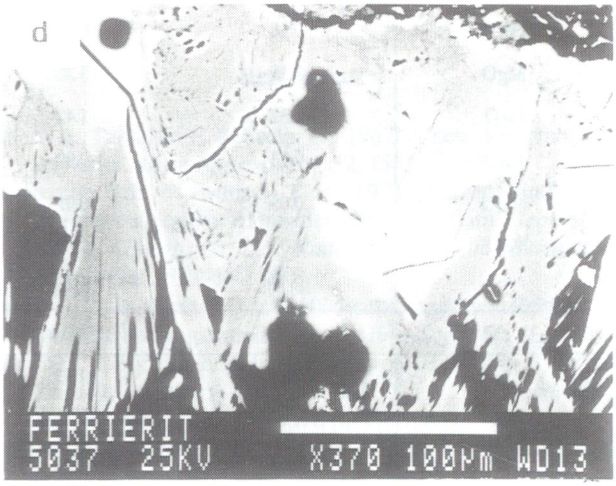

Fig. 1d. Backscattered electrons: two distinct phases with different equivalent Z. The dark part at the periphery of the aggregate differs from the core in lower Ca content.

Fig. 1 d). Fibrous crystals, distinguished at a greater magnification, are probably mordenites.

Thermometric properties

There are few published data on thermal properties of ferrierites and these data are not absolutely identical (Kirov & Filizova 1965; Yajima et al. 1971; Gottardi & Galli 1985).

As follows from DTA and TGA curves, the studied ferrierite having endotherms at 82, 220 and 649 °C, is closest to the ferrierite from the locality Alberto Bassi, Italy (Gottardi & Galli 1985). Total weight loss by TG is 15 wt. %, which corresponds to a loss near to the theoretical value of 20 water molecules per formula unit.

Electron-probe microanalysis

Since SEM study showed that the studied ferrierites are inhomogeneous, the both two lighter and darker parts were analyzed. The results of representative microanalyses are listed in Tab. 2.

Discussion

As follows from the crystal structure of ferrierite determined and refined by Vaughan (1966) and confirmed by Gramlich-Meyer et al. (1985), the alumosilicate framework consists of chains of five-member rings, linked in complex chains parallel to the orthorombic c-axis. Large cation cages between the chains contain hydrated cations and two channels containing the loosely bound and highly disordered remaining cations and water molecules.

According to published analytical data, chemical composition of real ferrierites often does not correspond to the idealised formula unit, where the ratio Si/Al approaches 5 and Mg content is predominant in relation to the other cations (Gottardi & Galli 1985). Following the chemical analyses compiled in the work of Wise & Tschernich (1976), the Si/Al ratio varies between 3.2 and 6.2. There is also a great variability in the content of exchangeable cations, while neither of them is indispensable for the formation of ferrierite structure. This fact is confirmed by the results of syntheses of ferrierite analogues without Mg, summarised in the paper of Gottardi & Galli (1985).

In ferrierite from the drillhole KR-1 (Tab. 2), the ratio Si/Al varying between 4.331 - 4.963 is close to the theoretical value. The exchangeable cations are predominantly the bivalent elements - Mg, Ba and Ca; while monovalent cations are represented by Na and K. The departure of Na may result in part from inaccuraces in the chemical composition determination. Magnesium occurs in ferrierite strictly as the hydrated ion $Mg(H_2O)_6^{2+}$, and is located at specific sites in channels

Table 2: Representative microprobe analyses [weight %].

	darker part			lighter part	
SiO_2	69.08	69.74	71.27	67.62	69.38
Al_2O_3	12.77	12.66	12.57	13.25	11.86
FeO*	0.10	0.32	0.32	0.19	0.38
MgO	3.35	3.35	3.09	2.26	2.84
BaO	1.32	1.42	1.37	1.75	1.13
CaO	0.73	0.80	0.71	2.56	1.37
Na_2O	0.05	0.01	0.10	-	0.02
K_2O	1.07	0.75	1.33	0.39	0.51
Σ	88.47	89.05	90.76	88.02	87.49
cation content based on 72 oxygens					
Si	29.630	29.705	29.852	29.351	29.995
Al	6.458	6.356	6.211	6.776	6.043
Fe*	0.036	0.114	0.113	0.068	0.136
Σ	36.124	36.175	36.176	36.195	36.174
Mg	2.141	2.129	1.937	1.464	1.828
Ba	0.222	0.237	0.225	0.298	0.192
Ca	0.334	0.364	0.320	1.190	0.636
Na	0.044	0.007	0.077	-	0.014
K	0.585	0.410	0.708	0.219	0.281
$\Sigma[+]_{ex}$	6.023	5.877	5.749	6.123	5.607
Σ_{total}	39.451	39.321	39.435	39.366	39.126
Si/Al	4.588	4.782	4.806	4.331	4.963

* all Fe formally as Fe^{2+}

$\Sigma[+]_{ex}$ is the sum of exchangeable cations

(Vaughan 1966). On the other hand, other, weakly bound cations, are coordinated only by oxygen atoms (Gramlich-Meier et al. 1985). In the studied ferrierite the Mg content (approximately two ions per formula unit) is predominant with respect to all exchangeable cations and close to the ideal formula-unit content.

Barium and strontium in ferrierites occur frequently in low concentrations. The ferrierites from the Silver Mountains (California) and Francois Lake (British Columbia), with Ba contents of 0.45 and 0.34 per formula unit, respectively are exceptions. Wise & Tschernich (1976) explained that the high barium content in ferrierite from the first locality is connected with the presence of barite in ferrierite-containing veins.

In our case, ferrierite occurs in veins as the only barium-bearing mineral and Ba concentrations in the analyses are remarkable constant. Geochemical study of rocks from the drillhole has shown that Ba and Sr in the surrounding rocks frequently reach values in the range 0.1 - 0.01 wt. %, but extreme Ba contents approached 1 wt. %. The strontium contents determined by semiquantitative spectral analyses are probably lower than the detection limit of the electron microprobe.

Ca contents are variable and they are higher in the lighter central parts (interval 0.636 - 1.190) of ferrierite aggregates. An increase in K concentration compensates for the decrease of Ca content in marginal parts (0.286 - 0.364). The position of Na is uncertain because of analytical difficulties in its determination by electron microprobe.

Ferrierites have a relatively simple linear correlation between the lattice parameter **a** and Si contents (Wise & Tschernich 1976), or Mg contents (Gramlich-Meier et al. 1985). The calculated lattice parameter **a** obtained from powder diffraction pattern corresponds to the above correlations. It is remarkable that an increased Ba content does not affect lattice parameters at all.

Conclusion

The broad range of chemical composition of ferrierites from various localities is evidence for the variability of chemical composition of source solutions from which this zeolite can crystallize. Wise & Tschernich (1976) stated that Si and H_2O activity are probably the main variables controlling the composition of high-silica zeolites.

Petrographical-mineralogical studies of the drillhole KR-1 has shown that hydrothermal mineralization in Badenian andesites resulted especially in low-temperature modifications of SiO_2 and these modifications occured only in tectonic zones, or in zones with increased porosity. In the Kremnica ore district such forms of SiO_2 (represented by opal and chalcedony without ore mineralization) are characteristic of the marginal and apical parts of quartz - noble metal veins connected with the Pannonian rhyolite volcanism (Böhmer 1966).

The ferrierite association (sometimes with sporadic mordenite) with low-temperature forms of SiO_2 indicates high Si activity in hydrothermal solutions and, at the same time, low temperature crystallization. The fact that ferrierite occurs in the studied drillhole as the only zeolite mineral indicates locally restricted conditions, which did not allow other high-silica zeolites to crystallize.

Exchangeable cations in the studied ferrierite are also affected by the composition of the surrounding rocks, through which hydrothermal solutions circulated. As indicated by the chemical composition of natural ferrierites and their synthetic analogues, magnesium is not absolutely necessary for the formation of ferrierite. However, in natural conditions it is Mg which may acts as stabilising agent of the ferrierite structure (Kirov & Filizova 1966). Barium contents are not genetically connected with hydrothermal processes (there is no evidence of barite mineralization in the ore field) and the barium seems to originate from the surrounding rocks.

The formation of ferrierite-opal mineralization is not connected with post-volcanic processes related to Badenian andesite volcanism, but it represents the last, lowest-temperature stage of the Pannonian ore-bearing rhyolite volcanism.

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References

Alietti A., Passaglia E. & Scaini G., 1967: A new occurrence of ferrierite. *Amer. Mineralogist,* 52, 1562 - 1563.

Appleman D.E. & Evans H.T. Jr., 1973: Indexing and least-squares refinement of powder diffraction data. *Geol. Surv. Comp. Contrib.* 20. *U.S. National Technical Information Service Doc. PB2-16 188.*

Barrel R.M. & Marshall D.J., 1950: Synthetic zeolites. Relation to ferrierite and yugawaralite. *Amer. Mineralogist,* 50, 484 - 489.

Barič L.J., 1965: Ferrierite from the quarry Golovec in Hrvatsko Zagorje (northern Croatia). *Bull. Sci. Cons. Acad. RSF Yougosl. sect. A*, 10, 177 - 178 (in German).

Böhmer M. & Mecháček E., 1964: O5-A-IX basic geological survey and mapping on the scale 1:25 000 and 1:50 000 on the map page Kremnica (Part Deposits). *Manuscript, Department of Economic Geology, Comenius University*, Bratislava, 1 - 60 (in Slovak).

Böhmer M., 1966: Depositional and paragenetic conditions of gold-bearing veins in the central part of the Kremnica ore field. *Acta Geol. Geogr. Univ. Comen., Geol.*, 11, 1 - 123 (in Slovak).

Gottardi G. & Galli E., 1985: Natural zeolites. *Springer-Verlag,* Heidelberg, New York, Tokio, 1 - 409.

Gramlich-Meier R., Gramlich V. & Meier W., 1985: The crystal structure of the monoclinic variety of ferrierite. *Amer. Mineralogist,* 70, 619 - 623.

Hayakawa N. & Suzuki S., 1969: Zeolitized tuffs and occurence of ferrierite in Tadami-Machi, Fukushima Pref. Japan. *Mining Geol.,* 20, 295 - 305.

Kirov G.N. & Filizova L., 1966: Calcium ferrierite from the Eastern Rhodopes. *An. Univ. Sofia Fac. Geol. Geogr. 1, Geol 59,* 237 - 246.

Konečný V., Lexa J. & Planderová E., 1983: Stratigraphic classification of central Slovakia neovolcanites. *GÚDŠ*, Bratislava, 1 - 203 (in Slovak).

Regis A.J., 1970: Occurrence of ferrierite in altered pyroclastics in central Nevada. *Geol. Soc. Amer. Abstr. Programs*, 2, 661 .

Smith B.K., 1986: Variations in the framework structure of the zeolite ferrierite. *Amer. Mineralogist*, 71, 989 - 998.

Vaughan P.A., 1966: The crystal structure of the zeolite ferrierite. *Acta Cryst.*, 21, 983 - 990.

Winchell A.N. & Winchell H., 1951: Elements of optical mineralogy. Part II. Description of Minerals. *John Wiley and Sons*, New York - London, 1 - 337.

Wise W.S., Nokleberg W.J. & Kokinos M., 1969: Clinoptilolite and ferrierite from Agoura, California. *Amer. Mineralogist*, 59, 887 - 895.

Wise W. & Tschernich R.W., 1976: Chemical composition of ferrierite. *Amer. Mineralogist*, 61, 60 - 66.

Yajima S., Nakamura T. & Ishii, 1971: New occurrence of ferrierite. *Mineral. J.*, 6, 343 - 364.

Zirkl E.J., 1973: Ferrierite in basalt from Weitendorf, Styria (Austria). *Neu. Jb. Miner., Mh.*, 11, 524 - 528 (in German).

FIRST SUBREGIONAL MEETING

CONSERVATION OF GEOLOGICAL HERITAGE IN SOUTH-EAST EUROPE

May 5 - 13, 1995
Sofia, Bulgaria

Scope of the Meeting

The combined efforts of many scientists within the frame of the **Working Group of Geological (incl. Fossil) Sites** (UNESCO, IUGS & IGCP) and the **European Association for the Conservation of Geological Heritage** marked a considerable progress in the establishment of the WORLD HERITAGE LIST, and in the study of important geological sites (geotopes) in the world. However, one of the important geological regions of Europe (the Balkan Peninsula) remained aside from these developments, mainly due to limited geological information, and to the turbulent political and military situation.

The aim of the planned meeting is to combine the efforts of Balkan geoscientists for to compile NATIONAL HERITAGE LISTS OF IMPORTANT GEOLOGICAL SITES as well as a BALKAN HERITAGE LIST OF IMPORTANT GEOLOGICAL SITES. A future international project in this respect would be most useful for the development of geosciences and geotope conservation in our subregion. The final result of our efforts could be a joint proposal for the inclusion of the most important Balkan geological sites into World Heritage List.

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