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Ravatite, $C_{14}H_{10}$, a new organic mineral species from Ravat, Tadzhikistan

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Abstract: The new organic mineral ravatite (analyzed as $C_{14.1}H_{9.9}$, idealized formula $C_{14}H_{10}$), identical with synthetic phenanthrene, is described as a sublimation product caused by the natural combustion of a brown coal seam near Ravat/Tadzhikistan (southwestern Tjan' Shan'). It forms thin, platelet-like individuals with diameters of mainly a few hundred micrometers which are usually aggregated to thin crusts on a bituminous, H_2SO_4-impregnated coaly-earthy material. Ravatite is colourless, or - dependent on the amount of coaly, gas and other inclusions - white to pale grey and transparent to translucent. It shows a vitreous to wax-like lustre. Ravatite has a monoclinic lattice (space group $P2_1$) with $a_o = 8.392(5)$Å; $b_o = 6.181(3)$Å; $c_o = 9.558(5)$Å; $\beta = 98.48(12)°$; $V = 490.4(4)$Å^3; $Z = 2$. The observed strongest five X-ray powder diffraction lines [d in Å (I_{rel}) (hkl)] are: 9.434(100)(001); 4.028(13)($20\bar{1}$); 4.941(11)(110); 4.724(11)(002); 3.371(10)($21\bar{1}$). The Mohs hardness is about 1; the calculated and the measured densities are 1.207(1) and 1.11(2) g/cm^3, respectively. Ravatite shows a whitish-yellow fluorescence under ultraviolet light. The initial temperature of melting is 94.3°C. Infrared absorption and Raman data do not differ significantly from data of synthetic phenanthrene.

Key-words: ravatite, phenanthrene, aromatic hydrocarbon, new mineral, Tadzhikistan.

Introduction

The cyclic hydrocarbon phenanthrene, $C_{14}H_{10}$, was first discovered in coal tar and named by Fittig & Ostermayer (1873). Until the end of the 1980's, the occurrence of phenanthrene in nature was known only in molecular form, for example as a component of oil (*e.g.* Gavat & Irimescu, 1942). However, phenanthrene crusts consisting of a multitude of crystalline individuals were found in geological samples taken in 1988 in the Jagnob valley in Tadzhikistan.

Natural phenanthrene was proposed as the new mineral ravatite - named after the locality of its discovery, which is situated near the former village Ravat. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the I.M.A. (92-019). The type specimen is deposited in the mineral collection of the Freiberg Mining Academy (sample 74120).

Occurrence: location and paragenesis

Ravatite was found in the Fan-Jagnob lignite basin, situated in north-western Tadzhikistan (about 100km north of Dushanbe; Fig. 1). Ravat, a former settlement, is situated in the valley of the Jagnob river, about 3km east of the confluence of the rivers Jagnob and Iskanderdar'ja to form the river Fandar'ja. Approximately 600m

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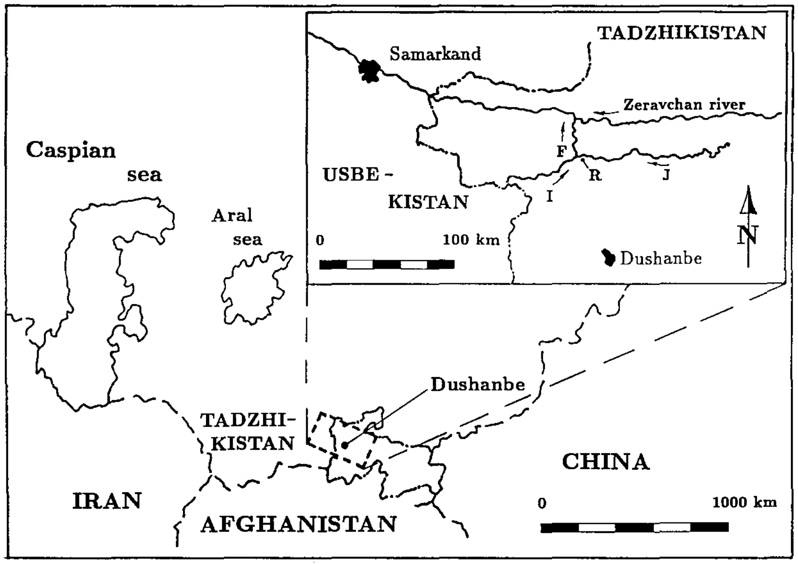

Fig. 1. Location map. F = Fandar'ja river; I = Iskanderdar'ja river; J = Jagnob river; R = point of discovery near Ravat.

east of the little tributary river Gaberut, at the south slope of the Jagnob valley (north slope of the Gissar mountain ridge), numerous thin, steeply dipping lignite seams are exposed. The seams are intercalated with a complex of Middle Jurassic molasse sediments, consisting primarily of sandstones and mudstones.

A combination of different processes, particularly the weathering of finely dispersed pyrite (*e.g.* Nikoloyannis, 1992) and the bacterial decay of coal have caused the seams to ignite spontaneously. Human influence can be ruled out, because the coal seam described here, as well as neighbouring seams and rocks in their vicinity have never been worked; there is no evidence of abandoned or active mining. Ignition and burning of coal seams in surface regions have taken place near Ravat for several thousand years. According to Belakovski (1990), mention was already made of this at the time of Alexander of Macedonia.

Due to the high temperatures, which can exceed 800°C, many new minerals are formed. A clear zonal distribution with respect to temperature, and therefore also to distance from the heat source, can be observed. A first short description of minerals of the present locality was given by Belakovski (1990). Belakovskiy & Moskalev (1988) described a similar association from Ravat, on the north slope of the Jagnob Valley (Zeravshan mountain ridge).

The lignite seam examined here has a thickness of 10 - 20cm. Temperatures ranging from 600 to >800°C were measured in the central zone of the source with a pyrometer. Here the coal has been completely consumed; the product is a slag-like 'buchite' which consists mainly of glass, quartz, labradorite, cordierite, and mullite. A superficial formation of sulphides such as galena, sphalerite, and greenockite is observed.

The seam is intercalated with a former argillite which shows intensive thermal and mechanical alteration. Where temperatures exceeded more than approximately 350°C, the highly H_2SO_4-impregnated metaargillite material contains ilsemannite, molybdite, and an anhydrous aluminium sulfate, which after sampling rapidly transforms to alunogen. At lower temperatures up to 100°C - conditions which can only be observed as a single zone of newly formed minerals in the hanging wall - the association sal ammoniac, mascagnite, hematite, and kremersite is found.

The footwall is composed of relatively unaffected sandstone (distance to the burning seam 20 - 30cm). In the hanging wall further newly formed minerals follow in an earthy or coaly-earthy to bituminous, similarly H_2SO_4-containing material. The boundary zone between this material and the decomposed argillite, where temperatures of approx. 120 - 50°C were reached, is char-

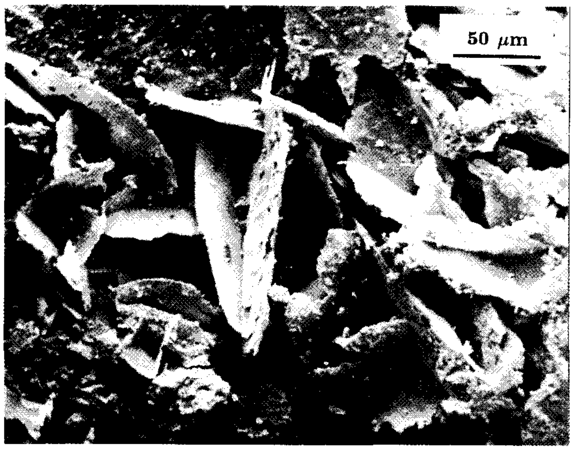

Fig. 2. Thin ravatite platelets with diameters of approximately 0.1mm. The two sides could be interpreted as (001) crystal faces.

acterized by the dominance of native sulphur (distance to the burning seam 10 - 50cm). In the outermost zone (60 - 25°C), which reaches an average thickness of one meter, ravatite occurs together with liquid bitumen and, very rarely, native selenium.

We interpret the formation of crystalline phenanthrene as a product of sublimation directly from a gas phase, at temperatures considerably below the melting temperature.

Appearance and physical properties

Ravatite forms thin, platelet-like individuals of irregular shape which mostly have sizes of a few hundred micrometers. The individuals are usually polycrystalline and only rarely monocrystalline, as indicated by the irregular extinction under crossed nicols. Ravatite often contains many gas inclusions so that the material has a 'porous' aspect (Fig. 2). Furthermore, coaly and mineral inclusions (especially quartz grains) occur. Dependent on the quantity and type of inclusions, ravatite is colourless and transparent to whitish or pale greyish and translucent. The lustre is vitreous to wax-like. The blades form crust-like aggregates which generally reach thicknesses of less than 1mm.

Ravatite shows a perfect {001} cleavage; the tenacity is wax-like. The density determined by floating in undersaturated NaCl-solutions is 1.11(2)g/cm^3. The relatively large discrepancy of this value with respect to the density calculated from the unit cell parameters (1.207(1)g/cm^3) is considered to be due to the the porosity of the individuals.

Optically, ravatite is biaxial with $2V_{meas} \approx 90°$. The indices of refraction could be assessed only by immersing in organic liquids, where ravatite shows a tendency towards dissolution. An accurate determination of n_α, n_β, and n_γ was not possible. For $\lambda = 5145Å$, minimum (≈ 1.75) and maximum (≈ 1.95) values can be reported. Due to the perfect {001} cleavage, a refractive index of about 1.95 was usually measured, which corresponds to a value near n_γ (for synthetic phenanthrene and $\lambda = 5145Å$ $n_\alpha \approx 1.56$; $n_\beta \approx 1.74$; $n_\gamma \approx 1.99$; *cf.* Gay *et al.*, 1961).

Under ultraviolet light ($\lambda \approx 3500Å$), ravatite shows a whitish yellow fluorescence with a broad maximum in the range 5900 - 5750Å.

Chemistry

The chemical composition of ravatite was determined by combustion in an element analyzer CHN-O-RAPID (Heraeus) as follows:

C	93.41 %
H	5.51 %
Total	98.92 %

On the basis of 24 atoms per formula unit, the empirical formula calculated from these data is $C_{14.1}H_{9.9}$. It shows good agreement with the idealized formula $C_{14}H_{10}$, which should be expected for the natural analogue of phenanthrene.

X-ray crystallography

A single-crystal study of ravatite was carried out by means of a STOE AED 2, 4-circle diffractometer with a Siemens Kristalloflex gener-

Table 1. X-ray powder data for ravatite compared with data of synthetic phenanthrene.

hkl	Ravatite from Ravat/Tadzhikistan			Powder data of synthetic phenanthrene [a]	
	d_{calc}	d_{obs}[b]	I/I_o	d_{obs}	I/I_o
001	9.453	9.434	100	9.381	100
100				5.869	<5
110	4.958	4.941	11	4.972	40
002	4.727	4.724	11	4.694	40
$11\bar{1}$	4.559	4.546	5	4.547	15
$10\bar{2}$	4.395	4.386	<1	4.361	5
111	4.240	4.230	1	4.245	10
200	4.150	4.148	2	4.194	10
$20\bar{1}$	4.025	4.028	13	4.042	50
201				3.643	5
$11\bar{2}$	3.582	3.579	1	3.565	5
210	3.446	3.441	3	3.470	10
$21\bar{1}$	3.373	3.371	10	3.386	60
003	3.151	3.151	2	3.130	10
$10\bar{3}$		(3.111)	<1	3.079	10
021		(2.921)	<1	2.9315	<5
$30\bar{1}$		(2.770)	<1	2.7885	<5
$11\bar{3}$				2.7514	<5
$31\bar{1}$	2.526	2.528	<1	2.5391	10
$21\bar{3}$				2.4709	<5
004	2.363	2.364	2	2.3466	15
014		(2.205)	<1	2.1946	<5
$11\bar{4}$, $12\bar{3}$				2.1781	<5
222				2.1263	<5
$40\bar{1}$				2.1106	<5
114	2.064	2.061	<1	2.0574	5
030	2.060				
223				2.0295	10
$41\bar{2}$		(1.934)	<1	1.9220	10
005		(1.892)	<1	1.8773	10
223				1.8729	10

a) according to Peters *et al.* (1966)
b) Values in brackets represent very low intensity, broadened peaks which were too inaccurate to be included in the refinement.

ator (MoK_α radiation, graphite monochromator). The X-ray powder diffraction data were obtained by a SEIFERT XRD 3000 TT powder diffractometer, using CuK_α radiation (silicon sample holder); these data are given in Table 1. It must be noted that due to the perfect {001} cleavage of ravatite and the resulting preferred orientation of the sample, the 00*l* reflections (especially the 001) show relative intensities considerably higher than those given in the literature for synthetic phenanthrene.

Table 2. Calculated unit cell parameters of ravatite, compared with literature data of synthetic phenanthrene.

	Ravatite		synthetic phenanthrene	
	calculated from		according to	
	powder data	4-circle study	Peters *et al.* (1966)	Petříček *et al.* (1990)
a_o (Å)	8.392(5)	8.42(1)	8.4744	8.441(2)
b_o (Å)	6.181(3)	6.21(1)	6.1720	6.140(1)
c_o (Å)	9.558(5)	9.43(1)	9.4805	9.438(1)
β	98.48(12)°	98.0(1)°	98°01'	97.96(1)°
V (Å^3)	490.4(4)	488(1)	491.02	484.4(1)

The mineral contains two formula units per unit cell. Table 2 shows a comparison of the calculated lattice parameters with those of synthetic phenanthrene.

Single-crystal and powder-diffraction studies indicate that ravatite is usually characterized by a relatively poor crystallinity. The calculations of cell parameters from the single-crystal data show considerable uncertainty; a structural refinement from these studies was not possible with sufficient accuracy. Therefore, the 4-circle investigations serve only to corroborate the space group $P2_1$ already known from the literature for synthetic phenanthrene (see Trotter, 1963; Petříček *et al.*, 1990).

Thermal and spectroscopic data

Thermal analysis carried out by means of a SETARAM DSC 92 thermal analyzer in the temperature range below 130°C at a heating and cooling rate of 1K/min revealed that the temperature of initial melting is 94.3°C. On cooling, the ravatite melt begins to crystallize at a temperature of 92.3°C.

A comparative analysis of synthetic ultrapure phenanthrene under the same analytical conditions (Fig. 3) showed that the melting point of ravatite is clearly lower than that of pure phenanthrene. Presumably, this and the large half-width of the endothermic melting peak of ravatite must be explained by the presence of foreign phases in the form of inclusions. The presence of a considerable number of solid inclusions is established by the small difference between the onset temperatures of melting and crystallization of

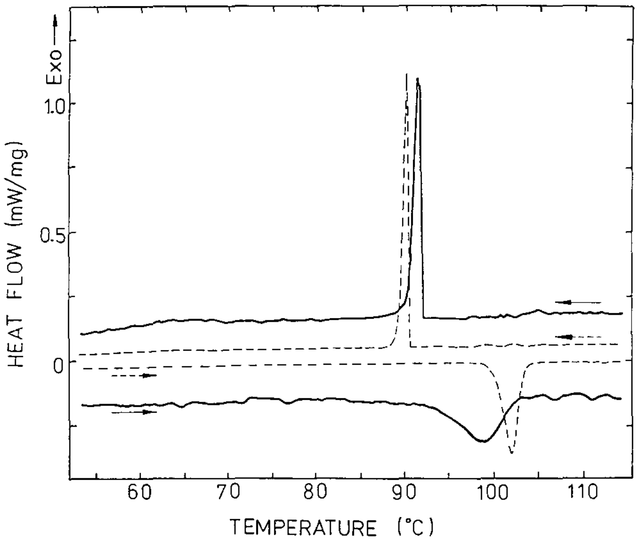

Fig. 3. Comparison of the heat flow curves of ravatite (solid line) and synthetic ultrapure phenanthrene (broken line). The lower curves show the behaviour during heating, the upper curves the behaviour during cooling. The heat flow is normalized with regard to the mass.

ravatite. Apparently, there are enough foreign nuclei or nucleation sites for crystallization, so that no pronounced supercooling is needed.

The endothermal phase transition of phenanthrene at about 72°C (Matsumoto, 1965; Kroupa *et al.*, 1988) could not be proved in ravatite, nor in the phenanthrene reference. Presumably, the quantities (sample: 1.78mg) were not sufficient to register this energetically weak reaction.

Infrared spectra of ravatite in the intermediate wavenumber range (400 - 4000cm^{-1}) were obtained with a Bruker IFS 66 apparatus. The KBr disk technique was employed (0.8mg sample/800mg KBr). The resolution was 4cm^{-1}. In addition, an IR spectrum of a ravatite single-crystal was obtained in reflectance mode with a Bruker IFS 86 IR microscope in the wavenumber range 600 - 3500cm^{-1} (resolution 2cm^{-1}). The beam diameter was about 50μm. 46 bands were registered in the IR spectra, from which 43 could be assigned to phenanthrene vibrations; the remaining three bands (471; 667; and 755cm^{-1}) presumably are due to impurities. The infrared data of ravatite (relative intensities measured from the KBr disk spectra) are listed in Table 3, again in comparison with data of pure synthetic phenanthrene. Infrared investigations on synthetic phenanthrene were also reported by Schettino *et al.* (1966) and Bree *et al.* (1972).

In addition, Raman microprobe spectra were also obtained. These analyses and results are presented and discussed elsewhere (Nasdala *et al.*, 1993). The strongest five Raman bands of ravatite observed are at 409; 709; 1035; 1350; and 1438cm^{-1}. As is the case for the IR data, the Raman wavenumbers and relative band intensities show good agreement with data published on synthetic phenanthrene (*cf.* Maddams & Royaud, 1990).

Discussion

Ravatite is the natural analogue of the synthetic hydrocarbon phenanthrene, which is an important, well-investigated chemical material. As was expected, the properties of both types of material are in good agreement with each other. The differences between ravatite and ultrapure phenanthrene can be explained by the relatively poor crystallinity as well as the presence of inclusions in the ravatite individuals and aggregates. Because these contaminants are predominantly of a mechanical nature, ravatite can be described as relatively pure and homogeneous in terms of chemistry. Significant contents of other hydrocarbons were not detected in ravatite.

The unequivocal identification of ravatite and

Table 3. Infrared data for ravatite in the wavenumber range 400 - 4000 cm^{-1}, compared with literature data of synthetic phenanthrene crystals.

Ravatite		**Infrared data of synthetic phenanthrene crystals**			
		b		*c*	
ν (cm^{-1})	Int. [a]	ν (cm^{-1})	Int. [a]	ν (cm^{-1})	Int. [a]
429	m	426 429	m m	429	vs
441	w	442	w	441	mw
471	w				
496	m	495	s	495	vs
546	w	547	m	547	m
617	w	618	w	616	m
667	vw				
713	s	713 716	s s	710 715	w ms
733	vs	735	vs	732	vs
755	w				
792	vw	794	vw	790	m
817	vs	816 819	vs vs	816	vs
832	w	831	sh	827	ms
870	m	865 868 872	m m s	866 873	ms vs
886	m			886	ms
949	m	950	s	950	ms
981	vw	980	vw	980	mw
1000	w	1001	vw	1000	mw
1036	m	1036 1040	vw m	1034	ms
1092	w	1093	m	1090	s
1143	m	1142 1147	m m	1140 1146	s s
1201	vw	1202	m	1198	ms
1243	m	1245	s	1240	s
1278	w	1280	vvw	1275	m
1301	m	1303	s	1300	s
1349	w	1350	w	1346	m
1421	w	1420	m	1425	s
1428	m	1430	s		
1443	m	1441 1446	m m	1440	s
1455	m	1457	w	1455	vs
1499	w	1500	w	1497	mw
1526	w	1522 1524	w w	1521	m
1532	vw				
1600	m	1602	m	1600	vs
1622	w	1622	w	1620	m
1688	w	1685	vw		
1810	w	1810	w		
1910	w	1910	w		
1937	w	1940	w		
2940	w	2940	vw		
3004	m	3006	w	3000	w
3016	w	3017	w	3015	vw
3045	m	3046	m	3035 3050	m m
3070	w	3071	w	3070	vw
3082	w	3086	w	3081	w
3113	w	3115	vw	3111	w

a) Intensities: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder
b) data according to Witt & Mecke (1967)
c) data according to Godec & Colombo (1976)
The literature data are not completely listed; those without an equivalent in the measured data are not given.

its distinction from other similar hydrocarbons, such as anthracene, fluorene, or naphthalene, is possible by vibrational spectroscopic methods. In the IR and Raman spectra - at least in the region of intramolecular vibrations - very sharp, easily measurable bands were registered. These methods allow the identification of poorly crystallized hydrocarbon samples in amounts of $\leq 10^{-10}$g. By contrast, X-ray reflections in powder diffractograms and especially in single-crystal patterns are broadened and asymmetric. Therefore, the relatively poor crystallinity of ravatite must be explained by irregularities in the position of the $C_{14}H_{10}$ molecules in the lattice and of the spaces between them, whereas the molecules themselves (atomic positions, intramolecular bond lengths and angles) show no significant differences with regard to the $C_{14}H_{10}$ molecules in ultrapure synthetic phenanthrene.

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