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PRELIMINARY DATA ON Fe-CELADONITE FROM RUDNO NEAR CRACOW

UKD 549.623. Fe-celadonit (438.31 Rudno)

Abstract. The paper deals with the results of mineralogical examination of celadonite from melaphyre quarry in Rudno near Cracow. This mineral has been identified by means of IR spectroscopic and X-ray diffractometric methods and the results confirmed by microscope observations and differential thermal analysis. Celadonite in question occurs in association with saponite, heulandite and quartz.

INTRODUCTION

Celadonite was found to occur among secondary alteration products of melaphyres from Rudno. This green mineral was observed already by Rozen (1909) and Gaweł (Piekarska, Gaweł 1954) but was determined as a member of chlorite group, though Gaweł did not exclude the possibility of occurrence of celadonite in Cracovian melaphyres.

Celadonite resembles glauconite in megascopic features, chemical composition and crystal structure and even the existence of isomorphous series celadonite-glauconite was suggested (Foster 1969).

FORMS OF OCCURRENCE AND OPTICAL PROPERTIES

In Rudno celadonite occurs within rock fractures and fissures in the form of green incrustations and fillings and as rims around other minerals. Moreover, it fills vacuoles and is colouring greenish other minerals. Celadonite display variable colouration ranging from light to dark green. Its aggregates are soft and show greasy or earthy lustre. When observed by means of binocular microscope some aggregates exhibit kidney-shaped or colloform structures. Some saponite, sepiolite, calcite and quartz specimens show greenish tint due to the presence of celadonite. It is particularly difficult to separate the mineral in question from saponite because of their

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very subtle intergrowths. Consequently, no matter of some differences in specific weights (density) these minerals could not be separated by sedimentation procedure in distilled water. A pearly-greenish suspension thus formed did not change for a long period of time. Attempts of electromagnetic separation were not succesful too.

When observed by microscope, celadonite presents an earthy substance or short fibrous forms, often developed in fan-shaped, sphaerolitic or vermicular aggregates. Fibrous celadonite usually occurs in association with saponite and sepiolite. Fibrous aggregates generally display distinct pleochroism from light to dark green while in earthy masses of celadonite this is not observed.

Elongated celadonite fibres were found to be optically positive. Refractive indices, measured using immersion technique, were found to vary between 1.59 and 1.64. Because of fine crystalline nature of celadonite under examination it was not possible to determine its other optical properties.

IR SPECTROSCOPIC STUDY

Identification of celadonite was carried out by means of infrared absorption spectroscopy using interferometric spectrometer DIGILAB (in the Institute of Material Engineering, Academy of Mining and Metallurgy,

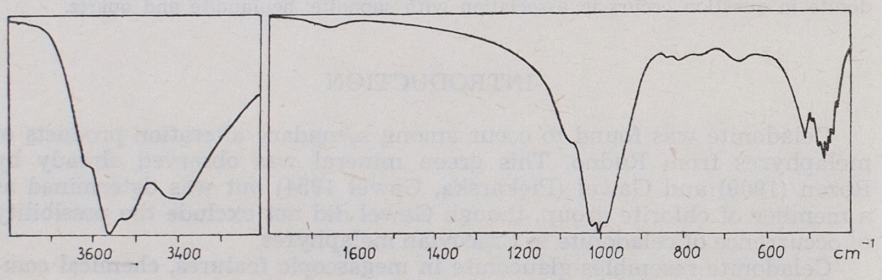

Fig. 1. IR spectrum of celadonite from Rudno

Cracow). Dark green pure celadonite sample was collected from a miarolitic cavity in melaphyre.

For sheet silicates particularly characteristic is the wave-number region corresponding to OH stretching vibrations since it reflects the structure of octahedral layer. In this range four distinct absorption bands are observed: 3600, 3560, 3535 and 3420 cm^{-1} (Fig. 1). The first three are characteristic of Fe-celadonite (Farmer *et al.* 1967, Kimbara, Shimoda 1973) whilst the latter one is due to adsorbed water molecules. In Farmer's opinion (1967) the 3600 cm^{-1} band results from hydroxyl stretching vibrations in Mg, Al, OH groupings, whilst 3560 cm^{-1} and 3535 cm^{-1} ones — in Mg, Fe^{3+}, OH and Fe^{2+}, Fe^{3+}, OH groupings, respectively. High intensity of 3560 cm^{-1} band and only slightly lower of the 3535 cm^{-1} indicate considerable content of Fe^{3+} and Fe^{2+} in octahedral layer. Consequently the mineral under examination can be determined as Fe-celadonite.

X-RAY STUDY

Because of impossibility of obtaining sufficient amount of pure celadonite samples X-ray diffractometric analyses were carried out using those containing some admixtures, mostly saponite. The study was performed by means of Rigaku-Denki diffractometer using filtered (Ni) CuK_α radiation. X-ray diffractometer patterns of some samples containing higher or lower amounts of celadonite and representing various forms of its occurrence in Rudno are presented in Figure 2. X-ray patterns of celadonite from Wind River, USA (Wise, Eugster 1964) is also presented for comparison purposes.

It can be observed distinct variability of reflection intensities of celadonite in X-ray patterns of investigated samples from Rudno containing this mineral. Sometimes there is even complete lack of basal reflection $d \approx 10$ Å. However, in all the oriented samples this reflection is very distinct as well as those coming from other *001* planes. Patterns of samples containing dark green seladonite distinguish by much more intense background.

In Wise and Eugster (1964) opinion reflections 3.64 and 3.09 Å are connected with ($11\bar{2}$) and (*112*) planes and indicate that celadonite belongs to 1*M* modification of sheet silicates and thus using this method it is possible to distinguish it from glauconite and other hydromicas. X-ray patterns of samples from Rudno (Fig. 2) are characterized by the presence of these

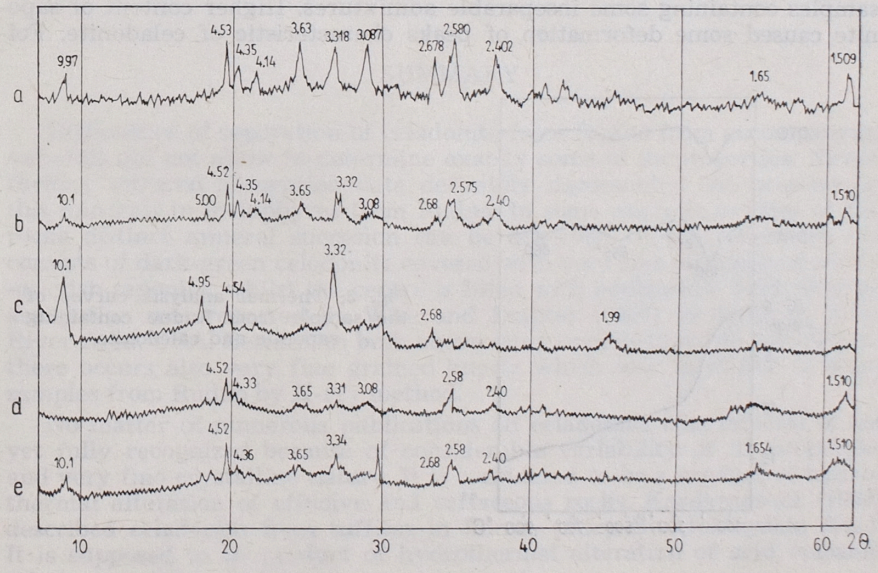

Fig. 2. X-ray diffractograms of celadonite from Wind River (USA) and of samples from Rudno containing celadonite

a — celadonite from Wind River (USA), *b* — Rudno — green mass filling rock fissures, *c* — Rudno — green mass (oriented sample), *d* — Rudno — green fillings of vacuoles, *e* — Rudno — green coating on calcite

reflections and, consequently, the celadonite in question should be assigned to 1*M* modification.

Wise and Eugster (1964) tried to find the relation between chemical composition of celadonites and the position of $d_{060} \approx 1.50$ Å or $d_{003} \approx$ $\approx$ 3.32 Å reflections but their attempts failed due to limited amount of X-ray data on various celadonites. However, on the ground of examination of synthetic celadonites these authors stated that the increase of Fe^{2+} content in octahedral layer causes parallel increase of d_{060} value.

In the case of celadonites from Rudno we observe that d_{060} values for some samples are slightly higher than that 1.50 Å and the background is considerably increased. Besides, celadonites in question are most probably very fine crystalline and show variable degree of structural ordering. Consequently, their X-ray diffraction patterns contain often diffuse reflections and their intensities are lowered. All these data suggest high iron content in celadonites from Rudno. As follows from electron microprobe analysis by means of Jeol JXA-50A apparatus, Fe content in them amounts to approx. 10 weight per cent.

It is supposed that saponite-celadonite association is purely mechanical since X-ray patterns of samples treated with glycol do not show reflections typical of mixed-layer structures.

THERMAL ANALYSIS

Similarly as X-ray study, thermal examinations were carried out on samples containing some inseparable admixtures. Higher content of saponite caused some deformation of peaks characteristic of celadonite. Following endothermal effects are observed on DTA curves: 180, 250, 565 and 860°C (Fig. 3). According to Stoch and Żabiński's data (1977), DTA curve for saponite from Rudno is characterized by double endothermal dehydration peak in the range 50—350°C and dehydroxylation one at approx.

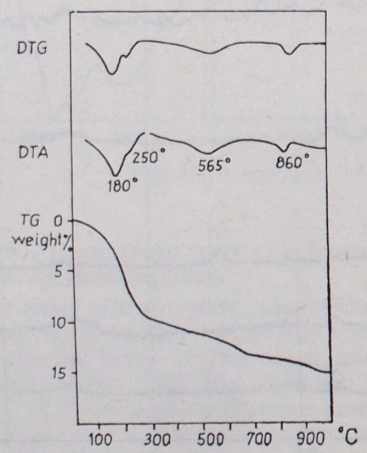

Fig. 3. Thermal analysis curves of the sample from Rudno containing saponite and caledonite

Table 1

Thermal effects of celadonites

Celadonites	Endothermal in °C			Exothermal in °C
Rudno	180—250	565	860	
Barcza (Kardymowicz 1960)	80	690	890	
(Stoch 1974)	100	560	910	330
Zavalie (Malkowa 1956)		680	940	340
Taihezan (Kimbara, Shimoda, 1973)	80	620	900	

850°C. Consequently, the observed endothermal effect at 565°C on DTA curve of the sample examined can be due to celadonite. The decrease of temperature of the maximum of this effect compared with other celadonites (Table 1) can be explained by dilution of celadonite by saponite admixture and/or its very fine grain size.

SUMMARY

Difficulties of separation of celadonite from Rudno from accompanying minerals did not allow to determine exactly some of its properties. Nevertheless, infrared absorption data definitely documented the presence of this minerals in melaphyres from Rudno. In some miarolic cavities of this rocks distinct mineral succesion can be observed — the outermost rim consists of dark-green celadonite covered with very fine envelope of white-greyish saponite, whilst the centre is filled with heulandite. Such mineral association was reported by Wise and Eugster (1964) to occur in Wind River Area, USA. Besides, in both above mentioned heulandite associations there occurs also very fine grained quartz which was identified in some samples from Rudno by X-ray method.

No matter of numerous publications on celadonite, this mineral is not yet fully recognized because of considerable variability of its properties and very fine crystalline nature. It is considered to be a product of hydrothermal alteration of effusive and tuffaceous rocks. Kardymowicz (1960) described celadonite from tuffites in Barcza (Góry Świętokrzyskie Mts.). It is supposed to be product of hydrothermal alteration of acid volcanic ashes.

It is difficult yet to present the conclusions on the formation of celadonite in melaphyre from Rudno. Further examinations of celadonite and accompanying minerals will, probably, allow to solve the problem of its origin. We may only suppose that hydrothermal processes which operated

within igneous rocks of Krzeszowice region, connected with so called *kalification processes* contributed to the formation of secondary minerals, including celadonite.

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Grażyna CICHOŃ

WYNIKI WSTĘPNYCH BADAŃ Fe-SELADONITU Z RUDNA KOŁO KRAKOWA

Streszczenie

W pracy przedstawiono wyniki badań mikroskopowych, rentgenowskich, termicznych i spektroskopowych w podczerwieni kilku próbek produktów wtórnych z melafirów z Rudna, zawierających seladonit. Jednoznaczną identyfikację tego minerału uzyskano metodą spektroskopii w podczerwieni, wykorzystując charakterystyczne dla tego minerału pasma absorpcji w zakresie drgań walencyjnych grup OH. Niewielką ilość próbki seladonitu, niezbędną do wykonania badań spektroskopowych, zdołano wyodrębnić w stanie czystym, wolnym od domieszek innych minerałów. Seladonit z Rudna odznacza się dużą zawartością Fe (około 10% wag.).

OBJAŚNIENIA FIGUR

Fig. 1. Widmo absorpcyjne w podczerwieni seladonitu z Rudna

Fig. 2. Dyfraktogramy rentgenowskie seladonitu z Wind River (USA) oraz próbek z Rudna zawierających seladonit
a — seladonit z Wind River (USA), *b* — Rudno — zielona masa wypełniająca szczeliny skały, *c* — Rudno — zielona masa (preparat orientowany), *d* — Rudno — zielone wypełnienia pęcherzy, *e* — Rudno — zielona otoczka na kalcycie

Fig. 3. Krzywe analizy termicznej próbki z Rudna zawierającej saponit i seladonit

Гражина ЦИХОНЬ

РЕЗУЛЬТАТЫ ПРЕДВАРИТЕЛЬНЫХ ИССЛЕДОВАНИЙ Fe-СЕЛАДОНИТА ИЗ РУДНА ВБЛИЗИ КРАКОВА

Резюме

В работе представлены результаты микроскопических, рентгеновских, термических и инфракрасных спектроскопических исследований нескольких образцов вторичных продуктов из мелафиров из Рудна, в которых содержится селадонит. Однозначное определение этого минерала было получено методом инфракрасной спектроскопии используя характерные для этого минерала полосы поглощения OH-валентных колебаний. Незначительное количество образца селадонита, необходимое для проведения спектроскопических исследований, удалось получить в чистом виде, свободном от примесей других минералов. Селадонит из Рудна отличается большим содержанием Fe (около 10% по весу).

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. ИК-спектр поглощения селадонита из Рудна

Фиг. 2. Рентгеновские дифрактограммы селадонита из Уинд Ривер (США) и образцов из Рудна, содержащих селадонит
a — селадонит из Уинд Ривер (США), *b* — Рудно — зелёная масса заполняющая трещины в скалах, *c* — Рудно — зелёная масса (орьентированный препарат), *d* — Рудно — зелёное вещество заполняющее пузыри, *e* — Рудно — зелёный покров кальцита

Фиг. 3. Кривые термического анализа образца из Рудна, содержащего сапонит и селадонит