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CHAMOSITE FROM OOLITIC IRONSTONES: THE NECESSITY OF A COMBINED XRD–EDX APPROACH

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ABSTRACT

Chemical compositions of fine flakes of chlorite within chamositic coated grains from ironstones in regressive and condensed Ordovician and Jurassic sequences in Poland, Germany, Czech Republic and India were established by energy-dispersion analysis (EDX). The chemical data are inaccurate, mainly owing to the presence of intergrowths with other mineral phases. Structural formulae of trioctahedral chlorites calculated from the EDX data show apparent vacancies in the octahedral site. A more accurate chemical composition was obtained using an X-ray-diffraction (XRD) method. Relationships between d_{001} and b and the chemical composition of trioctahedral chlorites enabled the determination of their structural formulae. A comparison of the experimental powder-diffraction patterns with calculated patterns allows the assignment of chlorites from Pasłęk to subfamilies C and D, and of chlorites in samples from other localities, to subfamily D. A sample from Pasłęk was identified as a mixture of two chlorite polytypes: $1A_C$–I–ho (82%) and $1M_D$–II–ho (8%) with quartz (10%). Both polytypes reveal homo-octahedral occupancy of cations, and differ slightly in their chemical composition, which is manifested in different values of d_{001} and b. The combination of XRD and EDX methods of determination of chemical composition of chamosite is superior to EDX analyses alone. From a simple measurement of d_{001} and b, one obtains five major chemical components: Si, ^{IV}Al, ^{VI}Al, Mg and Fe^{2+} not contaminated by mineral intergrowths. The EDX approach in addition provides information on specific heavy elements.

Keywords: chlorite, chamosite, coated grains, crystal chemistry, energy-dispersion analysis, X-ray diffraction.

SOMMAIRE

Il est possible d'établir par dispersion d'énergie (EDX) la composition chimique des fines particules de chlorite dans le revêtement de chamosite sur les grains provenant de formations de fer des séquences régressives et condensées d'âge ordovicien ou jurassique de Pologne, Allemagne, République Tchèque et en Inde. Toutefois, les résultats ne sont pas représentatifs de la chlorite elle-même, surtout à cause d'intercroissances avec d'autres phases minérales. D'après les formules structurales des chlorites trioctaédriques calculées à partir de ces données chimiques, il y aurait des lacunes dans le site octaédrique. Des données plus exactes à propos de la composition chimique ont été obtenues par diffraction X sur poudre. Les relations impliquant d_{001} et b et la composition chimique des chlorites trioctaédriques ont permis d'en établir les formules structurales. Une comparaison des spectres de diffraction expérimentaux avec des spectres simulés a permis l'attribution des chlorites de Pasłęk aux sous-familles C et D, et des chlorites d'échantillons d'autres endroits, à la sous-famille D. Dans un échantillon de Pasłęk, nous avons identifié un mélange de deux polytypes: $1A_C$–I–ho (82%) et $1M_D$–II–ho (8%), avec quartz (10%). Les deux polytypes contiennent une distribution homo-octaédrique des cations, et diffèrent légèrement dans leur composition chimique, comme le témoignent les valeurs distinctes de d_{001} et de b. La combinaison des approches, diffraction X et dispersion d'énergie, mène à une caractérisation supérieure de la composition chimique de la chamosite. A partir d'une simple mesure de d_{001} et b, on obtient cinq composants chimiques importants: Si, ^{IV}Al, ^{VI}Al, Mg et Fe^{2+} sans contamination due aux intercroissances. En plus, la dispersion d'énergie permet de spécifier les teneurs en éléments lourds.

(Traduit par la Rédaction)

Mots-clés: chlorite, chamosite, grains enrobés, chimie cristalline, dispersion d'énergie, diffraction X.

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INTRODUCTION

Results of electron-microprobe and wet-chemical analyses commonly reveal the presence of alkali and alkaline-earth cations in chlorite-group minerals from sedimentary rocks. Structural formulae of chlorites calculated from such chemical data show an apparent high proportion of vacancies in the octahedral sites. Using analytical data obtained with a transmission electron microscope (AEM), Jiang *et al.* (1994) noted a high correlation between such alkali contents and the proportion of vacancies in chlorite in pelitic rocks from Quebec and Texas. They attributed this correlation to the presence of intergrowths with other layer silicates; specifically, they found that the high K-content is due to the intergrowth of mica in chlorite. The chemical composition of chlorite-group minerals, contaminated in such a way by impurities, may thus not be sufficiently accurate for the purpose of geothermometry (De Caritat *et al.* 1993, Jiang *et al.* 1994, Essene & Peacor 1995), an evaluation of mineral-transformation processes, and an assessment of systematic changes in composition due to changing T, P and bulk-rock composition (Zane *et al.* 1998).

The X-ray method of estimating the chemical composition of chlorites (Rausell-Colom *et al.* 1991, Wiewióra & Wilamowski 1996) constitutes a valuable means of verifying the chemical composition of chlorite-group minerals in mixtures and in intergrowths with other minerals, especially with other phyllosilicates. An example of this approach is described below for a series of clinochlore–chamosite samples. In particular, we show how five major crystallochemical components of trioctahedral chlorite may be estimated simply with two X-ray-determined structural parameters, d_{001} and *b*. Also, a crystallochemical formula may be estimated separately for two structural modifications of chlorite intergrown in a sample.

SAMPLES STUDIED

In Poland, ironstones are mainly known from Ordovician (Arenigian–Caradocian) and Jurassic sequences. The mineral composition of the ooids is multiphase in most of these sediments owing to late diagenesis (siderite formation) and weathering (kaolinite formation). Among the sedimentary chlorites studied by us, those sampled from the horizons of condensed deposits within Caradocian marly limestones (Pasłęk) were found to be the most suitable for this study. This set of samples was complemented by ooid-bearing rocks in our collections, coming from the top of shoaling and coarsening-upward regressive sequences in Ejpovice near Prague in the Bohemian Massif, Czech Republic (Arenigian), in Echte (Liassic), Germany, and the Zangla nappe in the High Himalaya (Callovian), India. Such diversity in age and environments of formation allowed us to make an objective evaluation of the methods applied.

The concentric structure of chamosite-rich ooids is well defined in all samples investigated; however, the small and irregularly shaped platelets of chlorite within each lamina show a random orientation, without any tangential or radial fabric (Figs. 1a, b, c and d).

Condensed deposits within the calcareous Caradocian sequence of northern Poland (Pasłęk) consist of silty marl with numerous lenticular intercalations of marl enriched in chamositic ooids (Łącka 1990). Dark green ooids have an oblate shape and a well-defined concentric structure. They rarely have detrital material (quartz, heavy minerals, and bioclasts) in the core. The calcareous bioclasts were replaced by chlorite in the nucleus of the ooids (Fig. 1e).

The Arenigian Fe-bearing sediments outcrop in the Ejpovice quarry and occur within a shallow-marine clastic succession of sandstones and mudstones with some horizons rich in volcanogenic material (Babčan 1959). The oolitic ironstones are comprised of grains of layer silicates and detrital quartz cemented by siderite. The mineral composition of the grains varies from chamosite – illite within mudstones to hematite – kaolinite – illite in sandstone. The coated grains in both types of sediments are ellipsoidal in shape and are built up of concentric layers of phyllosilicates commonly separated from one another by thin laminae enriched in iron oxides. Grains of detrital quartz that acted as nuclei for the ooids are subordinate. Most of the ooids have a peloidal core. Secondary goethite and hematite commonly form irregular overgrowths (Fig. 1f).

The Jurassic oolitic ironstones were developed at the top of regressive cycles consisting of marls and limestones grading upward into Liassic marly sandstones at Echte (Schellmann 1969) or into Callovian sandstones in the Zangla nappe (Garzant *et al.* 1989). They are overlain by or interlayered with deposits rich in ferruginous grains that are coated and cemented by chamosite with authigenic siderite and subordinate calcite. Iron-bearing ooids from sandy marls (Liassic) are green in color, ellipsoidal in shape, and have a fine, concentric, commonly spastolithic structure. Well-sorted ooids from the Callovian sandstones (India) are black and spherical. Most of them have a peloidal nucleus. Secondary hematite or pyrite locally replaces chamosite in the outer shell of the ooid.

Studies with a petrographic microscope as well as with a scanning electron microscope (SEM) reveal the uniform size of the chlorite platelets in the nuclei and in the cortex of the investigated grains, with the exception of the Pasłęk sample. In the latter case, the core of the ooid is commonly built of coarse platelets of chlorite. In the coating, however, the chlorite is much finer (Fig. 1e).

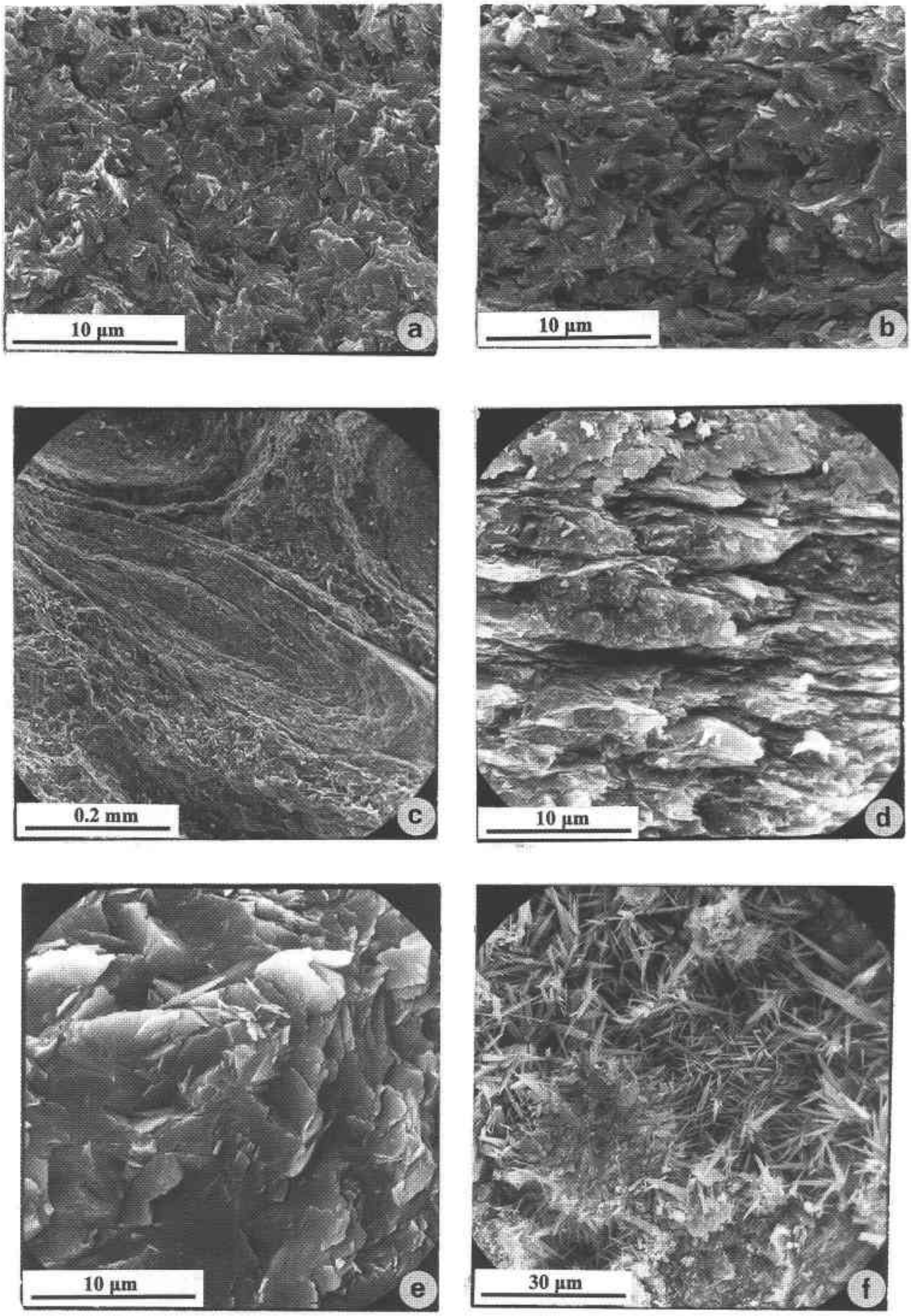

FIG. 1. a) Texture of the chamosite cortex on a coated grain from Pasłęk, b) texture of the chamosite cortex of a coated grain from Himalayas, c) chamosite-coated grain from Ejpovice, d) texture of the chamosite cortex of a coated grain from Ejpovice, e) texture of the chamosite nucleus of the coated grain from Pasłęk, f) hematitic intergrowth inside the cortex of the coated grain from Ejpovice. Note that in the core of the coated grain from Pasłęk, the chamosite is coarse grained (e), whereas in the cortex, the chamosite is fine grained (a).

TABLE 1. FORMULA UNIT OF Fe-RICH CHLORITES FROM EDX DATA*

Sample	^{IV}Si	^{IV}Al	^{VI}Al	Ti	Fe^{2+}	Mg	Σ_{oct}
Pasłęk shell							
1*-1**	2.71	1.29	1.09	0.03	3.49	1.46	6.07
1-2	2.78	1.22	1.23	0.10	3.10	1.47	5.90
1-3	2.64	1.36	1.13	0.09	3.14	1.67	6.03
2-1	2.93	1.07	1.42	0.04	2.87	1.46	5.79
2-2	2.86	1.14	1.34	0.06	2.85	1.60	5.84
2-3	2.90	1.10	1.24	0.06	2.92	1.66	5.87
2-4	3.05	0.95	1.43	0.04	2.75	1.50	5.72
Average	2.84	1.16	1.27	0.06	3.02	1.55	5.89
Pasłęk central part							
3-1	2.73	1.27	1.22	0.05	3.01	1.68	5.97
3-2	2.98	1.02	1.25	0.08	2.93	1.56	5.81
4-1	2.76	1.24	1.20	0	3.04	1.79	6.02
4-2	2.80	1.20	1.33	0.04	2.91	1.63	5.90
4-3	2.82	1.18	1.32	0	3.03	1.57	5.93
4-4	2.76	1.24	1.41	0.02	2.77	1.70	5.90
5-1	2.72	1.28	1.18	0.02	3.13	1.70	6.03
5-2	2.76	1.24	1.27	0.01	3.01	1.69	5.98
5-3	2.69	1.31	1.10	0.06	3.30	1.59	6.04
average	2.78	1.22	1.25	0.03	3.01	1.66	5.95
Himalayas							
6-1	2.65	1.35	1.55	0	3.80	0.55	5.90
6-2	2.60	1.40	1.50	0.01	3.78	0.65	5.94
6-3	2.61	1.39	1.50	0.01	3.95	0.47	5.93
6-4	2.60	1.40	1.44	0.06	3.78	0.65	5.93
7-1	2.54	1.46	1.33	0.09	4.15	0.41	5.97
7-2	2.63	1.37	1.65	0.03	3.59	0.54	5.82
7-3	2.61	1.39	1.58	0.02	3.85	0.43	5.88
7-4	2.62	1.38	1.57	0.02	3.84	0.45	5.88
8-1	2.59	1.41	1.42	0	3.77	0.81	6.00
9-1	2.68	1.32	1.58	0	3.73	0.57	5.87
9-2	2.58	1.42	1.51	0.02	3.43	0.96	5.93
9-3	2.93	1.07	1.59	0.01	3.40	0.74	5.73
9-4	2.57	1.43	1.35	0.02	3.77	0.87	6.02
9-5	2.65	1.35	1.48	0	3.74	0.72	5.94
10-1	2.68	1.32	1.46	0	3.84	0.62	5.93
10-2	2.56	1.44	1.44	0.01	3.74	0.79	5.99
10-3	2.68	1.32	1.61	0.02	3.29	0.89	5.83
10-4	2.66	1.34	1.53	0.01	3.46	0.89	5.89
average	2.64	1.36	1.51	0.02	3.72	0.67	5.91
Echte							
11-1	2.84	1.16	1.58	0	3.11	1.10	5.79
11-2	2.79	1.21	1.46	0.04	3.19	1.15	5.84
11-3	2.88	1.12	1.57	0.02	3.09	1.08	5.76
11-4	2.96	1.04	1.73	0	2.87	1.06	5.66
12-1	2.82	1.18	1.48	0.09	3.14	1.04	5.76
12-2	2.91	1.09	1.56	0.05	2.86	1.25	5.72
12-3	2.84	1.16	1.59	0.06	3.03	1.05	5.73
12-4	2.86	1.14	1.52	0.02	3.15	1.09	5.78
12-5	2.86	1.14	1.52	0.04	3.13	1.08	5.77
average	2.86	1.14	1.56	0.04	3.06	1.10	5.76
Ejpovice							
13-1	2.98	1.02	1.52	0	3.69	0.54	5.75
13-2	2.80	1.20	1.49	0	3.84	0.53	5.86
13-3	2.77	1.23	1.43	0	3.94	0.53	5.90
13-4	2.83	1.17	1.44	0	3.90	0.52	5.86
13-5	2.81	1.19	1.50	0	3.84	0.51	5.85
13-6	2.83	1.17	1.51	0	3.79	0.53	5.83
13-7	2.90	1.10	1.51	0	3.75	0.54	5.80
13-8	2.85	1.15	1.54	0	3.74	0.52	5.80
14-1	2.90	1.10	1.45	0	3.43	0.95	5.83
14-2	3.09	0.91	1.43	0	3.33	0.99	5.74
14-3	3.32	0.68	1.50	0	3.19	0.91	5.59
14-4	3.02	0.98	1.49	0	3.30	0.96	5.75
14-5	3.02	0.98	1.42	0	3.36	1.01	5.78
14-6	3.08	0.92	1.43	0	3.41	0.90	5.74
14-7	3.02	0.98	1.50	0	3.32	0.92	5.74
15-1	2.78	1.22	1.34	0	3.82	0.78	5.94
15-2	2.85	1.15	1.40	0	3.69	0.77	5.87
15-3	2.83	1.17	1.39	0	3.77	0.73	5.89
15-4	2.87	1.13	1.36	0	3.75	0.78	5.88
15-5	2.78	1.22	1.36	0	3.80	0.76	5.93
15-6	2.96	1.04	1.43	0	3.63	0.76	5.81
15-7	2.84	1.16	1.47	0	3.56	0.82	5.84
15-8	2.83	1.17	1.41	0	3.67	0.80	5.88
15-9	2.81	1.19	1.27	0	3.94	0.75	5.96
15-10	2.83	1.17	1.38	0	3.79	0.74	5.90
15-11	2.79	1.21	1.31	0	3.91	0.74	5.95
15-12	2.87	1.13	1.36	0	3.82	0.70	5.88
15-13	2.81	1.19	1.34	0	3.88	0.71	5.93
15-14	2.75	1.25	1.31	0	3.92	0.74	5.97
average	2.89	1.11	1.42	0	3.68	0.74	5.84

* Sample number, ** point-analysis number. The proportion of cations is reported in *apfu*, atoms per formula unit. Σ_{oct}: sum of octahedrally coordinated cations. Note that the raw data are available at the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Chemical Composition by Energy-Dispersion X-Ray Micro-Analysis

Chemical data were obtained by energy-dispersion X-ray micro-analysis (EDX) done on an Oxford Instrument AN10/85S combined with JEOL 840A scanning microscope, using an accelerating voltage of 15 kV. Concentrations of major elements were determined with a precision better than 2%. Table 1 shows the results of the EDX analyses, recalculated to the structural formula of chlorite based on $O_{10}(OH)_8$. The raw data are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

Only the samples from Ejpovice have an appreciable content of K (2 wt.% K_2O) due to the presence of fine-grained illite (X-ray determined), which contaminates the chlorite. To establish the most accurate EDX-determined composition of chlorite, a correction for the illite content was introduced assuming 0.8 K per formula unit $[O_{10}(OH)_8]$. Small amounts of titanium in the majority of samples were not taken into consideration

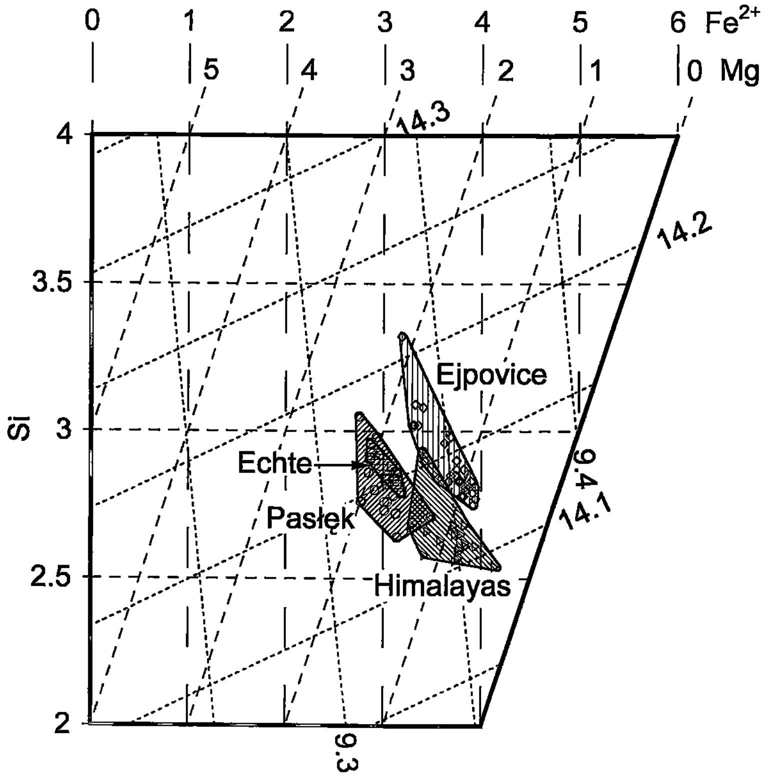

FIG. 2. Diagram of trioctahedral, vacancy-free chlorites with the projection of chemical compositions of chlorite samples, analyzed by the EDX method. Modified from Wiewióra & Weiss (1990).

in writing the structural formula of the chlorite, as the Ti may well reflect small quantities of an oxide phase.

The chemical composition of the chlorite samples, thus corrected for the presence of impurities, is projected onto the classification diagram of trioctahedral, vacancy-free chlorites (Fig. 2).

CHEMICAL COMPOSITION BASED ON X-RAY DIFFRACTION (XRD)

For the purpose of assessing the chemical composition of the chlorite in the samples, the d_{001} and b parameter of the unit cell have been used. This method is based on linear relationships between chemical composition and both d_{001} and b values in chlorites, as described by Rausell-Colom *et al.* (1991) and Wiewióra & Wilamowski (1996). The multiple regression analyses performed by these authors provided a coefficient of correlation R and standard error of estimation equal 0.976 and 0.0145 for b, and 0.883 and 0.0319 for d_{001}. Thus the precision of estimation of chemical composition from structural parameters justifies our approach. These numerical relationships are represented by contours of the d_{001} and b parameters on the classification diagrams of chlorites (Wiewióra & Weiss 1990).

Individual coated grains were crushed and placed in capillary tubes 0.5 mm in diameter. The samples were irradiated with Co$K\alpha_1$, and the diffraction patterns were recorded by means of a curved position-sensitive detector in the range of 2–120° 2θ. The detector channels were calibrated with an external standard composed of tetradecanol + böhmite + Si. The goodness of calibration was verified using quartz lines at 3.345 and 1.541 Å.

The unit-cell parameters were refined from the indexed powder-diffraction patterns by using a program for indexing and unit-cell calculation (UCIN). The refinement was based on 19 (Echte) to 41 (Pasłęk: triclinic polytype) reflections. The d_{001} values measured from d_{004} values ($d_{001} = 4 \cdot d_{004}$) are strictly identical with calculated those from unit-cell parameters: $d_{001} = c \cdot \sin\beta$ (Table 2).

TABLE 2. UNIT-CELL PARAMETERS AND CHEMICAL COMPOSITION OF Fe-RICH CHLORITES, OBTAINED BY THE XRD METHOD

	Pasłęk		Himal.*	Himal.**	Ejpovice	Echte
a (Å)	5.379(1)§	5.374(2)	5.394(3)	5.390(2)	5.376(4)	5.375(4)
b (Å)	9.316(2)	9.318(3)	9.349(3)	9.340(0)	9.315(4)	9.313(4)
c (Å)	14.25(0)	14.16(1)	14.12(2)	14.12(1)	14.15(1)	14.12(1)
α (°)	89.98(2)	90	90	90	90	90
β (°)	97.21(2)	89.72(5)	89.92(8)	89.95(6)	89.88(8)	89.98(7)
γ (°)	90.00(1)	90	90	90	90	90
d_{001} (Å)	14.14(1)	14.16(2)	14.12(2)	14.12(1)	14.15(1)	14.12(1)
Mg *apfu*	1.91	2.06	0.96	1.18	2.00	1.73
Fe^{2+} *apfu*	2.80	2.80	3.73	3.47	2.77	2.78
$^{VI}Al = {}^{IV}Al$ *apfu*	1.28	1.13	1.31	1.35	1.23	1.46
Si *apfu*	2.72	2.87	2.69	2.65	2.77	2.54
Polytype	$1A_C$-I-ho	$1M_D$-II-ho	$1M_D$-II-ho	$1M_D$-II-ho	$1M_D$-II-ho	$1M_D$-II-ho

Himal.*: Chlorite from ooids in sandstone from the Himalayas containing pyrite in cement. Himal.** Chlorite from ooids in sandstone from the Himalayas containing hematite in cement. § A short form of the standard deviation is given in brackets. In this case, the calculated value is 5.739 ± 0.0009 Å. The proportion of cations is expressed in *apfu*, atoms per formula unit.

Vacancy-free trioctahedral chlorites are characterized by equal amounts of $^{IV}(R^{3+})$ and $^{VI}(R^{3+})$, which enables compensation of the charges. The composition of the tetrahedral sheet is governed by the equation: [Si] = 4 – $^{VI}(R^{3+})$. The variation of the main chemical components in the octahedral sheet of trioctahedral chlorites may be expressed by the formula: [Mg] = 6 – [Fe] – [Al], where [Al] is the amount of Al in octahedral coordination. Taking into consideration these relationships, the classification diagram of Wiewióra & Weiss (1990) enables the estimation of the whole set of the main chemical constituents: [Fe] along the abscissa, [Si], [^{IV}Al] and [^{VI}Al] along the ordinate, and [Mg] along the oblique axis. Figure 3 shows the procedure of estimating the chemical composition of a sample of chlorite, the d_{001} and b values of which equal 14.12 and 9.31 Å, respectively. The estimated chemical composition established from the figure, assuming that only ^{IV}Al substitutes for Si, is: $(Fe_{2.8}\,Mg_{1.74}Al_{1.46})\,(Si_{2.54}\,Al_{1.46})\,O_{10}\,(OH)_8$.

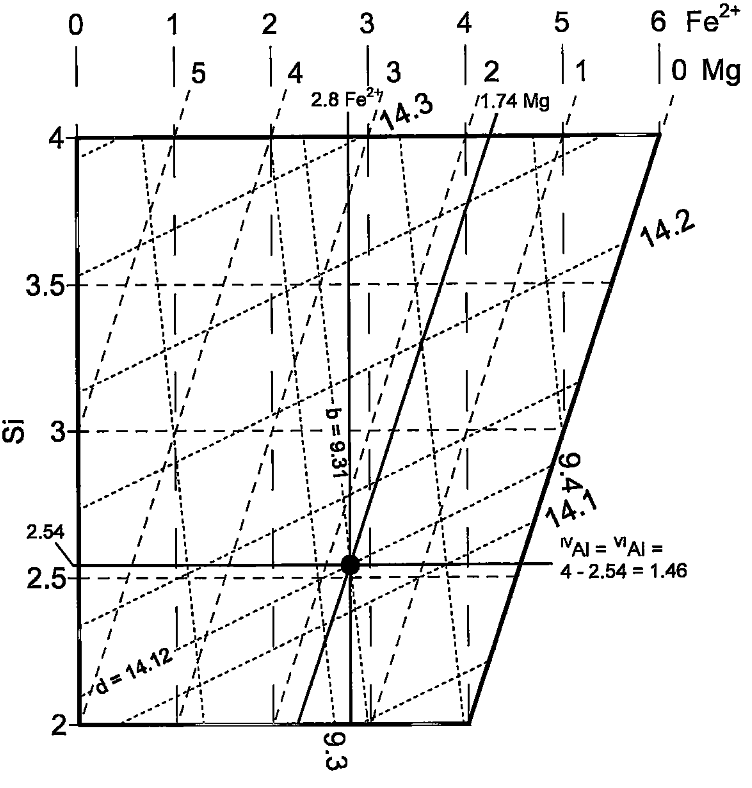

FIG. 3. An example of estimation of the chemical composition from the structural data: d_{001} and b. The values of d_{001} = 14.12 Å and b = 9.31 Å were projected on the diagram. Inside the diagram, lines parallel to the orthogonal axes and one line parallel to the isolines of the [Mg] value were drawn. The horizontal line cut off on the vertical axis indicates the value of [Si], [^{IV}Al] = 4 – [Si], and [^{VI}Al] = [^{IV}Al]; the vertical and the oblique lines indicate the values of [Fe^{2+}] and [Mg], respectively.

The left and right parts of the classification diagram (Figs. 4a, b) represent chlorites with and without vacancies, respectively. The right part (Fig. 4b), reproduced from Figure 2, shows solid symbols representing the average compositions, compared to the composition determined from XRD data. The chemical compositions of the chlorites studied may also be projected on the left part of this diagram owing to the presence of octahedral vacancies in their structural formulae (Table 1). However, the inconsistency of the *b* values on the left part of the diagram with the measured values indicates that all samples of chlorite studied here are vacancy-free. The right part of Figure 4 shows that the projected points derived from the structural parameters (open symbols) and the chemical composition (solid symbols) do not match. The points based on chemical results are shifted toward more ferrous compositions. The smallest differences are found in the samples from Pasłęk and the Himalayas, and the greatest, in the Echte and Ejpovice suites. This shift indicates the presence of phases other than chlorite that are rich in Fe. The SEM photographs of the samples from Ejpovice document the presence of rod-shaped goethite or platy crystals of hematite in between the chlorite platelets (Fig. 1f). The shift of points representing the Echte samples suggests the presence of an admixture of a phase richer in Si than chlorite.

IDENTIFICATION OF THE POLYTYPES

For identification of a chlorite polytype, one must have *XZ* and *YZ* projections of the structure. The distribution of intensity of reflections of the type 20*l* (and 13*l*) and 02*l* (and 11*l*) give information about the *XZ* and *YZ* projections, respectively. The presence of 20*l*, 13*l* reflections in the diffraction patterns enables us to classify all chlorite samples into one of four subfamilies allowed for chlorites: A, B, C and D (Weiss & Ďurovič 1983, Weiss 1991), which are equivalent to the symbols IIa, Ia, IIb, and Ib according to Brown & Bailey (1963) or IIaa, Iaa, IIbb and Ibb according to Bailey (1988a, b). Eight homo-homo-octahedral MDO groups can be distinguished on the basis of the distribution of the reflections 02*l*, 11*l* (Weiss & Ďurovič 1983).

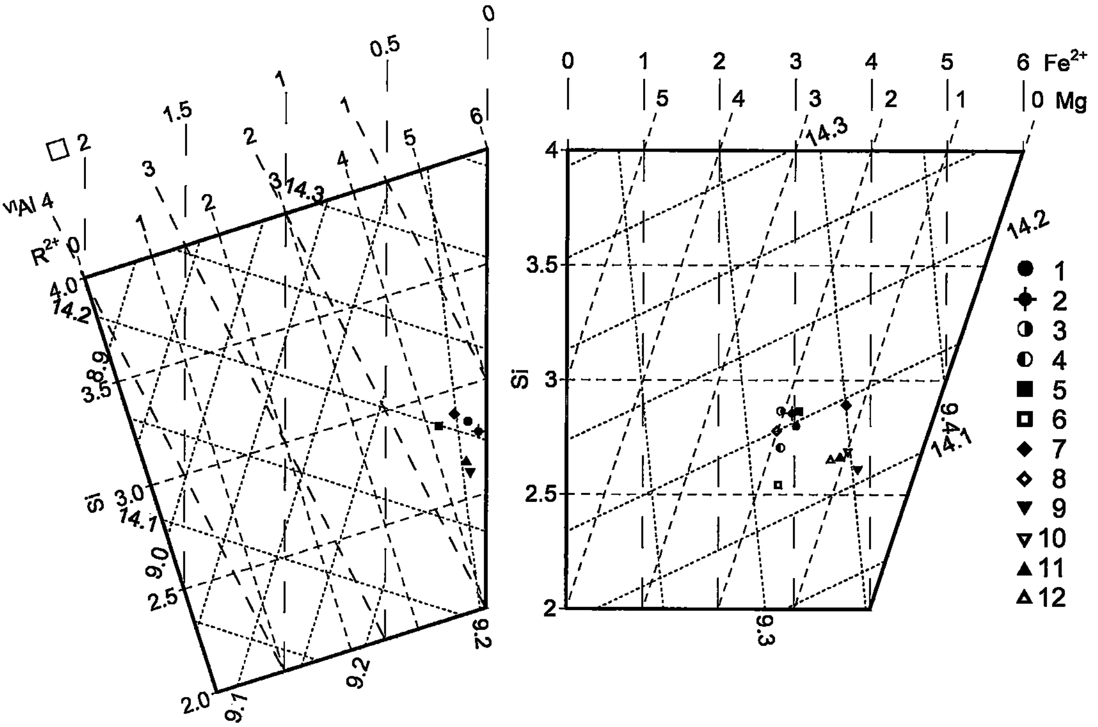

FIG. 4. Projection of the average EDX chemical compositions (solid symbols) of chlorites compared to the data from XRD composition determination (open symbols). Data points: 1) Pasłęk, ooid shell, 2) Pasłęk, central part of the ooid, 3) Pasłęk $1M_{D}$–II–ho, 4) Pasłęk $1A_{C}$–I–ho, 5, 6) Echte, 7, 8) Ejpovice, 9, 10) Himalayas (pyrite-bearing cement), 11, 12) Himalayas (hematite-bearing cement). Left and right parts of the diagram are appropriate for chlorites with and without vacancies, respectively.

X-ray-diffraction patterns of the samples are presented in Figure 5. To identify the subfamily, theoretical diffraction patterns of the chlorite samples were computed using the program DIFK (Smrčok & Weiss 1993). The published structural data were used, corrected both with the actual compositional data and calculated values of unit-cell parameters. The interval 40°–50° 2θ Co*K*α contains reflections suitable to identify the subfamilies (Fig. 6). Comparing the experimental and calculated diffraction-patterns led to unambiguous identification of two polytypes in the sample from Pasłęk. The main component belongs to subfamily C, and the secondary component, marked by the appearance of the 132, 201 composite reflection at 2.513 Å, to subfamily D (Fig. 7). The samples from the other localities are attributed to subfamily D. Chlorites occurring in sedimentary rocks usually belong to subfamily D (= Ibb), and subfamily C (= IIbb) is associated with metamorphic temperatures, as reported by Hayes (1970) and Whittle (1986). The coexistence of chlorites of both subfamilies in the sample from Pasłęk provides significant information about its origin.

The diffraction pattern of the chlorite from Pasłęk contains all reflections needed for the identification of polytypes and shows the presence of quartz (Fig. 5). Owing to the presence of reflections 02*l*, 11*l* in the diffraction pattern of this chlorite, the maximum degree of order (MDO) groups (Ďurovič *et al.* 1983) could be identified: I for the main component, and II for the secondary one. This enabled the full identification of the polytypes: $1A_C$–I–ho as a main component, and $1M_D$–II–ho as the admixed phase. The evaluation and transformation of these symbols result in a symbol IIbb–4 for the triclinic polytype, and Ibb–1 (β = 90°) for the monoclinic polytype according to Bailey (1988a, b). According to the fully descriptive crystallographic OD notation (Ďurovič *et al.* 1983, Weiss & Ďurovič 1983) the symbols of these polytypes are $\left|\begin{array}{ccc} u & e & .\,e \\ e & 1 & e \\ 5 & & \end{array}\right|$ and $\left|\begin{array}{ccc} u & u & .\,u \\ e & 0 & e \\ 3 & & \end{array}\right|$, respectively. The comparison of the simulated theoretical diffraction-patterns of those chlorite polytypes, quartz and their mixtures (Fig. 6) with the experimental data allowed us to establish the theoretical composition of the sample; the experimental and theoretical powder-diffraction patterns were found to coincide. The best consistency is observed for a composition with 82% of the polytype $1A_C$–I–ho, 8% of the polytype $1M_D$–II–ho, and 10% of quartz (Fig. 7). In case of an inhomogeneous distribution of octahedrally coordinated cations common in the meso-octahedral polytype, the homo-octahedral polytype $1A_C$–I–ho would be replaced by meso-octahedral polytypes:

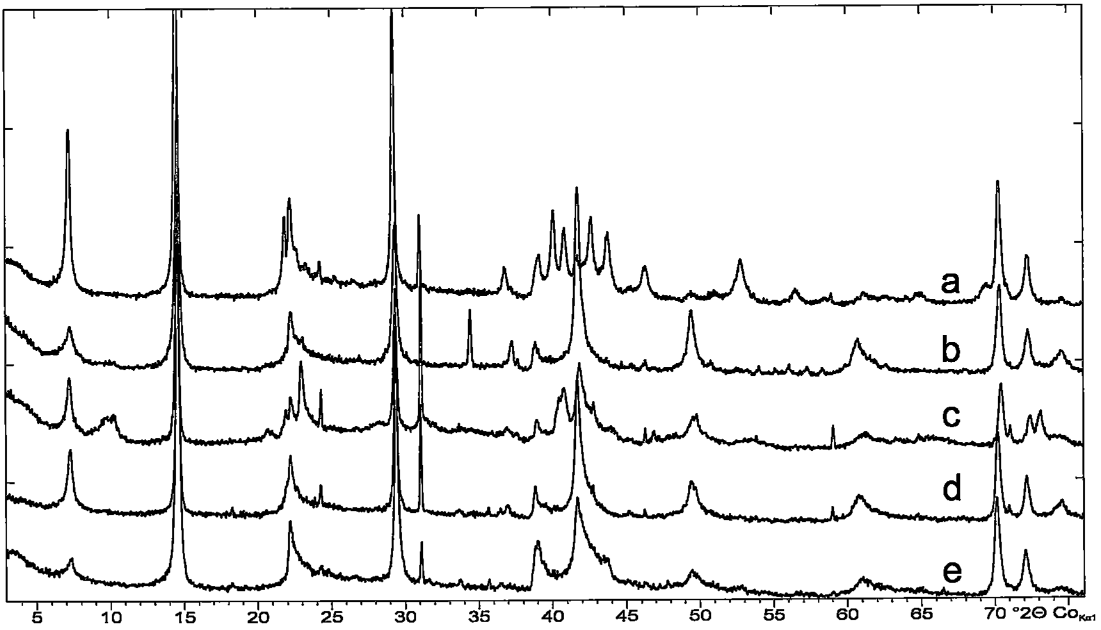

FIG. 5. Experimental powder-diffraction patterns of the chlorite samples studied: a) Pasłęk, b) Echte, c) Ejpovice, d) chlorite from ooids in sandstone from the Himalayas containing hematite in cement, e) chlorite from ooids in sandstone from the Himalayas containing pyrite in cement.

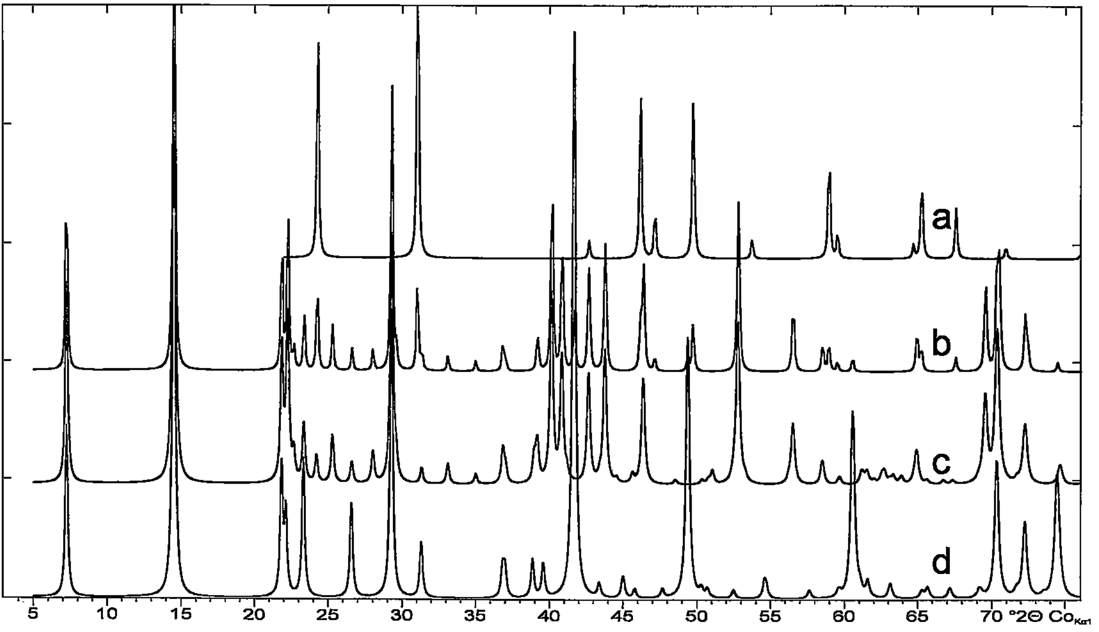

FIG. 6. Calculated powder-diffraction patterns from structural data: a) quartz, b) mixture of 82% $1A_C$–I–ho + 8% $1M_D$–II–ho polytypes + 10% quartz, c) $1A_C$–I–ho polytype, d) $1M_D$–II–ho polytype.

$1A_C$–I,1–me or $1A_C$–I,3–me. Similarly, the polytype $1M_D$–II–ho would be replaced by $1M_D$–II,1–me or $1M_D$–II,2–me. However, the intensities of reflections calculated for the models of the structures with homo- and meso-octahedral cation distribution differ radically. Therefore, a comparison of the experimental and calculated powder-diffraction patterns led to identification of the quasi-homogeneous distribution of the octahedrally coordinated cations in all samples of chlorite studied.

DISCUSSION

The determination of chemical composition of chamosite in ooids by X-ray diffraction is considered a superior method compared to EDX data, not because of its accuracy, which is limited by the accuracy of d_{001} and b measurements, but because it avoids contamination by the extraneous nano-phases, commonly intergrown with chlorites. From a simple measurement of two structural parameters, one obtains five major chemical components, namely the number of Si atoms per formula unit, ΣR^{3+} in the tetrahedral positions, ΣR^{3+} in the six octahedral positions, the number of Fe^{2+} atoms per six octahedral positions and the number of Mg atoms per six octahedral positions. In most cases, the ΣR^{3+} implies Al in equal quantities in the both tetrahedral and octahedral sites. The limitation of the method is that it does not distinguish specific heavy elements. On the other hand, the EDX results do provide this information. Therefore, it seems justified to apply both methods in a complementary way, EDX to determine all components of the chamosite, XRD to refine the crystallochemical formula.

In natural chlorites, semirandom stacking results in the smearing of reflections important for determination of polytypes. In the patterns of some samples studied here, *e.g.*, from Pasłęk and Echte, not only basal and $20l$ and $13l$ reflections are present, but also weak reflections of the type $02l$, which permit determination of polytype and calculation of the whole set of unit-cell parameters. This allowed us to use the b parameter for the evaluation of the chemical composition of the chamosite. The chamosite sample from Pasłęk is composed of two distinct polytypes: $1A_C$–I–ho and $1M_D$–II–ho, and quartz in the proportion 82:8:10, as shown by comparing the measured powder-diffraction pattern to the calculated pattern for such a mixture of the studied phases. In other samples, only the $1M_D$–II–ho polytype was found.

It should be stressed that the XRD method applied here for the determination of chemical composition is the only one which may be and was successfully used for the evaluation of chemical composition of the two individual polytypes occurring in the sample from Pasłęk (Table 2). This information could not have been achieved from the intensities of the basal reflections, as

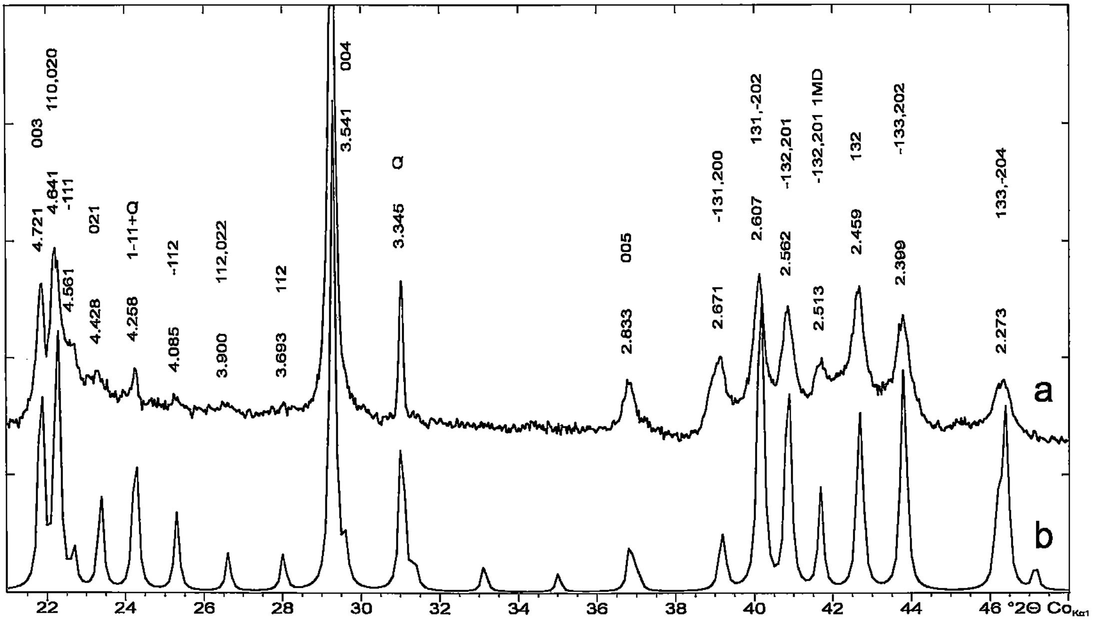

FIG. 7. Experimental (a) and calculated (b) powder-diffraction patterns of the sample from Pasłęk in the range of 21.5 – 48° 2θ. For the given composition (chlorites: 82% 1*A*_C–I–ho, 8% 1*M*_D–II–ho; quartz 10%), the computed pattern fits the experimental one. Indices of the reflections and spacings are given. Q: quartz, 1MD: 1*M*_D–II–ho polytype, other reflections: 1*A*_C–I–ho polytype.

basal reflections of different structural modifications of chlorites largely overlap. Reflections of the type 02*l* do not overlap, and thus may be used to determine MDO groups, which allows one to identify polytypes and measure their unit-cell parameters. Thus, the determined crystallochemical formulae (Table 2) for the studied chamosites are:

Pasłęk $1A_C$–I–ho: $(Fe^{2+}_{2.80}Mg_{1.91}Al_{1.28})(Si_{2.72}Al_{1.28})O_{10}(OH)_8$
Pasłęk $1M_D$–II–ho: $(Fe^{2+}_{2.80}Mg_{2.06}Al_{1.13})(Si_{2.87}Al_{1.13})O_{10}(OH)_8$
Himalayas*: $(Fe^{2+}_{3.73}Mg_{0.96}Al_{1.31})(Si_{2.69}Al_{1.31})O_{10}(OH)_8$
Himalayas**: $(Fe^{2+}_{3.47}Mg_{1.18}Al_{1.35})(Si_{2.65}Al_{1.35})O_{10}(OH)_8$
Ejpovice: $(Fe^{2+}_{2.77}Mg_{2.00}Al_{1.23})(Si_{2.77}Al_{1.23})O_{10}(OH)_8$
Echte: $(Fe^{2+}_{2.78}Mg_{1.73}Al_{1.46})(Si_{2.54}Al_{1.46})O_{10}(OH)_8$

The iron content of chamosite in the ooids from various localities and formations is strikingly consistent. Only ooids from the Himalayan locality contain chamosite richer in iron than the other samples studied.

The presence of the two different polytypes of chlorite, one typical of sedimentary layers and the second typical of higher temperatures of formation, indicates a detrital character of the 1*A*_C–I–me polytype, or else the sediment from Pasłęk underwent relatively important burial-induced recrystallization.

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