

STRUCTURE OF INORGANIC COMPOUNDS

Crystal Structure of Celadonite from the Electron Diffraction Data

A. P. Zhukhlistov

Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences,
Staromonetnyĭ per. 35, Moscow, 119017 Russia

e-mail: anzhu@igem.ru

Received March 14, 2005

Abstract—The crystal structure of the dioctahedral celadonite mica *1M* (space group *C2/m*; *R*, 2.98%; 184 unique reflections) is refined from the oblique-texture electron diffraction patterns obtained with the use of imaging plates. The maximum characterizing the location and potential of the hydrogen atom of the hydroxyl group oriented into the unoccupied *trans* octahedron at an angle of 4.4° with respect to the *ab* plane is revealed from the difference Fourier-potential syntheses. The O–H interatomic distance is equal to 0.98 Å. The superstructure reflections observed in the selected-area electron diffraction patterns for a number of particles arise from the superposition of two cells, namely, the main cell with a broken base-centered symmetry and the base-centered supercell with the triple parameter *a*. These reflections are caused by the ordered distribution of the trivalent and divalent cations Fe and Mg over the octahedral *cis* positions. © 2005 Pleiades Publishing, Inc.

INTRODUCTION

Celadonites belong to dioctahedral potassium micas in which the octahedral positions 2 : 1 in layers are almost equally occupied by trivalent and divalent cations with a predominance of the Fe³⁺ cations among the octahedral cations. Celadonite has the ideal crystal chemical formula K(Fe³⁺,Al)(Mg,Fe²⁺)Si₄O₁₀(OH)₂. Upon limited replacements of Si by Al in the tetrahedra, the layer charge is determined by the content of divalent cations in the octahedra.

Structural investigations of celadonite have been carried out only by electron diffraction methods because of the finely dispersed form of the celadonite samples. Zvyagin [1] was the first to perform an electron diffraction study of celadonite of the polytypic modification *1M* (Pobuzh'e, Ukraine). More accurate structural data were obtained for the celadonite *1M* from the Krivorozhskii iron-ore basin (Ukraine) [2]. The parameters of the base-centered monoclinic cell of celadonite with the crystal chemical formula (K_{0.83}Na_{0.01}Ca_{0.04})(Fe_{1.15}³⁺Fe_{0.36}²⁺Mg_{0.41}Al_{0.05})Ti_{0.01} · (Si_{3.94}Al_{0.06})O₁₀(OH)₂ are as follows: *a* = 5.23 Å, *b* = 9.05₅ Å, *c* = 10.15 Å, and β = 100°35'. According to the ratio Mg/(Mg + Fe²⁺) = 0.53, the sample studied is similar to ferroceldonite [3]. The use of the oblique-texture electron diffraction patterns recorded with a high-voltage electron diffraction camera, as well as the visual evaluation of the intensities in micrographs with multiple exposures, made it possible to determine the statistical distribution of the octahedral cations over the *cis* positions in the celadonite structure (space group *C2/m*, *R* = 10.8%); the average interatomic distances

M–O = 2.04₅ Å, *T*–O = 1.63₅ Å, and K–O = 3.07₅ Å; and the angles of ditrigonal rotation of the octahedron bases φ = 2.3° and tetrahedron bases ψ = 1.3° [2].

Using the electrometric recording of the intensities of reflections in the oblique-texture electron diffraction patterns, Tsipurskiĭ and Drits [4] refined the structure of the celadonite *1M* from Zaval'e (Pobuzh'e, Ukraine). It was found that this celadonite has a structure with the parameters of the base-centered monoclinic cell *a* = 5.223 Å, *b* = 9.047 Å, *c* = 10.197 Å, and β = 100.43° and the crystal chemical formula (K_{0.89}Ca_{0.10})(Fe_{0.90}³⁺Fe_{0.32}²⁺Mg_{0.73}Al_{0.05})(Si_{3.94}Al_{0.06})O₁₀(OH)₂ (*R* = 5.1%). The revealed lowering of the symmetry to *C2* was explained by the predominant location of Fe³⁺ cations in one of the two nonequivalent *cis* octahedra. The average interatomic distances are as follows: *M*–O = 2.027 and 2.060 Å, *T*–O = 1.616 and 1.618 Å, and K–O = 3.103 Å. The angle of ditrigonal rotation of the octahedron bases is equal to 0.54°, and the angles of ditrigonal rotation of the tetrahedron bases are 3.9° and 1.3°. The hydrogen atom inside the empty *trans* octahedron (the angle between the O–H bond and the layer plane is 14°) was located from the difference Fourier-potential syntheses. The O–H interatomic distance is 0.8 Å.

In this respect, it was of special interest to refine the celadonite structure from the oblique-texture electron diffraction patterns obtained with imaging plates. Experience on the application of digital imaging plates (DITABIS, Germany) in the study of layered minerals has opened up strong possibilities for their use in electron diffraction investigations. Owing to the wide dynamic range and the linearity of signal transmission,

all intensities of the reflections observed in the oblique-texture electron diffraction pattern can be recorded with the use of only one imaging plate [5]. The refinement of the crystal structure of brucite $\text{Mg}(\text{OH})_2$ ($R = 3.4\%$) from the oblique-texture electron diffraction patterns made it possible to reveal fine features in the brucite structure, such as the statistical distribution of hydrogen atoms over three positions located around the threefold axes, and clearly demonstrated the efficiency of using imaging plates in electron diffraction structure analysis, specifically in the study of hydroxyl-containing minerals [5].

EXPERIMENTAL TECHNIQUE

The structure of the previously studied celadonite sample from Krivoř Rog [2] was refined from the digital oblique-texture electron diffraction patterns measured using a high-voltage electron diffraction camera with imaging plates (resolution, 25 μm) and a DITABIS laser scanner. The intensities of diffraction reflections were estimated from the radial intensity distribution profiles obtained with the MICRON program package (DITABIS) [5]. The reflection profiles were approximated according to the Gaussian–Lorentzian Sum (Area) formula after subtracting the background (the PeakFit program). The intensities of the diffraction reflections were determined as the areas under the approximating curves. Partially overlapped or closely spaced reflections were separated using the profile analysis. The intensities of the reflections coinciding in the oblique-texture electron diffraction patterns were determined under the assumption that they are proportional to the corresponding values $IF_{\text{theor}}I^2$. The structure amplitudes were calculated from the intensities according to the following formula for local intensities:

$IF_{hkl}I_{\text{exp}} = \sqrt{I_{hkl\text{exp}}/d_{hkl}d_{hk0}p}$, where the indices $hk0$ refer to the reflections of the same ellipsis as the reflections with the indices hkl and p is the multiplicity factor [6]. The structural calculations were performed with the AREN-90 program package [7] and the electron atomic scattering factors for neutral atoms. We used 184 unique reflections with the maximum indices $l = 12$ in 12 ellipses up to $\sin\theta/\lambda = 0.69 \text{ \AA}^{-1}$. The parameters of the base-centered monoclinic cell [$a = 5.227(2) \text{ \AA}$, $b = 9.053(2) \text{ \AA}$, $c = 10.153(3) \text{ \AA}$, and $\beta = 100.53(3)^\circ$] were calculated from the electron diffraction patterns measured with TICl as an internal standard. The analysis of the intensities demonstrated that scattering for the majority of the reflections occurs according to the kinematic law. The intensities of eight strong reflections were corrected for primary extinction in the Blackman two-wave approximation [8] for the calculated average effective thickness of crystallites $t_{\text{av}} = 490 \text{ \AA}$.

The celadonite structure was refined in the space group $C2/m$ and also in the space group $C2$ in order to reveal the possible ordering of octahedral cations. As the starting models, we used the atomic coordinates

taken from [4] for the celadonite structure refined in the space group $C2$; the atomic coordinates in the space group $C2/m$, which were determined by averaging the coordinates of the atoms related by the m pseudoplane in the space group $C2$ [4]; and the atomic coordinates obtained in [2]. It should be noted that, in the starting models with space group $C2$, we varied the distributions of octahedral cations over two nonequivalent *cis* positions. It turned out that, when refining the models in the space group $C2$, the standard deviations of the coordinates of the atoms located in the vicinity of the m pseudoplane are considerably larger than those of the other atoms. Moreover, the average T –O distances in two tetrahedra also differ from each other. Crystal chemically, this is not justified in terms of the insignificant substitution of Al atoms for Si atoms in tetrahedra of the celadonite structure. For this reason, further refinement of the celadonite structure was carried out in the space group $C2/m$. A similar situation was considered in detail when refining the structure of the muscovite $1M$ [9].

After the least-squares refinement of the non-hydrogen atoms and their thermal parameters in the anisotropic approximation, the maximum associated with the hydrogen atom of the hydroxyl group was revealed from the difference Fourier-potential syntheses (Fig. 1). The final refinement of the celadonite structure was performed in the anisotropic approximations for all the atoms to $R = 2.98\%$. The atomic coordinates and the anisotropic thermal parameters are presented in Table 1. The interatomic distances are given in Table 2. The projection of the structure onto the ab plane is depicted in Fig. 2.

RESULTS AND DISCUSSION

It is established that celadonite from Krivoř Rog is characterized by a statistical distribution of octahedral cations with the average interatomic distance M –O = 2.042 \AA and the shortest distance M –OH = 2.025 \AA . The octahedra are slightly oblate; the average distances $(\text{O}–\text{O})_{\text{base}}$ and $(\text{O}–\text{O})_{\text{side}}$ are equal to 2.945 and 2.831 \AA , respectively; and the height of the octahedral sheet is 2.263 \AA . The octahedron bases are rotated through the angle $\varphi = 2.56^\circ$.

The tetrahedra are elongated along the normal to the layers. The average distances $(\text{O}–\text{O})_{\text{base}}$ and $(\text{O}–\text{O})_{\text{side}}$ are equal to 2.613 and 2.665 \AA , respectively. The tetrahedral cations are displaced to the O_{apex} atom shared by the octahedral and tetrahedral sheets. The T – O_{apex} and $(T–\text{O}_{\text{base}})_{\text{av}}$ distances are equal to 1.598 and 1.623 \AA , respectively. The average T –O distance is 1.617 \AA . The surface of the basal tetrahedral oxygen atoms is puckered. The O_{base} atom lying in the m plane is located 0.032 \AA closer to the octahedral sheet as compared to the other O_{base} atom.

For a small angle of ditrigonal rotation of the tetrahedron bases ($\psi = 0.5^\circ$) and a small interlayer displace-

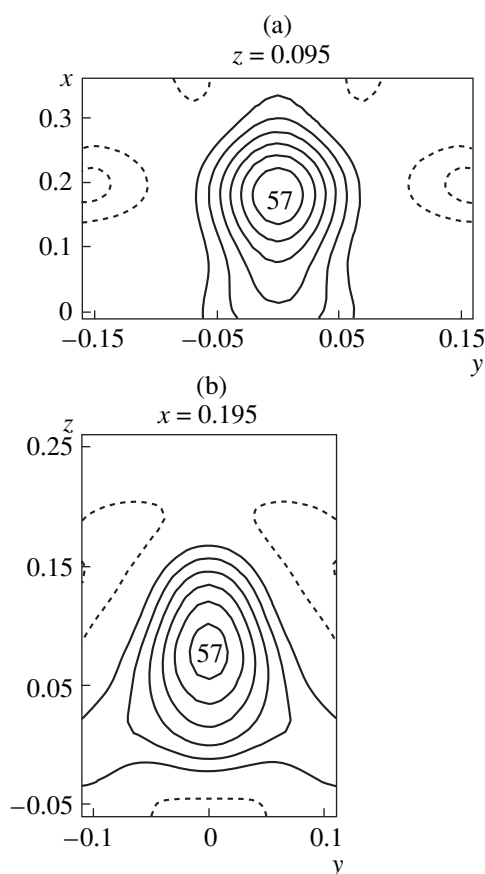


Fig. 1. Difference Fourier synthesis sections passing through the hydrogen atom and parallel to (a) the ab plane and (b) the bc plane of the celadonite structure. The contours are drawn at an interval of 10 V. Numbers indicate the potential at the maximum.

ment ($t = 0.003$), the interlayer cations K are located in a nearly regular hexagonal prism with average $(K-O)_{\text{inner}}$ and $(K-O)_{\text{outer}}$ distances equal to 3.084 and 3.107 Å, respectively [$(K-O)_{\text{av}} = 3.096$ Å]. For a small interlayer displacement t , the value of $-c \cos \beta / a =$

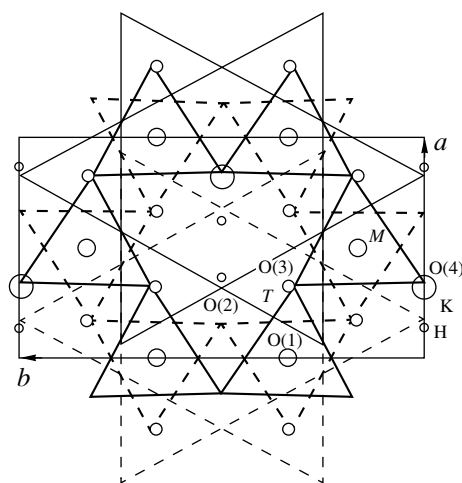


Fig. 2. Schematic drawing of the celadonite structure in the normal projection onto the ab plane. Heavy solid lines indicate the upper bases of the octahedra, heavy dashed lines correspond to the lower bases of the octahedra, thin solid lines represent the upper bases of the tetrahedra, and thin dashed lines show the lower bases of the tetrahedra.

0.355 (the ideal value is $1/3$) is provided by the intralayer displacement $s = 0.321$.

Compared to our earlier work [2], this study of the celadonite structure with modern digital methods used for recording the diffraction patterns made it possible to substantially refine a number of fine features in the celadonite structure. In particular, it should be noted that the data obtained in our present work confirmed neither the increase in the average $T-O$ distance nor the ratio between the $T-O_{\text{apex}}$ and $(T-O_{\text{base}})_{\text{av}}$ distances, which were found in [2].

The fact that we succeeded in determining the location and specific features of the hydrogen atom of the OH hydroxyl group is of particular importance. As can be seen from the difference Fourier-potential syntheses (Fig. 1), the maximum attributed to the hydrogen atom has an anisotropic shape and is extended in the ac plane. This agrees with the established anisotropy of

Table 1. Atomic coordinates and anisotropic thermal parameters ($\text{Å}^2 \times 10^{-4}$) for the celadonite structure

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
K	0.5	0	0.5	48(14)	18(5)	34(5)	0	12(11)	0
M	0.5	0.1663(2)	0	44(7)	16(3)	18(3)	0	8(7)	0
T	0.4139(3)	0.3329(2)	0.2736(1)	53(8)	19(3)	18(3)	4(9)	16(7)	0
O(1)	0.1879(6)	0.2507(3)	0.3348(3)	81(16)	36(6)	24(4)	-18(11)	7(11)	5(6)
O(2)	0.4426(7)	0.5	0.3315(3)	108(19)	20(7)	34(6)	0	11(17)	0
O(3)	0.3684(5)	0.3257(3)	0.1137(3)	115(16)	28(5)	32(4)	22(13)	22(12)	-13(7)
O(4)	0.3954(7)	0	0.1126(4)	56(20)	21(6)	30(6)	0	13(18)	0
H	0.204(6)	0	0.105(3)	579(141)	54(39)	137(46)	0	19(114)	0

Table 2. Interatomic distances (Å) in the celadonite structure

Octahedron					
$M-O(3) \times 2$	2.044(3)	Base edges		Side edges	
$-O(3') \times 2$	2.057(3)	$O(3)-O(3') \times 2$	2.951(4)	$O(3)-O(3')$	2.895(4)
$-O(4) \times 2$	2.025(3)	$O(3')-O(4) \times 2$	2.931(4)	$O(3')-O(4) \times 2$	2.917(4)
Average	2.042	$O(4)-O(3) \times 2$	2.952(3)	$O(4)-O(4)$	2.708(5)
		Average	2.945	$O(3)-O(3') \times 2$	2.774(3)
$O(4)-H$	0.98(2)			Average	2.831
Tetrahedron					
$T-O(1)$	1.613(4)	Base edges		Side edges	
$-O(1')$	1.638(3)	$O(1)-O(1')$	2.163(4)	$O(3)-O(2)$	2.686(4)
$-O(2)$	1.619(2)	$-O(2)$	2.603(3)	$-O(1')$	2.633(4)
$-O(3)$	1.598(3)	$O(2)-O(1')$	2.623(3)	$-O(1)$	2.674(4)
Average	1.617	Average	2.613	Average	2.665
Interlayer spacing					
	$K-O(1') \times 4$				3.077(3)
	$-O(2') \times 2$				2.097(3)
	$-O(1) \times 4$				3.102(3)
	$-O(2) \times 2$				3.118(4)
	Mean				3.096

Note: O and O' are the oxygen atoms related by the symmetry elements.

thermal vibrations of the hydrogen atom and reflects different configurations of the Fe and Mg trivalent and divalent cations distributed statistically over the *cis* positions in the nearest environment of the hydrogen atom. The O–H bond is oriented toward the empty octahedron and forms an angle of 4.4° with the *ab* plane (the hydrogen atom is slightly displaced inside the empty octahedron). The O–H interatomic distance is equal to 0.98(2) Å.

It should be noted that, among the dioctahedral micas, only the celadonite structure is characterized by the displacement of the hydrogen atom of the hydroxyl group inside the empty octahedron. In muscovites, the hydroxyl group is oriented toward the empty octahedron at an acute angle (15°–17°) with respect to the plane of the layer from the octahedral sheet [10]. The orientation of the hydroxyl group into the empty octahedron in the celadonite structure favors the interaction of the interlayer K cation with the oxygen atom of the hydroxyl group (the interatomic distance $K-OH = 3.870$ Å is the shortest among those observed in the mica structures). In the mica structures, this is the only oxygen atom that is located in the octahedral sheet at a sufficiently short distance from the interlayer cation and, moreover, is not shielded by the basal oxygen atoms. For a relatively weak interaction of the K cation with the basal oxygen atoms due to an insignificant

substitution of Al atoms for Si atoms in the tetrahedra, the interaction of the K cation with the oxygen atom of the hydroxyl group is an important factor stabilizing the celadonite structure. This can be judged, in particular, from the small interlayer spacing (3.325 Å as compared to $c \approx 3.40$ Å in muscovites), which is observed when the basal oxygen atoms of the adjacent tetrahedral sheets are superposed in the projection onto the *ab* plane. This superposition is favored by the small negative charge of the O_{base} atoms. In the present work, the angle of deviation of the O–H bond from the plane of the layer into the empty *trans* octahedron is smaller than that obtained in [4]. It seems likely that this deviation is associated both with the high content of trivalent cations in the octahedral sheet and with the deficit of interlayer cations in the structure of the celadonite from Krivoi Rog.

An interesting feature of the celadonite from Krivoi Rog is that the selected-area electron diffraction patterns of a number of band-shaped single-crystal particles extended along the *a* axis exhibit triads of weak additional reflections between strong reflections attributed to the main base-centered cell (Fig. 3). Similar electron diffraction patterns were also observed earlier [11]. The intensity ratio of reflections in triads (Fig. 3) varies both for different particles and within a single particle (the intensity of central reflections can be either

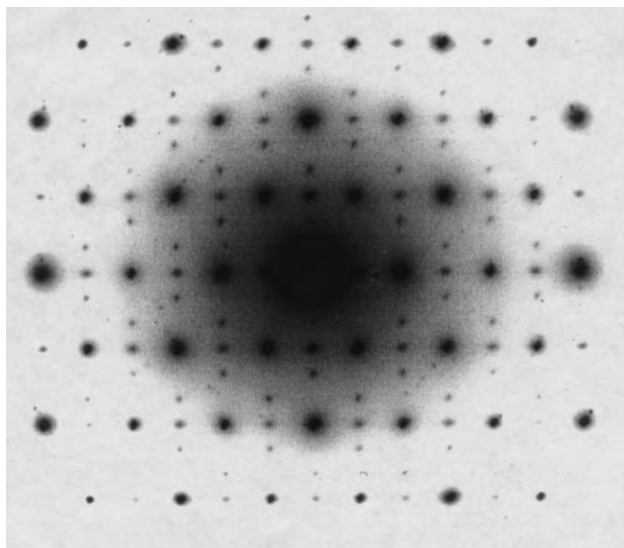


Fig. 3. Selected-area electron diffraction pattern of a single celadonite particle (the ab plane is oriented perpendicular to the incident beam). Triads of weak reflections extended along the a axis are seen. The central reflections in triads are attributed to the main cell with a broken base-centered symmetry. The extreme reflections correspond to the base-centered supercell with $a_s = 3a_0$ and $b_s = b_0$.

higher or lower than that of the extreme reflections, and the former reflection are always more smeared than the latter reflections). This indicates that the appearance of additional reflections is caused by the superposition of two cells. In triads, the extreme reflections correspond to the base-centered supercell with the triple parameter a , whereas the central reflections are attributed to the main cell with a broken base-centered symmetry. This feature of the celadonite apparently can be associated with the ordered distribution of trivalent and divalent cations Fe and Mg over the *cis* positions. The two models proposed for cation ordering are consistent with the observed intensity distribution. According to these models, when the octahedral cations are in the ratio $\text{Fe}^{3+} : \text{Fe}^{2+} : \text{Mg} = 2 : 1 : 1$, the Fe^{3+} cations occupy one system of octahedral *cis* positions (related by the C translation in the main cell), whereas the Fe^{2+} , Mg, and (Fe^{2+} , Mg) cations (the base-centered cell with $a_s = 3a_0$ and $b_s = b_0$) or the Fe^{2+} and Mg cations (the main cell with a broken base-centered symmetry) alternate in an ordered manner along the a axis in the other system of *cis* positions.

CONCLUSIONS

Thus, the above analysis of the selected-area electron diffraction patterns of single crystals confirmed the tendency (revealed from the oblique-texture electron diffraction patterns in [4]) toward ordered distribution of trivalent and divalent octahedral cations in celadonite and demonstrated that the Fe^{2+} and Mg^{2+} divalent cations are also ordered. The superstructure reflections observed only for particular particles most likely indicate that, in the vast majority of the celadonite particles, regions with ordered cations are characterized by incoherent scattering. This leads to an averaged structure with a statistical distribution of octahedral cations, as was established in the refinement of the celadonite structure from the oblique-texture electron diffraction patterns obtained with the use of imaging plates.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 02-05-64952.

REFERENCES

1. B. B. Zvyagin, *Kristallografiya* **2** (3), 393 (1957) [*Sov. Phys. Crystallogr.* **2**, 388 (1957)].
2. A. P. Zhukhlistov, B. B. Zvyagin, E. K. Lazarenko, and V. I. Pavlishin, *Kristallografiya* **22** (3), 498 (1977) [*Sov. Phys. Crystallogr.* **22**, 284 (1977)].
3. V. Rieder, G. Cavazzini, Y. S. Dyakonov, *et al.*, *Clays Clay Miner.* **46** (5), 586 (1998).
4. S. I. Tsipurskiĭ and V. A. Drits, *Mineral. Zh.* **8** (3), 32 (1986).
5. A. P. Zhukhlistov, M. S. Nickolsky, B. B. Zvyagin, *et al.*, *Z. Kristallogr.* **219**, 224 (2004).
6. B. K. Vainshteĭn, *Structural Electronography* (Akad. Nauk SSSR, Moscow, 1956) [in Russian].
7. V. I. Andrianov, *Kristallografiya* **32** (1), 228 (1987) [*Sov. Phys. Crystallogr.* **32**, 130 (1987)].
8. B. K. Vainshtein, B. B. Zvyagin, and A. S. Avilov, *Electron Diffraction Techniques* (Oxford University Press, Oxford, 1992), Vol. 1, p. 216.
9. S. I. Tsipurskiĭ and V. A. Drits, *Izv. Akad. Nauk SSSR* **41** (11), 2363 (1977).
10. R. F. Giese, *Rev. Mineral.* **13**, 105 (1984).
11. B. B. Zvyagin, *Electron Diffraction Analysis of Clay Minerals* (Nauka, Moscow, 1964; Plenum, New York, 1967).

Translated by O. Borovik-Romanova