GEOLOGICA CARPATHICA - SERIES CLAYS, 1, BRATISLAVA, JUNE 1992

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RELATIONS BETWEEN UNIT-CELL PARAMETERS AND CATION COMPOSITION OF SHEET SILICATES II: TRIOCTAHEDRAL CHLORITES

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Abstract: Relation between unit cell parameters - d_{001} and b-value of trioctahedral chlorites is detaily discussed. b-parameter of the unit cell allows to estimate the total content of the cations Fe, Mn, Cr, Ni. The method for determination of the chlorite composition using val chemical analysis is described. Coordinates of atoms in the unit cell and the distribution of octahedral cations is possible to calculate on the basis of the chlorite composition.

Key words: trioctahedral chlorite, cation composition, b-parameter, d_{001}-parameter.

Introduction

One of the most important problems of crystallochemistry of sheet silicates, which has been given great attention in literature, is the dependence of unit-cell parameters on the chemical composition of minerals. The determination of such relations is not only of theoretical, but also of practical importance. Thus, in the case of finely-dispersed samples, which can contain several phases, direct determination of composition by chemical analysis is often difficult. In connection with this, the question appears, to which extent we can estimate chemical composition of a mineral using its unit-cell parameters.

The paper deals with the analysis of relations between the parameters b and d_{001} of trioctahedral chlorites and their chemical compositions. Such relations can be used e.g. in testing changes in the composition of chlorites during post-sedimentary alterations of sedimentary rocks, and also in determining the content of chlorite in mixtures by using the method of quantitative phase analysis based on a combination of data obtained from X-ray diffraction with results of the chemical analysis.

Relation between cell parameters and composition

It is well known that the structure of chlorites consists of regularly alternating 2 : 1 layers of mica type and brucite-like octahedral layers (see e.g. Bailey 1975, 1988). It has been stated that the parameter b of trioctahedral chlorites increases with increasing content of Fe^{2+} cations in octahedra. There is also a trend to decrease the d_{001} value with increasing substitution of Si cations by Al in tetrahedra of 2 : 1 layers.

In papers of Brindley (1961), Bailey (1975), Shirozu (1958), Von Engelhardt (1942), equations of the following type have been presented:

$$b = b_0 + k\,(Fe^{2+}, Mn^{2+}) \qquad (1)$$

where b_0 and k are constants, (Fe^{2+}, Mn^{2+}) content of octahedral cations of bivalent iron (or iron and manganese) in atoms per formula unit of chlorite. Hey (1954) obtained different k-coefficients for Fe^{2+} and Mn^{2+}. In the book of Kepezhinskas (1965) a more complex relation has been suggested:

$$b(kX) = 9.3274 - 0.009\,Mg - 0.0195\,Si - 0.0220\,Al^{VI} + \\ + 0.0208\,Fe^{3+} + 0.02141\,Fe^{2+} \qquad (2)$$

Bailey (1975) applied the relations mentioned above on four chlorite samples with known compositions and cell parameters and he came to the conclusion that the best agreement between experimental and calculated data is obtained in the case of the equation of Von Engelhardt (1942) of the type (1), with the coefficients $b_0 = 9.22$ Å and $k = 0.028$ Å, if the total content of all transition elements (Fe^{2+}, Fe^{3+}, Cr, Mn, Ni) is included. Satisfactory results have been obtained also using the equations of Shirozu (1978) of the type (1), with the coefficients $b_0 = 9.21$ Å, $k = 0.039$ Å as well as with the equation (2). An analysis of recent crystallochemical data confirms these conclusions.

Less successful proved to be the attempts to relate the d_{001} value to cationic composition of chlorites. The following type of equations have been presented by Albee (1962), Brindley(1961):

$$d_{001} = d - kX \qquad (3)$$

where k, d are constants, X - number of Al^{VI} atoms (Brindley 1961), or total number of Al^{IV} + Al^{VI} + Cr (Albee 1962) (per 10 cations). For chlorites containing more than 4% of Fe_2O_3, Brindley (1961) included an additional number into the equation (3), representing the content of Fe^{3+}. For d_{001} Kepezhinskas (1965) suggested a linear function analogous to the equation (2), with positive coefficients for Si, Fe^{3+} and Mg and negative ones for Al^{VI} and Fe^{2+}. Analysing data of the four chlorites mentioned earlier, Bailey came to the conclusions that the thicknesses of the tetrahedral sheet, octahedral sheets of brucitic and

Table 1: Experimental and calculated values of b and d_{001} for chlorites with refined structures (Nos 1-9) or with known distribution of octahedral cations (No. 10).

No.	Mineral	b [Å] exp.	b [Å] calc.	d_{001} [Å] exp.	d_{001} [Å] calc.	References
1	Penninite IIb-4	9.232	9.228	14.287	14.288	Joswig et al. (1980)
2	Cr-clinochlor IIb-4 (Day Duke Body)	9.227	9.229	14.238	14.263	Phillips et al. (1980)
3	Cr-clinochlor IIb-4 (Siskiu)	9.228	9.230	14.250	14.257	Phillips et al. (1980)
4	Fe-clinochlor IIb-2 (Washington)	9.267	9.272	14.182	14.161	Rule & Bailey (1987)
5	Clinochlor IIb-4 (Kenya)	9.228	9.234	14.251	14.262	Zheng & Bailey (1989)
6	Clinochlor IIb-2 (Kenya)	9.228	9.234	14.263	14.262	Zheng & Bailey (1989)
7	Clinochlor IIb-4 (Ural)	9.234	9.233	14.240	14.229	Joswig & Fuess (1990)
8	Clinochlor IIb-2 (Ural)	9.227	9.234	14.227	14.229	Joswig et al. (1989)
9	Cr-chlorite Ia-4	9.246	9.243	14.332	14.289	Bailey (1986)
10	Baileychlor (Zr - chlorite)	9.257	9.255	14.290	14.282	Rule & Radke (1988)

Table 2: Experimental and calculated structural characteristics of 2:1 layers in chlorites.

No.	Composition of tetrahedral net	d_t [Å] exp.	d_t [Å] calc.	l_b [Å] exp.	l_b [Å] calc.	l_p [Å] exp.	l_p [Å] calc.	h_t [Å] exp.	h_t [Å] calc.
1	$Si_{3.16}Al_{0.84}$	1.651	1.648	2.681	2.60	2.709	2.712	2.223	2.227
2	$Si_{3.02}Al_{0.98}$	1.654	1.653	2.686	2.64	2.716	2.718	2.227	2.233
3	$Si_{2.99}Al_{1.01}$	1.656	1.654	2.691	2.68	2.717	2.720	2.234	2.234
4	$Si_{2.622}Al_{1.378}$	1.668	1.668	2.705	2.77	2.740	2.741	2.251	2.252
5	$Si_{3.056}Al_{0.944}$	1.652	1.651	2.683	2.61	2.712	2.714	2.227	2.229
6	$Si_{3.056}Al_{0.944}$	1.653	1.651	2.683	2.63	2.714	2.716	2.228	2.231
7	$Si_{2.85}Al_{1.15}$	1.656	1.659	2.683	2.68	2.725	2.720	2.234	2.234
8	$Si_{2.85}Al_{1.15}$	1.654	1.659	2.686	2.64	2.714	2.718	2.226	2.233
9	$Si_{3.15}Al_{0.85}$	1.652	1.648	2.679	2.64	2.710	2.708	2.225	2.225

No.	Composition of octahedral net of 2:1 layer*	d_{oct}[1] [Å] exp.	d_{oct}[1] [Å] calc.	< h_{oct} > exp.	< h_{oct} > calc.	ΔOH exp.	ΔOH calc.
1	$Mg_{2.4}Al_{0.3}Fe_{0.3}$	2.080	2.073	2.161	2.159	0.056	0.05
2	$Mg_{2.97}Al_{0.03}$	2.075	2.083	2.148	2.154	0.058	0.05
3	$Mg_{2.94}Al_{0.06}$	2.078	2.082	2.150	2.157	0.044	0.05
4	$Mg_{1.68}Fe^{2+}_{0.91}Fe^{3+}_{0.136}Cr_{0.004}$	2.087	2.079	2.166	2.166	0.047	0.05
5	$Mg_{2.715}Fe^{3+}_{0.156}Cr_{0.128}$	2.081	2.074	2.171	2.160	0.044	0.05
6	$Mg_{2.715}Fe^{3+}_{0.156}Cr_{0.128}$	2.081	2.074	2.168	2.160	0.042	0.05
7	$Mg_{2.75}Fe^{2+}_{0.25}$	2.078	2.088	2.157	2.157	0.052	0.05
8	$Mg_{2.75}Fe^{2+}_{0.25}$	2.077	2.088	2.157	2.156	0.064	0.05
9[2]	Mg_3	2.082	2.085	2.161	2.167	0.045	0.05

[1] in all structures, except No.4, octahedral cations are rndoml distributed over the positions M1 and M2. In the case f No.4, average composition according to M1 and M2 and average d_{oct} are given;

[2] the composition of the sample is taken from Bailey (1986).

2 : 1 layers and the distance between brucitic and 2 :1 layers in chlorite structures vary in a wide range and they can differ even at the same composition of tetrahedral cations. He mentioned that, besides by the grade of substitution of Si by Al, the value of d_{001} should be affected also by such factors as the general composition of octahedral cations, the number of vacant octahedra and the distribution of trivalent cations between the octahedral sheet of the 2 : 1 layer and brucitic layer (Bailey 1975). Regardless of this, Bailey (l.c.) believes that equations presented above can be used for the estimation of Al^{VI} content in the majority of trioctahedral chlorites. However, an analysis of recent precise experimental data carried out in this work has shown that neither of these relations allows to predict the values of d_{001} and, consequently, to estimate the composition of chlorites. The differences between experimental and calculated values of d_{001} reach 0.05 - 0.1 Å, which causes these equations to the practically useless.

At present, there are data in the literature on 12 trioctahedral chlorites, for which precise measurements of unit-cell parameters and reliable determinations of chemical composition have been made. These data allow to analyse the character of the relation of b and d_{001} parameters to the cationic composition of chlorites on a new level. Thus it have been shown that the values of b in these structures are very accurately (see Tab. 1, Tab. 4, samples 1, 2) described by the regression equation

$$b = 9.912 + 0.030\Sigma_{tr} \qquad (4)$$

where Σ_{tr} is total content of Fe, Cr, Mn, and Ni (in atoms per formula unit). The equation (4) is very similar to the relation of Van Engelhardt (1942) mentioned above.

Rich factografic material about chlorites can be found in the book of Kepezhinskas (1965). However, since the book was published in the year 1965 and many data in it are even older, we cannot be absolutely sure that chemical compositions and unit-cell parameters have been determined with sufficient reliability for all samples. Therefore, for an additional testing of the equation (4), 44 samples have been selected, for which the calculations of crystallochemical formulae related to the anionic part $O_{10}(OH)_8$, yields a sum of octahedral cations approaching six. For these samples, the equation (4) yields values with a standard deviation of 0.016 Å.

Table 3: Experimental and calculated structural characteristics of the brucitic layer

No.*	Composition of brucitic layer	
	M3	M4
1	2x(Mg0.875Al0.125)	Mg0.75Al0.25
2	2x(Mg0.99Al0.01)	$\mathrm{Al0.67Cr0.23Fe^{2+}0.04Fe^{3+}0.04Ni0.02}$
3	2x(Mg0.98Al0.02)	$\mathrm{Al0.62Cr0.25Fe^{2+}0.06Fe^{3+}0.06Ni0.01}$
4	$\mathrm{2x(Mg0.64Fe^{2+}0.32Al0.04)}$	Al0.965O0.035
5	2x(Mg1.0)	$\mathrm{Al0.694Fe^{2+}0.113Fe^{3+}0.109Ni0.011O0.073}$
6	2x(Mg0.9Al0.1)	$\mathrm{Mg0.2Al0.494Fe^{2+}0.113Fe^{3+}0.109Ni0.011O0.073}$
7	$\mathrm{2x(Mg0.65Al0.25Fe^{2+}0.015Fe^{3+}0.09Mn0.005)}$	Mg0.5Al0.5
8	$\mathrm{2x(Mg0.65Al0.25Fe^{2+}0.015Fe^{3+}0.09Mn0.005)}$	Mg0.5Al0.5
9	2x(Mg0.9Al0.05Cr0.05)**	Mg0.21Fe0.14Cr0.65

	d_{br} M3		d_{br} M4		s		h_{br}		$h_{sep.}$	
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
1	2.045	2.063	2.023	2.042	2.038	2.055	1.995	1.993	2.824	2.822
2	2.069	2.078	1.963	1.946	2.034	2.034	1.979	1.989	2.810	2.808
3	2.075	2.077	1.960	1.951	2.037	2.035	1.986	1.992	2.806	2.804
4	2.117	2.087	1.929	1.933	2.054	2.036	2.024	2.009	2.730	2.738
5	2.079	2.080	1.957	1.961	2.038	2.040	1.994	1.993	2.802	2.812
6	2.064	2.065	1.990	1.993	2.042	2.041	2.005	1.997	2.803	2.812
7	2.057	2.038	1.991	2.005	2.035	2.027	1.985	1.990	2.792	2.784
8	2.055	2.038	1.997	2.005	2.036	2.027	1.990	1.991	2.797	2.784
9	2.068	2.066	2.007	2.001	2.048	2.044	2.031	2.003	2.827	2.821

* Sample Nos. correspond to table 1;

** the scheme of cation distribution in the positions M3 and M4 has been suggested by the present authors.

An analysis of data from the literature has been shown that the value of d_{001} cannot be related directly to the composition of tetrahedral and octahedral cations by a linear function. Regression equations obtained by the present authors of the type $d_{001} = d + k_1Al^{IV} + k_2X$, where Al^{IV} is the content of Al in tetrahedra, X the content of dioctahedral cations in octahedra, d, k_1 are constants, do not allow to predict with sufficient accuracy the unknown quantities (the errors frequently reach 0.04Å). This confirms the complex character of the relation of d_{001} to chlorite composition mentioned by Bailey (1975). Therefore, we have used the method of structure modelling for the determination of d_{001} in trioctahedral chlorites.

The value of d_{001} in chlorites can be given in the form:

$$d_{001} = 2h_t + h_{oct,max} + h_{br} + 2h_{sep} \qquad (5)$$

where h_t is the thickness of tetrahedral sheet, $h_{oct,max}$ is the thickness of the tetrahedral sheet in the 2 : 1 layer calculated from non-hydroxyl oxygen atoms, h_{br} the thickness of brucitic layer, h_{sep} the distance separating the brucitic and the 2 : 1 layers. An analysis of precise structural data on one-layer trioctahedral chlorites has shown that 2 : 1 layers are very similar to 2 : 1 layers of trioctahedral micas of corresponding composition as far as their structural features are concerned. Thus, tetrahedra of 2 : 1 layers are elongated along the normal to the layers and rotated alternatively in opposite directions around it; the fitting of tetrahedra does not exceed 0.01 Å; the octahedra of 2 : 1 layers are flattened, while oxygen atoms of the hydroxyl groups are shifted relative to the non-hydroxyl oxygen atoms along the $\bar{z}$ axis by Δ_{OH}.

The basic structure characteristic of 2 : 1 layers of trioctahedral chlorites can be predicted using the following empirical relations:

$$d_t = 1.616\, C_{Si} + 1.766\, C_{AlIV} \qquad (6)$$

$$l_b = 1.623\, d_t \qquad (7)$$

$$l_p = 3.266\, d_t - l_b \qquad (8)$$

$$h_t = (l_p^2 - l_b^2/3)^{1/2} \qquad (9)$$

$$d_{oct} = \Sigma\, C_{Ri} .\, d_{Ri} \qquad (10)$$

where C_{Ri} is the relative content of R_i cations in octahedra of 2 : 1 layers, $d_{Mg} = d_{Zn} = 2.085$; for other cations d_{Ri} coincides with values obtained for trioctahedral micas in the work of Smoliar-Zviagina & Drits (1991), i.e. $d_{Fe3+} = 1.99$, $d_{Fe2+} = 2.12$, $d_{Mn} = 2.20$, $d_{Cr3+} = 1.95$, $d_{Ti4+} = 1.94$, $d_{Ni2+} = 2.03$ Å;

$$< h_{oct} > = 1.038\, d_{oct} \qquad (11)$$

$$OH = (0.051\ \ 0.007) \qquad (12)$$

$$h_{oct,max} = < h_{oct} > + 2/3\, \Delta_{OH} \qquad (13)$$

We shall note that the values of d_t, d_{oct} and $<h_{oct}>$ calculated by using the formulae obtained by Smoliar-Zviagina & Drits (1991) for trioctahedral micas correspond to experimental values within 0.01Å, however, better results are obtained by using the equations (6), (10), (11). A comparison of experimental and calculated structural characteristics of 2 : 1 layers of chlorites is given in Tab. 2.

It is evident that this set of relations principially allows us to calculate the coordinates of atoms in 2 : 1 layers of chlorite from data on the chemical composition and unit-cell parameters.

The average interatomic distance cation-anion in octahedra of the brucitic layer d_{br} is slightly shorter than the value of d_{oct} in octahedra of 2 : 1 layers of the same composition and it can be calculated using the formula (10) and by the values of d_{Ri} obtained for trioctahedral micas (Smoliar-Zviagina & Drits 1991). Octahedra of the brucitic layer are flattened more than those in 2 : 1 layers, while the value of h_{br} can be described by the relation

$$h_{br} = 0.978\, d_{br} \qquad (14)$$

In Tab. 3 we can see that the calculated values of h_{br} agree well with the experimental ones ($\sigma = 0.008$ Å). The Cr-chlorite Ia-4 (Bailey 1986) in which the thickness of brucite sheet is anomalously large (2.031 Å in contrast to the expected 2.002 Å) is the only exception. Since all other characteristics of this structure calculated from its chemical composition correspond closely to experimental values (Tab. 2 and Tab. 3),we can assume that either is the increased value h_{br} is caused by an unusually high Cr content (0.75 at.u.), or there is an error in the experiment.

The distance h_{sep} decreases with increasing degree of substitution of Si by Al in tetrahedra, since then the effective negative charge on basal oxygen atoms of tetrahedral sheets is increased and this leads to shortening of hydrogen bonds. The following regression equation has been obtained:

Table 4: Crystallochemical formulae, experimental and calculated values of b and d_{001} for chlorites without refined structures.

No.	Sample	Crystallochemical formula	b [Å]		d_{001} [Å]		Reference
			exp.	calc.	exp.	calc.	
1	IIb-chlorite (N. Hampshire)	$(Mg_{1.42}Al_{1.47}Fe_{3.09})(Si_{2.46}Al_{1.54})O_{10}(OH)_8$	9.298	9.312	14.083	14.07	Hazen & Finger (1978)
2	Corundophyl.	$(Mg_{4.64}Al_{0.83}Fe_{0.37}Cr_{0.15}Ni_{0.01})(Si_{3.02}Al_{0.98})O_{10}(OH)_8$	9.235	9.235	14.270	14.26	Bailey (1975)
3	Sayama mine	$(Mg_{1.02}Al_{1.23}Fe^{2+}_{3.26}Fe^{3+}_{0.41})(Si_{2.55}Al_{1.45})O_{10}(OH)_8$	9.354	9.330	14.100	14.14	Shirozu (1978)
4	No. 22	$(Mg_{4.538}Al_{0.791}Fe^{2+}_{0.552}Fe^{3+}_{0.112}Mn_{0.007})(Si_{3.096}Al_{0.904})O_{10}(OH)_8$	9.240	9.239	14.300	14.27	Kepezhinskas (1965)
5	No. 156	$(Mg_{3.548}Al_{1.095}Fe^{2+}_{1.245}Fe^{3+}_{0.090}Mn_{0.008})(Si_{2.844}Al_{0.156})O_{10}(OH)_8$	-	9.257	14.220	14.23	Kepezhinskas (1965)
6	No. 247	$(Mg_{4.268}Al_{1.069}Fe^{2+}_{0.503}Fe3^{+}_{0.151}Mn_{0.006})(Si_{2.786}Al_{1.214})O_{10}(OH)_8$	-	9.238	14.200	14.20	Kepezhinskas (1965)
7	No. 257	$(Mg_{4.574}Al_{1.296}Fe^{2+}_{0.027}Fe^{3+}_{0.101})(Si_{2.608}Al_{1.392})O_{10}(OH)_8$	9.228	9.223	14.158	14.13	Kepezhinskas (1965)
8	No. 271	$(Mg_{4.755}Al_{0.931}Fe^{2+}_{0.124}Fe^{3+}_{0.146})(Si_{3.010}Al_{0.990})O_{10}(OH)_8$	9.240	9.227	14.258	14.25	Kepezhinskas (1965)
9	No. 296	$(Mg_{3.329}Al_{1.165}Fe^{2+}_{1.086}Fe3^{+}_{0.358})(Si_{2.597}Al_{1.403})O_{10}(OH)_8$	9.260	9.262	14.170	14.14	Kepezhinskas (1965)

Table 5: Calculation of d_{001} for chlorites without refined structures.

No.	dt	lb	lp	ht	doc	hoct,max	dbr	hbr	hsep	d001
1	1.675	2.718	2.752	2.261	2.094	2.208	2.018	1.973	2.684	14.072
2	1.653	2.682	2.716	2.232	2.080	2.193	2.041	1.996	2.807	14.267
3	1.670	2.711	2.743	2.253	2.105	2.219	2.025	1.981	2.719	14.144
4	1.650	2.678	2.711	2.227	2.081	2.194	2.048	2.003	2.818	14.283
5	1.659	2.693	2.725	2.238	2.085	2.198	2.037	1.992	2.782	14.230
6	1.662	2.697	2.730	2.242	2.081	2.194	2.031	1.987	2.772	14.208
7	1.668	2.707	2.741	2.251	2.078	2.191	2.018	1.973	2.734	14.133
8	1.653	2.683	2.716	2.231	2.081	2.194	2.033	1.989	2.806	14.257
9	1.669	2.708	2.743	2.253	2.086	2.199	2.022	1.977	2.731	14.144

$$h_{sep} = 2.847 - 0.042\,(Al^{IV})^3 \qquad (15)$$

where Al^{IV} is the number of Al atoms in tetrahedra per $O_{10}(OH)_8$. Experimental and calculated values of h_{sep} are also listed in Tab. 3. There were used experimental values of the structural parameters in calculations according to the formulae 7 - 9, 11, 13.

The obtained empirical relations were used for the calculation of the parameter d_{001} of chlorites with defined structures or with known distribution of octahedral cations. As it is evident from Tab. 1, the accuracy of such calculations is sufficiently high* ($\sigma \neq 0.013$ Å).

In the case when only the crystallochemical formula of chlorite is known but precise structural data and information on the distribution of octahedral cations are missing, the value of d_{001} can be calculated if another important structural feature of trioctahedral chlorites is used. It turned out that the ratio of b/d_{oct} in trioctahedral chlorites is constant:

$$b/d_{oct} = 4.440 \pm 0.004 \qquad (16)$$

This circumstance can be easily explained. An octahedral sheet of 2 : 1 layers in chlorites occupied predominantly by bivalent cations is only very little distorted. In reality, there is practically no counter-relation of the upper and lower bases of octahedra. It is easy to show that in the case, with $<h_{oct}>> = 1.038\, d_{oct}$, the condition $b/d_{oct} = 4.44$ is fulfilled automatically.

Having calculated d_{oct} according to formula (16) (where b is determined experimentally or according to formula (14), the value of d_{br} can be obtained easily:

$$d_{br} = 2 <d> - d_{oct} \qquad (17)$$

where $<d>$ is determined using the equation (10), in which C_{Ri} is the common relative content of cation of the type R_i in octahedra of brucitic and 2 : 1 layers and d_{Ri} are the same as those used above. In the same way, some structural restrictions are imposed upon the distribution of octahedral cations in chlorites with given composition. This distribution should be such that average interatomic distances cation - anion in octahedra of 2 : 1 and brucitic layers comply with the conditions (16) and (17).

It is possible to calculate d_{001} value according to the formula (5), using the relations (6 - 9, 11- 15), when d_{oct} and d_{br} values are known. For a number of chlorites, the structure of which have not been refined, good correspondence of calculated and experimental values of d_{001} and b has been obtained (Tab. 4 and Tab. 5).

There is also one more simple method for calculating the d_{001} value, but it is not quite correct. Considering the relatively small differences between the values of d_{oct}, d_{br} and $<d>$, it can be assumed that

$$h_{oct} + h_{br} = (1.038 + 0.978) <d>$$

and

$$d_{001} \approx 2\,(h_t + h_{sep}) + 2.016 <d> + 0.034$$

where h_t and h_{sep} are calculated using the formulae (9) and (15).

It has to be noted that it is by far not always possible to make an unambignous decision on the distribution of octahedral cations on the basis of data on bulk chemical composition and the parameter b. This problem can be relatively easily solved when octahedra are occupied essentially by Mg and Al cations (see Tab. 6). As it can be seen from the same table in the case of chlorites with high iron content, the number of possible variations increases, and the solution can become ambigous, even if we take into account that, according to Bailey (1986), the absolute values of charges of brucitic and 2 : 1 layers are almost in any case close to 1. It could be expected that, after having determined the distribution of iron cations according to the intensities of basal reflexions from X-ray diffraction patterns, this problem can be solved. However, from Tab. 6 it can be seen that for Fe-chlorites there are different possibilities of cation distribution, which, in this case (IIb-chlorite - New Hampshire), do not distinguish between the variants (b) and (c).

It is also neccessary to bear in mind that all above mentioned empirical relations have been obtained on the basis of an analysis of data from the literature, on the structures of manganese and magnesium-iron-containing chlorites, for which the b parameter does not exceed 9.3 Å. To establish reliably the laws controlling fine structural features of chlorites with high iron content and b > 9.3 Å, additional experimental material will be necessary.

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* With the exception of the Cr-chlorite Ia-4, since in this case the large discrepancy between d_{001}^{calc} and d_{001}^{exp} is caused by an anomalously high value of h_{br}^{exp}.

Conclusions

The analysis presented in this paper has shown that the value of the *b* parameter of the unit cell of trioctahedral chlorites allows us to estimate the content of the cations Fe, Mn, Cr and Ni. To obtain information on the cationic composition of chlorites according to the value of d_{001} is obstructed by the complicated dependance of this parameter on the composition. However, the suggested method of calculation can be used for the determination of the composition, on the basis of data from val chemical analysis, of individual phases of two-phase samples of the type chlorite-mica, characteristic for certain facies of early metamorphism. On the other hand, when the composition of chlorite is known, it is possible to calculate not only *b* and d_{001} parameters, but principially also coordinates of atoms in the unit cell, and in some cases also to make certain conclusions on the character of distribution of octahedral cations.

Translated by K. Janáková

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