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RELATIONS BETWEEN UNIT-CELL PARAMETERS AND CATION COMPOSITION OF SHEET SILICATES I: WHITE MICAS

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Abstract: The relation between b-value, d_{002}-parameter and chemical composition of the white micas has been studied. A simple method for quantitative estimation of "paragonite" and "leucophyllite" components in white micas in the range of compositions of muscovite-phengite and muscovite-paragonite is presented.

Key words: white micas, cation composition, b-parameter, d_{001}-parameter.

Introduction

Information about the chemical composition of white micas (muscovite, phengite, paragonite) frequently occurring in rocks of the initial metamorphic stage can be very useful for the estimation of the conditions in which these rocks were formed. Thus, on the qualitative level it has been determined (Guidotti 1984) that with increasing pressure the content of the so-called "celadonite" or, more precisely, "leucophyllite" (LPh) component in white micas increases and variations of the "paragonite" component (PG) contents are conected with changes of temperature and (to a lesser extent) of pressure. Direct determination of chemical composition of white micas is difficult, since these finely dispersed minerals usually occur in mixtures. Considering that lattice parameters of micas depend on their cation composition, many authors attempted to use b and d_{002} parameters of white $2M_1$ micas as indicators of pressure and temperature. In this way, in a number of works (Cipriani, Sassi & Viterbo-Bassani 1968; Frey et al. 1983; Guidotti 1974; Guidotti & Sassi 1976; Lindquist & Widmark 1986), regressive equations have been obtained relating b and d_{002} values with the contents of LPh and PG components.

Thus it has been proposed, that the content of the "leucophyllite" component be determined using equations of the type:

$$d_{060} = d_0 + k\,RM \qquad (1)$$

where $RM = MgO + FeO + 2Fe_2O_3$ (in mole per cent), d_0 and k are constants (different in different papers). To examine these relations, we used data on the cell parameters and chemical composition of muscovites, phengites and paragonites with refined structures, obtained from literature. It has been shown that the most optimal of all equations appears to be the one suggested by Frey et al. (1983) ($d_0 = 1.498 Å, k = 0.082 Å$). This equation satisfactorily describes the values of muscovite-phengite micas ($\sigma = 0.012 Å$). The authors presented an equation relating b with the contents not only of the "celadonite" but also of the "paragonite" component:

$$b = 8.995 + 0.321\,RM - 0.039\,Na/(Na + K) \qquad (2)$$

where Na / (Na + K) is the relative content of Na cations in interlayer space. This formula describes the values of b in muscovites and phengites with a trend of reducing them, however, it definitely cannot be used for paragonites. We shall note that in the case of Mn-containing $2M_1$ phengite with unusually high b parameter (Smoliar et al. 1989), out of all mentioned equations only the formula of Frey et al. (1983) gives a value approaching the experimental one.

As we can see, formulae of the type (1), (2) suggested in literature can be used in the best case for a very limited range of compositions. On the basis of this, Lindquist & Widmark (1986) and Naef & Stern (1982) came to the conclusion that these relations can be applied only for semiquantitative analysis of finely dispersed micas.

Relation between cell parameters and composition

A relation relating the b-values in dioctahedric micas of any composition to the character and content of cations in tetrahedra and octahedra of 2 : 1 layers and in the interlayer spaces has been obtained by Smoliar & Drits (1988). However, this relation is too complicated to estimate the composition of the white micas using the parameter b.

In the present work, the following, simpler relation has been obtained for the particular case of $2M_1$ white micas (isomorphous series muscovite-phengite and muscovite-paragonite):

$$b = 9.005 + 0.102\,\Sigma - 0.104\,Na/(Na + K) \qquad (3)$$

where Σ is the sum of the contents of the cations Mg, Fe, Cr, Mn (in atoms per $O_{10}(OH)_2$). In contrast to the known formulae of the type (1) and (2), this equation can be applied for Na-containing muscovites and phengites as well as for K-containing paragonites. Table 1 lists experimental and calculated values of b for white micas with refined structures (samples 1 - 12), as well as of a number of samples (samples 13, 14, 20 - 23) for which the precise data of cell parameters and chemical composition have been kindly provided by Prof. C. V. Guidotti (Maine State University, U.S.A.).

Table 1: Experimental and calculated values of b, d_{002}, Na / (Na + K), and t for white micas $2M_1$.

No.	Sample	b [Å]		d [Å]		Na/(Na + K)		Σ[a.u.]		t	
		exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
1	Muscovite $2M_1$	9.008	9.007	9.973	9.971	0.104	0.100	0.130	0.131	0.387	0.387
2	Muscovite $2M_1$	9.015	9.011	9.973	9.972	0.095	0.085	0.155	0.185	0.386	0.389
3	Muscovite $2M_1$	9.000	9.017	9.974	9.990	0.048	0.115	0.170	0.068	0.386	0.390
4	Muscovite $2M_1$	9.018	9.027	9.985	9.977	0.050	0.056	0.268	0.185	0.391	0.390
5	Muscovite $2M_1$	9.027	9.025	10.002	9.986	0.033	0.006	0.230	0.222	0.390	0.391
6	Muscovite $2M_1$	8.994	8.998	10.011	9.996	0.079	0.061	0.010	0.000	0.392	0.390
7	Phengite $2M_1$	9.038	9.062	9.923	9.922	0.075	0.126	0.640	0.452	0.385	0.382
8	Phengite $2M_1$	9.043	9.052	9.936	9.948	0.051	0.092	0.512	0.466	0.386	0.387
9	Phengite $2M_1$	9.080	9.067	9.942	9.958	0.000	0.002	0.610	0.737	0.382	0.386
10	Na-muscovite $2M_1$ [5]	8.976	8.970	9.890	9.885	0.340	0.330	0.000	0.050	0.374	0.369
11	K-paragonite $2M_1$	8.907	8.921	9.656	9.668	0.850	0.878	0.040	0.000	0.304	0.304
12	Paragonite $2M_1$	8.898	8.909	9.616	9.622	0.958	0.972	0.040	0.000	0.285	0.287
13	O-C-35	9.001	8.991	9.943	9.940	0.214	0.206	0.085	0.170	0.387	0.380
14	O-S-53	9.005	8.994	9.946	9.943	0.210	0.199	0.105	0.202	0.387	0.381
15	O-S-73	-	-	9.947	9.949	0.193	0.197	0.100	-	-	-
16	O-S-55	-	-	9.947	9.951	0.187	0.197	0.105	-	-	-
17	O-K-57	-	-	9.954	9.958	0.172	0.181	0.090	-	-	-
18	O-J-89	-	-	9.959	9.963	0.160	0.169	0.090	-	-	-
19	O-C-17	-	-	9.963	9.967	0.150	0.159	0.090	-	-	-
20	O-J-16	9.016	9.012	9.982	9.982	0.079	0.067	0.145	0.176	0.391	0.389
21	O-K-31	9.004	8.999	9.962	9.964	0.157	0.161	0.105	0.154	0.390	0.384
22	O-K-9	9.010	9.012	9.984	9.983	0.074	0.076	0.140	0.126	0.388	0.388
23	O-K-8	9.011	9.017	9.981	9.985	0.058	0.070	0.180	0.139	0.389	0.389
		σ =0.010		σ =0.008		σ =0.021		σ =0.074		σ =0.004	
		η =0.969		η =0.996		η =0.996		η =0.919		η =0.993	

It is known that the value of interplanar spacing (c.sinβ/2, or d_{002}) of white micas depends also on the contents of Na cations in the interlayer and of the "leucophyllite" component. If we should succeed in obtaining a regression equation describing adequately this dependance for the same range of mica compositions as the equation (3), it would be possible to use these two relations for the estimation of the contents of "LPh" and "PG" components.

In a number of earlier papers (Zen E-an & Albee 1964; Cipriani, Sassi & Viterbo-Bassani 1968; Guidotti 1974, 1984), the following equations have been proposed, respectively:

$$d_{002} = 10.034 - 0.427\, Na / (Na + K) \qquad (4)$$

$$d_{002} = 10.023 - 0.316\, Na / (Na + K) - 0.484\, RM \qquad (5)$$

$$d_{002} = 10.0000 - 0.2584\, Na / (Na + K) \qquad (6)$$

$$d_{002} = 10 - 0.00217\, X - 0.0000259\, X^2 \qquad (7)$$

where X = % Na / (Na + K). However, none of them can be used for the whole range of white mica compositions. Thus, the equations (4, 6, 7) yield considerably higher values of d_{002} for phengites (at $RM \geq 0.1$). The values calculated for paragonites correspond to experimental ones only in the case of equation (4). The formulae (5) and (6) considerably increase these values and the relation (7) strongly reduces them.

Thus, the formula (4) can be used only for micas of the muscovite-paragonite series at $RM \leq 0.05$, formula (7) at $RM \leq 0.05$ and Na / (Na + K) $\leq$ 0.3, No.(5) for potassium micas of the muscovite-phengite series, and (6) only for muscovites.

An analysis of data on 12 well refined structures of muscovites, phengites and $2M_1$ paragonites, and 11 samples of Prof. Guidotti, carried out in the present work has shown, that the values of d_{002} in these micas can be described with great accuracy (σ = 0.008 Å) by the following relations:

a - for $d_{002} > 9.06$ Å and $d_{002} \leq 9.96$ Å ; $b > 9.02$ Å
(corresponding to Na / (Na + K) < 0.15)

$$d_{002} = 10.031 - 0.120\, \Sigma - 0.427\, Na / (Na + K) \qquad (8a)$$

b - for $d_{002} \leq 9.96 Å$; $b \leq 9.02 Å$
(corresponding to Na/(Na + K) < 0.15)

$$d_{002} = 10.031 - 0.427 Na / (Na + K) \quad (8b)$$

Thus, for sufficiently high contents of Na cations, the value of d_{002} is fully determined by the value of Na / (Na + K). Thus, if b and d_{002} are known, we can successfully estimate the values of Na / (Na + K) and Σ in muscovites, phengites and paragonites using the relations (3) and (8). Tab. 1 lists corresponding experimental and calculated values for the samples of white micas mentioned above. It can be seen that relative error increases with the decrease of Na / (Na + K) and Σ. Besides this, additional testing of the suggested method has been done by including data on six white micas presented in the paper of Velde (1970). As we can see in Tab. 2, close correspondence of calculated and experimental values of b, d_{002} and, correspondingly, of Na / (Na + K) and Σ, can be observed also in these samples.

Another parameter, clearly dependent on the composition of white micas, is the value of $c.cos\beta/\alpha$. Bailey (1984) noted that the shift of centres of ditrigonal rings of adjacent tetrahedral sheets in paragonites is more significant with respect to value and opposite with respect to the direction, in comparison with the corresponding shift in K micas. Therefore the resulting shift along the axis a, $t = c.cos\beta/a$ decreases its absolute value with an increase of Na cation contents in the interlayer. Besides this, at similar composition of interlayer cations, the value of $|t|$ in phengites is as a rule lower than in muscovites. From an analysis of existing experimental data the following relation has been obtained:

$$|t| = 0.393 - 0.112\,[Na / (Na + K)]^{1.414} - 0.016 Mg \quad (9)$$

where the Mg cation content is expressed in atom units per $O_{10}(OH)_2$. The calculated and experimental data are listed in Tab. 1. The equation (9) can be used as an independent method of the Na-content estimation in cases where Na / (Na + K) > 0.3, since Mg content is then as a rule negligible. This relation could be also used for the estimation of Mg cation contents, however, this requires that the value of Na / (Na + K) should be determined earlier by an another method. The reliability of the determination of Na / (Na + K) according to the equation (3) and (8) increases with the increasing contents of PG-component, however, in this case the content of Mg is low and the accuracy of its determination is also low. On the other hand, at high Mg contents the PG-component is as a rule negligible and the relative error of the Na / (Na + K) determination according to the formulae (3) and (8) increases. Thus, from the studied phengite samples, the experimental and calculated values of Mg cation contents are in satisfactory accordance in two cases (Nos. 8 and 9, Tab. 1; correspondingly, 0.27 and 0.20, 0.53 and 0.69), and for sample No.7 they differ considerably (0.50 and 0.13) due to a great relative error in the estimation of Na / (Na + K). Disregarding the limits mentioned above, we can expect that additional experimental data will allow to define more precisely the character of the dependence from the character and contents of interlayer and octahedral cations and use it for the estimation of the composition of white micas.

In this way, the procedure suggested in the present work allows us to estimate quantitativly the contents of the "paragonite" and "leucophyllite" components in white micas in the range of compositions of muscovite-phengite and muscovite-paragonite, which can be used for mapping of pre-metamorphic alteration zones of sedimentary rocks.

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Table 2: Experimental and calculated values of b, d_{002}, Na / (Na + K), and t for samples of white micas $2M_1$ (Velde, 1970).

No.	Sample	b [Å]		d_{002} [Å]		Na / (Na + K)		(see text)		t	
		exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.
1	BRIG 13	8.900	8.922	9.643	9.647	0.900	0.930	0.100	0.000	0.280	0.296
2	BOU 15	8.900	8.918	9.628	9.621	0.960	0.940	0.200	0.000	0.283	0.286
3	FAY	9.050	9.046	9.920	9.921	0.110	0.110	0.520	0.550	0.378	0.381
4	CAMP	9.040	9.044	9.916	9.930	0.100	0.140	0.490	0.480	0.379	0.382
5	BRIG 14	9.060	9.053	9.926	9.922	0.090	0.070	0.570	0.610	0.380	0.383
6	B 8	9.050	9.071	9.929	9.902	0.090	0.090	0.740	0.530	0.386	0.380

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