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THE RELATIONSHIP BETWEEN COMPOSITION AND *b* FOR CHLORITE

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Abstract: On the basis of the outlines of the crystallochemical classification of chlorites (Wiewióra & Weiss 1990), the authors postulate regression equations for the *b* parameter, derived from the published structural and chemical data of chlorites:

— trioctahedral chlorites

$b=9.225+0.0270Al^{IV}-0.0386Al^{VI}+0.0376Fe^{2+}-0.0376Cr^{3+}+0.0665Mn^{2+}$

— di-tri- and di-dioctahedral chlorites

$b=8.860+0.112Al^{IV}+0.0524Mg^{2+}+0.0752Fe^{2+}+0.0600Fe^{3+}-0.0523Li^{+}$

These equations, together with the similar regression equation for $d_{(001)}$ derived by Raussel-Colom, Wiewióra & Matesanz (1991), were used to prepare 2D and 3D diagrams. They may be used for estimation of the chemical composition of any chlorite from the XRD analysis.

Key words: phyllosilicates, chlorites, unit-cell parameter *b*, composition, XRD.

Introduction

The relationship between chemical composition of chlorites and *b* parameter has been studied by many authors in the last 50 years. Von Engelhardt (1942), Shirozu (1958), Brindley (1961), and Bailey (1972) presented the correlation between the *b* value and the Fe and Mn contents, expressed as a number of atoms per formula unit per 2:1 layer in a unit cell, in the form of a linear equation: $b=b_o+k(Fe^{2+}, Mn^{2+})$.

The validity of the most frequently used equations was tested by Bailey (1975, 1988). He obtained the best correlation between experimental and calculated *b* value for 4 trioctahedral chlorite specimens of the known structure by using the equation of von Engelhardt (1942): $b(Å)=9.22+0.028(Fe^{2+}, Fe^{3+}, Cr^{3+}, Mn^{2+}, Ni^{2+})$.

Drits & Smoliar-Zvyagina (1992) derived a similar equation from the structural data of 12 trioctahedral chlorites: $b(Å)=9.912+0.03(Fe^{2+}, Fe^{3+}, Cr^{3+}, Mn^{2+}, Ni^{2+})$ in which the value of the intercept is incorrect, evidently due to print error.

Kepezhinskas (1965) proposed another equation, in which *b* is expressed in kX units:

$$b(kX)=9.3274-0.0094Mg^{2+}-0.0195Si^{4+}-0.0220Al^{VI}+0.0208Fe^{3+}+0.0241Fe^{2+}.$$

The obtained *b* value should be recalculated to angstroms according to the equation: 1kX=1.002056Å.

It is to be mentioned that none of these equations take into consideration the dependence of *b* on the octahedral sheet geometry. From published refinements of chlorite structures it is clear that trioctahedral chlorites have a homooctahedral sheet in the 2:1 layer and the mesooctahedral sheet in the interlayer. On the other hand the dioctahedral chlorites reveal the meso-dioctahedral distribution of cations in both octahedral sheets. The manner of occupancy of the octahedral sites influences the value of parameter *b*. Therefore, it is suitable to distinguish these two cases while formulating the regression equations.

Composition and XRD data

114 examples were taken from the published chlorite chemical analyses for which values of *b* or $d_{(060)}$ were given. The reliability of the chemical data was critically examined and discussed by Raussel-Colom et al. (1991). All the structural formulae were presented as the number of atoms per half formula unit, i.e. $O_{10}(OH)_8$. In some cases the data required recalculation. In the formulae of Cr-rich chlorites of Lapham (1958), Cr^{3+} was reallocated to octahedral sites because the structural refinements of Phillips et al. (1980) indicated no evidence for Cr^{3+} in tetrahedral coordination. Fig. 1 based on Wiewióra & Weiss (1990) projection system is a graphical presentation of the compositional vari-

Table 1: Compositions, *b* values and references of chlorite samples.

(a) Trioctahedral chlorites

	b	R^{IV}	Al	Mg	Fe^{2+}	Fe^{3+}	Cr	Mn	Ni	Zn	Li	☐	References
1	9.5	1.429	1.16	0.139	0	0.36	0	4.295	0	0	0	0.05	Bannister F. A. et al., 1955
2	9.4	1.3	1.3	0.6	0.2	0	0	2.6	0	1.3	0	0	Bayliss P., 1983
3	9.47	1.278	1.363	0.262	0	0.393	0	3.952	0	0	0	0.03	Bayliss P., 1983
4	9.216	0.6	0.84	4.6	0.28	0.11	0.02	0	0.07	0	0	0.12	Besnus Y. et al., 1976
5	9.242	1	0.2	5	0.1	0	0.7	0	0	0	0	0	Brown B. E., Bailey S. W., 1963
6	9.29	1.2	1.2	2.6	2.2	0	0	0	0	0	0	0	Brown B. E., Bailey S. W., 1962
7	9.29	0.7	0.87	3.13	2	0	0	0	0	0	0	0	Brown B. E., Bailey S. W., 1962
8	9.297	1.6	0.85	0.7	0.75	3.7	0	0	0	0	0	0	Engelhardt W. von, 1942
9	9.29	1.38	1.17	2.82	1.24	0.52	0	0	0	0	0	0.25	Hayashi H., Oinuma K., 1967
10	9.22	1.2	1.28	4.3	0.3	0.06	0	0	0	0	0	0.06	Hayashi H., Oinuma K., 1967
11	9.17	1.33	2.099	3.345	0.034	0.09	0	0	0	0	0	0.342	Hayashi H., Oinuma K., 1967
12	9.35	1.13	1.453	0.789	2.823	0.123	0	0.588	0	0	0	0.224	Hayashi H., Oinuma K., 1967
13	9.336	1.45	1.405	0.775	3.88	0	0	0	0	0	0	0	Ijima A., Matsumoto R., 1982
14	9.234	1.15	0.97	4.54	0.28	0.18	0	0.01	0	0	0	0.02	Joswig W., Fuess H., 1990
15	9.232	0.84	0.82	4.9	0.285	0	0	0.005	0	0	0	0	Joswig W. et al., 1980
16	9.216	0.78	0.65	5.04	0.1	0.17	0	0.01	0	0	0	0.03	Kowalew G. A., 1956
17	9.216	0.99	0.92	4.75	0.13	0.14	0	0	0	0	0	0.004	Kowalew G. A., 1956
18	9.24	1.36	1.17	4.02	0.65	0.13	0	0.02	0	0	0	0	Kowalew G. A., 1956
19	9.258	1.313	1.421	2.355	1.722	0.264	0	0.052	0	0	0	0.186	Kowalew G. A., 1956
20	9.306	1.4	1.23	2.16	2.11	0.3	0	0.04	0	0	0	0.09	Kowalew G. A., 1956
21	9.354	1.49	1.04	0.37	3.57	0.79	0	0.01	0	0	0	0.21	Kowalew G. A., 1956
22	9.207	1.035	0.946	4.618	0.137	0.14	0.086	0	0.007	0	0	0.066	Lapham D. M., 1958
23	9.22	0.93	0.627	4.945	0.109	0.032	0.257	0	0.007	0	0	0.003	Lapham D. M., 1958
24	9.231	0.809	0.202	5.175	0.114	0.036	0.507	0	0	0	0	-0.03	Lapham D. M., 1958
25	9.215	0.893	0.19	5.101	0.16	0	0.602	0	0	0	0	-0.05	Lapham D. M., 1958
26	9.219	1.09	0.36	5.03	0.23	0.11	0.27	0	0.02	0	0	0	Lapham D. M., 1958
27	9.192	1.167	1.257	4.057	0.416	0.149	0	0	0	0	0	0.102	Lis J., Sylwestrzak H., 1986
28	9.222	1.121	1.002	4.564	0.155	0.218	0	0	0.011	0	0	0.032	Lis J., Sylwestrzak H., 1986
29	9.192	0.447	0.97	4.198	0.056	0.195	0	0	0.223	0	0	0.351	Lis J., Sylwestrzak H., 1986
30	9.24	1	0.2	5	0.1	0	0.7	0	0	0	0	0	Lister J. S., Bailey S. W., 1985
31	9.17	0.792	0.555	4.717	0.104	0	0.473	0.001	0.032	0	0	0.118	McCormick G.R., 1975
32	9.187	1	1	5	0	0	0	0	0	0	0	0	McMurchy G. C., 1934
33	9.246	0.831	0.825	4.276	0.203	0.277	0.023	0	0.249	0	0	0.147	Montoya J. W., Baur G. S., 1963
34	9.306	1.279	1.352	0.408	3.416	0.455	0	0.015	0	0	0	0.33	Novak, 1967
35	9.35	1.46	0.84	0.7	2.51	1.15	0	0.53	0	0	0	0.27	Petruk W., 1964
36	9.227	0.98	0.72	4.95	0.04	0.04	0.23	0	0.02	0	0	0.02	Philips T. L. et al., 1980
37	9.228	1.01	0.71	4.92	0.06	0.06	0.25	0	0	0	0	0	Philips T. L. et al., 1980
38	9.23	0.83	0.77	4.82	0.17	0.18	0	0	0	0	0	0.06	Post J. L., Plummer C. C., 1972
39	9.286	1.36	0.85	3.1	1.82	0.32	0	0	0	0	0	0	Post J. L., Plummer C. C., 1972
40	9.241	1.31	1.55	3.47	0.86	0	0	0	0	0	0	0.12	Post J. L., Plummer C. C., 1972
41	9.236	1.13	0.79	4.6	0.48	0.21	0	0	0	0	0	0	Post J. L., Plummer C. C., 1972
42	9.267	1.378	1.316	2.847	1.533	0.222	0.002	0	0	0	0	0.08	Rule A. C., Bailey S. W., 1987
43	9.257	0.45	1.17	0.76	1.2	0	0	0.01	0	2.5	0	0.36	Rule A. C., Radke F. 1988
44	9.344	1.157	0.951	0.794	3.053	0.65	0	0.327	0	0	0	0.225	Shirozu H., 1955
45	9.21	1.27	1.155	4.736	0	0.074	0	0.054	0	0	0	-0.019	Shirozu H., 1958
46	9.24	0.9	0.79	4.54	0.55	0.11	0	0.01	0	0	0	0	Shirozu H., 1958
47	9.29	1.306	1.127	2.86	1.846	0.144	0	0.041	0	0	0	0	Shirozu H., 1958
48	9.35	1.44	1.25	1.02	3.49	0.19	0	0.05	0	0	0	0	Shirozu H., 1958
49	9.365	1.57	1.54	0.2	4.17	0.03	0	0.06	0	0	0	0	Shirozu H., 1958
50	9.348	1.463	1.204	1.012	3.242	0.405	0	0.053	0	0	0	0.08	Shirozu H., 1958
51	9.208	1.271	1.154	4.739	0	0.074	0	0.055	0	0	0	-0.021	Shirozu H., 1958
52	9.354	1.463	1.204	1.012	3.242	0.405	0	0.053	0	0	0	0.072	Shirozu H., 1978
53	9.282	1.033	1.346	2.242	1.437	0.447	0	0.031	0	0	0	0.382	Shirozu H., 1978
54	9.27	0.83	0.885	3.16	1.583	0.201	0	0.009	0	0	0	0.154	Shirozu H., 1978
55	9.216	1.219	1.241	4.265	0.294	0.06	0	0	0	0	0	0.117	Shirozu H., 1978
56	9.198	1.7	2.14	3.21	0.06	0.2	0	0	0	0	0	0.35	Shirozu H., 1980
57	9.216	1.23	1.76	3.58	0.29	0.03	0	0.02	0	0	0	0.32	Shirozu H., 1980
58	9.336	1.3	1.3	1.3	3.4	0	0	0	0	0	0	0	Shirozu H., Bailey S. W., 1965
59	9.314	1.09	1.56	1.11	3.04	0	0	0	0	0	0	0.29	Spötl Ch. et al., 1994
60	9.326	1.36	1.76	0.82	3.19	0	0	0	0	0	0	0.23	Spötl Ch. et al., 1994
61	9.324	1.41	1.84	0.83	3.006	0	0	0	0	0	0	0.25	Spötl Ch. et al., 1994
62	9.324	1.33	1.73	0.79	3.26	0	0	0	0	0	0	0.22	Spötl Ch. et al., 1994
63	9.319	1.38	1.68	0.93	3.23	0	0	0	0	0	0	0.16	Spötl Ch. et al., 1994
64	9.311	1.39	1.72	1.19	2.9	0	0	0.02	0	0	0	0.17	Spötl Ch. et al., 1994
65	9.27	1.5	0.6	5	0.4	0	0	0	0	0	0	0	Steinfink H., 1958b
66	9.214	0.99	0.985	1.665	0.495	0.14	0	0.005	2.615	0	0	0.07	Wall de S.A., 1970
67	9.209	1.74	1.33	4.42	0	0.03	0.19	0	0	0	0	0	unpublished author's data
68	9.245	0.89	0.69	4.44	0.2	0.4	0	0.01	0.01	0	0	0.19	unpublished author's data
69	9.256	1.12	0.75	4.47	0	0.57	0	0	0	0	0	0.07	unpublished author's data
70	9.264	1.46	0.81	2.38	0.9	1.41	0	0.09	0.01	0	0	0.4	unpublished author's data
71	9.233	0.99	1	4.12	0.34	0.3	0	0.01	0	0	0	0.18	unpublished author's data
72	9.362	1.35	1.18	0.63	3.19	0.52	0	0.09	0	0	0	0.19	unpublished author's data
73	9.206	1.6	1.14	4.59	0	0.08	0.25	0	0	0	0	0	unpublished author's data
74	9.192	1.8	1.67	3.97	0	0.17	0.12	0	0	0	0	0.07	unpublished author's data
75	9.237	0.47	0.47	4.74	0.28	0.29	0	0.01	0.02	0	0	0.19	unpublished author's data
76	9.331	1.19	1.39	0.82	3.69	0	0	0	0	0	0	0.1	unpublished author's data
77	9.222	1	0.96	3.93	0.95	0.1	0	0.02	0	0	0	0.03	unpublished author's data
78	9.224	0.87	0.65	4.38	0	0.54	0	0.01	0	0	0	0.29	unpublished author's data
79	9.215	1.03	0.98	4.43	0.17	0.25	0	0	0.07	0	0	0.1	Wiewióra A., 1978
80	9.228	1.05	1.05	4.51	0.14	0.17	0	0	0.02	0	0	0.11	Wiewióra A., 1978
81	9.336	1.364	1.451	1.295	3.116	0	0	0.084	0	0	0	0.046	unpublished author's data
82	9.228	0.944	0.694	4.175	0.109	0.269	0.128	0	0.011	0	0	0.073	Zheng H., Bailey S. W., 1989
83	9.228	0.944	0.694	4.175	0.109	0.269	0.128	0	0.011	0	0	0.073	Zheng H., Bailey S. W., 1989

(b) Di-tri- and di-dioctahedral chlorites

	b	R^{IV}	Al	Mg	Fe^{2+}	Fe^{3+}	Cr	Mn	Ni	Zn	Li	□	References
1	9.058	1.14	2.98	1.95	0.14	0.08	0	0	0	0	0	0.85	Aleksandrova V. A. et al., 1973a
2	8.956	0.86	4.1	0.08	0.01	0.04	0	0	0	0	0.26	1.51	Aleksandrova V. A. et al., 1973b
3	9.06	0.94	2.45	2.54	0.01	0.03	0	0	0	0	0	0.97	Alysheva E. I. et al., 1977
4	9.034	0.7	2.7	2.3	0	0	0	0	0	0	0	1	Bailey S. W., Tyler S. A., 1960
5	9.216	0.939	0.278	4.563	0.06	0.013	0.46	0.001	0.029	0	0	0.588	Besnus Y. et al., 1976
6	9.314	1.52	1.52	0.32	3.46	0.04	0	0	0	0	0	0.63	Brindley G. W., 1951
7	9.054	1.14	2.9	1.96	0.22	0	0	0	0	0	0	0.96	Drits V. V., Lazarenko E. K., 1967
8	8.94	0.88	4	0.24	0	0	0	0	0	0	0	1.76	Drits V. V., Lazarenko E. K., 1967
9	8.89	0.915	3.9	0.11	0	0.015	0.005	0.01	0	0	0.815	1.09	Černý P., 1970
10	8.885	0.96	3.8	0.135	0	0.015	0	0	0.005	0	1.13	0.85	Černý P., 1970
11	9.07	0.7	2.7	2.3	0	0	0	0	0	0	0	1	Eggleston R. A., Bailey S. W., 1967
12	9.08	0.99	2.84	1.91	0.02	0.19	0	0.02	0	0	0	1.02	Fransolet A.-M., Bourgignon P., 1978
13	9.083	1.01	2.88	1.94	0	0.17	0	0.02	0	0	0	1	Fransolet A.-M., Bourgignon P., 1978
14	9.042	0.57	2.7	1.97	0.04	0.09	0	0	0	0	0	1.2	Frenzel G., Schembra F. W., 1965
15	8.93	1.05	3.89	0.02	0.05	0	0	0	0	0	1.11	0.865	Ginzburg A. I., 1953
16	9.05	0.739	3.017	1.175	0.033	0.345	0	0.004	0	0	0	1.39	Hayashi H., Oinuma K., 1967
17	9.19	1.118	2.351	2.905	0	0.012	0	0	0	0	0	0.623	Hayashi H., Oinuma K., 1967
18	9.18	1.214	1.337	2.226	0.288	0.693	0	0	0	0	0	1.409	Hayashi H., Oinuma K., 1967
19	9.063	0.991	2.924	1.885	0.124	0.076	0	0.024	0	0	0	0.97	Kramm U., 1980
20	9.067	1.001	2.829	2.002	0	0.184	0	0.001	0	0	0.015	0.97	Lin Cheng-yi, Bailey S. W., 1985
21	9.09	0.7	2.86	1.92	0.13	0	0	0	0	0	0	1.09	Percival J. B., Kodama H., 1989
22	8.929	0.73	4.02	0.013	0	0.003	0	0	0	0	0.66	1.287	Ren S. K. et al., 1988
23	8.92	1.04	3.97	0	0	0	0	0	0	0	1.11	0.9	Sahama Th. G. et al., 1968
24	8.957	0.92	3.961	0.017	0	0.007	0	0	0	0	0.979	1.036	Shimada N. et al., 1985
25	9.054	0.8	3.2	1.6	0	0	0	0	0	0	0	1.2	Shirozu H., 1978
26	9.054	0.978	3.049	1.786	0	0.059	0	0	0	0	0	1.085	Shirozu H., 1978
27	9.054	0.715	3.075	1.186	0.033	0.348	0	0.004	0	0	0	1.354	Shirozu H., 1978
28	9.3	1.8	1.2	2.6	0.3	1.5	0	0	0	0	0	0.5	Steinfink H., 1958a
29	8.9	0.62	3.96	0	0.04	0.09	0	0	0	0	0.7	1.21	Vrublevskaja, Z. V. et al., 1975
30	9.207	1.64	3.14	1.8	0	0.1	0.12	0	0	0	0	0.84	unpublished author's data
31	8.93	1.02	3.77	0.06	0.12	0.15	0	0	0	0	1.27	0.65	Zvyagin B. B., Nefedov E. I., 1954

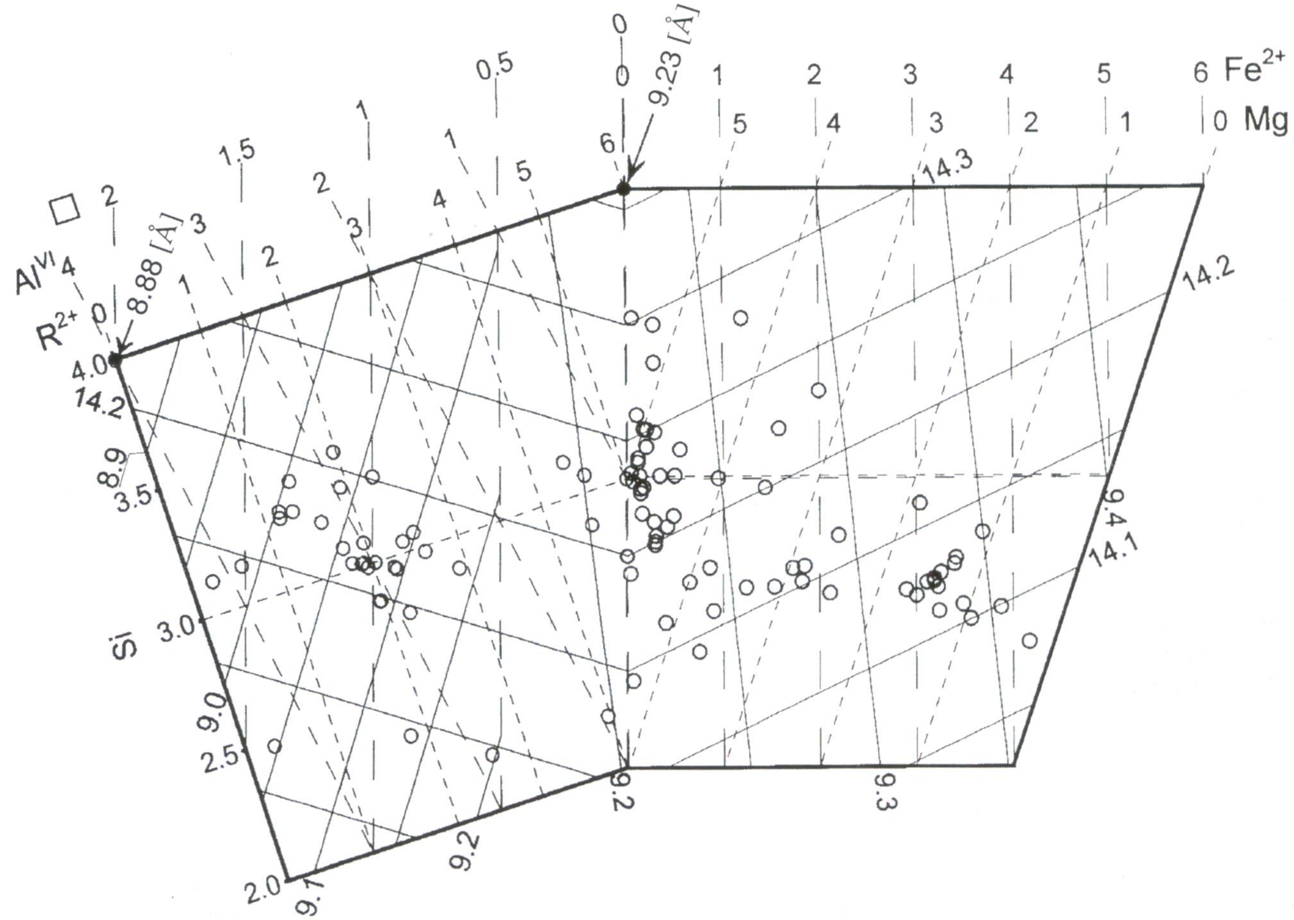

Fig. 1. $d_{(001)}$ and *b* isolines in the diagram of the chlorite composition normalized to $O_{10}(OH)_8$ in the coordinate system Si-Mg-Fe^{2+}(R^{2+})-Al^{VI}-□ (□=octahedral vacancies). Solid circles designate compositions for trioctahedral, di-tri- and di-dioctahedral chlorites for which the calculated *b* values are represented by the intercept in equations *(1)* and *(2)*. Open circles designate projection points of reference data (Table 1).

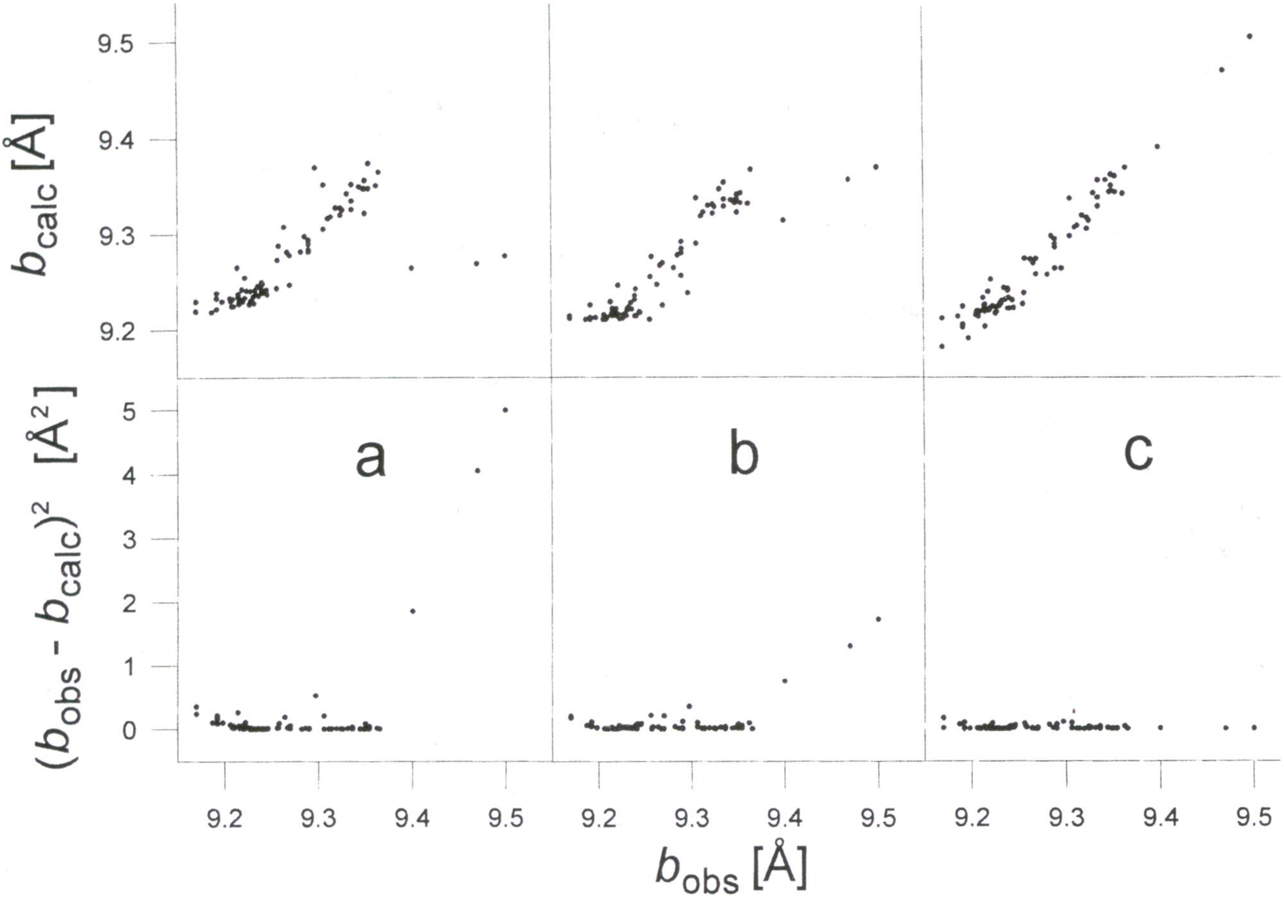

Fig. 2. Plots of b_{calc} and of square of residuals vs. b_{obs} for the trioctahedral chlorite specimens (Table 1a): (**a**) *b* from Kepezhinskas (1965); (**b**) *b* from Brindley (1961); (**c**) *b* from this work, equation *(1)*.

ability of all the chlorite samples used for the calculation of regression equations. Chemical analyses of lithium-bearing chlorites, after recalculation according to the rule: $2Mg^{2+}=Al^{3+}+Li^{+}$ (Raussel-Colom et al. 1991) were also put on this common diagram. A list of *b* values, compositions and references is given in Table 1.

Taking into account the different geometry of octahedral sheets one obtains two regression equations: one for trioctahedral and one for di-tri- and di-dioctahedral chlorites. For the trioctahedral chlorites, the intercept value corresponds to the chemical composition of a theoretical Mg-chlorite end-member. The intercept value of the equation for the dioctahedral chlorites refers to a purely alumineous chlorite end-member (Fig. 1).

Trioctahedral chlorites (□< 0.5)

Multiple regression analysis has been performed for the unit cell *b* parameter and compositions, by using the computer program Statistica for Windows (ver. 4.3). The number of variables was 11 including the dependent variable *b* and the vacancy. The raw data preparation for the statistical computation was described by Raussel-Colom et al. (1991). In total, 83 compositions were considered (Table 1a). Table 2 gives the descriptive statistics and the correlation matrix for the input variables. Tetrahedral occupancy may be expressed in number of Si atoms or tetrahedral Al atoms (in vast majority of cases only Al is present in tetrahedra). Because of colinearity with Al^{IV}, Si was then excluded from the set of variables. The correlations marked with a star are significant by a *p-level* of 0.05 and they were included in the regression model. The value of the *p-level* = 0.05 means that the probability of an error, involved in accepting the observed result as representative of the population, equals 5%. Mg was not considered as an independent variable because the $Mg_6Si_4O_{10}(OH)_8$ was considered to be the departure composition and thus the Mg and Si effect on *b* parameter was enclosed in the value of the intercept. Thus, for the computation of the linear regression equation, the following independent variables were chosen: Al^{IV}, Al^{VI}, Fe^{2+}, Cr and Mn. The resulting equation is:

$$b=9.225+0.0270Al^{IV}-0.0386Al^{VI}+0.0376Fe^{2+}-0.0376Cr^{3+}+0.0665Mn^{2+} \quad (1)$$

with *b* in Å and the compositional variables in numbers of atoms per half formula unit i.e. $O_{10}(OH)_8$.

The value of the tolerance test was set to 0.01 in order to exclude redundant variables. A multiple R factor equal

Table 2: Multiple regression analysis for trioctahedral chlorites.

Correlations

	b	Al^{IV}	Al^{VI}	Mg	Fe^{2+}	Fe^{3+}	Cr	Mn	Ni	Zn	□
b	1.00										
Al^{IV}	0.39 *	1.00									
Al^{V}	0.29 *	0.57 *	1.00								
Mg	-0.84 *	-0.46 *	-0.57 *	1.00							
Fe^{2+}	0.65 *	0.38 *	0.45 *	-0.80 *	1.00						
Fe^{3+}	0.17	0.23 *	-0.13	-0.26 *	0.02	1.00					
Cr	-0.28 *	-0.19	-0.56 *	0.41 *	-0.31 *	-0.17	1.00				
Mn	0.63 *	0.14	0.09	-0.35 *	-0.12	0.05	-0.09	1.00			
Ni	-0.12	-0.12	-0.04	-0.07	-0.08	-0.02	-0.05	-0.03	1.00		
Zn	0.09	-0.22 *	0.05	-0.21	-0.03	-0.08	-0.06	0.16	-0.02	1.00	
□	0.05	-0.04	0.41 *	-0.34 *	0.21	0.16	-0.31 *	-0.09	-0.01	0.17	1.00

Marked correlations are significant at $p < 0.05$
N = 83 (casewise deletion of missing data)

Descriptive statistics

	Mean	Minimum	Maximum	Std.Dev.
b	9.2668	9.170	9.500	0.0644
Al^{IV}	1.1643	0.447	1.800	0.2872
Al^{VI}	1.0776	0.190	2.140	0.4128
Mg	3.0956	0.139	5.175	1.7171
Fe^{2+}	1.1554	0.000	4.170	1.3270
Fe^{3+}	0.2368	0.000	3.700	0.4569
Cr	0.0595	0.000	0.700	0.1537
Mn	0.1596	0.000	4.295	0.6940
Ni	0.0410	0.000	2.615	0.2885
Zn	0.0458	0.000	2.500	0.3077
□	0.1055	-0.050	0.400	0.1183

Analysis of variance

	Sum of squares	df	Mean square	F
Regression	0.3244	5	0.0649	309.779
Residual	0.0161	77	0.0002	

tolerance = 0.01
df = degrees of freedom, F = regression mean square/residual mean square.

Regression summary

Variable	Coefficient	Std. error	t
Intercept	9.22514		
Al^{IV}	0.02698	0.0071	3.81
Al^{VI}	-0.03863	0.0058	-6.65
Fe^{2+}	0.03761	0.0014	26.70
Cr	-0.03760	0.0129	-2.91
Mn	0.06651	0.0024	27.92

Multiple R=0.9760
Std. error of estimation: 0.01447
t = Coefficient/Std. error

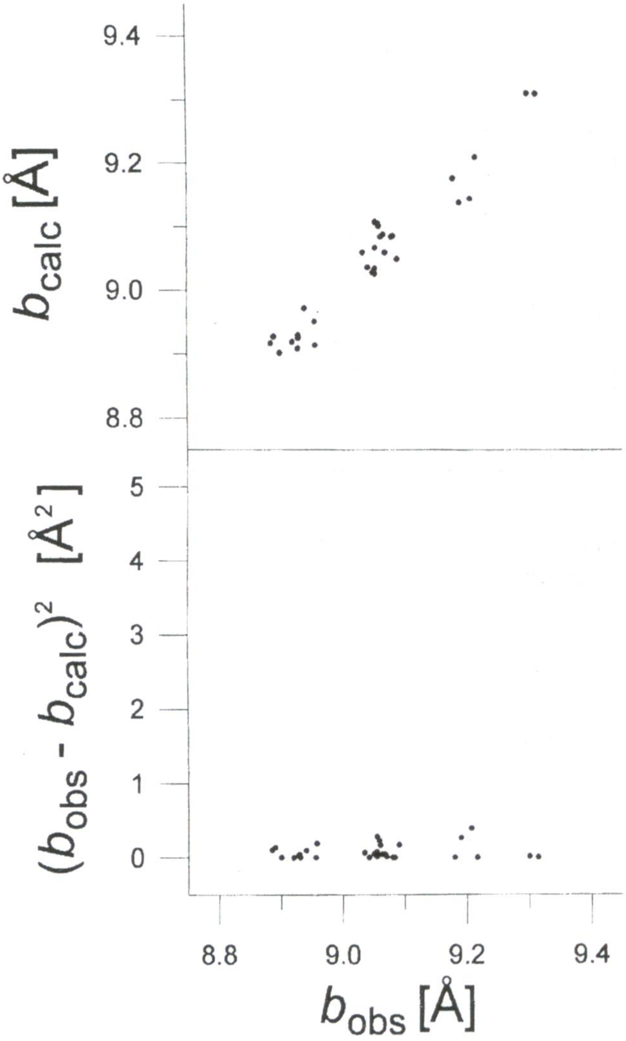

Fig. 3. Plots of b_{calc} (equation *2*) and of square of residuals vs. b_{obs} for the di-tri- and di-dioctahedral chlorite specimens in Table 1b.

0.9760 indicates that more than 95% of the variability in *b* could be explained by this equation. The standard error of estimation is 0.01447 and the F ratio (Regression Mean Square/Residual Mean Square), equals 310.

The value of the intercept 9.225 Å implicitly contains the contribution of Mg and Si to the spacing and corresponds to the basal spacing for the ideal composition $Mg_6Si_4O_{10}(OH)_8$, the theoretical end-member talc-chlorite (Fig. 1). The coefficients are both positive and negative and this implies that the intercept value does not reflect the minimum or maximum of the possible *b* values. It may be

Table 3 Multiple regression analysis for di-tri and di-dioctahedral chlorites

Correlations

	b	Al^{IV}	Al^{VI}	Mg	Fe^{2+}	Fe^{3+}	Cr	Mn	Ni	Li	□
b	1.00										
Al^{IV}	0.62 *	1.00									
Al^{VI}	-0.88 *	-0.40 *	1.00								
Mg	0.69 *	0.14	-0.81 *	1.00							
Fe^{2+}	0.48 *	0.42 *	-0.35	-0.14	1.00						
Fe^{3+}	0.47 *	0.52 *	-0.45 *	0.23	0.03	1.00					
Cr	0.33	0.09	-0.52 *	0.52 *	-0.04	-0.08	1.00				
Mn	0.01	-0.03	0.01	0.10	-0.08	0.01	-0.06	1.00			
Ni	0.22	-0.03	-0.51 *	0.47 *	-0.04	-0.09	0.95 *	-0.06	1.00		
Li	-0.69 *	-0.10	0.61 *	-0.72 *	-0.13	-0.21	-0.13	-0.16	-0.05	1.00	
□	-0.45 *	-0.56 *	0.44 *	-0.34	-0.28	-0.15	-0.31	0.02	-0.30	-0.13	1.00

Marked correlations are significant at $p < 0.05$
N = 31 (casewise deletion of missing data)

Descriptive statistics

	Mean	Minimum	Maximum	Std.Dev.
b	9.0502	8.885	9.314	0.1142
Al^{IV}	0.9787	0.570	1.800	0.2786
Al^{VI}	2.9775	0.278	4.100	0.9243
Mg	1.4036	0.000	4.563	1.1415
Fe^{2+}	0.1638	0.000	3.460	0.6175
Fe^{3+}	0.1371	0.000	1.500	0.2919
Cr	0.0189	0.000	0.460	0.0847
Mn	0.0027	0.000	0.024	0.0065
Ni	0.0011	0.000	0.029	0.0053
Li	0.2596	0.000	1.270	0.4427
□	1.0260	0.500	1.760	0.2839

Analysis of variance

	Sum of squares	df	Mean square	F
Regression	0.3666	5	0.0733	74.815
Residual	0.0245	25	0.0010	

tolerance = 0.01
df = degrees of freedom, F = regression mean square/residual mean square.

Regression summary

Variable	Coefficient	Std. error	t
Intercept	8.86020		
Al^{IV}	0.11193	0.02822	3.97
Mg	0.05238	0.00796	6.58
Fe^{2+}	0.07518	0.01166	6.44
Fe^{3+}	0.05998	0.02414	2.48
Li	-0.05229	0.02027	-2.58

Multiple R= 0.9682
Std. error of estimation: 0.03131

seen that the contribution of octahedral Al and/or Cr cause diminishing of the value of *b*, while the contribution of the remaining elements occurring in the equation should cause an increase in *b*.

The reliability of analysis was verified using relation between *b* observed (b_{obs}) and *b* calculated (b_{calc}) as well as ($b_{obs} - b_{calc}$) for our *equation (1)*(Fig. 2c) and the two other published by Kepezhinskas (1965): $b(kX)=9.3274-0.0094Mg^{2+}-0.0195Si^{4+}-0.0220Al^{VI}+0.0208Fe^{3+}+0.0241Fe^{2+}$ (Fig. 2a), and Brindley (1961): $b=9.21+0.037(Fe^{2+}+Mn)$(Fig. 2b). In the upper part of Fig. 2 there are plots of b_{calc} and in the lower part plots of square of residuals: both versus b_{obs}. The grouping of data points on diagrams in Fig. 2 confirms that the accuracy of fitting the experimental points by the equation used in part (c) in Fig. 2 is better than that of (a) and (b). Unlike (c) some of the projection points of (a) and (b) do not plot along the line of the ideal inclination in the upper part, and parallel to the X-axis in the lower part of the diagram. This happens because special chemical compositions represented by these points are not expressed by equations used in (a) and (b). Higher Mn contents underestimate *b* in (a) and (b). Low Mg contents overestimate *b* in (a).

Di-tri- and di-dioctahedral chlorites (□> 0.5)

Unlike trioctahedral chlorites, there have been no published equations expressing *b* as a function of compositional variables for di-tri- and di-dioctahedral chlorites. To obtain the present equation,

$$b=8.860+0.112Al^{IV}+0.0524Mg^{2+}+0.0752Fe^{2+}+0.0600Fe^{3+}-0.0523Li^{+} \qquad (2)$$

chemical compositions of 31 samples were used (Table 1b). In comparison to the case of trioctahedral chlorites, the set of variables was identical with exception of Li in the case of equation 2 (Zn in equation 1). Table 3 lists the details of the multiple regression analysis. R equal 0.9682 indicates, that 93% of the variability in *b* could be explained by equation *(2)*.

The value of the intercept 8.860 Å implicitly contains the contribution of Si and Al^{VI} to the spacing and corresponds to the basal spacing for the ideal composition $Al_4Si_4O_{10}(OH)_8$, a purely alumineous chlorite end-member. The coefficients of Al^{IV}, Mg, Fe^{2+}, and Fe^{3+} are positive, thus the contribution of these elements makes the *b* value greater

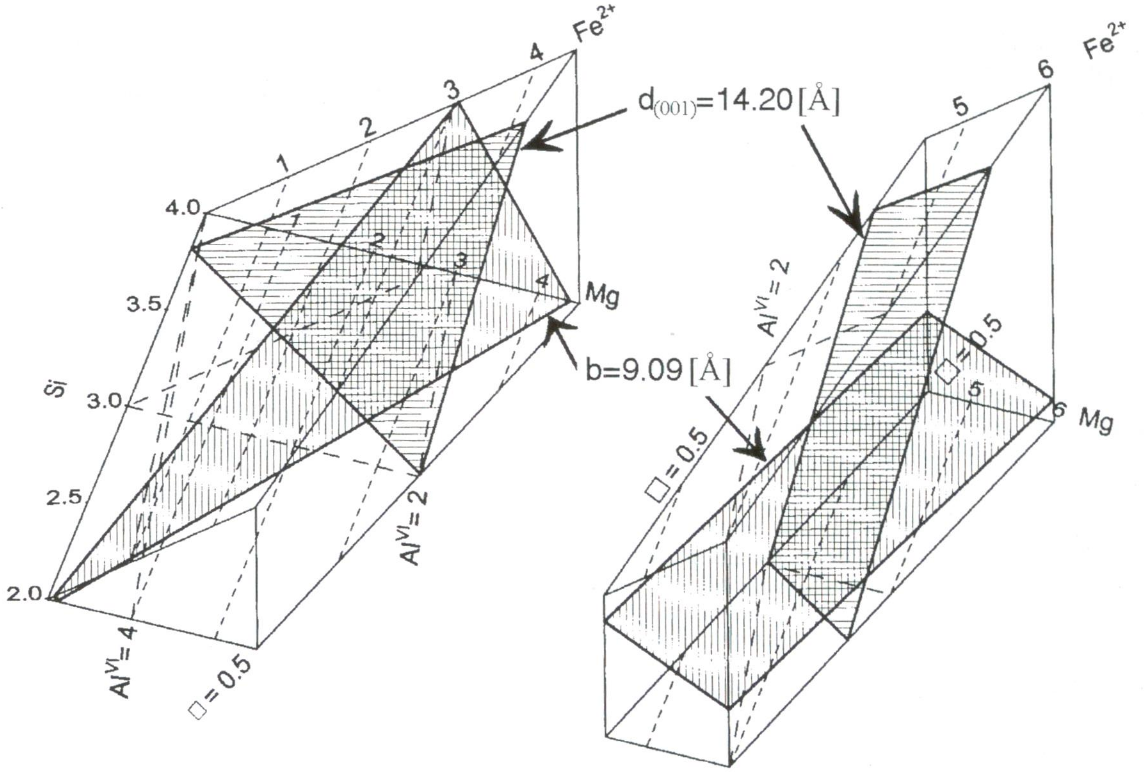

Fig. 4. 3D diagram of trioctahedral (right) and di-tri- and di-dioctahedral (left) chlorite compositions normalized to $O_{10}(OH)_8$ in the coordinate system Si-Mg-Fe^{2+}-Al^{VI}-□(□=octahedral vacancies). The points of the *b* value of 9.09 Å (exemplary value) constitute planes of different position in the left (□>0.5) and right (□<0.5) parts of the diagram. The plane representing the $d_{(001)}$ spacing of 14.20 Å is common for both parts of the diagram.

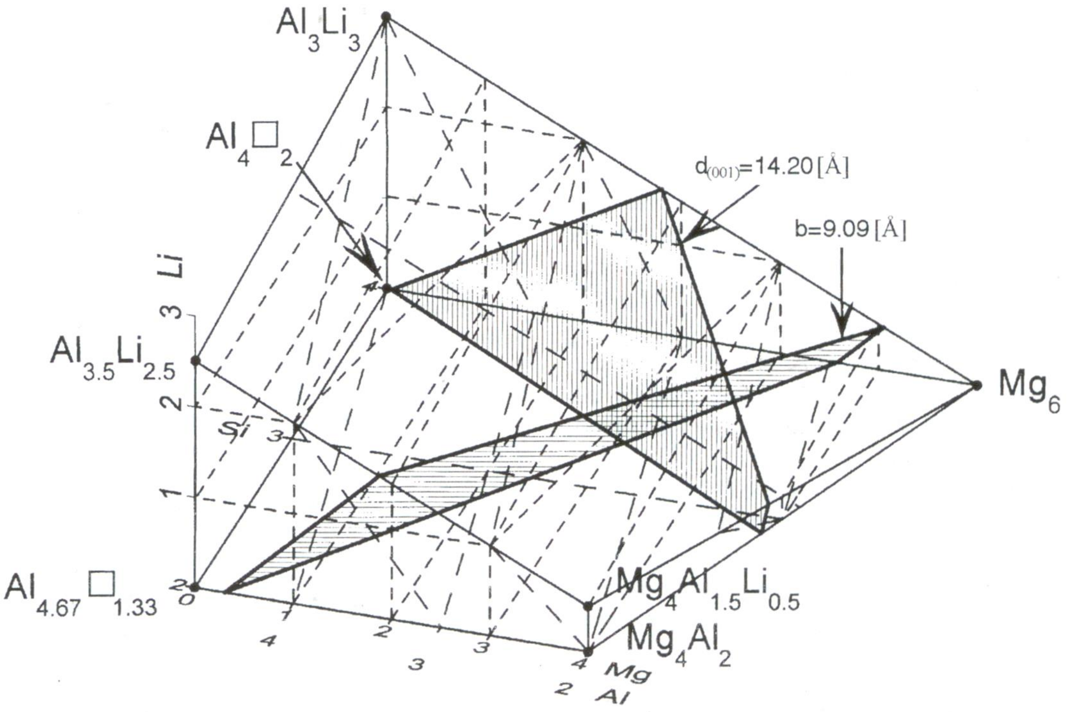

Fig. 5. 3D diagram of chemical composition normalized to $O_{10}(OH)_8$ of lithium-bearing chlorites in the coordinate system Si-Mg-Al^{VI}-Li^+. Two exemplary planes represent points of *b* and $d_{(001)}$ values equal to 9.10 Å and 14.22 Å, respectively.

than the intercept value. Only the contribution of lithium lowers the value of *b*.

As in the case of trioctahedral chlorites Fig. 3 presents plots of b_{calc} vs. b_{obs}, and plots of the square of residuals vs. b_{obs} for di-tri- and di-dioctahedral chlorites. The reliability of fitting is comparable to the fitting for trioctahedral chlorites.

As shown on Fig. 1 lines of constant *b* drawn by using equations *(1)* and *(2)* are oblique and the ranges of variability of *b* on both sides of the line, representing vacancy 0.5, are different. This is in accordance with the pronounced change of the geometry of the octahedral layer as described previously. This phenomenon is also distinctly visible on a 3D diagram (Fig. 4). The range of variability of chemical compositions presented in this diagram corresponds to the left side of the Fig. 1. Fig. 4 was divided into two parts, for better clarity, along the plane of □ = 0.5. The points of the *b* value of 9.09 Å (exemplary value) constitute planes of a different position in two parts of the diagram. Another plane represents the $d_{(001)}$ spacing of 14.20 Å and is common for both parts of the diagram.

The variation of chemical composition of lithium-bearing chlorites might be presented on a separate 3D diagram (Fig. 5). Two exemplary planes represent points of *b* and $d_{(001)}$ values equal to 9.10 Å and 14.22 Å, respectively.

Estimation of the chemical composition of chlorites from XRD data

The classification diagrams of chlorites (Wiewióra & Weiss 1990) together with the plotted lines of the constant *b* and $d_{(001)}=14.359-0.0905Al^{IV}-0.035Al^{VI}-0.0201Fe^{2+}+0.0938Cr^{3+}+0.0283Mn^{2+}-0.0519Li^{+}$ (Raussel-Colom et al. 1991) can be used for estimating the chemical composition of chlorites based on powder diffraction patterns (Fig. 1). For this purpose, the values of *b* and $d_{(001)}$, obtained by the XRD method are to be projected onto the diagram (Fig. 1). These two oblique coordinates determine the composition of interest. Lines of constant values of *b* and $d_{(001)}$ provide an accurate definition of the resulting projection point because they cross at wide angles. Chemical composition of chlorite specimen, represented by this point, can be established by projecting it onto the compositional axes of the diagram.

Although Fig. 1 represents all possible chlorite compositions, lithium content has to be recalculated before plotting on this diagram, as described above. Therefore, a separate diagram is used (Fig. 6) for classifying lithium-bearing chlorites. Lithium content is explicitly expressed as a compositional variable on this diagram.

To the contrary, on the basis of the same diagrams, it is also possible to estimate *b* and $d_{(001)}$ when the chemical composition of chlorites is known.

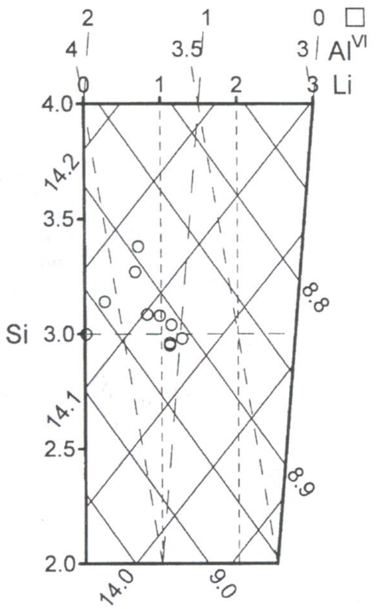

Fig. 6. $d_{(001)}$ and *b* isolines in the diagram of lithium-bearing chlorites in the coordinate system Si-Li^{+}-Al^{VI}-□ (□ =octahedral vacant sites). Open circles designate projection points of reference data (Table 1b).

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