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Relationship between composition and d_{001} for chlorite

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ABSTRACT

The relationship between chemical composition and interplanar spacing d_{001} for chlorite minerals has been determined by multiple regression analysis using data for 98 natural chlorite samples (trioctahedral, di,trioctahedral and dioctahedral). The regression equation is

$$d_{001}\ (\text{Å}) = 14.359 - 0.0905\ {}^{[4]}\text{Al} - 0.035\ {}^{[6]}\text{Al} - 0.0201\ \text{Fe}^{2+} + 0.0938\ \text{Cr}^{3+} + 0.0283\ \text{Mn}^{2+} - 0.0519\ \text{Li}^{+}$$

with the compositional variables as number of atoms per half formula unit, i.e., per $O_{10}(OH)_8$. The multiple R factor for the regression is 0.883, and the standard error of estimation is 0.032. The predictions from the equation above are compared with those from other equations formerly used, and it is concluded that the expression proposed here is best suited for chlorite compositions of the tri-, di,tri-, or dioctahedral series.

INTRODUCTION

The relationship between chemical composition of chlorites and d_{001} and d_{060} interplanar spacings has been studied by Engelhardt (1942), Hey (1954), Shirozu (1958), Brindley (1961), Albee (1962), Radoslovich (1962), and Kepezhinskas (1965). In his review of chlorites, Bailey (1975) provided a summary of the main conclusions of these studies. According to Brindley (1961), d_{001} is correlated with $^{[4]}$Al content by the equation

$$d_{001}\ (\text{Å}) = 14.55 - 0.29x \qquad (1)$$

where x = number of Al atoms per four tetrahedral atoms. Although this equation is currently in use and is recommended for estimation of chlorite composition (Bailey, 1988), several authors (Hey, 1954; Kepezhinskas, 1965; Bailey, 1975, 1988; Whittle, 1986) showed that octahedral composition may affect basal spacings quite independently of $^{[4]}$Al content. For example, Kepezhinskas (1965) proposed the equation

$$d_{001} = 13.496 + 0.232\ \text{Si} - 0.0064\ {}^{[6]}\text{Al} + 0.107\ \text{Fe}^{3+} - 0.001\ \text{Fe}^{2+} + 0.01\ \text{Mg}^{2+} \qquad (2)$$

in which the significance of the octahedral cation population is apparent. Here compositional variables are in numbers of ions per $O_{10}(OH)_8$ and spacings in KX units.

The validity of the most frequently used equations has been tested by Bailey (1975) by comparing the predictions with experimental data for chlorite specimens whose structures had been determined in detail. It was found that the content of both $^{[6]}$Al and total octahedral cations ($^{[6]}$Al + Fe^{3+} + Fe^{2+} + Cr + Mn + Ti + Mg) could be estimated from the interplanar spacings with errors averaging 0.05 atoms per $O_{10}(OH)_8$ for $^{[6]}$Al or Fe^{2+}; errors may increase to 0.1 atoms for some individual determinations. The same author (Bailey, 1988) advises that XRD estimates of composition not be extended to dioctahedral chlorite specimens because the regression equations were derived from data for trioctahedral chlorite. In fact, many chlorite samples considered as trioctahedral have as many as 0.5 octahedral vacant sites per $O_{10}(OH)_8$. Whittle (1986) analyzed 18 sedimentary chamosite samples by XRD and TEM/EDAX and found overestimation of $^{[4]}$Al by Brindley's equation (Eq. 1). He stated that the equation might not be applicable even for trioctahedral chlorite containing some vacancies.

In the present communication, an expression has been derived for the relationship between composition and d_{001} for a large number of chlorite specimens covering a wide range of tri-, di,tri-, and dioctahedral chlorite compositions. It has been found for micas that the b dimension is related to chemical composition as well as to the geometrical characteristics of the octahedral sheet. As the latter are known only for 14 chlorite samples for which crystal structure refinement has been performed, we will not now consider the study of the relationship between b and chemical composition.

COMPOSITIONAL AND XRD DATA

Mineralogical formulas or chemical analyses for over 100 chlorite specimens for which d_{001} had also been measured were obtained from published mineralogical reports. Twelve compositions are from reports of crystal structure refinements, and the remaining data were included after their reliability was critically examined as discussed below.

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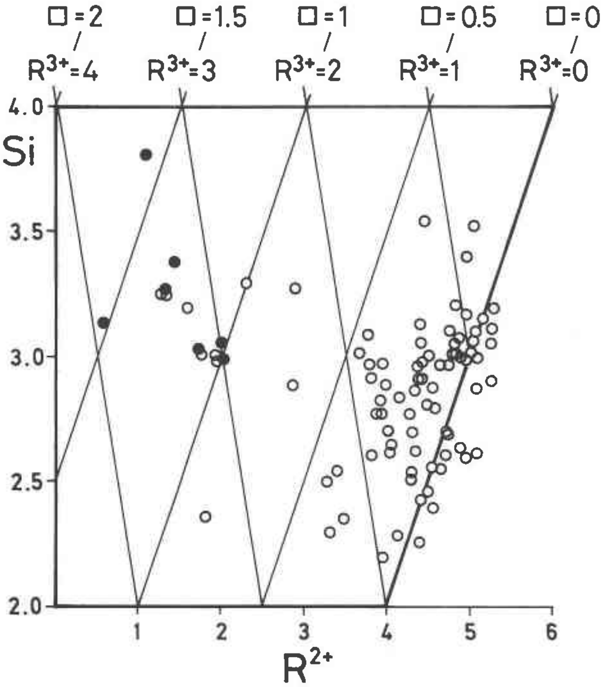

Fig. 1. Plot of the chlorite compositions in Table 1. For the Li-bearing compositions, represented as black points, the coordinates R^{2+} and R^{3+} are taken as $R^{2+} = Mg + Fe^{2+} + Mn + Zn + Ni + Ca + 2Li$; $R^{3+} = {}^{[6]}Al + Fe^{3+} + Cr + \frac{4}{3}Ti - Li$; □ = octahedral vacant sites. Normalized to $O_{10}(OH)_8$.

Most of the reported d_{001} values are based on rational series of 001 reflections extending to ten orders, although in a few cases spacings are based on five orders. All mineralogical formulas were accepted after ensuring their conformity to the general expression

$$^{[6]}(R^{2+}_u R^{3+}_y \square_z)^{[4]}(Si_{4-x}Al_x)O_{10}(OH)_8$$

where R^{2+} and R^{3+} stand for octahedral divalent and trivalent cations, respectively; x, y, and u are numbers of cations in the tetrahedral and octahedral sheets; and z is the number of octahedral vacant sites, represented as □. Thus, $u + y + z = 6$, and if the calculation of the formula from the analytical data is correct, equal values of z should result after computation from either $z = 6 - (u + y)$ or from $z = (y - x)/2$ (Wiewióra and Weiss, 1990). Any significant deviation would indicate that the formula has been normalized to the wrong quantity [i.e., that normalization to $O_{10}(OH)_8$ is incorrect], that there are inaccuracies in the analytical data such as errors in estimation of Fe^{2+}/Fe^{3+}, or that extraneous mineral phases are present as impurities in the analyzed samples. Accordingly, some compositions were rejected because the corresponding analyses indicated appreciably high K_2O or CaO contents.

In other cases, mineralogical formulas were recalculated after correcting the Fe^{3+} content according to the condition $^{[6]}Al + Fe^{3+} = 2z + x$, which is valid only for compositions that do not contain other octahedral trivalent cations such as Cr^{3+}. In this manner, the values of z computed in the two ways mentioned above were as nearly equal as possible. Structure refinements by Phillips et al. (1980) indicated no evidence of Cr^{3+} in tetrahedral coordination for Cr^{3+}-bearing chlorite, and for compositions rich in Cr^{3+}, the formulas of Lapham (1958) were modified by reallocating $^{[4]}Cr^{3+}$ to octahedral sites. A list of d_{001} values, compositions, and references is given in Table 1.[1]

Figure 1 shows the selected compositions plotted in the compositional field for chlorite. The largest population of points falls within the range of trioctahedral chlorites, i.e., between the boundaries for □ = 0 and □ = 0.5, and fewer points are within the range of di,trioctahedral and of dioctahedral chlorites, i.e., between the boundaries for □ = 0.5 and 2. However, most of the compositional field is covered, ensuring a continuous variation of all the important crystallochemical variables. Because Li enters the structure by the substitution 2Mg → Al + Li, all the Li-containing compositions are plotted in Figure 1 by including twice the Li content in R^{2+} and decreasing R^{3+} by the Li content (Wiewióra, 1990). Thus, the tosudite composition of Merceron et al. (1988), $(Al_{3.81}Mg_{0.01}Fe_{0.01}Mn_{0.01}Li_{0.52}Ca_{0.02}\square_{1.62})(Si_{3.81}Al_{0.19})O_{10}(OH)_8$, is rewritten as $(Al_{3.29}Mg_{1.05}Fe_{0.01}Mn_{0.01}Ca_{0.02}\square_{1.62})(Si_{3.81}Al_{0.19})O_{10}(OH)_8$ and plotted at the top left corner of Figure 1 as a black point with coordinates (1.09, 3.81) on the orthogonal axes R^{2+}, Si or coordinates (3.29, 1.62) on the inclined axes R^{3+}, □.

THE REGRESSION EQUATION

Multiple linear regression analysis has been performed for the interplanar spacings and compositions used by means of the program P1R (Dixon, 1983). The number of variables was 12 (d_{001} as dependent variable) after excluding Ti and Ca, whose contents in chlorites are too small to be considered. In total, 98 compositions were considered. Because of collinearity with $^{[4]}Al$, $^{[4]}Si$ was not included as an independent variable. Table 2 gives the univariate statistics and the correlation matrix for the input variables. The variables Mg^{2+} and □ are most highly correlated to other compositional variables, so they can be excluded from the regression model. For the first computation, the variables tested were $^{[4]}Al$, $^{[6]}Al$, Fe^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, and Li^{+}, with the value for the tolerance test set at 0.01. A multiple R factor of 0.88 was obtained, indicating that 78% of the variability in d_{001} could be explained by these variables. The standard error of estimation was 0.0325, and the F ratio was 34. However, the regression coefficients for Fe^{3+} and Zn^{2+} were very small, i.e., less than 0.01, and the corresponding T values were smaller than 1. Also, the coefficient for Ni^{2+} was small (-0.011, with $T = 1.21$). Therefore, these three variables were also excluded from the regression model, and for the

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[1] A copy of Table 1 may be ordered as Document AM-91-468 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 2. Multiple regression analysis

Univariate statistics

Variable	Mean	Standard deviation	Minimum	Maximum
d_{001}	14.1944	0.0659	14.067	14.368
$^{[4]}$Al	1.1217	0.3057	0.190	1.800
$^{[6]}$Al	1.4667	0.9251	0.190	4.100
Mg	2.8683	1.6877	0	5.213
Fe^{2+}	0.8522	1.1743	0	4.170
Fe^{3+}	0.2196	0.2817	0	1.510
Cr	0.0559	0.1451	0	0.700
Mn	0.0850	0.4672	0	3.830
Ni	0.0567	0.3739	0	2.650
Zn	0.0388	0.2834	0	2.500
Li	0.0408	0.1699	0	0.980
□	0.3022	0.4104	0	1.600

Correlation matrix

	d_{001}	$^{[4]}$Al	$^{[6]}$Al	Mg	Fe^{2+}	Fe^{3+}	Cr	Mn	Ni	Zn	Li	□
d_{001}	1.0000											
$^{[4]}$Al	−0.4032	1.0000										
$^{[6]}$Al	−0.5469	−0.1564	1.0000									
Mg	0.6270	−0.0469	−0.6381	1.0000								
Fe^{2+}	−0.4656	0.3393	−0.1429	−0.5299	1.0000							
Fe^{3+}	−0.0096	0.1617	−0.1949	−0.0906	0.1575	1.0000						
Cr	0.5257	−0.0978	−0.3852	0.4513	−0.2506	−0.2357	1.0000					
Mn	0.1264	0.2133	−0.0262	−0.2506	−0.0300	0.0351	−0.0697	1.0000				
Ni	0.0094	−0.0693	−0.0817	−0.0961	−0.0469	−0.0531	−0.0530	−0.0262	1.0000			
Zn	0.1641	−0.1722	−0.0377	−0.1771	−0.0007	−0.1077	−0.0533	0.2400	−0.0209	1.0000		
Li	−0.2960	−0.2923	0.6487	−0.4087	−0.1740	−0.1690	−0.0934	−0.0434	−0.0367	−0.0332	1.0000	
□	−0.3070	−0.4308	0.8930	−0.5528	−0.2354	−0.0069	−0.2453	−0.1063	−0.0904	−0.0220	0.5433	1.0000

Analysis of variance
(tolerance = 0.01)

	Sum of squares	DF	Mean square	*F* ratio
Regression	0.3278	6	0.0546	53.559
Residual	0.0928	91	0.0010	

Regression coefficients

Variable	Coefficient	Std. error	*T*
Intercept	14.35890		
$^{[4]}$Al	−0.0905	0.0120	−7.54
$^{[6]}$Al	−0.0350	0.0052	−6.74
Fe^{2+}	−0.0201	0.0031	−6.45
Cr	0.0938	0.0264	3.56
Mn	0.0283	0.0072	3.94
Li	−0.0519	0.0264	−1.97

Multiple *R* = 0.8828 Std. error of estimation = 0.0319

Note: □ = octahedral vacancies. Normalized to $O_{10}(OH)_8$. DF = degrees of freedom.

final computations, only $^{[4]}$Al, $^{[6]}$Al, Fe^{2+}, Cr^{3+}, Mn^{2+}, and Li^{+} were retained as independent variables. The coefficients, standard errors, and corresponding *T* values are given in Table 2. The multiple *R* factor was 0.883. The analysis of variance yielded an *F* ratio of 54. Consequently, the equation proposed is

$$d_{001} = 14.359 - 0.0905\,^{[4]}\mathrm{Al} - 0.035\,^{[6]}\mathrm{Al} - 0.0201\,\mathrm{Fe}^{2+} + 0.0938\,\mathrm{Cr}^{3+} + 0.0283\,\mathrm{Mn}^{2+} - 0.0519\,\mathrm{Li}^{+} \qquad (3)$$

with d_{001} in Å and the compositional variables in numbers of atoms per half formula unit, i.e., $O_{10}(OH)_8$.

DISCUSSION

Tetrahedral Si^{4+} and octahedral Mg^{2+} contents are not considered as independent variables in Equation 3 because they are collinear with other variables. Therefore, the value of the intercept, 14.36 Å, implicitly contains the contribution of these elements to the spacing and corresponds to the basal spacing for the ideal composition $Mg_6Si_4O_{10}(OH)_8$. With the exception of the coefficients for Cr^{3+} and Mn^{2+}, all other coefficients in Equation 3 are negative, implying that d_{001} for chlorite free of Cr^{3+} and Mn^{2+} should never exceed 14.36 Å. Increasing Cr^{3+} content should result in a large increase in the spacing. Increasing Mn^{2+} content should cause an increase in d_{001} to a lesser extent. Calculated values for d_{001} for ideal end-member compositions in the Mg-Al-□ solid solution series decrease in the sequence clinochlore (14.231 Å) to donbassite (14.127 Å). For intermediate compositions, the spacings are 14.197 Å for Al-rich clinochlore

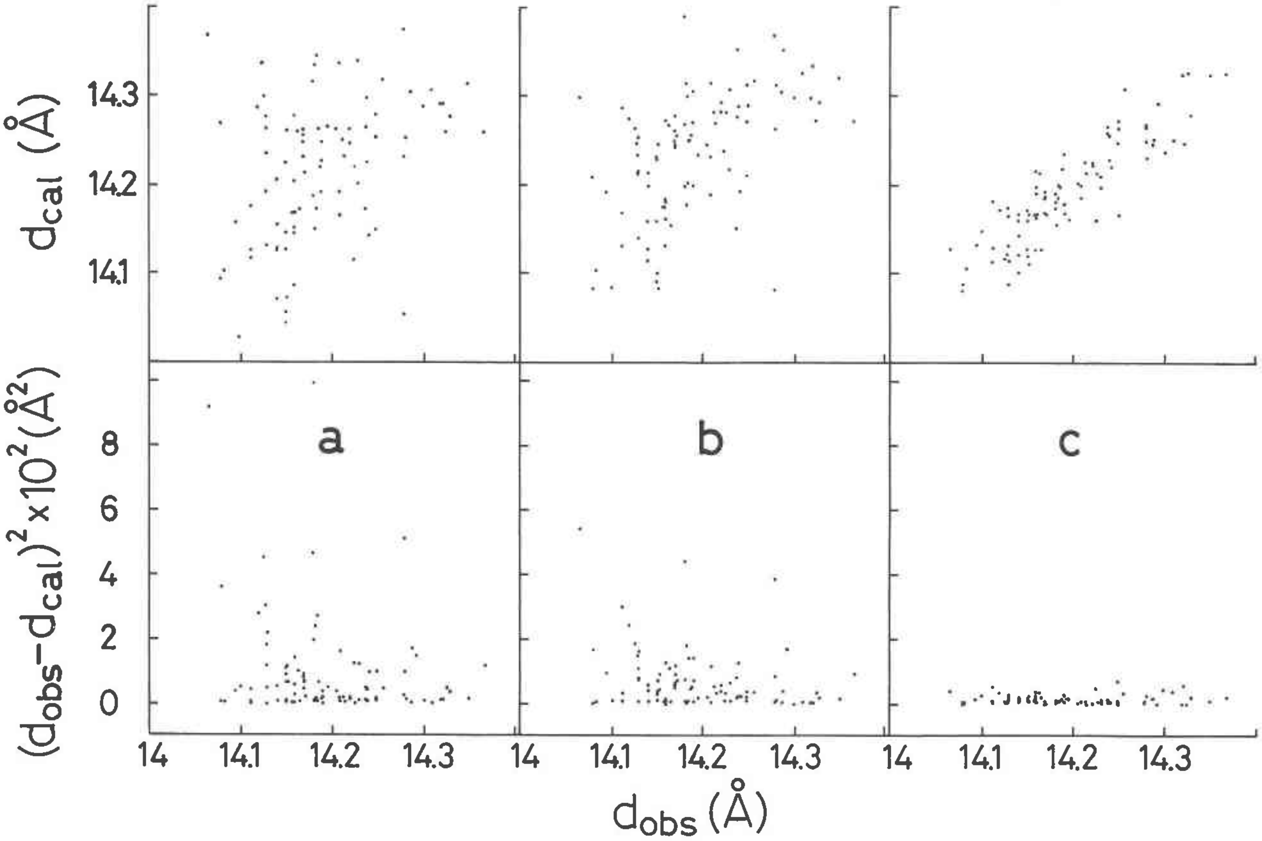

Fig. 2. Plots of d_{cal} and of square of residuals vs. d_{obs} for the chlorite specimens in Table 1: **(a)** d_{cal} from Brindley (1961), Equation 1; **(b)** d_{cal} from Kepezhinskas (1965), Equation 2; **(c)** d_{cal} from this work, Equation 3.

$(Mg_{3.5}Al_2)(Si_3Al)O_{10}(OH)_8$ and 14.162 Å for sudoite. Concerning other common octahedral substitutions, Li^+ markedly reduces d_{001} so that the spacing decreases to approximately 14.08 Å for end-member cookeite. Substitution of Mg^{2+} for Fe^{2+} has a less pronounced effect, and for solid solutions from clinochlore to chamosite the spacing decreases to 14.132 Å.

Comparison with previous results

Equation 3 predicts that d_{001} decreases with increasing $^{[4]}Al$ and $^{[6]}Al$, as is also predicted by previous results (Eqs. 1 and 2, respectively). However, the coefficients in Equations 1 to 3 differ considerably for the same variables. The largest coefficient in Equation 2 (from Kepezhinskas, 1965) corresponds to Fe^{3+}, whereas our regression equation contains no coefficient for this consituent. Weiss (personal communication, 1989) claims that d_{001} values calculated from Equation 2 for Fe^{3+}-rich chlorite compositions are unreasonably high and never observed in natural specimens. Both Equation 3 of this study and Equation 2 of Kepezhinskas have a negative coefficient for Fe^{2+}, but the absolute value for the coefficient is 20 times larger in the former than in the latter.

In view of the different contributions to the spacing for the same compositional variables in Equations 1 to 3, in Figure 2 we compare the observed spacings of Table 1 with those calculated from each equation. Plots of d_{cal} vs. d_{obs} show a rather shapeless array of points for Equation 1, a better grouping for Equation 2, and a well-defined band extending along the ideal 1:1 line for Equation 3

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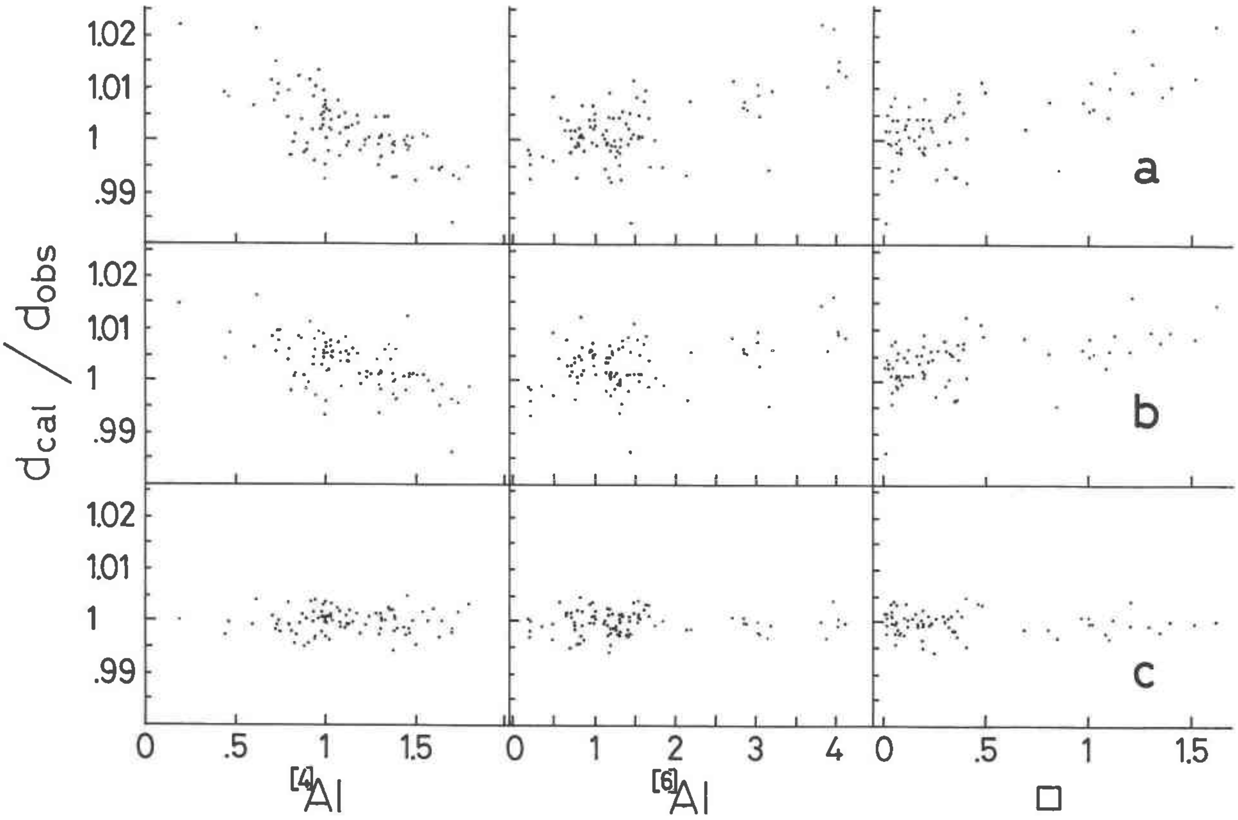
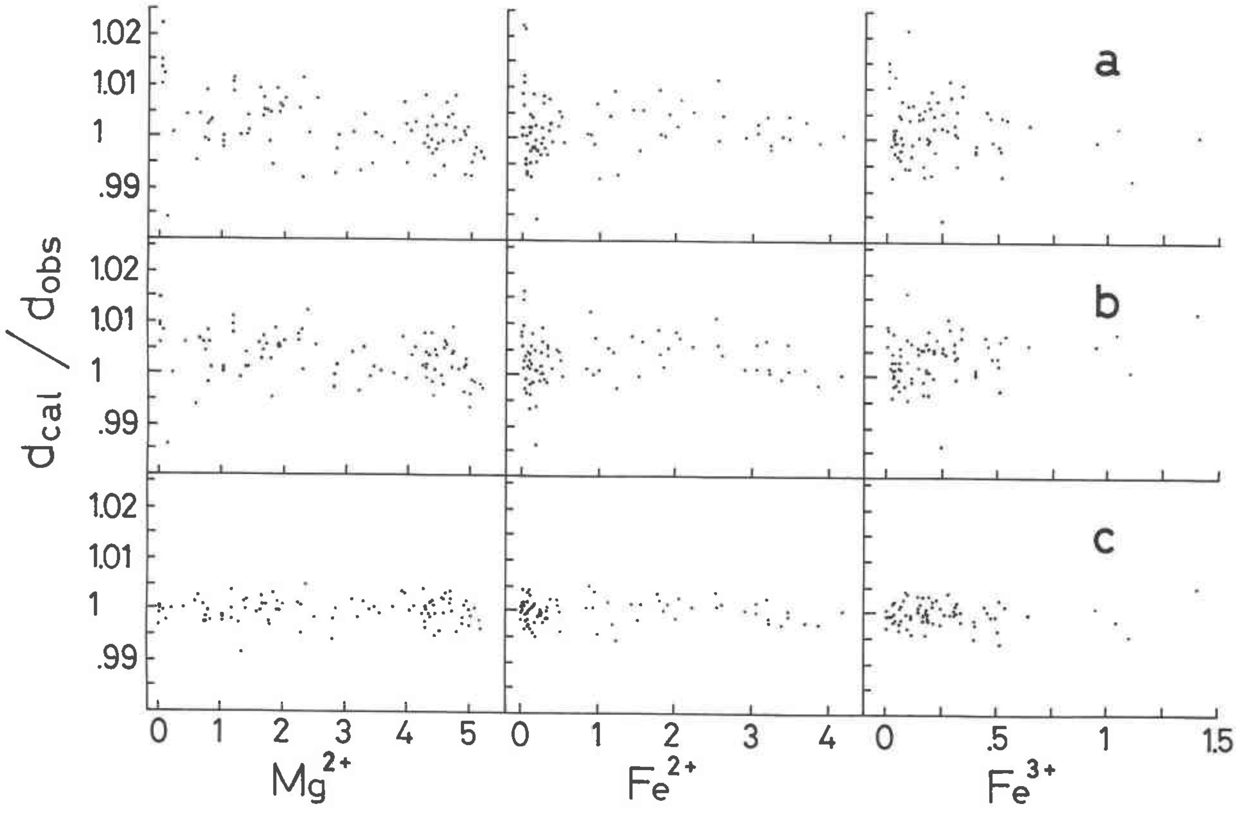
Fig. 3. **(top of next page)** Plots of the ratio d_{cal}/d_{obs} against amount of $^{[4]}Al$, $^{[6]}Al$, and vacancies for the chlorite specimens in Table 1. Normalized to $O_{10}(OH)_8$. Values of d_{cal} in **(a)**, **(b)**, and **(c)** are as in Figure 2.

Fig. 4. **(bottom of next page)** Plots of the ratio d_{cal}/d_{obs} against content of Mg^{2+}, Fe^{2+}, and Fe^{3+} for the chlorite specimens in Table 1. Normalized to $O_{10}(OH)_8$. Values of d_{cal} in **(a)**, **(b)**, and **(c)** are as in Figure 2.


d_{cal} / d_{obs}
1.02
1.01
1
.99
a
b
c
0
.5
1
1.5
2
3
4
[4]Al
[6]Al
□


d_{cal} / d_{obs}
1.02
1.01
1
.99
a
b
c
0
1
2
3
4
5
.5
1.5
Mg2+
Fe2+
Fe3+

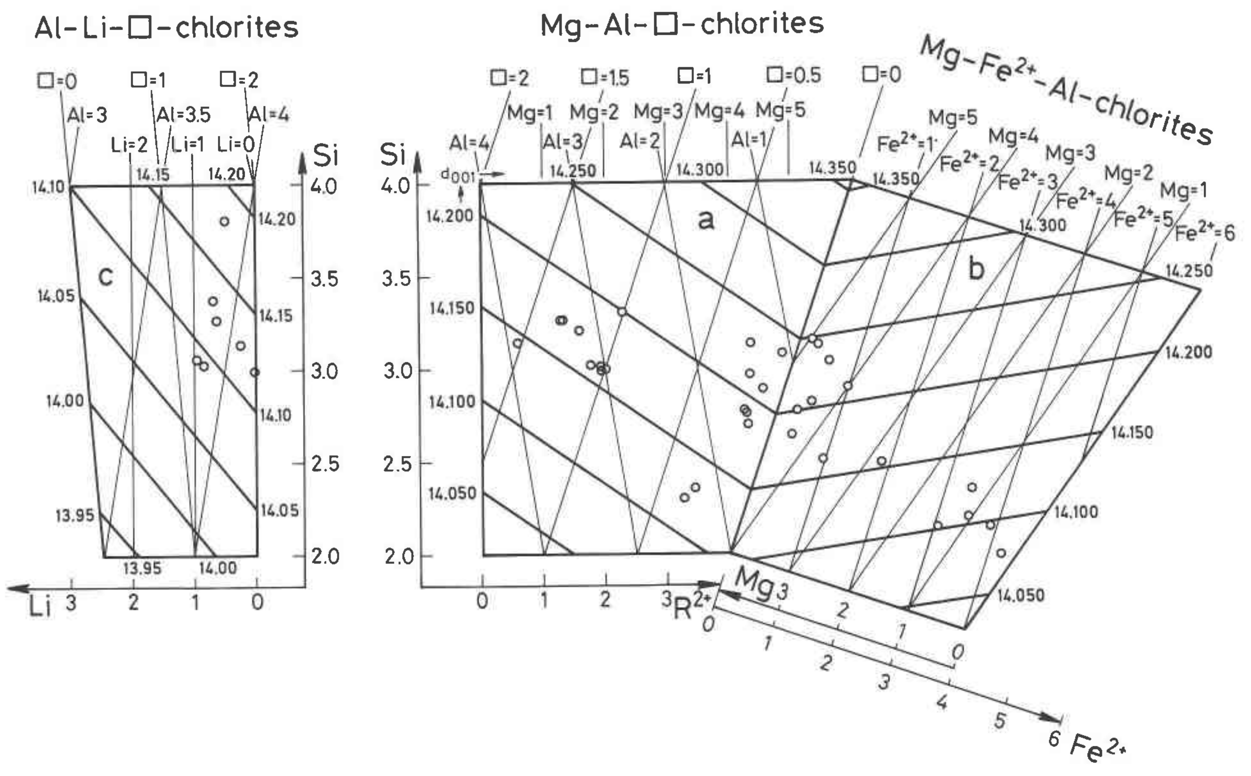


Fig. 5. Lines of constant d_{001} from Equation 3 in diagrams for the field of compositions of chlorites: a: chlorites of the system Mg-Al-□; b: chlorites of the system Mg-Fe^{2+}-Al; c: chlorites of the system Al-Li-□. Compositions of natural chlorites in Table 1 that fit into the respective systems are plotted in the diagrams. Normalized to $O_{10}(OH)_8$.

(Fig. 2, top). Similarly, plots of the square of residuals vs. d_{obs} give the best concentration of points along the line of equation y = 0 for Equation 3 (Fig. 2, bottom).

Chlorite composition vs. d_{cal}/d_{obs}

Except for the case of Equation 3, plots of d_{cal}/d_{obs} against the amounts of $^{[6]}$Al and vacancies (Fig. 3) show a scatter of points along lines of positive slope, indicating that Equations 1 and 2 overestimate the spacing when composition departs significantly from those of trioctahedral chlorites. The opposite trend is observed in plots against $^{[4]}$Al, probably because the coefficient for that element in Equation 1 or for Si in Equation 2 are both too high.

For the other compositional variables (Fig. 4), data are more or less evenly distributed along the line of ideal ratio $d_{cal}/d_{obs} = 1$. Again, the largest deviations are for Equation 1, the smallest for Equation 3, and intermediate values for Equation 2.

CONCLUSIONS

It has been shown in the discussion above that the regression equation proposed here is better suited than the previously proposed Equations 1 and 2 for the range of compositions in Table 1, indicating that it could be safely applied to chlorites of all compositions (tri-, di,tri-, or dioctahedral).

The correlation between d_{001} and composition of Equation 3 may be represented as lines of constant d_{cal} in diagrams showing the range of compositions of chlorites. This has been done in Figure 5 for octahedral compositions of the three series Mg-Al-□, Mg-Fe^{2+}-Al, and Al-Li-□. Plotted points are for the compositions in Table 1 that correspond to the respective series. Values of d_{cal} for any given composition may be obtained from the diagram and compared with the spacing observed. A large departure from d_{obs} indicates that the composition is in error.

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