Supplemental Discussion to

"Structural regularities in 2M_1 dioctahedral micas: the structure modeling approach"

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In the initial review of the manuscript "Structural regularities in 2M_1 dioctahedral micas: the structure modeling approach" a question was raised as to how the various ways of predicting mean octahedral and tetrahedral bond lengths, d(M-O,OH) and d_T, suggested by previous authors compare with Equations 1 and 7 obtained in the present work. A comprehensive discussion on this issue is beyond the scope of the primary paper and is therefore dealt with in the following Supplemental Discussion.

Mean octahedral bond lengths

The coefficients d_i for the equation $d(\text{M-O,OH}) = \sum_i c_i d_i$ suggested by Baur (1981), Weiss et al. (1992), Smoliar-Zviagina (1993), Mercier et al. (2006), and the present authors are listed in Supplement Table 1.

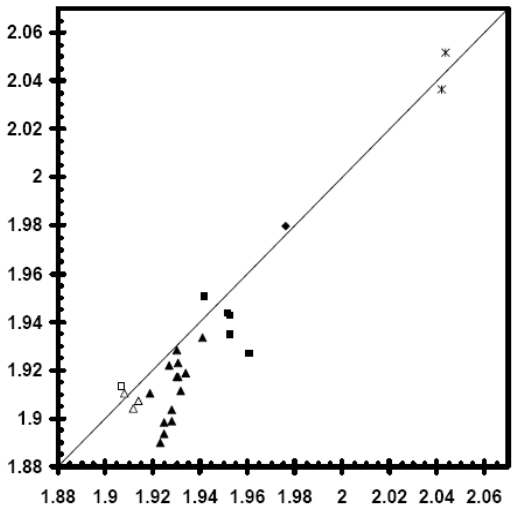
Supplementary Table 1. Coefficients d_i for the equation $d(\text{M-O,OH}) = \sum_i c_i d_i$

Cation	Baur (1981)	Weiss et al. (1992)	Smoliar-Zviagina (1993)	Mercier et al. (2006)	This work
Al	1.909	1.919	0.816+0.214*b**	1.945	1.918
Mg	2.085	2.083	2.060	2.076	2.065
Fe^{2+}	2.136	2.11	2.120	2.126	2.063
Fe^{3+}	2.011	2.053	1.980	2.026	2.028
Ti	-	2.073	1.945	-	1.900
Cr	1.999	2.04	1.950	-	2.000
Mn^{2+}	-	2.14	-	-	2.200
Mn^{3+}	-	-	1.980	-	2.000

* b = unit-cell parameter

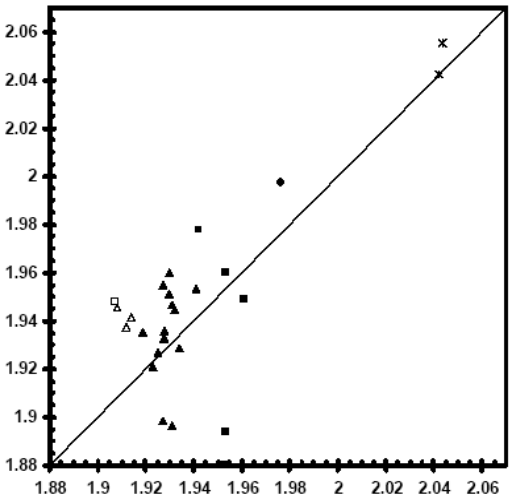
The d_i values of Drits (1969, 1975) are not given, as they were generalized in the equation of Smoliar-Zviagina (1993).

Supplement Figure 1, where the mean octahedral bond lengths calculated using the d_i values of Baur (1981) are plotted against the observed mean octahedral bond lengths in refined dioctahedral mica structures, shows that the predicted d(M-O,OH) values are severely underestimated (on average, by 0.015 Å), with reasonable agreement only for paragonites and margarites.



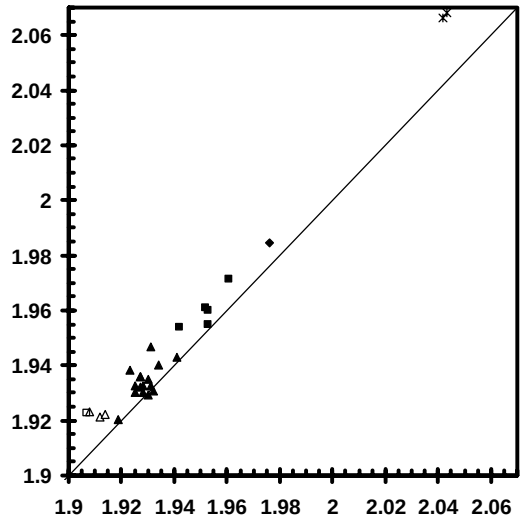
Supplement Figure 1. Comparison of predicted (Baur, 1981) and observed mean octahedral bond lengths *d*(M-O,OH) in dioctahedral micas. Symbols: black triangle = muscovite-2M_1, black square = Fe- and/or Mg-rich muscovite and phengite-2M_1, diamond = aluminoceladonite-2M_1, open triangle = paragonite-2M_1, open square = margarite-2M_1, asterisk =

The d(M-O,OH) values calculated according to Mercier et al. (2006) (Supplement Figure 2) show a wide scatter of points, with esd=0.03 Å and the discrepancies between the calculated and observed values up to 0.04 Å.



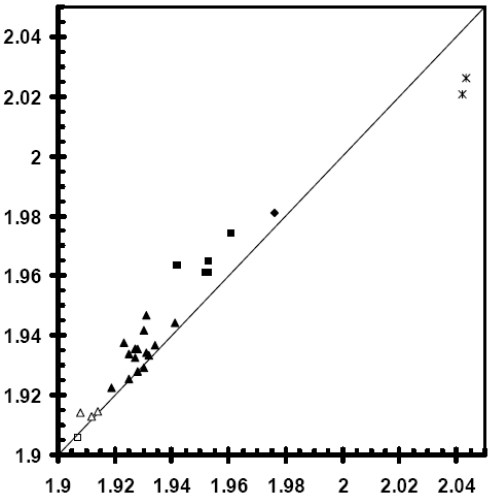
Supplement Figure 2. Comparison of predicted (Mercier et al., 2006) and observed *d*(M-O,OH) values in dioctahedral micas (symbols as in Supplement Figure 1).

The approach of Weiss et al. (1992) provides better agreement between the predicted and observed d(M-O,OH) values, although the latter are systematically overestimated, on average, by 0.008 Å (Supplement Figure 3).



Supplement Figure 3. Comparison of predicted (Weiss et al., 1992) and observed *d*(M-O,OH) values in dioctahedral micas (symbols as in Supplement Figure 1).

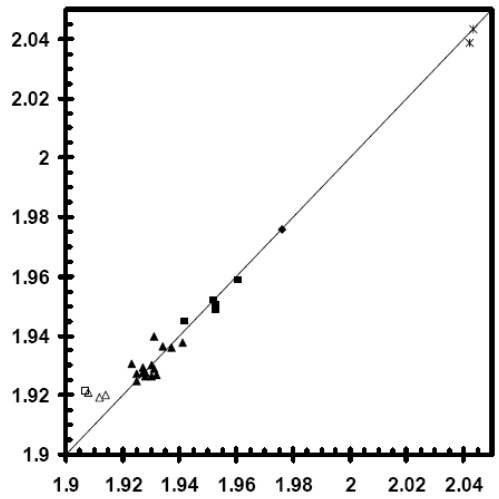
The equation of Smoliar-Zviagina (1993) overestimates the d(M-O,OH) values for dioctahedral micas-2M_1 by, on average, 0.005 Å, and underestimates those for celadonites-1*M* by about 0.02 Å (Supplement Figure 4).



Supplement Figure 4. Comparison of predicted (Smoliar-Zviagina, 1993) and observed *d*(M-O,OH) values in dioctahedral micas (symbols as in Supplement Figure 1).

The equation obtained in the present work (Eq. 1) describes the d(M-O,OH) values in K-dioctahedral micas with esd = 0.003 Å, r^2 = 0.983, p-value $<10^{-10}$, whereas those for paragonites and margarite are overestimated by 0.006-0.014 Å, so that the overall esd and r^2 are 0.005 Å and 0.979, respectively (Supplement Figure 5). The best agreement between the calculated and observed mean octahedral bond lengths in K-dioctahedral micas is therefore provided by

Equation 1 of the present work, whereas the d(M-O,OH) in paragonites and margarites are best described using either the approach of Smoliar-Zviagina (1993) or that of Baur (1981).



Supplement Figure 5. Comparison of predicted (this work) and observed *d*(M-O,OH) values in dioctahedral micas (symbols as in Supplement Figure 1).

Mean tetrahedral bond lengths

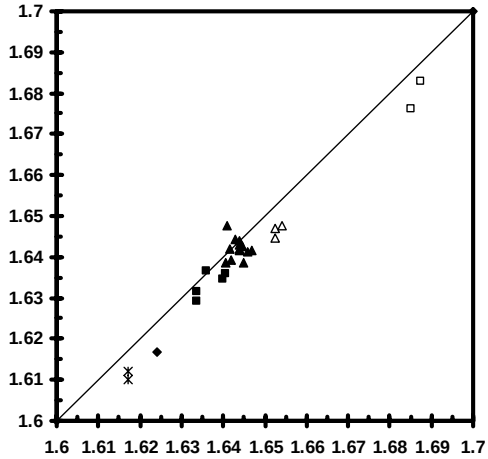
The equations for predicting mean tetrahedral bond lengths suggested in different works including the present study are given in Supplement Table 2.

Supplement Table 2. Equations for predicting mean tetrahedral bond lengths (Si and Al^{IV} are amounts of Si and Al cations in tetrahedra (phfu)).

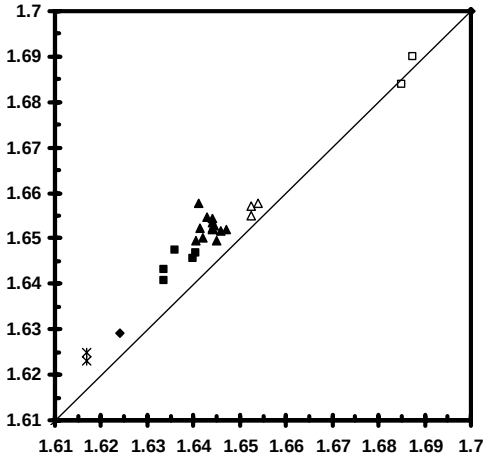
Reference	Equation
Drits (1975)	$d_T = 1.61(Si/4) + 1.75(^{IV}Al/4)$
Baur (1981)	$d_T = 1.623(Si/4) + 1.752(^{IV}Al/4)$
Hazen and Burnham (1973)	$d_T = 1.608 + 0.163(^{IV}Al/4)$
Brigatti and Guggenheim (2002)	$d_T = 1.607 + 0.042\ ^{IV}Al = 1.607 + 0.168(^{IV}Al/4)$
Mercier et al. (2006)	$d_T = 1.610(Si/4) + 1.787(^{IV}Al/4)$
Smoliar-Zviagina (1993)	$d_T = 1.616 + 0.160(^{IV}Al/4)^{1.25}$
This work	$d_T = 1.6192 + 0.1569(^{IV}Al/4)^{1.25}$

The d_T values calculated using the approach of Drits (1975) are systematically underestimated, the average discrepancy between the calculated and observed values being -

0.003 Å, reaching -0.007 to -0.009 Å in the case of aluminoceladonite-2M_1 and celadonites-1M (Supplement Figure 6).



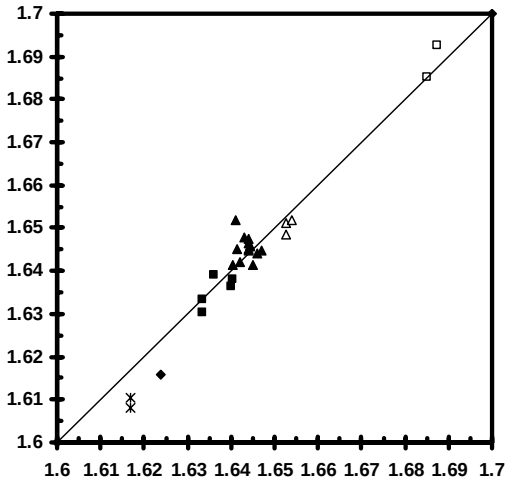
Supplement Figure 6. Comparison of predicted (Drits, 1975) and observed d_T values in dioctahedral micas (symbols as in Supplement Figure 1).



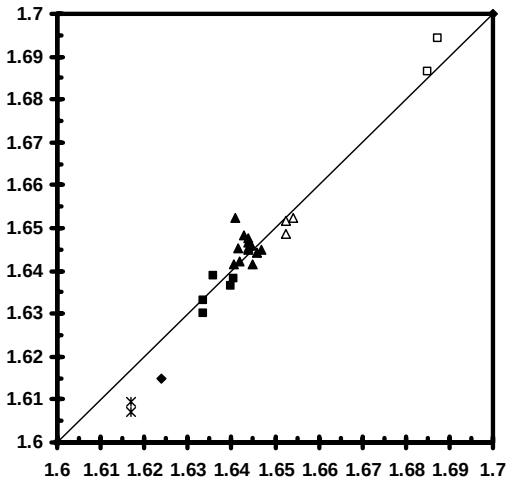
Supplement Figure 7. Comparison of predicted (Baur, 1981) and observed d_T values in dioctahedral micas (symbols as in Supplement Figure 1).

The equation of Baur (1981) provides close agreement between predicted and observed d_T values for paragonites and margarites, whereas the predicted d_T in K-dioctahedral micas are systematically overestimated, on average, by 0.007 Å (Supplement Figure 7).

The equations of Hazen and Burnham (1973) and Brigatti and Guggenheim (2002) are very similar (Supplement Table 2) and therefore lead to virtually identical results (Supplement Figures 8 and 9): good agreement between calculated and observed d_T (esd = 0.004 Å and 0.005 Å, respectively; r^2= 0.95), with the d_T in micas having low tetrahedral Al contents (aluminoceladonite-2M_1 and celadonites-1M) underestimated by 0.007-0.010 Å.

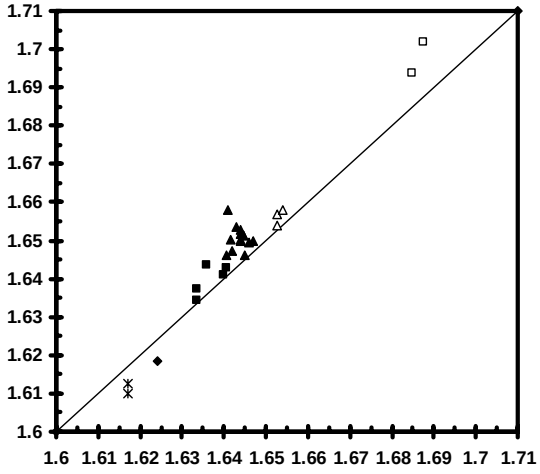


Supplement Figure 8. Comparison of predicted (Hazen and Burnham, 1973) and observed d_T values in dioctahedral micas (symbols as in Supplement Figure 1).



Supplement Figure 9. Comparison of predicted (Brigatti and Guggenheim, 2002) and observed d_T values in dioctahedral micas (symbols as in Supplement Figure 1).

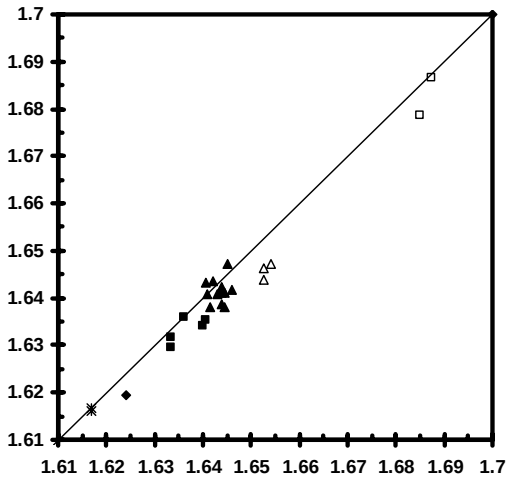
The d_T values calculated using the equation of Mercier et al. (2006) are systematically overestimated (on average, by 0.006 Å, with discrepancies up to 0.017 Å) for all the samples except aluminoceladonite-2M_1 and celadonites 1M, where the d_T are underestimated by up to 0.007 Å (Supplement Figure 10)



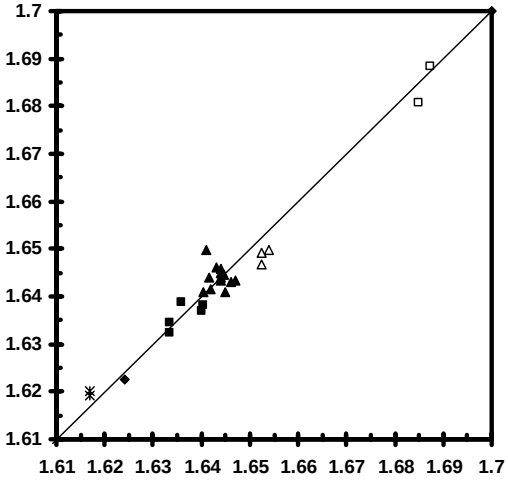
Supplement Figure 10. Comparison of predicted (Mercier et al., 2006) and observed d_T values in dioctahedral micas (symbols as in Supplement Figure 1).

The equatiom of Smoliar-Zviagina (1993) was only slightly modified in the present work to account for contemporary high-precision refined structural data (Supplement Table 2). The two regressions provide similar results (esd = 0.003 Å, r^2 = 0.958, p-value $<10^{-10}$ in both cases) but

that of Smoliar-Zviagina (1993) tends to systematically underestimate the d_T values (on average, by 0.003 Å) (Supplement Figures 11 and 12).



Supplement Figure 11. Comparison of predicted (Smoliar-Zviagina, 1993) and observed d_T values in dioctahedral micas (symbols as in Supplement Figure 1).



Supplement Figure 12. Comparison of predicted (this work) and observed d_T values in dioctahedral micas (symbols as in Supplement Figure 1).

To summarize, Equation 7 of the present work shows the best statistical parameters and describes equally well the d_T at both high and low tetrahedral Al contents, although the regression of Hazen and Burnham (1973)/ Brigatti and Guggenheim (2002) is of comparable predictive quality and provides slightly better agreement between the calculated and observed d_T values in paragonites.

References to Supplemental Discussion

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