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GLADSTONE–DALE CONSTANTS FOR THE MAJOR ELEMENTS IN SILICATES: COORDINATION NUMBER, POLARIZABILITY, AND THE LORENTZ–LORENTZ RELATION

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ABSTRACT

Least-squares analysis of the Gladstone–Dale constants (*GDCs*) on the basis of data from 574 silicates confirms Jaffe's (1988) conclusion that the *GDC* for an oxide in a silicate structure depends on the cation's coordination number. The effect is most prominent for Al and Ca; the *GDC* for $^{IV}Al_2O_3$ is 0.221, and for $^{VI}Al_2O_3$ it is 0.188. The *GDC* for ^{VI}CaO is 0.221, and for ^{VIII}CaO it is 0.205. The new *GDCs* yield better agreement between observed and calculated mean indices of refraction than previous compilations (all but one sample agree to within 4%) and bring the garnets into conformity with the other silicate groups. The Gladstone–Dale relation appears to be a special case of Anderson's (1975) general refractivity equation, applicable to structures with intermediate ionic–covalent bonding.

Keywords: coordination, Gladstone–Dale, Lorentz–Lorentz relation, index of refraction, silicates.

SOMMAIRE

Une analyse selon la méthode des moindres carrés des constantes de Gladstone et Dale tirées des données pour 574 silicates confirme la conclusion de Jaffe (1988), qui avait prédit que la constante d'un oxyde dans une structure silicatée dépend de la coordinence du cation. L'effet est surtout marqué pour Al et Ca. La constante pour $^{IV}Al_2O_3$ est 0.221, et pour $^{VI}Al_2O_3$, 0.188. La constante pour ^{VI}CaO est 0.221, et pour ^{VIII}CaO, 0.205. Les nouvelles constantes de Gladstone et Dale assurent une meilleure concordance entre l'indice moyen de réfraction observé et calculé que les constantes déjà dans la littérature (à ±4% près, sauf dans un cas). Avec ces nouvelles valeurs, les grenats se conforment enfin aux autres groupes de silicates. La relation de Gladstone et Dale serait un cas spécial de la relation générale de la réfractivité de Anderson (1975), qui s'applique aux structures à liaisons à caractère ionique-covalent intermédiaire.

(Traduit par la Rédaction)

Mots-clés: coordinence, relation de Gladstone et Dale, relation de Lorentz-Lorentz, indice de réfraction, silicates.

INTRODUCTION

The concept of refractivity of an ion or oxide in crystalline solids is firmly enshrined in the mineralogical literature through the Lorentz–Lorentz (L–L) and Gladstone–Dale (G–D) relationships. The Lorentz–Lorentz law has a theoretical basis, and has been used in a general way by a number of authors, including McConnell (1965) and Anderson (1975), to demonstrate consistency of optical properties in minerals. Batsanov (1961) summarized extensive analyses of refractivity based on the L–L law, and among other variables demonstrated that the refractivity of an ion pair in a silicate depends on the coordination number of the cation.

In contrast to the L–L law, the Gladstone–Dale relation does not appear to have any theoretical basis, but nonetheless has been widely used by mineralogists. In a major series of publications, Mandarino (1976, 1978, 1979, 1981) developed a new series of empirical Gladstone–Dale constants (*GDCs*) for many constituents, improving on those of Larsen & Berman (1934) and Jaffe (1956). The *GDCs*, g_i, relate the mean index of refraction (n) and density (d) of a phase to its composition, expressed as weight fraction of oxide (w_i), by the equation $(n - 1)/d = \Sigma g_i w_i$.

Mandarino (1979) introduced the concept of "compatibility" as a measure of the degree of agreement between the two sides of the G–D equation. Mineral data for which the agreement lies within 2% he rated as "superior", between 2% and 4%, as "excellent", between 4% and 6%, as "good", between 6% and 8%, as satisfactory, and worse than 8%, as "poor". Mandarino (1981) noted that ortho- and inosilicates seem to require a slightly different set of *GDCs* than were suited to other compounds, and that garnets required yet another set. Bloss *et al.* (1983) examined two sets of accurate data obtained by spindle stage collected from an andalusite-kanonaite suite, and from plagioclase samples. By least-squares analysis, they derived *GDC*s for the component oxides of these minerals, and noted that there was an appreciable difference between their results and those of Mandarino, and that even the *GDC* for SiO_2 ranged from 0.211 for tridymite to 0.188–0.190 for stishovite. Much of the large difference between the results of Bloss *et al.* and Mandarino can be attributed to the use of the least-squares method by the former authors. There are really only two variables in the andalusite–kanonaite series (those appropriate to the two end-member compositions); hence use of four variables allows spurious minima in the least-squares refinement. Almost any values for SiO_2 and Al_2O_3 that give the same sum will provide a "good" set of constants.

Jaffe (1988) presented new Gladstone–Dale constants that take into account valency and coordination number for minerals in general and for a variety of silicate structure-types. He found significant variation in *GDC* with coordination number (for example, from 0.218 for $^{IV}Al_2O_3$, to 0.187 for $^{VI}Al_2O_3$), and with silicate structure-type (for example, from 0.20 for CaO in scapolite to 0.228 for CaO in epidote). Jaffe (1988) did not describe his method for estimating the *GDC*, nor the numbers of minerals used to determine each constant, nor did he indicate how successful the resulting compilations are in terms of compatibility, although it is clear from his examples that the new values are an improvement on previous compilations.

Despite the clear limitations recognized by all the above authors in the application of the G–D relation to minerals, the compatibility concept is routinely used to assess the quality of mineralogical data; it has value in this regard, as well as for estimation of density from indices of refraction and results of chemical analysis, and for its intrinsic worth as an empirical but unfounded relationship. The present study was undertaken initially to establish a *GDC* for Mn_2O_3 in silicates as part of an investigation of a suite of manganese minerals from Grenfell in New South Wales, Australia (Ashley 1986). It became quickly apparent that the existing *GDC*s had only limited applicability to layer silicates, and the scope of the investigation widened.

METHOD AND RESULTS

The accuracy with which an empirical *GDC* can be determined depends on the accuracy of the data. Results of a chemical analysis are generally held to be accurate to within 1%, measurements of indices of refraction, to within 0.5% (0.002 in 0.4 at the low end, 0.005 in 0.8 at the high end), and cell volumes, to about 0.5%. This indicates that the limit on accuracy for a *GDC* would be about 2% if it is derived from a mixed oxide mineral. For simpler compositions, 1% or better may be attainable.

Mandarino (1976), McConnell (1965), and Bloss *et al.* (1983) all pointed out that a major weakness in the application of the G–D relationship was the difficulty in measuring density. These authors avoided the problem by using density calculated from the composition and cell volume. This approach has been followed here; only mineral data providing cell parameters were used, with the exception of a few olivine compositions, for which there are good relationships between composition and volume, and the feldspar data of Bloss *et al.* (1983).

Earlier data were obtained from the compilations by Deer *et al.* (1962, 1963, 1978, 1982, 1986) and in the Russian text "Minerals" (Chukhrov 1981). Data published after those compilations were largely culled from mineralogical abstracts. Hydrous minerals were included only if H_2O was reported in the analysis; both structural and zeolitic water were included. Weight fractions were corrected to total 1.00. Mean indices of refraction were taken as the average of the three principal indices.

It is impossible to separate the methodology of this study from the results, because each result dictates the next step in the method. It is possible that a different pathway could lead to a different result, although other routes tried here did not do so. This study was limited to establishing *GDC*s for the major elements in silicates: H, Li, Be, Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn and Fe. Constants for minor elements (Cs, Rb, Ba, Sr, and other transition elements) were taken from Mandarino's compilation. Minerals containing B, C, N, P, S, Cl and Zr were not included.

The *GDC* for SiO_2 was taken as 0.207, the value derived from quartz, and this was used in all subsequent determinations. Similarly, the value for H_2O of 0.333 was derived from water, and not varied. The polymorphs of Al_2SiO_5 give three different values for Al_2O_3, 0.188 from kyanite, 0.200 from andalusite, 0.205 from sillimanite, consistent with Jaffe's (1988) results. With Al split between 4, 5, and 6 coordinations in the aluminosilicates, the *GDC*s are: 0.188 for $^{VI}Al_2O_3$, 0.211 for $^{V}Al_2O_3$, and 0.222 for $^{IV}Al_2O_3$.

Further calculation of *GDC*s was done with the inclusion of separate variables for Al depending on coordination number, and also for Fe and Mg where in 4-fold coordination (*e.g.*, in akermanite). Constants were independently calculated for the major groups of silicates by least squares using data from 94 garnets, 156 orthosilicates, sorosilicates and cyclosilicates, 54 pyroxenes, 129 amphiboles, 74 layer silicates and 65 framework silicates. At all stages of calculation, oxides present in minor quantities in a mineral group (*e.g*, $^{IV}Al_2O_3$ in orthosilicates) were held constant at a value previously determined, or at the Mandarino (1981) value. Calculations for amphiboles and layer silicates were made after those for the simpler orthosilicates, pyroxenes and framework silicates; oxides whose *GDC* had been established earlier were not varied in these later groups (*e.g.*, MgO, $^{IV}Al_2O_3$, $^{VI}Al_2O_3$). For each group, a subset was taken having less than 1% Fe_2O_3, or Cr_2O_3, or Mn_2O_3, or TiO_2, and these were used to derive *GDC*s for the remaining major oxides (MgO, CaO, FeO, MnO, Na_2O). Constants for other oxides were then derived from the full data-set, with the values for the previously determined oxides held constant. This procedure was adopted because the trivalent transition metals introduce color and high indices, which render measurements of index of refraction more liable to error. The results are tabulated by mineral group in Table 1, where only the oxides varied for that group are listed, with the standard deviations of the *GDC*s in parentheses. The oxides held invariant for a group were set to the value listed in the average column. For all data sets, there is better than 2% agreement for 93% of the minerals used, that is to say the compatibility is superior for 93% of minerals. The constants show quite good agreement with those of Jaffe (1988). Major differences are noted in the discussion.

TABLE 1. GLADSTONE-DALE CONSTANTS FOR SILICATES

Oxide of	ortho-soro-ring-	garnets	pyrox & pyxoids	amphi-boles	layer silic.	frame-works	averages	Jaffe (1988)
H							0.333	0.340
^{IV}Li						0.269(17)	0.269	
^{VI}Li			0.323(11)		0.264(23)		0.3	
Be	0.307(2)						?	0.252
F	0.071(5)				0.086(20)		0.075	0.043
^{V}Na			0.184				0.184	
^{VI}Na	0.165(12)						0.179	
^{VIII}Na			0.162(7)	0.127(9)*	0.098(22)*	0.155(45)	0.158	0.178
^{IV}Mg	0.222(7)						0.222	0.241
^{VI}Mg	0.197(1)		0.196(2)		0.189(3)		0.196	0.200
^{VIII}Mg		0.195(3)					0.195	0.201
^{IV}Al	0.226(2)					0.218(2)	0.221	0.218
^{V}Al	0.212(2)						0.212	
^{VI}Al	0.188(1)		0.184(2)				0.188	0.187
Si						0.207	0.207	0.206
K					0.152(7)	0.185(3)	0.17	0.186
^{VI}Ca	0.221(1)		0.218(2)	0.211*			0.220	0.226
^{VIII}Ca		0.205(2)			0.203(8)	0.207(5)	0.205	0.215
^{IV}Ti		0.461(12)					0.46	
$^{VI}Ti^{4+}$	0.353(6)			0.336			0.340	0.398
$^{VI}Ti^{3+}$			0.294(11)				0.30	
V		0.331(6)					0.33	0.247
Cr^{3+}		0.242(5)	0.246(8)				0.244	0.229
$^{VI}Mn^{2+}$	0.188(1)		0.185(2)				0.186	0.190
$^{VIII}Mn^{2+}$		0.176(2)					0.176	
Mn^{3+}	0.267(4)	0.270					0.269	0.259
$^{IV}Fe^{2+}$	0.199(10)						0.199	0.205
$^{VI}Fe^{2+}$	0.187(1)		0.188(2)	0.180*	0.186		0.187	0.185
$^{VIII}Fe^{2+}$		0.180(2)					0.180	0.180
Fe^{3+}	0.285(5)	0.281(2)	0.276(3)	0.251*	0.262		0.277	0.280
Number	156	94	56	129	74	65	574	
Superior	149	88	54	112	65	65	533	
Excellent	7	6	2	17	8	0	40	
Good					1		1	
Superior	96%	94%	96%	87%	88%	100%	93%	

* not included in average, largely because of uncertainty in coordination number.

DISCUSSION

The Gladstone–Dale constants

Na_2O: From synthetic $Na_2Si_2O_6$, 5-coordinated Na yields a *GDC* of 0.184. Octahedrally coordinated Na in cyclosilicates yields a *GDC* of 0.179. From pyroxenes, the *GDC* is 0.162, for amphiboles, 0.127, for layer silicates, 0.098, and for framework silicates, the *GDC* is 0.155. Jaffe's average value for $^{VII}Na_2O$ is 0.178, but it is not clear how this figure was derived. Because *GDC*s for a compound are additive, some difference in the result for framework silicates is to be expected because of difference in the values found for $^{IV}Al_2O_3$ (0.226 for layer silicates, 0.218 for framework silicates).

MgO: Six-fold Mg occurs in olivines and pyroxenes; both data sets yield 0.196. Pyrope has Mg in 8-coordination; a least-squares analysis of 93 garnets with the *GDC*s for SiO_2 and $^{VI}Al_2O_3$ held invariant yields 0.195 for MgO, not significantly different from the value for ^{VI}MgO. Akermanite has Mg in tetrahedral coordination; the refined *GDC* for MgO is 0.222, somewhat lower than Jaffe's figure of 0.239 for melilite.

Al_2O_3: Al in six-fold coordination to oxygen occurs as a major component in kyanite, topaz, and staurolite among orthosilicates, and in the pyroxenes jadeite, aegirine, and spodumene. Both mineral groups yield a *GDC* for Al_2O_3 of 0.188 by least-squares analysis. Al in four-fold coordination occurs in framework silicates, in cordierite and the osumilite group, and in sillimanite. For the feldspar data-set of Gunter & Bloss (1982), the least-squares method will give equally good results for any *GDC* for Al_2O_3 within reasonable limits because the values for Ca and Na simply adjust to fit the observed indices, and consequently these data cannot define a value for $^{IV}Al_2O_3$. A data-set of 65 framework silicates samples yielded a *GDC* of 0.218 for $^{IV}Al_2O_3$. The cordierite–osumilite data and sillimanite (two samples) yield 0.226 for $^{IV}Al_2O_3$, and andalusite samples yield 0.212 for $^{V}Al_2O_3$ with $^{VI}Al_2O_3$ = 0.188. These values for Al_2O_3 were used in all other group refinements, and are similar to Jaffe's.

CaO: From shannonite, larnite, rankinite, and wollastonite, a *GDC* of 0.222 was derived for ^{VI}CaO. In pyroxenes and amphiboles, Ca has six nearest neighbors, and two are somewhat further away; the *GDC*s are 0.218 and 0.211, respectively. In layer silicates, Ca lies in the interlayer space, and has six nearest neighbors, and six further away; the *GDC* is 0.203. Framework silicates have Ca in relatively large cavities with a high coordination number (8, commonly); the *GDC* for CaO in framework silicates is 0.207. From grossular, the *GDC* for ^{VIII}CaO is 0.205. The differences in *GDC* for CaO may be attributed to differences in coordination number. The lower value obtained from amphiboles than from pyroxenes may reflect the more layer-like structure of the amphiboles.

FeO: Many silicates contain octahedrally coordinated Fe^{2+}; the average *GDC* from orthosilicates, pyroxenes, and layer silicates is 0.187. The value derived from amphibole is lower, 0.180, the same as the value found in garnets (0.180), in which Fe^{2+} is in 8-coordination. In melilites and epidotes, Fe^{2+} is in tetrahedral coordination, and these minerals yield a *GDC* for FeO of 0.199.

MnO: A *GDC* of 0.188 for ^{VI}MnO was derived from orthosilicates and pyroxenes. For the 8-fold site in garnet, the *GDC* is 0.176.

TiO_2: Ti in garnet largely substitutes for Si in tetrahedrally coordinated sites (Huggins *et al.* 1977), whereas in pyroxenes and orthosilicates, it is in 6-fold coordination. There is also some question regarding the valence of Ti in silicates, although in the NaTi-pyroxene, Ti is clearly trivalent, and in titanite it is tetravalent. The *GDC*s for TiO_2 vary from 0.465 in garnets to 0.353 in orthosilicates (a value dominated by titanite), and 0.294 in pyroxenes. The variation probably reflects changes in valence and coordination number.

Li_2O and BeO: *GDC*s for these oxides vary widely with mineral group, as can be seen from Table 1. The reason does not appear to be coordination number, as the extreme values are from silicates with Li in octahedral coordination, the intermediate value from tetrahedrally coordinated Li. The *GDC* for BeO ranges from 0.236 in phenacite to 0.307 in beryl, with no change in coordination number.

Mn_2O_3: Trivalent manganese occurs in few silicates; the best known are kanonaite and piemontite; these yield a *GDC* of 0.267. Henritermierite garnet gives a *GDC* of 0.270. The new NaMn-bearing pyroxene described by Lucchetti *et al.* (1988) and Basso *et al.* (1989) also contains Mn^{3+}; the data for this sample give a *GDC* of 0.260. The new mica norrishite (Eggleton & Ashley 1989) gives a *GDC* for Mn_2O_3 of 0.254. Jaffe's figure of 0.259 is said to be applicable to epidote. Until more data become available for Mn^{3+}-bearing silicates, an average figure of 0.265 would seem to be the most appropriate.

Discussion of the silicate groups

Except for Na_2O and CaO, the *GDC*s listed in the "average" column of Table 1 are applicable to all the major groups of silicates, provided the coordination number of the cations is taken into account. Some structures have cations spread over more than one site, and consequently yield an average *GDC*. Amphiboles show this effect most markedly; the relatively large *M*(4) site has some similarity to the interlayer site in a layer silicate, and consequently the *GDC*s for CaO and FeO are significantly lower than in other structures in which Ca and Fe are octahedrally coordinated. The *GDC* for Na_2O decreases from pyroxenes to layer silicates, possibly a result of an increasing number of second-nearest neighbors. However, much of the variation is not significant; the standard deviations for Na_2O are higher than for most other oxides, and holding the *GDC* for Na_2O constant during refinement of the other *GDC*s gives little increase in the sum of the squares of the residuals. Some of the variation may be a consequence of the distribution of Na over the *M*(4) and *A* sites in amphiboles, but the data are not of sufficient quality to assess this hypothesis. CaO shows a similar variation with extent of Si–O polymerization. Excluding garnets, the *GDC* for CaO varies from 0.221 in orthosilicates, to 0.218 in pyroxenes, 0.211 in amphiboles, 0.203 in layer silicates and 0.207 in framework silicates. This variation correlates well with the coordination number for Ca from orthosilicates to framework silicates (Table 2).

TABLE 2. VARIATION OF GLADSTONE-DALE CONSTANTS WITH COORDINATION

	IV	V	VI	VIII
Na		0.184	0.179	0.151
Mg	0.222		0.196	0.195
Al	0.226	0.212	0.188	
Si	0.207		0.189	
Ca			0.221	0.200
Ti^{4+}	0.461		0.340	
Mn^{2+}			0.188	0.176
Fe^{2+}	0.199		0.187	0.180

Comparison with the Lorentz–Lorentz relation

The L–L law has a theoretical basis; it is expressed, following Lasaga & Cygan (1982), as $\Sigma\alpha_i = 3V(n^2 - 1)/4\pi(n^2 + 2)$, where α_i is the polarizability of the i^th^ atom in a molecule, V is the molecular volume (the molar volume in A^3 divided by Avogadro's number, or the unit-cell volume/*Z*, where *Z* is the number of formula units in the cell), and *n* is the mean index of refraction. The units of α_i are thus the same as those of V, A^3 in this case. Some authors express α_i in cm^3, using the molar volume for V. Numerically, the two usages are related by $N/10^{24}$, or 0.6022.

Anderson (1975) developed the L–L law to include the effects of electron overlap, significant where covalent bonding is important, as it is in silicates. Anderson's equation (17) can be expressed as:

$$\frac{(n^2 - 1)\ V}{4\pi + b\ (n^2 - 1)} = \Sigma\alpha_i \tag{1}$$

where $b = 4\pi/3 - c$. In this equation, $4\pi/3$ is the Lorentz factor and accounts for the spherically symmetrical field around a molecule, and *c* is an electron-overlap factor. Anderson pointed out that if *c* is equal to zero, (1) yields the L–L relation, appropriate to ionic crystals. Where electron overlap is significant, as in covalent bonding, *b* may be zero (if $c = 4\pi/3$), yielding the Drude relation, $V(n^2 - 1)4\pi = \Sigma\alpha_i$.

If the electron-overlap term *c* (incorporated in the term *b* of equation 1) is not zero, the denominator of equation (1) varies; in particular, where *c* equals 2.26 (found by trial and error), the denominator of (1) becomes very close to $6\ (n+1)$ for $1.4 < n < 1.8$, the range of *n* for silicates. That is, where *c* equals 2.26, the left side of equation (1) becomes $(n + 1)(n - 1) / 6(n+1) = (n - 1)/6$ (see Table 3).

TABLE 3. COMPARISON BETWEEN $(n-1)/6$ AND $Q = (n^2-1)/[4\pi+b(n^2-1)]$ WHERE $b = 1.93$ (GLADSTONE-DALE), AND SIMILAR COMPARISONS FOR $b = 0$ AND $b = 4\pi/3$ (LORENTZ-LORENTZ)

n	Q $b=1.93$	$\frac{(n-1)}{6}$	Q $b=0$	$\frac{(n-1)}{4.835}$	Q $b=4\pi/3$	$\frac{(n-1)}{7.34}$
1.4	0.0666	0.0666	0.0764	0.0827	0.0578	0.0545
1.5	0.0834	0.0833	0.0995	0.1034	0.0702	0.0681
1.6	0.1001	0.1000	0.1241	0.1241	0.0817	0.0817
1.7	0.1166	0.1167	0.1504	0.1448	0.0922	0.0954
1.8	0.1333	0.1326	0.1782	0.1655	0.1030	0.1090

n is the mean index of refraction.

Thus:

$$V(n - 1)/6 = \Sigma a_i \tag{2}$$

The G–D relation is $(n - 1)/d = \Sigma w_i g_i$. If w_i is replaced by $p_i m_i/M$, where p_i is the number of moles of the i^th^ oxide, m_i the molecular weight of the i^th^ oxide, and M the molecular weight of the mineral, and if *d* is replaced by mass/V, where mass (= M/N) is the unit-cell mass and V the cell volume, then the G–D relation can be recast in a form similar to equation (2): $(n - 1)VN/M = \Sigma p_i m_i g_i/M$. Whence:

$$V(n - 1) = \Sigma p_i m_i g_i/N \tag{3}$$

Combining with equation (2):

$$\Sigma\alpha = \Sigma p_i m_i g_i/6N(A^3) \tag{4}$$

Thus the polarizability is simply related to the G–D constants, and is directly proportional to the index of refraction where *c* equals 2.26. This result suggests a reason for the success of the G–D relation. By chance (?), it fits the theoretical relation if covalent bonding is significant. Other values of *c* do not match the G–D relation as well over the range in index of refraction of minerals (see Table 3) and require a factor different from 6. Jaffe (1988) listed the polarizability of a number of minerals using the G–D relation, and assumed that the Lorentz factor $4\pi/3$ was appropriate. As the derivation from Anderson's equation shows, the G–D relation requires a factor of about 6; thus Jaffe's figures for polarizability are larger than those indicated here by about 1.5.

The simple oxides MgO, CaO, Al_2O_3 and TiO_2 themselves yield significantly different polarizabilities from those found for these oxides in silicates (Table 4). Use of a smaller value for *c* in equation (1) brings these polarizabilities into conformity, and so implies a more ionic bond for the simple oxides. For this argument to have any significance, it must be assumed that the Gladstone–Dale relation is valid for structures with the degree of electron overlap found in silicates, and therefore that the oxide polarizabilities derived from its use are correct for all oxide structures. Compounds with a degree of ionicity different from that in silicates can therefore have their ionicity assessed by determining *b* from the indices of refraction and molar volume using equation (1).

TABLE 4. POLARIZABILITY (α) FOR OXIDES IN SILICATES CALCULATED FROM AVERAGE GLADSTONE–DALE CONSTANTS, COMPARED WITH POLARIZABILITY FOR SIMPLE OXIDES ASSUMING C = 2.26

column 1 oxide in silicates		column 2 simple oxide		C required to equate col 2 to col 1
MgO	2.19	periclase	2.30	1.87
^{VI}CaO	3.43	lime	3.88	1.37
$^{VI}Al_2O_3$	5.30	corundum	5.43	2.11
SiO_2	3.44	quartz	3.43	2.26
TiO_2	7.52	rutile	8.85	2.07

TABLE 5. POLARIZABILITY (α, Å^3) FOR MINERALS CALCULATED BY ADDITION OF POLARIZABILITY OF THEIR COMPONENT OXIDES DERIVED FROM AVERAGE GLADSTONE–DALE CONSTANTS, COMPARED WITH POLARIZIBILITY DETERMINED FROM INDICES OF REFRACTION AND MOLECULAR VOLUME ASSUMING C = 2.26

mineral	α by addition	α from $V(n-1)/6 = \Sigma\alpha_i$	Reference
spinel	7.91	7.90	W & W
gibbsite	10.29	10.13	W & W
brucite	3.85	3.81	W & W
tridymite	3.44	3.44	Dana vol. 3
coesite	3.44	3.45	Dana vol. 3
natrolite	7.53	7.53	DHZ (1963)
microcline	15.8	15.6	B & T
anorthoclase	15.2	15.0	DHZ (1963)
albite	14.7	14.8	Bloss #1
plagioclase (An_{50})	15.4	15.5	Bloss #18
anorthite	16.0	16.1	Bloss #26
grossular	26.7	26.8	DHZ (1962a) #9
andradite	31.3	31.3	DHZ (1978) #59.11
almandine	25.0	25.0	DHZ (1978) #55.3
spessartine	26.3	26.4	DHZ (1978) #56.27
pyrope	23.7	23.9	DHZ (1978) #52.8
olivine (Fo_{90})	8.1	8.4	R & B #9150
titanite	14.1	14.2	DHZ (1978) #46.5

References: B & T: Bailey & Taylor (1955); DHZ(date): Deer, Howie & Zussman (date); R & B: Rodgers & Brothers (1969); Bloss: Bloss et al. (1983); Dana vol. 3: Frondel (1962); W & W: Winchell & Winchell (1964).

An important property of oxide polarizability is that of additivity (Lasaga & Cygan 1982). Table 5 demonstrates the consistency between molecular polarizability for complex silicates derived by summation of oxide polarizabilities and that determined directly from index of refraction using equation (2). The summation for Table 5 uses polarizabilities derived from the average *GDC*s listed in Table 1, not those that best fit each silicate group.

Consideration of electron overlap may also explain why the *GDC*s for Li and Be are inconsistent. The bonds in silicates are generally held to be about 50% ionic, and the value for *c* in equation (1) of 2.26 is about half-way between zero and its maximum value of $4\pi/3$. Possibly 4-coordinated Li and Be introduce differing extents of covalency in the bonding, resulting in less close adherence to the G–D equation.

SUMMARY

The Gladstone–Dale constants for oxides in silicates are dependent on coordination number; the *GDC* for an oxide decreases with increasing coordination number. Gladstone–Dale constants calculated separately for garnets, other orthosilicates, pyroxenes, amphiboles, layer silicates and framework silicates do not show significant variation among these major silicate groups, with the exception that the range in site size and coordination in amphiboles causes averaging of the *GDC*s for the larger cations (CaO, FeO). Values determined for the trivalent and tetravalent transition metals show more inconsistency among groups than do most other oxides, possibly because of uncertainty in coordination number, possibly from errors in determination of indices of refraction because of intense color. The G–D equation is consistent with Lorentz–Lorentz theory if silicates are regarded as having intermediate bonds (50% ionic, 50% covalent). The new *GDC*s for silicates bring 93% of 574 sets of mineral data into Mandarino's "superior" category.

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