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GLADSTONE–DALE CALCULATIONS APPLIED TO FLUORIDES

HANS PAULY

Mineralogical Institute, Technical University of Denmark,
DK-2800 Lyngby, Denmark

ABSTRACT

Gladstone–Dale calculations, using the constants given by Mandarino (1976, 1978, 1981), were carried out for fluorides. In many cases, the results were much poorer than expected considering the accuracy of the data. Use of a new set of constants, derived from data for a number of simple fluorides, gave anomalous results for compound fluorides containing ^{viii}Na, ^{iv}Li *and* ^{xii}K. In the simple fluorides, these elements are all *vi*-co-ordinated. Supplementary constants for these elements were, therefore, considered necessary: $K = 0.1086$ for ^{viii}Na was derived from cryolite, $K = 0.1553$ for ^{iv}Li was derived from cryolithionite and $K = 0.1336$ for ^{xii}K was derived from elpasolite. Further constants for $Al(OH)_3$, $K = 0.2335$ derived from prosopite, and for H_2O, $K = 0.322$ derived from gearksutite, were also found necessary. The new constants are considered as accurate as the physical data from which they were derived. The new constants were used to calculate the expression $1-(K_P/K_C)$ for twenty-three fluorides; eighteen (78%) sets of data were characterized as superior, three (13%) as excellent, one as good and one as poor. Within such a limited group of compounds, with good physical data and precisely known chemical compositions, Gladstone–Dale calculations may give information about the co-ordination of the elements involved.

Keywords: Gladstone–Dale constants, fluorides, co-ordination, Ivigtut (Greenland).

SOMMAIRE

On a effectué les calculs de Gladstone–Dale pour certains fluorures au moyen des constantes de Mandarino (1976, 1978, 1981). Dans de nombreux cas, la concordance des valeurs calculées avec celles des données expérimentales est beaucoup moins bonne que ne le faisait espérer l'exactitude des données. De nouvelles constantes, établies pour des fluorures simples, donnent des résultats anormaux pour les fluorures composés dans lesquels Na, Li et K se trouvent en coordinence *viii*, *iv* et *xii*, respectivement. Dans les fluorures simples, ces éléments sont hexacoordonnés. On a ensuite établi les constantes K supplémentaires qui s'avéraient nécessaires: 0.1086 pour ^{viii}Na (à partir de a cryolite), 0.1553 pour ^{iv}Li (cryolithionite) et 0.1336 pour ^{xii}K (elpasolite). De plus, de nouvelles valeurs de K pour $Al(OH)_3$ (0.2335, à partir de prosopite) et pour H_2O (0.322, géarksutite) ont aussi été déterminées. Ces nouvelles valeurs sont jugées aussi exactes que les données physiques de départ. En utilisant ces valeurs nouvelles pour calculer l'indice de compatibilité $1 - (K_P/K_C)$ pour vingt-trois fluorures, les résultats sont jugés supérieurs dans 18 cas (78%), excellents dans 3 cas (13%), bons dans un cas et mauvais dans le dernier cas. Dans un groupe de composés aussi restreint, avec des mesures adéquates des propriétés physiques et la composition chimique exactement connue, on pourrait utiliser pareils calculs pour déterminer la coordinence des éléments constitutifs.

(Traduit par la Rédaction)

Mots-clés: constantes de Gladstone–Dale, fluorures, coordinence, Ivigtut (Groënland).

INTRODUCTION

The K_P values $[K_P = (\bar{n}-1)/d]$ given in Table 1 were calculated from physical data of high accuracy for eight simple fluorides that are chemically well characterized. The K_C values calculated from the chemical compositions and the individual Gladstone–Dale constants k given by Mandarino (1981) show some large deviations from the corresponding values of K_P. Using the $1-(K_P/K_C)$ compatibility scale proposed by Mandarino (1979), the eight sets of data are characterized as follows: superior (2), excellent (1), good (2), fair (1) and poor (2). Calculations carried out with the data for compound fluorides gave similar results. Because the data for these compounds are considered quite accurate, such results are hard to reconcile. The deviations could be explained, in part, by the nature of the constants used. Those of Larsen (1921) and Mandarino (1981) were calculated from compounds based on oxygen frameworks. It was decided to calculate new Gladstone–Dale constants that could be used specifically with fluorides. Because compound fluorides can be considered as combinations of simple fluorides and few other constituents, the K_P values listed in Table 1 were used as individual Gladstone–Dale constants. However, even with the constants derived from fluorides, certain compound fluorides showed discrepancies between K_C and K_P

TABLE 1. DATA USED IN CALCULATIONS OF GLADSTONE-DALE RATIOS - OR CONSTANTS - FOR SIMPLE COMPOUNDS

	Coordination	$\bar{n}$	d	Data from	K_p or constants	K_c
LiF	VI	1.3915	2.638	PDF 4-857	0.1484	0.1486
NaF	VI	1.3270	2.802	PDF 4-793	0.1167	0.1228
KF	VI	1.352	2.524	PDF 4-726	0.1395	0.1463
MgF_2	VI	1.382 WW	3.17	PDF 6-290	0.1205	0.1059
CaF_2	VIII	1.43385	3.180	Allen(1952)	0.1364	0.1321
SrF_2	VIII	1.435	4.28	PDF 6-262	0.1016	0.1018
BaF_2	VIII	1.472	4.886	PDF 4-452	0.0966	0.1036
AlF_3	VI	1.3767	3.197	PDF 9-138	0.1178	0.0996
$AlPO_4$		1.528	2.618	PDF 10-423	0.2017	0.1930
$SrCO_3$		1.618	3.75	L&B	0.1648	0.1647
LiF	IV	calculated from cryolithionite			0.1553	-
NaF	VIII	calculated from cryolite			0.1086	-
KF	XII	calculated from K_2NaAlF_6 PDF 22-1235			0.1336	-
$Al(OH)_3$		calculated from prosopite			0.2335	0.2531
H_2O		calculated from gearksutite			0.322	0.340

$\bar{n}$: n for cubic compounds, $(2\omega+\epsilon)/3$ or $(\alpha + \beta + \gamma)/3$.

d: Where possible d_x - from X-ray data - has been used.

PDF: Powder Diffraction File Card No., Joint Committee on Powder Diffraction Standards, Swarthmore, PA, USA.

WW: Winchell & Winchell (1964).

L&B: Strontianite from Larsen & Berman (1934).

K_c: For comparison these values have been calculated from the constants given in Mandarino (1976).

that could not be explained by inacccuracies in the data or in the constants.

According to Larsen & Berman (1934), "Every liquid has a specific refractive energy composed of the specific refractive energies of its component elements, *modified by the manner of combination*, and which is unaffected by changes of temperature and accompanies it when mixed with other liquids. The product of this specific refractive energy and the density is, when added to unity, the refractive index." In order to explain the observed deviations, it seems reasonable to contemplate that part of the statement italicized by the present author: "modified by the manner of combination". Whereas the co-ordination of Na in the simple fluoride villiaumite is VI in regard to F, we rather often find in compound fluorides a co-ordination VIII for Na [*e.g.*, in the mineral cryolite, as shown by Hawthorne & Ferguson (1975)]. Similar deviations in co-ordination are observed for Li and K when the structure of their simple compounds are compared to the structure of the compound fluorides containing these elements.

In order to establish constants for these elements in co-ordinations corresponding to the situations in the compound fluorides, a few well-documented fluorides have been chosen: cryolite, cryolithionite and synthetic elpasolite. On the assumption that their K_C values are identical with their K_P values and applying the constants for the other simple fluoride constituents given in Table 1, supplementary constants for NaF, LiF and KF have been calculated; they are included in Table 1 together with constants for $Al(OH)_3$ and H_2O calculated from prosopite and gearksutite. These two constants were found to give better results for the fluorides than K_C for $Al(OH)_3$ calculated from the Gladstone–Dale constants given by Mandarino (1981) and the *k* value for H_2O 0.340 (Mandarino 1981). Certain other constants have been given in Table 1 for simple constituents that are present in some compound fluorides.

CALCULATION OF SUPPLEMENTARY CONSTANTS

The fluorides given in Table 2 are regarded as particularly well suited for the calculations. According to all existing analytical data [for published compositions, see Bøggild (1953)], cryolite, cryolithionite and chiolite are stoichiometric. Weberite (Bøgvad 1938) contains 1.19% K substituting for Na in the formula, but otherwise it is stoichiometric.

The crystal structure of cryolite was refined by Hawthorne & Ferguson (1975), that of cryolithionite by Geller (1971) and that of weberite by Giuseppetti & Tadini (1978). Note that the D_x value of weberite (Table 2) is calculated from the X-ray data taking into account the 1.19% K substitution mentioned. The D_x of chiolite has been calculated from unit-cell dimensions determined by Dr. E.L. Leonardsen of The Geological Museum, Copenhagen (pers. comm.).

Recently, the optical data for these minerals have been revised by Pauly (1977) and Pauly & Petersen (1981). The newly established indices of refraction are believed accurate to ±0.0003. One notes, in particular, the slight but real difference between the highest index of refraction of cryolite and the index of cryolithionite.

TABLE 2. DATA FOR FLUORIDES FROM IVIGTUT, SOUTH GREENLAND

Cryolite Na_3AlF_6	Cryolithionite $Na_3Li_3Al_2F_{12}$	Chiolite $Na_5Al_3F_{14}$	Weberite Na_2MgAlF_7
$\alpha = 1.3382$		$\epsilon = 1.3431$	$\alpha = 1.3440$
$\beta = 1.3383$	$n = 1.3395$	$\omega = 1.3497$	$\beta = 1.3455$
$\gamma = 1.3392$			$\gamma = 1.3470$
$\bar{n} = 1.3386$	$\bar{n} = 1.3395$	$\bar{n} = 1.3475$	$\bar{n} = 1.3455$
$d_x = 2.973$	$d_x = 2.771$	$d_x = 2.996$	$d_x = 2.980$
$K_p = 0.1139$	$K_p = 0.1225$	$K_p = 0.1160$	$K_p = 0.1159$

The densities of these minerals are probably accurate to within at least ±0.2%. The K_P values given in Table 2 should, therefore, be accurate to within at least ±0.3%. The constants (K_P values) for the simple constituents, given in Table 1, are probably of a corresponding accuracy.

Cryolite contains 60% NaF and 40% AlF_3. With the constants (K_P values) for these two constituents (see Table 1), one finds K_C = 0.1171. This is 2.8% higher than the K_P of the mineral, or about 10 times as much as could be expected from the uncertainty in K_P. According to Hawthorne & Ferguson (1975), Na occurs in two different positions in the structure, with two different co-ordinations. One Na is situated in a fairly regular octahedron, and the other two Na are situated in a highly distorted cubic antiprism of eight fluorine ions. In calculating K_C, a constant for NaF having the co-ordination VI was used, but this, it is assumed, is only valid for the first type of Na in the structure; another constant must be sought for ^{viii}Na. Setting $K_C = K_P$ and using the constant for ^{vi}Na for 20% NaF and the constant for ^{vi}Al for 40% AlF_3, calculations show that NaF with co-ordination VIII has a K of 0.1086.

Weberite has, according to Giuseppetti & Tadini (1978), Na in co-ordination VIII, Mg and Al in VI. It can be recast as 34.99% NaF and 1.78% KF, 26.83% MgF_2 and 36.40% AlF_3; with the constant for NaF in VIII and the other constants from Table 1, this gives a K_C of 0.1157, in good agreement with the K_P of 0.1159.

Chiolite has, according to Brosset (1942), one Na co-ordinated by 8 fluorine ions and four Na co-ordinated by six fluorine ions. Here, as in the other fluorides, Al has co-ordination VI. This gives 9.09% NaF in VIII, 36.36% NaF in VI and 54.55% AlF_3 in VI. With the appropriate constants from Table 1, one finds K_C = 0.1166. The deviation from K_P (= 0.1160) is higher than what one might expect from the uncertainties in the physical data of the mineral. The deviation must, therefore, be connected with the constants used. As ^{viii}Na makes up only a small amount of the composition, an unrealistically large change in that constant would be necessary. Therefore, assuming $K_C = K_P$, a value has been calculated for "Na in VI". The result is K =0.1151. This is 1.4% lower than the value given in Table 1. Accepting this as a value attributable to these Na ions in the chiolite structure must indicate that they have a co-ordination slightly higher than VI. In this connection, note that Vlasse *et al.* (1976) reported, for a synthetic analogue to chiolite $Na_5Fe_3F_{14}$, the same overall structure; whereas one Na has VIII co-ordination, the remaining four Na have VII co-ordination because the co-ordination polyhedra of Fe are clearly distorted. If the co-ordination polyhedra of Al in chiolite also are slightly distorted, this might give rise to an increase in the number of co-ordinating F ions around Na, which is here assumed to be in six-fold co-ordination.

Cryolithionite has, according to Geller (1971), Na in co-ordination VIII, Li in IV and Al in VI. From the data for the mineral, a constant for ^{iv}Li has been calculated assuming $K_C = K_P$ and applying the constants from Table 1. For Li in IV co-ordination with respect to F the calculations show K = 0.1553.

Synthetic elpasolite K_2NaAlF_6 has, according to PDF 22–1235, $\bar{n}$ = 1.376 and D_x = 3.003, in good agreement with data obtained on the natural occurrences. It is seen that K_P = 0.1252. This compound has the perovskite structure, so that a constant for potassium in co-ordination XII has to be established. Using the constants for the other elements from Table 1 and setting $K_C = K_P$, a constant K of 0.1336 is found for potassium in XII co-ordination with respect to F.

Prosopite $CaAl_2F_4(OH)_4$ has, according to Palache *et al.* (1951), $\bar{n}$ = 1.504 and D_x = 2.89, which are in good agreement with data obtained on prosopite from Ivigtut by the present author. It is seen that K_P = 0.1744. Chemical analyses of prosopite from Ivigtut were made in 1935 by H. Buchwald, chief chemist at the Kryolitselskabet Øresund A/S (pers. comm.): 16.80% Ca, 22.65% Al, 31.81% F and 28.52% OH. The latter was calculated to balance charges. Weight loss on ignition at 1100°C (assumed to be caused by liberation of HF only) was found to indicate the presence of 31.85% F and 28.51% OH, in fine agreement with the direct determination. It is clear, in other words, that the mineral is stoichiometric. Recalculation in terms of simple compounds gives: 32.80% CaF_2, 23.52% AlF_3 and 43.68% $Al(OH)_3$. Setting $K_C = K_P$ and using the constants from Table 1, a constant K for $Al(OH)_3$ of 0.2335 is found. The much higher value of K_C for this compound (0.2531), obtained by using the constants of Mandarino (1981), results in a K_C for prosopite 4.8% higher than its K_P. This is out of proportion with the uncertainties of the physical data of the mineral.

Gearksutite $CaAlF_4(OH)H_2O$ has, according to Larsen & Berman (1934), $\bar{n}$ = 1.453 and D = 2.77. The index of refraction is in keeping with results obtained on material from Ivigtut by the present author. The mineral clearly is stoichiometric, as can be seen from the compositions given by Ermilova (1963). It contains 43.84% CaF_2, 31.44% AlF_3, 14.60% $Al(OH)_3$ and 10.12% H_2O. If the constant for H_2O is taken as 0.322, one finds $K_C = 0.1635 = K_P$, applying the other constants from Table 1. The value 0.340 for H_2O would give K_C about 1% higher than K_P, and this might well be accepted. However, the new value for H_2O seems to match the water-bearing fluorides better and is, therefore, preferred.

GLADSTONE–DALE CALCULATIONS

β-Li_3AlF_6: $\bar{n} = 1.364$, $D_x = 2.785$, $K_P = 0.1307$

On a sample of this compound, obtained from Dr. J.L. Holm, Trondheim, Norway, the indices of refraction were found to lie between 1.360 and 1.368. The value of D_x is taken from Holm & Jenssen (1969). Burns *et al.* (1968) stated that Li ions are in a very distorted VI co-ordination polyhedron which, for two thirds of the ions, is close to IV co-ordination. Using the constants for Li and Al in VI from Table 1, calculations give $K_C = 0.1325$. Use of the value for Li in IV would increase K_C 1.4%. Re-examination of the physical data might be useful.

Na_2LiAlF_6: $\bar{n} = 1.355$, $D_x = 3.02$, $K_P = 0.1176$

The indices of refraction of some samples of this compound were determined by Mrs. I.L. Olsen, Mineralogical Institute of the Technical University of Denmark (pers. comm.). The value of D_x is taken from Holm & Holm (1970). Assuming Na in VIII and Li in VI co-ordinations, calculations give $K_C = 0.1180$.

K_2LiAlF_6: $\bar{n} = 1.3907$, $D_x = 3.018$, $K_P = 0.1295$

The index of refraction is taken from Winchell & Winchell (1964); D_x is from Grjotheim *et al.* (1971). According to Winkler (1953), this compound has the perovskite structure, with K in XII co-ordination, Li in VI and Al in VI. Calculation, using the constants from Table 1, gives $K_C = 0.1295$.

$NaMgF_3$: $\bar{n} = 1.364$, $D_x = 3.06$, $K_P = 0.1190$

Data for neighborite (Chao *et al.* 1961) are closely similar to the results obtained on the synthetic material (PDF 13–303); using the constants from Table 1 for ^{vi}Na and ^{vi}Mg gives a K_C of 0.1190. As the structure of this compound is considered to be of the perovskite type, one would expect Na to have a higher co-ordination number. The constant for Na in VIII gives, however, a 3% lower K_C. The required changes in the physical data are probably not acceptable.

$KMgF_3$: $\bar{n} = 1.404$, $D_x = 3.17$, $K_P = 0.1274$

Data are from DeVries & Roy (1953). As this compound has the perovskite structure (Winkler 1953), the constants for ^{xii}K and ^{vi}Mg are used (Table 1); these give $K_C = 0.1269$.

K_2MgF_4: $\bar{n} = 1.378$, $D_x = 2.85$, $K_P = 0.1326$

The index of refraction is taken from Winchell & Winchell (1964), who referred to DeVries & Roy (1953) for the value of D_x. Assuming the co-ordination for K and Mg to be VI, K_C is equal to 0.1329. If the index of refraction ($\bar{n} = 1.383$) of DeVries & Roy (1953) is used, K_P has a value of 0.1344.

Colquiriite $CaLiAlF_6$: $\bar{n} = 1.387$, $D_x = 2.95$, $K_P = 0.1312$

Data are taken from Walenta *et al.* (1980). In view of the character of the chemical analyses, calculations here have been based on the idealized formula. If Li is in co-ordination VI, one finds, with the constants from Table 1, $K_C = 0.1297$. If Li is in co-ordination IV, one finds $K_C = 0.1306$. The data for the mineral probably need some refinement before a decision about the co-ordination can be reached.

$LiBaF_3$: $\bar{n} = 1.544$, $D_x = 5.242$, $K_P = 0.1038$

Data are taken from PDF 18–715. Use of the constants from Table 1, with Li in co-ordination VI, gives $K_C = 0.1033$. If the constant for Li in co-ordination IV is used, $K_C = 0.1041$. The data do not allow one to judge which co-ordination number should be preferred.

Thomsenolite $NaCaAlF_6 \cdot H_2O$: $\bar{n} = 1.412$, $D_x = 2.974$, $K_P = 0.1385$

Pachnolite $NaCaAlF_6 \cdot H_2O$: $\bar{n} = 1{,}412$, $D = 2.98$, $K_P = 0.1383$

For thomsenolite, the index of refraction is obtained from Bøggild (1913), who also noted a value of D_x of 2.982. Cocco *et al.* (1967) are cited for D_x and the co-ordination of the constituent atoms. For pachnolite, the density is taken from Bøggild (1913). Concerning the indices of refraction (not given), Bøggild observed that no difference could be found between the two minerals when they were examined in Thoulet's solution; he attributed the same average index of refraction $\bar{n}$ to both minerals: 1.4119. This value was also found by the present author by measuring polished faces of larger

TABLE 3. ANALYSIS OF THOMSENOLITE AND PACHNOLITE FROM IVIGTUT, SOUTH GREENLAND

	THOMSENOLITE		PACHNOLITE	
	ORIGINAL ANALYSIS	F & H_2O CORRECTED	ORIGINAL ANALYSIS	F & H_2O CORRECTED
Na	10.45%	10.32%	10.03%	10.00%
K	nil	-	nil	-
Mg	nil	-	0.09%	0.09%
Ca	17.96%	17.75%	17.31%	17.25%
Sr	0.51%	0.51%	1.63%	1.62%
Ba	nil	-	nil	-
Al	12.28%	12.13%	12.11%	12.07%
F	48.90%	51.20%	47.96%	50.96%
$H_2O^{+110°C}$	9.07%	8.09%	8.87%	8.01%
	99.17%	100.00%	98.00%	100.00%

crystals from Ivigtut on the refractometer. Cocco *et al.* (1967) reported that for thomsenolite, Na has the co-ordination VIII. It is surrounded by 6 F situated at the corners of a distorted triangular prism and further, 2 F atoms are placed beyond two of the prism faces. Ca is in co-ordination VIII, bonded by 6 F and 2 O atoms. The Al shows the known regular octahedral co-ordination with F. Using the constants from Table 1, one finds $K_C = 0.1392$ for the theoretical composition. As published compositions for these minerals (Bøggild 1953) were based on rather old analyses, material for new analyses was obtained and analyzed in 1962 in the laboratories of the Kryolitselskabet Øresund A/S. The results of these analyses are given in Table 3. The chemist, Mrs. E.-L. Mortensen, M.Sc., noted: "In order to balance charges, part of H_2O was calculated as OH. Uncertainties, particularly for Sr, may be rather great due to the large amounts of Ca. The uncertainty on the determination of F and notably on the determination of H_2O is considerable. The F value may be too low. Concerning the H_2O determination no indication can be given because it is influenced by the F content of the samples."

In recalculating the analytical results into simple compounds, OH was combined with Al to form $Al(OH)_3$. Assuming Na to be in VIII co-ordination in both minerals and using the constants from Table 1, a K_C value of 0.1425 was found for thomsenolite and 0.1421 for pachnolite. These values are quite different from the K_P values of the two minerals. Comparison with the value found for the theoretical composition (0.1392) indicates that the higher K_C values may be due to the introduction of OH.

When the analytical results are recalculated as if all metals were bound to F, it is seen that, for thomsenolite, F is increased to 51.83% and, for pachnolite, to 51.13%, in terms of the original analytical data. Under these conditions, the water determined analytically corresponds to 1.1 mol in both minerals. For the recalculation it was decided to reduce the amounts of water so as to correspond to just 1 mol in each of the minerals. The results are given in Table 3 under the heading "F & H_2O corrected", and they are recalculated to give 100%. Values of K_C based on these corrected compositions are 0.1389 for thomsenolite and 0.1384 for pachnolite. It is, therefore, assumed that the corrections were justified.

Tikhonenkovite $SrAlF_4(OH)\cdot H_2O$: $\bar{n} = 1.455$, $D = 3.26$, $K_P = 0.1397$

Data are taken from Fleischer (1964). From the analytical data given in the reference, calculations give $K_C = 0.1395$ when the constants of Table 1 are used.

Yaroslavite $Ca_3Al_2F_{10}(OH)_2\cdot H_2O$ [*or* $Ca_2AlF_6(OH)\cdot H_2O$?]: $\bar{n} = 1.418$, $D = 3.09$, $K_P = 0.1353$

Data are taken from Fleischer (1966). The present author finds that the alternative formula may also be deduced from the analysis. This resembles an OH-bearing carlhintzeite (see the following paragraph). The optical and powder-diffraction data given in the reference also come rather close to carlhintzeite. The reason for these considerations is to be found in the calculated K_C of 0.1509. The pronounced discrepancy between K_C and K_P called for a detailed examination of the data given in the reference. As some inconsistencies seem to be present among these data, a re-examination of the mineral should probably be undertaken.

Carlhintzeite $Ca_2AlF_7\cdot H_2O$: $\bar{n} = 1.4163$, $D_x = 2.89$, $K_P = 0.1441$

The data are taken from Dunn *et al.* (1979). Using the constants from Table 1, the results of the analysis give a value K_C of 0.1437. Calculations based on the constants of Mandarino (1981) give a K_C of 0.136.

Usovite $Ba_2MgAl_2F_{12}$: $\bar{n} = 1.4423$, $D = 4.18$, $K_P = 0.1058$

Data are taken from Fleischer (1967) and Mineralogical Abstracts (1967, p. 284). Assuming all metals found in the analysis to be bound to F requires an increase from 39.8% to 40.5% F. This is regarded as being within the uncertainty of the determination. Thus calculated, one finds from the analytical data $K_C =$

0.1057 using the constants of Table 1. If OH is introduced to compensate for the F deficit, one finds a K_C of 0.1069. The former is thus preferred.

Jarlite $NaSr_3Al_3F_{15}(OH)$: $\bar{n} = 1.431$,
$D = 3.87$, $K_P = 0.1114$

"Metajarlite" $NaSr_3Al_3F_{15}(OH)$: $\bar{n} = 1.431$,
$D = 3.72$, $K_P = 0.1159$

Data and analyses are taken from Bøgvad (1933), but values of D for jarlite (Ferguson 1949) and for "metajarlite" D has been corrected downward from 3.78 (given by Bøgvad) with a factor corresponding to Ferguson's correction of D for jarlite (from originally 3.93 to 3.87). This is done because Bøgvad (1933) indicated the same procedure for the determination of density for both minerals. Assuming Na to have co-ordination VIII and using the constants of Table 1, one finds $K_C = 0.1142$ for jarlite and 0.1149 for "metajarlite". Better ajustment of K_C to K_P might be obtained by assuming smaller amounts of OH in the minerals than indicated in the analyses; as long as a final solution has not been found for the discrepancies between the chemical data and the X-ray data (Brosset 1942, Ferguson 1949), it is hardly reasonable to attempt a refinement of the K_P/K_C ratios. These problems were taken up earlier by Bøgvad (1951); based on new analytical data, he proposed the formula $NaSr_2Al_2(F,OH)_{11}$, but this formula also is at variance with the X-ray data. The problems are once again under examination, and it may be noted that the original formula now seems the more promising. This viewpoint is further supported by the existence of the mineral calcjarlite (see the following paragraph). It should be noted that the Gladstone–Dale calculations do not allow a distinction between the various proposed formulas for jarlite. Even a formula like $NaSrAlF_6$ gives a K_C value exactly the same as the two formulas given above.

Calcjarlite $NaCa_3Al_3F_{14}(OH)_2$: $\bar{n} = 1.428$
$D = 3.51$, $K_P = 0.1220$

Data are from Fleischer (1974). Assuming Na in co-ordination VIII and using the constants of Table 1, calculations give a K_C of 0.1287. If the calculations are based on a composition involving only ½ mol OH, one finds a K_C of 0.1218. This demands an increase from 47.5% to 51.9% F and corresponding reduction in the H_2O^+ determined in the analysis.

Ralstonite $Na_{0.88}Mg_{0.88}Al_{1.12}F_{5.5}(OH)_{0.5}\cdot H_2O$: $\bar{n}$
$= 1.37$, $D = 2.67$, $K_P = 0.1390$

$Na_{0.54}Mg_{0.34}Al_{1.66}F_4(OH)_2\cdot H_2O$: $\bar{n} = 1.419$,
$D = 2.54$, $K_P = 0.1650$

Data for the first ralstonite are taken from Pauly (1965) and for the second from Stepanov & Moleva (1962). Assuming Na to be in VIII co-ordination and using the constants of Table 1, K_C is found to be 0.1423 for the first and 0.1687 for the second composition. In view of the variability of the mineral (even single grains show variations in optical properties), these results seem rather acceptable.

Stenonite $Sr_2Al(CO_3)F_5$: $\bar{n} = 1.506$,
$D_x = 3.848$, $K_P = 0.1315$

The data are from Pauly (1962). Using the constants from Table 1, calculations give a K_C of 0.1317.

Bøggildite $Na_2Sr_2Al_2(PO_4)F_9$: $\bar{n} = 1.466$,
$D_x = 3.707$, $K_P = 0.1257$

The index of refraction and the analytical data are from Pauly (1956); D_x is calculated from the chemical analysis using the X-ray data in Hawthorne (1982). The latter indicates that one Na has co-ordination VII and one Na has co-ordination IX. Because constants for these co-ordination states are not known, that for ^{viii}Na is used as an approximation. Sr occurs in two co-ordination states: VIII and IX. As no

TABLE 4. K_p, K_c AND COMPATIBILITY INDEX FOR 28 FLUORIDES

Mineral or Compound	K_p	K_c	$1-K_p/K_c$
Neighborite	0.1190	0.1190	0.000 S
$KMgF_3$	0.1274	0.1269	-0.004 S
$LiBaF_3$	0.1038	0.1033	-0.005 S
K_2MgF_4	0.1326	0.1329	0.002 S
Weberite	0.1159	0.1157	-0.002 S
Cryolite	0.1139	$K_c = K_p$	
Chiolite	0.1160	0.1166	0.005 S
Cryolithionite	0.1225	$K_c = K_p$	
β-Li_3AlF_6	0.1307	0.1325	0.014 S
Na_2LiAlF_6	0.1176	0.1180	0.003 S
K_2LiAlF_6	0.1295	0.1295	0.000 S
Elpasolite	0.1252	$K_c = K_p$	
Colquiriite	0.1312	0.1297	-0.012 S
Thomsenolite	0.1385	0.1389	0.003 S
Pachnolite	0.1383	0.1384	0.001 S
Prosopite	0.1744	$K_c = K_p$	
Gearksutite	0.1635	$K_c = K_p$	
Yaroslavite	0.1353	0.1509	0.103 P
Carlhintzeite	0.1441	0.1437	-0.003 S
Tikhonenkovite	0.1397	0.1395	-0.001 S
Usovite	0.1058	0.1057	-0.001 S
Jarlite	0.1114	0.1142	0.025 E
"Metajarlite"	0.1159	0.1149	-0.009 S
Calcjarlite	0.1220	0.1287	0.052 G
Ralstonite	0.139	0.1423	0.023 E
Ralstonite	0.1650	0.1687	0.022 E
Stenonite	0.1315	0.1317	0.002 S
Bøggildite	0.1257	0.1259	0.002 S

$K_c = K_p$ indicates that the mineral has been used for the calculation of new constants. S: superior, E: excellent, G: good, P: poor, according to Mandarino (1981).

constant for the second is known, that for ^{viii}Sr is used. With the constants from Table 1, one finds a K_C of 0.1278. If, however, the value of K for $AlPO_4$ calculated from the constants given in Mandarino (1981) is used, a K_C of 0.1259 is found. As the accuracy of the physical and chemical data for this mineral seems to allow for less than 1% deviation between K_C and K_P, the latter value is preferred.

CONCLUSION

As seen in Table 4, the use of the constants proposed here for fluorides gives rather satisfactory results in most cases. Of the 23 minerals or compounds for which Gladstone–Dale calculations have been carried out using these constants, the compatibility of the data for eighteen (78%) are classed as superior, three (13%) as excellent, one as good and one as poor. As mentioned in the discussion for calcjarlite, classed as good, errors in the chemical determinations of F and H_2O may account for the rather large difference between K_P and K_C. The discussion concerning the chemical data for thomsenolite and pachnolite illustrates the particular difficulties connected with these determinations. For yaroslavite, classed as poor, the calculations strongly suggest errors in the data.

The suggested influence of the co-ordination state of the elements constituting the compounds on the Gladstone–Dale constants seems to obtain some support in the present, though rather limited, study. This should, of course, be further examined. It might be appropriate here to point out that determination of the indices of refraction is such a small task compared to the synthesis and X-ray examination of compounds that optical data should really be included in all such works. If the idea holds, Gladstone–Dale calculations might help in estimating the co-ordination relations in a number of compounds for which good physical data exist, provided they are stoichiometric in composition or the chemical analysis is of good quality. On the other hand, the Gladstone–Dale calculations may also be most valuable in cases where the chemical analyses have shortcomings due to scarcity of material or for other reasons, provided the physical data are of a reasonably high quality.

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