

GLADSTONE - DALE CONSTANTS: A NEW APPROACH

F. DONALD BLOSS*, MICKEY GUNTER**, SHU-CHUN SU*** AND H. E. WOLFE****

Department of Geology, University of New Mexico, Albuquerque, New Mexico 87131, U.S.A.

ABSTRACT

Multiple linear regressions, if performed with a no-intercept option on data for density, compositions and optical constants derived by spindle stage for a solid-solution series, yield Gladstone-Dale values specific for the series. Applied to 20 crystals ranging in composition from andalusite ${}^{\text{VI}}\text{Al}^{\text{VI}}\text{AlO}[\text{SiO}_4]$ to kanonaite ${}^{\text{VI}}(\text{Mn}^{3+}, \text{Al})^{\text{VI}}(\text{Al}, \text{Mn}^{3+})\text{O}[\text{SiO}_4]$, some also containing Fe^{3+} , the regressions generate the following Gladstone-Dale values: $k(\text{SiO}_2) = 0.285$ (0.054), $k(\text{Mn}_2\text{O}_3) = 0.243$ (0.027), $k(\text{Fe}_2\text{O}_3) = 0.341$ (0.031) and $k(\text{Al}_2\text{O}_3) = 0.153$ (0.032). Applied to 26 members of the plagioclase series, the regression yield: $k(\text{SiO}_2) = 0.211$ (0.015), $k(\text{Al}_2\text{O}_3) = 0.179$ (0.032), $k(\text{CaO}) = 0.266$ (0.052), $k(\text{Fe}_2\text{O}_3) = 0.250$ (0.051), $k(\text{Na}_2\text{O}) = 0.202$ (0.082) and $k(\text{K}_2\text{O}) = 0.223$ (0.060). The calculations yield inflated standard errors (the values in parentheses) because of the high correlation between the normalized independent variables (weight fraction oxides), whose sum necessarily equals 1. For andalusite, kanonaite and plagioclases, observed and calculated indices usually differ in the third decimal place with the new values, but in the second place with the Mandarino (1981) values of the Gladstone-Dale constants. For the SiO_2 polymorphs, the Gladstone-Dale values range from 0.188-0.190 (stishovite) to 0.222 (silicalite). This suggests that for SiO_2 the Gladstone-Dale values are modified by structure or degree of covalency of the Si-O bond.

Keywords: Gladstone-Dale constants, andalusite, plagioclase, kanonaite.

SOMMAIRE

Exécutées avec la contrainte d'ordonnée à l'origine nulle sur les données d'une solution solide

*Permanent address: Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A.

**Department of Geology, Southern Illinois University, Carbondale, Illinois 62901, U.S.A.

***Permanent address: Institute of Geology, Chinese Academy of Sciences, Beijing, The People's Republic of China.

****Harbison-Walker Refractories, Garber Research Center, Pittsburgh, Pennsylvania 15122, U.S.A.

densité, composition, constantes optiques obtenues à la "platine universelle" à un axe, les régressions linéaires multiples donnent aux constantes de Gladstone-Dale des valeurs spécifiques à cette série. Les régressions effectuées sur les données provenant de 20 cristaux dont la composition s'étend de l'andalousite ${}^{\text{VI}}\text{Al}^{\text{VI}}\text{AlO}[\text{SiO}_4]$ à la kanonaïte ${}^{\text{VI}}(\text{Mn}^{3+}, \text{Al})^{\text{VI}}(\text{Al}, \text{Mn}^{3+})\text{O}[\text{SiO}_4]$, et dont certains contiennent aussi du Fe^{3+} , ont fourni les valeurs suivantes: $k(\text{SiO}_2) = 0.285$ (0.054), $k(\text{Mn}_2\text{O}_3) = 0.243$ (0.027), $k(\text{Fe}_2\text{O}_3) = 0.341$ (0.031) et $k(\text{Al}_2\text{O}_3) = 0.153$ (0.032). Pour 26 compositions de la série des plagioclases, les régressions donnent: $k(\text{SiO}_2) = 0.211$ (0.015); $k(\text{Al}_2\text{O}_3) = 0.179$ (0.032); $k(\text{CaO}) = 0.266$ (0.052); $k(\text{Fe}_2\text{O}_3) = 0.250$ (0.051); $k(\text{Na}_2\text{O}) = 0.202$ (0.082); $k(\text{K}_2\text{O}) = 0.223$ (0.060). Les calculs donnent des écarts normaux exagérés (chiffres entre parenthèses), dûs à la corrélation prononcée entre les variables indépendantes normalisées (fractions pondérales d'oxydes), dont la somme doit nécessairement évaluer l'unité. Les indices de réfraction mesurés et calculés pour l'andalousite, la kanonaïte et les plagioclases diffèrent dans la troisième décimale avec les nouvelles valeurs, dans la deuxième avec les valeurs de Mandarino (1981). Les valeurs Gladstone-Dale pour les polymorphes de SiO_2 s'évalent de 0.188-0.190 (stishovite) à 0.222 (silicalite), ce qui indiquerait qu'elles sont affectées par la structure ou le degré de covalence de la liaison Si-O.

(Traduit par la Rédaction)

Mots-clés: constantes Gladstone-Dale, andalousite, plagioclase, kanonaïte.

INTRODUCTION

The Gladstone-Dale rule

$$K = \frac{\bar{n} - 1}{D} = \sum k_i w_i \quad (1)$$

relates a material's mean index of refraction \bar{n} and density D to the weight fractions w_i of its i components and to the coefficients k_i . These latter were originally called the *specific refractive energies* of the components but were renamed *Gladstone-Dale constants* by Mandarino (1981). In addition, Mandarino (1979) proposed that K_p represent K calculated from the observed mean index \bar{n}_o and density, thus

$$K_p = \frac{\bar{n}_o - 1}{D} \quad (2)$$

and that K_C represent K calculated from the material's composition and Gladstone–Dale constants, thus

$$K_C = k_1w_1 + k_2w_2 \dots + k_iw_i \quad (3)$$

Given D , a crystal's mean index refraction \bar{n}_c can be calculated from K_C since

$$K_C = \frac{\bar{n}_c - 1}{D} \quad (4)$$

To assess the internal consistency of the data (\bar{n} , D , w_1 , $w_2 \dots w_i$, k_1 , $k_2 \dots k_i$) for a material, Mandarino (1979, 1981) introduced the *compatibility index*, $[1 - (K_P/K_C)]$, here symbolized C_1 . Using equations (2) and (4), it can be rewritten as

$$C_1 = (\bar{n}_c - \bar{n}_o)/(\bar{n}_c - 1) \quad (5)$$

For materials with \bar{n}_c equal to 1.5, Mandarino's (1981) scale for compatibility will equate to index differences ($\bar{n}_c - \bar{n}_o$) of 0 to ± 0.009 (his *superior* category), ± 0.010 to ± 0.019 (*excellent* category), ± 0.020 to ± 0.029 (*good*), ± 0.030 to ± 0.039 (*fair*) and beyond ± 0.039 (*poor*). For \bar{n}_c values that differ from 1.5 these tolerances will change somewhat, but it is conceptually instructive to express C_1 in terms of differences between calculated and observed mean index of refraction.

With the spindle-stage techniques of Bloss (1981), the principal indices of refraction of a crystal can be measured to within 0.0005 and, from this same crystal, the unit-cell constants can be determined by X-ray techniques and composition by subsequent microprobe analysis. A tight control between \bar{n} , composition and density calculated from unit-cell volume thus results. If such data fall outside Mandarino's superior category, then the applicability of the Gladstone–Dale values used (for the minerals involved) becomes suspect. Such has occurred for two sets of superior data, one for 26 samples of plagioclase and the other for 20 members of the andalusite–kanonaite series. On each of the two data-sets, a multiple linear regression was performed by computer using the GLM procedure of the SAS Institute (Helwig & Council 1979). Using the no-intercept (NOINT) option for this procedure, the model

$$K_P = k_1w_1 + k_2w_2 \dots + k_iw_i \quad (6)$$

was fit by least squares to each data-set where the input data consisted of K_P , in other words $(\bar{n}_c - 1)/D$, as the dependent parameter, and weight fractions w_i of the component oxides for each crystal as the independent variables.

The values generated for the coefficients k_i then represent Gladstone–Dale values for each oxide composing the crystal. These differ from the Gladstone–Dale constants tabulated by Mandarino (1981), but compared to them, as will be seen, they permit more precise calculations of \bar{n}_c for samples of andalusite and for plagioclase both within and outside the data-sets used.

For oxide components, a single set of Gladstone–Dale constants that would place all minerals in the superior category defined by Mandarino (1981) is unlikely. This has been recognized by Mandarino (1981) where, for a given oxide, he provides several different Gladstone–Dale constants, depending upon the crystal structure. Such structural dependence becomes obvious if we calculate the Gladstone–Dale value for SiO_2 from Tröger's (1979) data for the various SiO_2 polymorphs. We thus obtain 0.188–0.190 (stishovite), 0.204 (coesite), 0.207 (quartz), 0.209 (cristobalite), 0.207–0.211 (tridymite) and, using the data of Flanigen *et al.* (1978), 0.222 for silicalite, a recently discovered synthetic polymorph of SiO_2 . G. V. Gibbs (pers. comm.) notes that the degree of covalency of the Si–O bond roughly increases from stishovite to coesite to quartz to cristobalite (and tridymite). The possibility exists that the Gladstone–Dale value for SiO_2 increases with degree of covalency of the Si–O bond.

DATA ANALYZED AND RESULTS

Andalusite–kanonaite

Table 1 summarizes the data for the samples

TABLE 1. COMPOSITION, DENSITY, AND REFRACTIVE INDICES (FOR LIGHT VIBRATING ALONG THE a , b , AND c AXES) FOR 20 ANDALUSITES AND KANONAITES*

Crystal	Weight Fractions (normalized)				Density D	Indices (589.3 nm)				
	SiO_2	Al_2O_3	Mn_2O_3	Fe_2O_3		n_a	n_b	n_c	\bar{n}	
1	0.3699	0.6283	0.0000	0.0018	3.146	1.6439	1.6386	1.6329	1.6385	
2	0.3698	0.6279	0.0000	0.0023	3.142	1.6439	1.6395	1.6342	1.6392	
3	0.3731	0.6245	0.0001	0.0023	3.147	1.6448	1.6398	1.6340	1.6395	
4	0.3685	0.6285	0.0000	0.0030	3.148	1.6444	1.6397	1.6340	1.6394	
5	0.3714	0.6245	0.0001	0.0040	3.146	1.6446	1.6403	1.6351	1.6400	
6	0.3670	0.6284	0.0000	0.0046	3.150	1.6446	1.6404	1.6350	1.6400	
7	0.3699	0.6204	0.0028	0.0069	3.156*	1.6460	1.6417	1.6363	1.6413	
8	0.3738	0.6142	0.0001	0.0119	3.153	1.6458	1.6427	1.6385	1.6423	
9	0.3719	0.6150	0.0001	0.0130	3.151	1.6490	1.6445	1.6385	1.6440	
10	0.3656	0.6138	0.0006	0.0201	3.158	1.6497	1.6476	1.6433	1.6449	
11	0.3662	0.6117	0.0150	0.0071	3.172	1.6498	1.6460	1.6437	1.6465	
12	0.3683	0.5926	0.0153	0.0238	3.172	1.6551	1.6572	1.6599	1.6574	
13	0.3630	0.5975	0.0120	0.0274	3.175	1.6539	1.6551	1.6556	1.6549	
14	0.3686	0.5867	0.0278	0.0168	3.176	1.6543	1.6581	1.6668	1.6597	
15	0.3667	0.5859	0.0300	0.0175	3.176	1.6565	1.6597	1.6662	1.6608	
16	0.3667	0.5796	0.0367	0.0170	3.195	1.6546	1.6589	1.6675	1.6603	
17	0.3661	0.5783	0.0430	0.0126	3.181	1.6565	1.6609	1.6685	1.6620	
18	0.3594	0.5514	0.0643	0.0249	3.203	1.6663	1.6753	1.6927	1.6781	
19	0.3606	0.4669	0.1365	0.0359	3.250	1.6844	1.7124	1.7649	1.7206	
20	0.3527	0.3804	0.2598	0.0071	3.313	1.7022	1.7273	1.7920	1.7405	

* Descriptions and localities for these crystals are given by Guntter & Bloss (1982, Table 1).

of andalusite and kanonaite used in the regressions. From each individual crystal, three sets of data were collected: (1) by spindle-stage methods (Bloss 1981), its principal indices of refraction were determined for sodium light vibrating parallel to the a , b and c crystallographic axes (respective symbols: n_a , n_b and n_c), (2) by back-reflection Weissenberg photography, the crystal's cell edges and cell volume were evaluated and finally, (3) by electron-microprobe analysis, the weight fractions of the component oxides (normalized to total 1.0) were determined. From these data the computer calculated, for each crystal, its density D , its mean index of refraction \bar{n} , and its value K_P , namely $(\bar{n} - 1)/D$. It then fitted Equation 6 by least squares to the data using the SAS GLM procedure with the no-intercept option.

The regressions were performed on data involving \bar{n} and also on data wherein n_a , n_b and n_c respectively, were used instead of \bar{n} . Gladstone-Dale values were thus obtained (Table 2), not only for \bar{n} , but also for n_a , n_b and n_c . In this we followed Pabst (1975), who had similarly obtained Gladstone-Dale values that permitted prediction of principal indices; however, Pabst derived such values for end members rather than individual oxides. For comparison, the Gladstone-Dale constants given by Mandarino (1976) for silicates, and for island and chain silicates in particular (Mandarino 1981), are added to Table 2.

Using the Gladstone-Dale values in Table 2, the indices of refraction n_a , n_b , n_c and \bar{n} were calculated using our new values. In addition, \bar{n} was calculated using the constants recommended for silicates in general (Mandarino 1976) and for island and chain silicates in particular (Mandarino 1981). The differences between observed indices of refraction and the indices thus calculated (Table 3) disclose the superiority of our new Gladstone-Dale values

TABLE 2. GLADSTONE-DALE VALUES FOR CALCULATION OF n_a , n_b , n_c AND \bar{n} FOR ANDALUSITES AND KANONAITES

Index	SiO ₂	Al ₂ O ₃	Mn ₂ O ₃	Fe ₂ O ₃
New values specific for andalusites and kanonaites				
n_a	0.220 (31)	0.195 (18)	0.224 (15)	0.255 (18)
n_b	0.272 (49)	0.161 (29)	0.233 (24)	0.343 (28)
n_c	0.365 (98)	0.102 (58)	0.271 (48)	0.422 (55)
\bar{n}	0.285 (54)	0.153 (32)	0.243 (27)	0.341 (31)
Mandarino (1976) values				
\bar{n}	0.208	0.207	0.301	0.268
Mandarino (1981) values				
\bar{n}	0.208	0.176	0.256	0.268

TABLE 3. OBSERVED INDICES MINUS CALCULATED INDICES FOR ANDALUSITE-KANONAITES*

Crystal	n_a	n_b	n_c	Differences ($\times 10^{-4}$)		
				\bar{n}	\bar{n} (81)	\bar{n} (76)
1	9	18	41	24	470	-143
2	16	33	58	37	483	-129
3	14	15	19	17	474	-136
4	9	23	47	28	473	-140
5	11	18	28	20	477	-132
6	5	23	50	27	472	-141
7	-2	-6	-11	-6	457	-154
8	-8	-27	-52	-28	461	-139
9	27	-4	-43	-8	481	-120
10	12	-7	-31	-8	482	-120
11	-5	-11	-6	-7	452	-171
12	14	-4	-33	-7	509	-95
13	-5	-27	-58	-29	481	-125
14	-1	7	28	12	512	-106
15	20	22	21	22	519	-101
16	-45	-40	-38	-40	460	-167
17	6	23	17	16	502	-130
18	21	24	29	25	536	-104
19	15	58	128	67	648	-22
20	6	21	-63	-25	490	-288

* For n_a , n_b , n_c and \bar{n} , the calculated indices resulted from use of the new Gladstone-Dale values summarized in Table 2.

For \bar{n} (81) and \bar{n} (76), the calculated values for \bar{n} resulted from use of the Mandarino (1981) constants and of the Mandarino (1976) constants, respectively.

relative to the general values of Mandarino for predicting the indices of refraction of andalusite or kanonaite. Curiously, the Gladstone-Dale values intended for island or chain silicates (Mandarino 1981) predict values of \bar{n} that are far too low and lead to either fair or poor values for the compatibility index, whereas the earlier constants (Mandarino 1976) predict values of \bar{n} that are too high but yield better results.

A comparative test of the three sets of Gladstone-Dale values on aluminosilicates outside our data-set poses a problem because (1) the indices of refraction reported in the literature are commonly optimistic, even when reporting values to ± 0.003 and (2) the measured indices are commonly linked to a composition derived either from another grain or, in the majority of cases, obtained from bulk analysis of a 1- or 2-gram sample. Such an analysis, because of the presence of inclusions or of extraneous minerals, may thus include elements not actually in the mineral. In spite of this drawback, we tested the three sets of Gladstone-Dale values relative to two samples of andalusite described by Carlino (1972) and, extending the test, to one sample of sillimanite and two of kyanite. As summarized in Table 4, the Mandarino (1981) constants again yield values of \bar{n} that are too low, the Mandarino (1976) constants yield values of \bar{n} that are too high but closer, and our new values provide values that are, as a rule, closest to the observed value for \bar{n} .

TABLE 4. COMPARISON OF OBSERVED MEAN INDICES OF ALUMINOSILICATES WITH THOSE CALCULATED USING THE NEW GLADSTONE-DALE VALUES AND THOSE OF MANDARINO

	I	II	III	IV	V
Composition in weight fractions (normalized)					
SiO ₂	0.3683	0.3661	0.3642	0.3654	0.3758
Al ₂ O ₃	0.6167	0.6083	0.6254	0.6333	0.6171
Fe ₂ O ₃	0.0150	0.0256	0.0094	0.0013	0.0071
Observed physical constants					
D	3.147	3.162	3.25	3.65	3.63
α	1.632	1.638	1.6595	1.7140	1.713
β	1.636	1.642	1.6609	1.7236	1.720
γ	1.643	1.647	1.6812	1.7296	1.728
\bar{n}	1.637	1.642	1.667	1.722	1.720
Calculated mean refractive indices*					
\bar{n} (new)	1.643	1.652	1.659	1.735	1.740
\bar{n} (76)	1.655	1.661	1.675	1.757	1.754
\bar{n} (81)	1.595	1.601	1.612	1.686	1.685

* These were calculated using as Gladstone-Dale values: (1) Our new values for \bar{n} in Table 2; (2) Those suggested by Mandarino (1976) for silicates in general; and (3) Those which Mandarino (1981) suggests be used for Al₂O₃ and Mn₂O₃ in island and chain silicates.

- I, II Andalusites: data from Carlino (1972) but with CaO and MgO values omitted and with remaining weight fractions normalized to total 1.0.
- III Sillimanite: data from Peterson & McMullen (1980) and Peterson (personal communication). Optical data by Gunter (this laboratory) but not from crystal analyzed.
- IV Kyanite: compositional and density data from R. C. Peterson (personal communication). Optical data by Gunter but not from crystal analyzed.
- V Kyanite: all data from Deer, Howie & Zussman (1966).

Plagioclase

Table 5 summarizes the empirical data for 26 plagioclase crystals whose optical properties were measured with a spindle stage by Wolfe (1976). For each crystal, the measured indices of refraction ($\lambda = 589.3$ nm) usually permitted a calculation for $2V$ within 1° of that independently determined for the crystal using the extinction method of Bloss & Riess (1973). Compositions for these same 26 crystals were later determined by electron microprobe by Professor Paul Ribbe. Density values were lacking and hence had to be calculated from the contents and volume of the unit cell. Since unit-cell volumes were not available, the volume of the unit cell (V_{uc}) was calculated for each crystal from its composition in terms of mole fractions of albite (X_{ab}), anorthite (X_{an}) and orthoclase (X_{or}), after these mole fractions had been normalized to total 1.0. After such normalization, the equation used was $V_{uc} = X_{ab}V_{ab} + X_{an}V_{an} + X_{or}V_{or}$, where V_{ab} , V_{an} and V_{or} , respectively, represent the unit-cell volume for low albite

TABLE 5. WEIGHT FRACTIONS OF OXIDES AND MEASURED REFRACTIVE INDICES (± 0.0005 FOR SODIUM LIGHT) FOR 26 PLAGIOCLASE CRYSTALS

SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	K ₂ O	Fe ₂ O ₃	α	β	γ	* x_{AB}	* x_{AN}	* x_{OR}
0.6840	0.1980	0.1157	0.0007	0.0015	---	1.5292	1.5330	1.5387	0.98	0.01	0.01
0.6713	0.2068	0.1089	0.0087	0.0041	---	1.5301	1.5344	1.5407	0.93	0.04	0.02
0.6543	0.2178	0.1030	0.0227	0.0019	.0004	1.5343	1.5395	1.5430	0.88	0.11	0.01
0.6429	0.2262	0.0962	0.0319	0.0028	---	1.5361	1.5404	1.5443	0.82	0.15	0.02
0.6318	0.2316	0.0892	0.0439	0.0026	.0008	1.5399	1.5440	1.5477	0.77	0.21	0.01
0.6180	0.2404	0.0782	0.0522	0.0098	.0014	1.5419	1.5458	1.5495	0.67	0.25	0.06
0.6130	0.2451	0.0803	0.0586	0.0029	.0001	1.5418	1.5465	1.5500	0.69	0.28	0.02
0.6217	0.2396	0.0862	0.0512	0.0013	---	1.5433	1.5477	1.5512	0.74	0.24	0.01
0.6054	0.2475	0.0749	0.0618	0.0097	.0008	1.5429	1.5480	1.5515	0.65	0.30	0.05
0.5936	0.2557	0.0705	0.0719	0.0074	.0009	1.5465	1.5506	1.5538	0.61	0.34	0.04
0.5907	0.2603	0.0720	0.0760	0.0010	---	1.5469	1.5507	1.5546	0.62	0.36	0.01
0.5906	0.2584	0.0694	0.0741	0.0067	.0009	1.5478	1.5511	1.5548	0.60	0.36	0.04
0.5840	0.2640	0.0690	0.0811	0.0020	.0001	1.5481	1.5515	1.5558	0.60	0.39	0.01
0.5758	0.2694	0.0641	0.0884	0.0024	---	1.5505	1.5537	1.5581	0.56	0.42	0.01
0.5765	0.2640	0.0623	0.0884	0.0049	.0040	1.5510	1.5549	1.5593	0.54	0.43	0.03
0.5615	0.2771	0.0564	0.0984	0.0046	.0020	1.5533	1.5560	1.5606	0.49	0.48	0.03
0.5543	0.2808	0.0539	0.1042	0.0046	.0020	1.5549	1.5576	1.5618	0.47	0.50	0.03
0.5539	0.2825	0.0537	0.1053	0.0029	.0017	1.5555	1.5581	1.5622	0.47	0.51	0.02
0.5387	0.2915	0.0474	0.1176	0.0029	.0021	1.5576	1.5606	1.5650	0.41	0.57	0.02
0.5358	0.2941	0.0461	0.1191	0.0022	.0029	1.5584	1.5613	1.5656	0.40	0.58	0.01
0.5346	0.2928	0.0445	0.1216	0.0026	.0039	1.5587	1.5620	1.5670	0.39	0.59	0.02
0.5286	0.2975	0.0437	0.1255	0.0016	.0031	1.5597	1.5632	1.5683	0.38	0.61	0.01
0.5198	0.3026	0.0397	0.1310	0.0021	.0050	1.5609	1.5650	1.5695	0.35	0.64	0.01
0.4866	0.3283	0.0244	0.1588	0.0001	.0017	1.5656	1.5718	1.5768	0.22	0.78	---
0.4811	0.3303	0.0227	0.1639	0.0001	.0020	1.5669	1.5724	1.5770	0.20	0.80	---
0.4544	0.3484	0.0100	0.1861	---	.0012	1.5716	1.5791	1.5841	0.09	0.91	---

* Compositions recalculated as mole fractions of albite (x_{AB}), anorthite (x_{AN}) and orthoclase (x_{OR}) prior to normalization to total 1.0.

(663.57 Å³ according to Stewart 1975), one-half that for anorthite (1336.3 Å³/2 according to Smith 1974), and that for maximum microcline (723.4 Å³ according to Stewart 1975). Density was then calculated by computer from V_{uc} and the weight of the unit-cell contents for each crystal.

After normalization of the weight fractions in Table 5 and calculation of \bar{n} and then $(\bar{n}-1)/D$, the SAS GLM procedure (with NOINT option) fitted equation (6) to the data by least squares. The resultant Gladstone-Dale values, *specific for plagioclase*, are compared in Table 6 to those cited by Mandarino (1976). However, the plagioclase-specific values cited for K₂O and Fe₂O₃ may not be reliable because these components are so minor in the 26 plagioclase samples studied.

Using the plagioclase-specific values from Table 6, the indices α , β , γ and \bar{n} (for sodium light) were calculated and subtracted from the observed values. In addition, \bar{n} was calculated using the Mandarino (1976) constants and subtracted from its observed value. The differences (Table 7) clearly show the superiority of the specific values. The specific values also prove superior to the Mandarino (1976) constants if applied to several plagioclases for which data on index of refraction, composition and density are given in the literature (Table 8).

CONCLUSIONS

1. Gladstone-Dale values need to be calculated, as described here, for each mineral group using spindle-stage-derived optical data in conjunction with cell-edge data and compositional data derived from the same grain by electron-microprobe analysis.

TABLE 6. GLADSTONE-DALE VALUES FOR PLAGIOCLASES COMPARED TO MANDARINO'S (1976) VALUES*

	SiO ₂	Al ₂ O ₃	Na ₂ O	CaO	K ₂ O	Fe ₂ O ₃
Specific Gladstone-Dale values						
α	0.228 (24)	0.147 (51)	0.140 (132)	0.277 (84)	0.207 (97)	0.289 (82)
β	0.207 (20)	0.188 (41)	0.207 (107)	0.259 (69)	0.237 (79)	0.194 (67)
γ	0.197 (20)	0.202 (41)	0.258 (107)	0.263 (68)	0.226 (79)	0.266 (66)
\bar{n}	0.211 (15)	0.179 (32)	0.202 (82)	0.266 (52)	0.223 (60)	0.250 (51)
Mandarino (1976) values						
\bar{n}	0.208	0.207	0.190	0.210	0.196	0.268

* The large standard errors of estimate (values in parentheses) are likely the result of (a) the strong interdependence of the independent variables (weight fractions oxides) which necessarily total 1.0 and (b) the discontinuities in the variation of refractive index with composition that appear to exist at one or more compositions for the plagioclase series (Wolfe *et al.*, in preparation). The microprobe analyses for Na₂O may also involve higher errors than for SiO₂ and Al₂O₃. The small amounts of K₂O and Fe₂O₃ in the plagioclases analyzed caused high relative errors in their determination. Hence these Gladstone-Dale values for K₂O and Fe₂O₃ should only be used if these oxides constitute less than 1% by weight of the plagioclase.

TABLE 7. OBSERVED INDICES FOR PLAGIOCLASES MINUS THOSE CALCULATED USING GLADSTONE-DALE VALUES FROM TABLE 6

Crystal	α	β	γ	\bar{n}	\bar{n} (76)*
Differences ($\times 10^4$)					
1	-5	-7	2	-10	-63
2	-8	-9	9	-9	-58
3	2	9	-5	-4	-46
4	1	-2	-9	-9	-46
5	-2	2	-6	-8	-34
6	-1	3	3	-4	-24
7	-11	-6	-14	-16	-35
8	24	25	14	15	-9
9	-9	0	-3	-9	-23
10	5	4	-4	-3	-12
11	5	-4	-11	-9	-19
12	13	3	-1	0	-8
13	4	-10	-12	-11	-17
14	9	-6	-5	-5	-6
15	-6	5	3	-4	-2
16	7	-7	-4	-6	-1
17	12	-3	-5	-3	7
18	15	-2	-6	-2	7
19	6	-7	-9	-7	10
20	7	-6	-11	-8	9
21	-10	-3	0	-5	15
22	5	-1	1	-2	19
23	0	4	-4	-4	20
24	-8	3	6	-3	36
25	-8	-3	-5	-8	36
26	-12	9	13	1	59

*Mandarino's (1976) Gladstone-Dale values used.

TABLE 8. COMPARISON OF REFRACTIVE INDICES REPORTED BY OTHER AUTHORS WITH THOSE CALCULATED USING NEW GLADSTONE-DALE VALUES AND THOSE OF MANDARINO (1976)

	I	II	III
Composition in weight fractions (normalized)			
SiO ₂	0.6874	0.4319	0.6729
Al ₂ O ₃	0.1944	0.3665	0.2018
Na ₂ O	0.1182	—	0.1154
CaO	—	0.2016	0.0070
K ₂ O	—	—	0.0024
Fe ₂ O ₃	—	—	0.0005
Observed physical constants			
D	2.62	2.76	2.626
α	1.529	1.575	1.532
β	1.533	1.583	1.536
γ	1.539	1.588	1.541
\bar{n}	1.5337	1.582	1.5363
Indices calculated using new values			
α	1.5289	1.5746	1.5300
β	1.5327	1.5810	1.5346
γ	1.5376	1.5855	1.5399
\bar{n}	1.5337	1.5806	1.5355
Indices from Mandarino's (1976) values			
\bar{n}	1.5389	1.5742	1.5403

- I. Low albite physical data from Tröger (1979, p. 120), composition assumed to be pure albite.
- II. Anorthite physical data from Tröger (1979, p. 120), composition assumed to be pure anorthite.
- III. Albite physical and compositional data from Chaudhry (1971, p. 180, specimen MN.57). The index β was here calculated from his α , γ and 2γ values.

2. Such values will greatly enhance, for mineralogists, the uses described by Mandarino (1979) for Gladstone–Dale constants; these can be developed to predict principal indices of refraction (α , β , γ or ϵ , ω) or their mean value to within 0.003 (*ca.*) for members of the group, as demonstrated here for members of the andalusite–kanonaite and plagioclase series. The greater precision of Gladstone–Dale values specific for a mineral series will thus permit more precise crosschecks between measured composition, indices of refraction, density and unit-cell volume when members of the series are studied in the future. For example, if density calculated from the unit-cell volume and contents deviates significantly from measured density, the value that best predicts indices of refraction from the Gladstone–Dale relationship should be favored.

3. The Gladstone–Dale value for a given oxide will vary with the structure accommodating that oxide. Mandarino (1981) recognized this by providing, for several trivalent oxides, one set of Gladstone–Dale values for application to island or chain silicates and another for silicates in general. Further support for the structural dependence of Gladstone–Dale values derives from the changing values, calculated from \bar{n} , for SiO₂ in the silica polymorphs, namely: 0.188–0.190 (stishovite), 0.204 (coesite), 0.207 (quartz), 0.209 (cristobalite), 0.207–0.211 (tridymite) and 0.222 (silicalite). The comparable value we obtain for SiO₂ in the plagioclase series, namely 0.211, falls within this range, but our value for SiO₂ in the series andalusite–kanonaite, 0.285, falls well outside the range.

4. Ultimately, Gladstone–Dale values, or similar values such as those based on the Clausius–Mosotti relation discussed by Lasaga & Cygan (1982), if evaluated for different mineral groups, may provide a parameter for determining the proportion of covalency to ionicity in, say, the Si–O bond.

ACKNOWLEDGEMENTS

The Caswell Silver Foundation of the University of New Mexico kindly provided the support that facilitated much of the preparation and writing of this paper. F.D. Bloss, in particular, thanks the Foundation for the opportunity to experience, as the first Caswell Silver Distinguished Professor at the University of New Mexico, a stimulating academic year devoted to research of his own choosing. Support from the National Science Foundation (NSF EAR-8018492) is also gratefully acknowledged. The

writers owe much to Dr. Joseph Mandarino whose study and publications relative to Gladstone–Dale constants set the stage for this paper. We thank him (and two anonymous reviewers) for suggestions that materially improved the manuscript. Professor Paul Ribbe kindly made available his microprobe results for the plagioclase samples studied optically by Wolfe. We thank Judy Metelits and Hersha Evans-Wardell for skillful typing of the manuscript.

REFERENCES

- BLOSS, F.D. (1981): *The Spindle Stage: Principles and Practice*. Cambridge University Press, Cambridge, England.
- & RIESS, D. (1973): Computer determination of 2V and indicatrix orientation from extinction data. *Amer. Mineral.* 58, 1052-1061.
- CARLINO, P. (1972): L'andalusite di S. Giorgio Morgeto (Reggio Calabria). *Soc. Ital. Mineral. Petrog. Rend.* 28, 413-421.
- CHAUDHRY, M.N. (1971): Feldspars from the Meldon aplite, Devonshire, England. *Mineral. Mag.* 38, 179-185.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1966): *An Introduction to the Rock-Forming Minerals*. John Wiley & Sons, New York.
- FLANIGEN, E.M., BENNETT, J.M., GROSE, R.W., COHEN, J.P., PATTON, R.L., KIRCHNER, R.M. & SMITH, J.V. (1978): Silicalite, a new hydrophobic crystalline silica molecular sieve. *Nature* 271, 512-516.
- GUNTER, M. & BLOSS, F.D. (1982): Andalusite–kanonaite series: lattice and optical parameters. *Amer. Mineral.* 67, 1218-1228.
- HELWIG, J.T. & COUNCIL, K.A., eds. (1979): *SAS User's Guide*. SAS Institute Inc., Cary, North Carolina.
- LASAGA, A.C. & CYGAN, R.T. (1982): Electronic and ionic polarizabilities of silicate minerals. *Amer. Mineral.* 67, 328-334.
- MANDARINO, J.A. (1976): The Gladstone–Dale relationship. I. Derivation of new constants. *Can. Mineral.* 14, 498-502.
- (1979): The Gladstone–Dale relationship. III. Some general applications. *Can. Mineral.* 17, 71-76.
- (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* 19, 441-450.

- PABST, A. (1975): Modified Gladstone and Dale calculations for carbonates. *Fortschr. Mineral.* **52**, 605-09.
- PETERSON, R.C. & McMULLEN, R.K. (1980): Neutron structure refinements of the Al_2SiO_5 polymorphs. *Amer. Geophys. Union Trans.* **61**, 409 (abstr.).
- SMITH, J.V. (1974): *Feldspar Minerals. 1. Crystal Structure and Physical Properties*. Springer-Verlag, Heidelberg, Germany.
- STEWART, D.B. (1975): Lattice parameters, composition, and Al/Si order in alkali feldspars. In *Feldspar Mineralogy* (P.H. Ribbe, ed.). *Mineral. Soc. Amer., Rev. Mineral.* **2**, St1-20.
- TRÖGER, W.E. (1979): *Optical Determination of Rock-Forming Minerals* (translated by Bambauer, H.U., Taborszky, F. & Trochim, H.D.) E. Schweitzerbart'sche Verlagsbuchhandlung, Stuttgart, Germany.
- WOLFE, H.E. (1976): *Optical and X-Ray Study of the Low Plagioclases*. M.S. thesis, Virginia Polytechnic Inst. and State Univ., Blacksburg, Va.

Received March 26, 1982, revised manuscript accepted August 20, 1982.