

- ²⁵A. V. Lesikar, O. H. El-Bayoumi, C. J. Simmons, and C. T. Moynihan, "Secondary Electrical Relaxations in Alkali Silicate Glasses"; for abstract see *Am. Ceram. Soc. Bull.*, **58** [3] 384 (1979).
- ²⁶T. J. Higgins, P. B. Macedo, and V. Volterra, "Mechanical and Ionic Relaxation in Na₂O·3SiO₂ Glass," *J. Am. Ceram. Soc.*, **55** [10] 488–91 (1972).
- ²⁷M. Tomozawa, pp. 283–345 in *Treatise on Materials Science and Technology*, Vol. 12 (Glass 1: Interaction with Electromagnetic Radiation), Edited by M. Tomozawa and R. H. Doremus. Academic Press, New York, 1977.
- ²⁸A. E. Owen, pp. 77–196 in *Progress in Ceramic Science*, Vol. 3. Edited by J. E. Burke. Pergamon, Elmsford, N.Y., 1963.
- ²⁹C. T. Moynihan, J. H. Simmons, and P. B. Elterman, "Source of Dielectric Relaxation in Ionically Conducting Glasses"; for abstract see *Am. Ceram. Soc. Bull.*, **55** [8] 745 (1976).
- ³⁰C. Lim and D. E. Day, "Sodium Diffusion in High Silica Glass," *J. Am. Ceram. Soc.*, **61** [7–8] 329–32 (1978).
- ³¹J. H. Simmons, P. B. Elterman, C. J. Simmons, and R. K. Mohr, "Dielectric Relaxation in High-Silica Borosilicate Glasses," *ibid.*, **62** [3–4] 158–61 (1979).
- ³²C. T. Moynihan and R. W. Laity, "Relative Cation Mobilities in KCl-LiCl Melts," *J. Phys. Chem.*, **68** [11] 3312–17 (1964).
- ³³O. V. Mazurin, pp. 5–55 in *Structure of Glass*, Vol. 4. Edited by O. V. Mazurin. Translated by E. B. Uvarov. Consultants Bureau, New York, 1965.
- ³⁴O. J. Kleppa and L. S. Hersh, "Heats of Mixing in Liquid Alkali Nitrate Systems," *J. Chem. Phys.*, **34** [2] 351–58 (1961).
- ³⁵L. S. Hersh and O. J. Kleppa, "Enthalpies of Mixing of Some Binary Liquid Halide Mixtures," *ibid.*, **42** [4] 1309–22 (1965).
- ³⁶O. J. Kleppa and H. C. Ko, "Thermochemical Studies of Liquid Alkali Metaphosphates," *Inorg. Chem.*, **10** [4] 771–75 (1971).
- ³⁷J. R. Hendrickson and P. J. Bray, "A Theory for the Mixed Alkali Effect in Glass: Part 1," *Phys. Chem. Glasses*, **13** [2] 43–49 (1972); "Part 2," *ibid.*, [4] 107–15.
- ³⁸H. M. J. M. van Ass and J. M. Stevels, "Internal Friction of Mixed Alkali Metaphosphate Glasses: II," *J. Non-Cryst. Solids*, **16** [1] 27–45 (1974).
- ³⁹Y. H. Han, N. J. Kreidl, and D. E. Day, "Alkali Diffusion and Electrical Conductivity in Sodium Borate Glasses," *ibid.*, **30** [3] 241–52 (1979).
- ⁴⁰J. C. Maxwell, *A Treatise on Electricity and Magnetism*, 3d ed.; p. 440. Oxford University Press, London, 1904.
- ⁴¹E. A. Moelywyn-Hughes, *Physical Chemistry*, 2d rev. ed; pp. 890–94. Pergamon, New York, 1961.
- ⁴²O. V. Mazurin and E. S. Borisovskii, "Neutralization Reduction of Electrical Conductivity in Silica Glasses," *Sov. Phys.-Tech. Phys.*, **2** [2] 243–54 (1957).
- ⁴³J. M. Stevels, pp. 350–91 in *Handbook of Physics (Handbuch der Physik)*, Vol. XX, Edited by S. Flügge. Springer-Verlag, Berlin, 1957.
- ⁴⁴M. D. Ingram, "Conduction and Dielectric Loss Mechanisms in β -Alumina and Glass: A Discussion Based on the Paired Interstitialcy Model," *J. Am. Ceram. Soc.*, **63** [5–6] 248–53 (1980).
- ⁴⁵C. T. Moynihan and A. V. Lesikar, "Weak Electrolyte Models for the Mixed-Alkali Effect in Glass;" submitted to the *Journal of the American Ceramic Society*.

The Stability of Bredigite and Other Ca-Mg Silicates

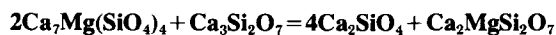
ERIC ESSENE

Department of Geological Sciences, The University of Michigan, Ann Arbor, Michigan 48109

The phase Ca₇Mg(SiO₄)₄, bredigite, is chemically and structurally distinct from α' -Ca₂SiO₄. Experiments on its lower stability limit represent a synthesis limit which is not likely to be an equilibrium boundary. Equilibrium experiments place its upper stability limit at 1372°C and 98 kPa by the reaction



The experimental data also require a second reaction



at the same pressure and temperature and imply that two other reactions relating these phases are located near 1372°C and 98 kPa. Location of these four reactions around an invariant point in *P-T* space shows that bredigite is on the low-pressure side of the reactions.

I. Introduction

THE mineral bredigite, originally identified as the α' polymorph of Ca₂SiO₄,¹ has since been shown to have essential magnesium with compositions usually estimated at values between Ca₅Mg(SiO₄)₃ [=Ca_{1.67}Mg_{0.33}SiO₄] and Ca₇Mg(SiO₄)₄ [=Ca_{1.75}Mg_{0.25}SiO₄].^{2–11} Experimental studies have placed the composition of synthetic bredigite at Ca_{1.67}Mg_{0.33}SiO₄ to Ca_{1.8}Mg_{0.2}SiO₄.^{2–6,9} Based on crystal-chemical arguments, Moore⁸ estimated the bredigite composition to be Ca_{1.75}Mg_{0.25}SiO₄ with solid solutions ranging to Ca_{1.88}Mg_{0.12}SiO₄. Saalfeld¹⁰ X-rayed a synthetic bredigite to obtain cell dimensions; he concluded that bredigite possesses the same structure type as α' -Ca₂SiO₄. His chemical analysis of the same material gave the formula Ca_{1.75}Mg_{0.25}SiO₄. Moore and Araki¹¹ refined the structure of a synthetic bredigite from a slag and found that it is an ordered Ca-Mg silicate with a structure distinct from α' -Ca₂SiO₄ and with several 8 to 12-coordinated

polyhedral sites. These large sites suggest that it will concentrate large cations and analysis must include elements such as Ba, Sr, and K to ensure that the proper composition is inferred. Microprobe analyses of three natural bredigites yield (Ca_{1.76}Na_{0.01})(Mg_{0.26}Mn_{0.007}Fe_{0.006})(Si_{0.94}P_{0.012}S_{0.012})O₄.⁷ (Ca_{1.74}Na_{0.02})(Mg_{0.18}Fe_{0.07})(Si_{0.99})₄,¹² and Ca_{1.77}Mg_{0.21}(Si_{1.01})₄.¹³ These analyses are near Ca_{1.75}Mg_{0.25}SiO₄ but Ba, K, and Sr were not determined. The apparent discrepancy between the inferred compositions of some synthetic bredigite and analyses of natural materials is unexplained. To establish that bredigite must contain more Mg than Ca_{1.75}Mg_{0.25}SiO₄, it should be reacted to form Ca₃Mg(SiO₄)₂ + a bredigite containing more magnesium, thus showing that Ca_{1.75}Mg_{0.25}SiO₄ is unstable. Although bredigite's formula is still somewhat uncertain, Ca_{1.75}Mg_{0.75}SiO₄ is used in the present discussion. Only the coefficients of the reactions would change if a formula higher in magnesium were chosen.

II. Upper Stability Limit

There is some controversy as to the upper stability limit of bredigite at atmospheric pressure (98 kPa), as experiments on its thermal limit yield temperatures of 1372° to 1500°C.^{3–5,9} Only the experiments of Lin and Foster⁸ involved equilibrium reversals, showing that bredigite decomposes to Ca₂SiO₄ + Ca₃Mg(SiO₄)₂ (merwinite) at >1374°C and that these products in turn react to bredigite at <1370°C. These data are definitive in placing the upper stability of bredigite at 1372±2°C, locating the boundary only 9°C lower than the synthesis experiments of Schlaudt and Roy.⁴ Lin and Foster identified the Ca₂SiO₄ polymorph as β -Ca₂SiO₄ (larnite), whereas Schlaudt and Roy identified it as α' -Ca₂SiO₄ and Gutt³ as α -Ca₂SiO₄. The β - α' transition in Ca₂SiO₄ has been reversibly located at ≈700°C for 98 kPa pressure^{14–17} and it decreases in the presence of excess Mg since α' -Ca₂SiO₄ concentrates Mg over β -Ca₂SiO₄.⁴ When quenched, α' -CaSiO₄ inverts to β so rapidly that α' does not

Table I. Volume Data and Volume Change for Reactions (4)-(7)

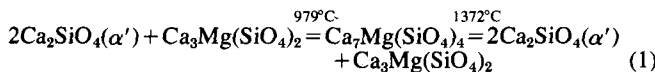
Phase	Abbrev.	Formula	$V_{25^\circ\text{C}}^\circ$ (cm ³)	Ref.	$V_{1200^\circ\text{C}}^\circ$ (cm ³)	Ref.
Bredigite	Bd	Ca ₇ Mg(SiO ₄) ₄	204.53	10	215.21	*
Rankinite	Rn	Ca ₃ Si ₂ O ₇	95.8	18	100.65	19
Larnite	Ln	β-Ca ₂ SiO ₄	51.6	18	54.49	19
α'-Ca ₂ SiO ₄	α'	α'-Ca ₂ SiO ₄	51.8	21	54.49	*
Akermanite	Ak	Ca ₂ MgSi ₂ O ₇	92.81	18	96.27	19
Merwinite	Me	Ca ₃ Mg(SiO ₄) ₂	98.54 [†]	16	103.08	19
			$\Delta V_{25^\circ\text{C}}^\circ$ (cm ³)		$\Delta V_{1200^\circ\text{C}}^\circ$ (cm ³)	
Reaction (4)			-2.4		-3.2	
Reaction (5)			-0.3		-1.6	
Reaction (6)			+2.1		+1.5	
Reaction (7)			+4.5		+4.7	

*The thermal expansions of bredigite and α'-Ca₂SiO₄ are assumed to be equal to those of larnite. This assumption is justified by the closely related structures of these phases. †The volume of this phase given in Ref. 16 is considerably smaller than that given in Ref. 18. The former is preferred because it is derived as part of a detailed crystallographic study.

survive.⁴ Schlautd and Roy identified α'-Ca₂SiO₄ by high-temperature X-ray and DTA methods only. This reaction presumably explains why Lin and Foster reported β-Ca₂SiO₄ as a reaction product and why α'-Ca₂SiO₄ has not been found in nature. It is assumed that Lin and Foster's experiments demonstrated the upper stability of bredigite compared to α'-Ca₂SiO₄ and merwinite at 1372°C. In contrast, the lower stability of bredigite has not been investigated by equilibrium reversals.

III. Lower Stability Limit

Schlautd and Roy⁴ investigated the system Ca₂SiO₄-Mg₂SiO₄ and concluded that bredigite was unstable at <979°C. They noted the general difficulty of growing bredigite and that some starting materials yielded Ca₂SiO₄ + merwinite instead. Nevertheless, they assumed that their lower synthesis boundary for bredigite was an equilibrium feature. They inferred that the same assemblage (α'-Ca₂SiO₄ + merwinite) was more stable than bredigite at both lower and higher temperatures:



This reaction requires that bredigite have a higher entropy than α'-Ca₂SiO₄ + merwinite at 972°C but a lower entropy at 1372°C, since

$$d\Delta G_T = -\Delta S_r dT \quad (2)$$

where the assemblage with the more negative free energy has a higher entropy with increasing temperature. If pressure is considered as a variable, bredigite should break down with increasing pressures to form Ca₂SiO₄ + Ca₃Mg(SiO₄)₂ because it has a larger volume (Table I). The phase diagram consistent with Schlautd and Roy's experiments requires that bredigite be restricted to low pressures (Fig. 1(A)). It is conceivable that the ΔS_r is relatively small and that a sign reversal occurs at high temperatures.

One way to obtain a sign reversal in small ΔS_r is to have a phase in the low-temperature assemblage undergo cation disorder at high temperatures, which would anomalously increase its entropy. Merwinite does have some potential for Ca-Mg disorder. However, the high-temperature entropy of merwinite has been measured¹⁹; it shows no particular anomalous increase up to 1300°C. If ΔS_r is very small (<4.2 J/mol K), the entropy associated with disorder could still cause a sign change in ΔS_r and be spread over several hundred degrees. High-temperature X-ray refinement of the structures of merwinite (and bredigite) are necessary to resolve the possibility of some positional disorder in these phases.

An alternative explanation is that α'-Ca₂SiO₄ undergoes a phase transition between 979° and 1372°C with a sufficient change in

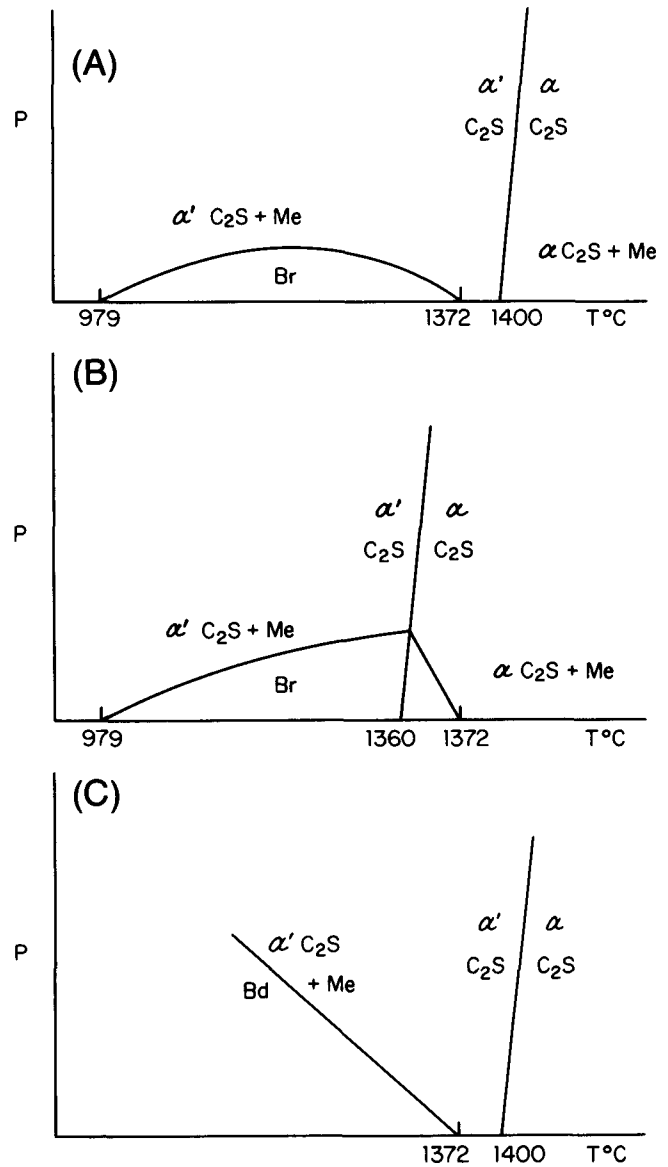
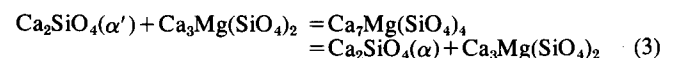


Fig. 1. Possible P-T equilibria for bredigite required by breakdown below 979°C and above 1372°C to Ca₂SiO₄ and Ca₃Mg(SiO₄)₂. (A) Diagram required for a change in sign of ΔS_r, as indicated by data of Ref. 4. (B) Possible diagram if α'-α inversion occurs below 1372°C (Ref. 3). (C) Diagram obtained by thermodynamic calculations.

entropy to change the slope of the bredigite reaction. Schlautd and Roy⁴ showed that the α'-α transition of Ca₂SiO₄ is within 20°C of the upper limit of bredigite and they noted the difficulty in identifying the equilibrium high-temperature Ca₂SiO₄ phase due to reaction on quenching. Gutt³ reported that the α'-α transition of Mg-containing Ca₂SiO₄ in equilibrium with bredigite occurs at 1360°C (based on high-temperature X-ray studies). The entropy change of α'-to-α-Ca₂SiO₄ is 12.4 J/mol K²⁰ and, if the bredigite reaction has a smaller entropy change, the slope of the reaction could reverse at 1360°C. In this case the proper sequence of reactions for bredigite stability would be:



The phase diagram consistent with Gutt's α'-α inversion and Schlautd and Roy's experiments on bredigite stability is shown in Fig. 1(B)).

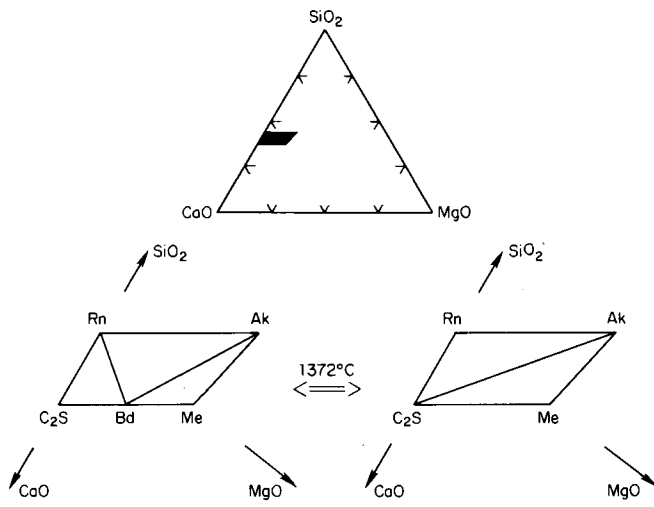
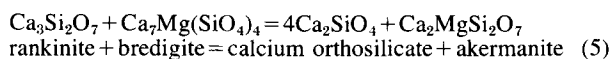
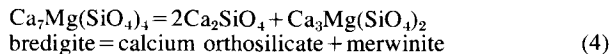


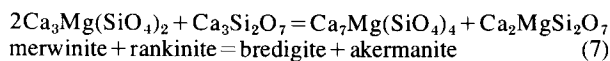
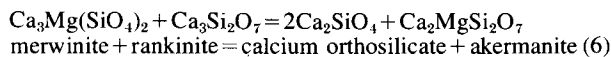
Fig. 2. A portion of the system CaO-MgO-SiO₂, showing phase compatibility regions below and above 1372°C at 98 kPa (modified from Ref. 9).

Another alternative is that Schlaudt and Roy's⁴ lower stability limit for bredigite may represent a synthesis rather than an equilibrium boundary and bredigite may be stable to relatively low temperatures (Fig. 1(C)). This explanation is consistent with other measurements showing stable bredigite down to 500°C. It seems likely that this boundary has not been properly located and its use in predicting minimum temperatures for bredigite rocks¹² may be in error. Carefully reversed experiments in this reaction are needed at <1000°C to evaluate the lower stability of bredigite.

In addition to the stability limits of bredigite, reactions between bredigite and other phases are also of interest. Lin and Foster⁹ concluded that bredigite decomposes at 1372°C with the tie line to Ca₃Si₂O₇ (rankinite) simultaneously breaking (Fig. 2), which means that two equilibria coincide:



This reaction requires an invariant point at 1372°C and 98 kPa, and all other univariant equilibria related by algebraic combination of Eqs. (4) and (5) must pass through the same invariant point. These reactions are:



Reactions (4) to (7) can be positioned in *P-T* space so that the equilibria are consistent (Fig. 3) with Lin and Foster's experiments⁹ and with available volume data (Table I). It is clear that Lin and Foster's composition diagrams (Fig. 2) must be separated by either one or two compositional configurations except through the invariant point itself. The chance that the invariant point is located exactly at 98 kPa is small, but experimental reversals⁹ allow reaction (4) to be inferred between 1370° and 1374°C and reaction (5) between 1371° and 1372°C. Based on these data, the invariant point must be near 1372°C and 98 kPa, assuming that the slopes of reactions (4) and (5) are significantly different. If the slopes are similar, the invariant point could be located at higher pressures and lower temperatures or it need not even exist (i.e. it may be located at "negative" pressures and higher temperatures). The latter possibility would make reaction (5) metastable at real *P-T*. Accurate high-temperature entropy data on bredigite and rankinite and/or experiments at different pressures are needed to identify the exact position of reactions (4) to (7).

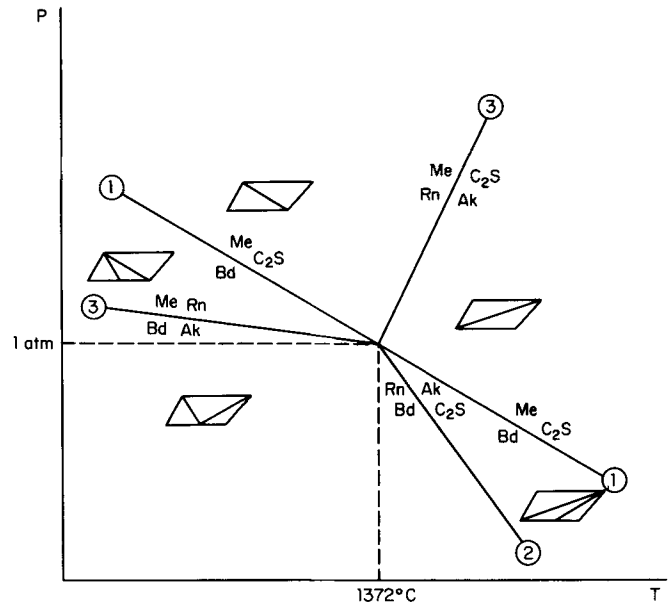


Fig. 3. *P-T* projection around the invariant point at 1372°C and 98 kPa for part of the system CaO-MgO-SiO₂ (compatibility quadrilaterals as in Fig. 2).

Acknowledgments: The writer thanks W. R. Foster, D. Perkins, and J. Valley for reviewing the manuscript.

References

1. C. E. Tilley and H. C. G. Vincent, "Occurrence of an Orthorhombic High-Temperature Form of Ca₂SiO₄ (Bredigite) in the Scawt Hill Contact Zone and as a Constituent of Slags," *Mineral. Mag.*, **28**, 255-71 (1948).
2. W. Gutt, "A New Calcium Magnesiumsilicate," *Nature (London)*, **190** [4773] 339-40 (1961).
3. W. H. Gutt, "System Dicalcium Silicate-Merwinite," *ibid.*, **207** [4993] 184-85 (1965).
4. C. M. Schlaudt and D. M. Roy, "The Join Ca₂SiO₄-CaMgSiO₄," *J. Am. Ceram. Soc.*, **49** [8] 430-32 (1966).
5. M. J. O'Hara and G. M. Biggar, "Phase Equilibria Aspects of the Performance of Basic Refractories," *Trans. Br. Ceram. Soc.*, **69** [6] 243-51 (1970).
6. G. M. Biggar, "Phase Relationships of Bredigite (Ca₃MgSi₃O₁₂) and of the Quaternary Compound (Ca₆MgAl₃Si₂O₂₁) in the System CaO-MgO-Al₂O₃-SiO₂," *Cem. Concr. Res.*, **1** [4] 493-513 (1971).
7. H. G. Midgley and M. Bennett, "A Microprobe Analysis of Larnite and Bredigite from Scawt Hill, Larne, Northern Ireland," *ibid.*, pp. 413-51 (1970).
8. P. B. Moore, "Bracelets and Pinwheels: A Topological-Geometrical Approach to the Calcium Orthosilicate and Alkali Sulfate Structure," *Am. Mineral.*, **58** [1-2] 32-42 (1973).
9. H. C. Lin and W. R. Foster, "Stability Relations of Bredigite (5CaO-MgO-3SiO₂)," *J. Am. Ceram. Soc.*, **58** [1-2] 73 (1975).
10. H. Saalfeld, "Crystallographic Investigation of the Compound Ca₇MgSi₃O₁₆ (Phase T) in the System Ca₂SiO₄-Ca₃Mg(SiO₄)₂," *Ber. Dtsch. Keram. Ges.*, **51** [10] 295-98 (1974).
11. P. B. Moore and T. Araki, "The Crystal Structure of Bredigite and the Genealogy of Some Alkaline Earth Orthosilicates," *Am. Mineral.*, **61** [1-2] 74-87 (1976).
12. R. Joesten, "Metasomatism and Magmatic Assimilation at a Gabbro-Limestone Contact, Christmas Mountains, Big Bend Region, Texas," *Univ. Microfilms Int.* (Ann Arbor, Mich.) Order No. 74-14276, 417 pp.; *Diss. Abstr. Int. B*, **35** [1] 325 (1974).
13. S. L. Sarkar and J. W. Jeffery, "Electron Microprobe Analysis of Scawt Hill Bredigite-Larnite Rock," *J. Am. Ceram. Soc.*, **61** [3-4] 177-78 (1978).
14. J. Forest, "Knowledge of Dicalcium Silicate," *Bull. Soc. Fr. Mineral. Crystallogr.*, **94** [2] 118-37 (1971).
15. D. M. Roy, "Studies in the System CaO-Al₂O₃-SiO₂-H₂O: III," *J. Am. Ceram. Soc.*, **41** [8] 293-99 (1958).
16. P. B. Moore and T. Araki, "Atomic Arrangement of Merwinite, Ca₃Mg(SiO₄)₂, an Unusual Dense-Packed Structure of Geophysical Interest," *Am. Mineral.*, **57** [9-10] 1355-74 (1972).
17. L. B. Pankratz and K. K. Kelley, "High-Temperature Heat Contents and Entropies of Akermanite, Cordierite, Gehlenite, and Merwinite," *U.S. Bur. Mines Rept. Invest.*, **1964**, No. 6555, 7 pp.
18. R. A. Robie, P. M. Bethke, and K. M. Beardsley, "Selected X-Ray Crystallographic Data, Molar Volumes, and Densities of Minerals and Related Substances," *Geol. Surv. Bull. (U.S.)*, **1967**, No. 1248, 87 pp.
19. G. R. Rigby and A. T. Green, "Reversible Thermal Expansion of Refractory Materials," *Trans. Ceram. Soc. (Engl.)*, **37** [9] 355-403 (1938).
20. J. P. Coughlin and C. J. O'Brien, "High-Temperature Heat Content of Calcium Orthosilicate," *J. Phys. Chem.*, **61**, 767-69 (1957).
21. W. Klement, Jr. and L. H. Cohen, "Determination of the β↔α_L Transition in Ca₂SiO₄ to 7 kbar," *Cem. Concr. Res.*, **4** [6] 939-43 (1974).