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Chemical variation of clinopyroxene phenocrysts from the trachybasaltic lavas of Mount Etna, Sicily

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SUMMARY. The chemical variation of clinopyroxene phenocrysts from the trachybasaltic lavas of Etna volcano is described. The phenocrysts show a limited, but distinct trend in chemical variation from calcic-augite in the hawaiites to augite in the benmoreites. The trend of this variation is unusual, being one of Mg-enrichment with differentiation of the magma. Ca shows a steady decrease in the clinopyroxenes from the hawaiites to the benmoreites. Na, however, shows little chemical variation in the pyroxenes. The trace element chemistry is briefly examined. The clinopyroxenes show well-developed oscillatory and sector zoning. The basal $\{11\bar{1}\}$ sectors are enriched in Si and Mg and depleted in Ti, Al, and Fe relative to the $\{100\}$, $\{110\}$, and $\{010\}$ prism sectors.

THE trachybasaltic lavas of Mount Etna comprise a suite ranging from hawaiite through mugearite to benmoreite. The chemical variation shown by these lavas can be largely explained in terms of moderate- to low-pressure crystal fractionation of augite, plagioclase, olivine, and titanomagnetite from a parental magma of hawaiite composition (Duncan, 1978).

Clinopyroxene is present as phenocrysts in all the trachybasaltic lavas, though most abundant in the more basic members. Oscillatory and sector zoning are well developed in these pyroxenes. The chemical variation shown by the phenocrysts throughout the lava suite and the variation within zoned crystals form the basis of this account. The chemistry of the groundmass pyroxenes is not considered here.

Chemical variation of clinopyroxene phenocrysts

The phenocrysts show a limited, but distinct trend in chemical variation from calcic-augite in the hawaiites to augite in the benmoreites (Table I). The trend of this variation is unusual, being one of Mg-enrichment with differentiation of the magma (fig. 1). In a review of recent work on pyroxenes (Deer *et al.*, 1978) it becomes apparent that most study has been concentrated on tholeiitic volcanics and intrusive rocks and that there is little information available on pyroxenes from lavas of alkalic affinity.

There is reasonable correlation between the over-all trend in the Si-content of the phenocrysts from the hawaiites to the benmoreites and the chemical variation in the lavas. There is an increase in Si and a decrease in Al and Ti of the pyroxenes as the whole-rock chemistry becomes progressively more silicic; a similar relationship occurs in clinopyroxenes from the Hawaiian alkalic lavas (Fodor *et al.*, 1975). In the clinopyroxene structure Al is assumed to be admitted into tetrahedral, 'z', sites to make good any deficiency in Si. The presence of Al_z may be balanced by Ti^{4+} being accepted into octahedral, 'y', sites with the effective substitution $Ti_y^{4+} + 2Al_z \rightleftharpoons M_y^{2+} + 2Si_z$ (Le Bas, 1962). Though there is reasonable correlation between Al_z and Ti, as can be seen from fig. 2 there is an excess of Al_z relative to the Ti with all values plotting above the line 2Al:Ti. This excess of Al_z is probably partly balanced by Al entering the octahedral, 'y', sites with the effective substitution $2Al \rightleftharpoons M_y^{2+} + Si_z$ leading towards $M^{2+}Al(AlSiO_6)$. Scott (1976) describes a similar relationship for pyroxenes from the alkalic lavas of Tenerife. It seems likely that the increase in Si of the augites from the more evolved lavas of the trachybasaltic suite reflects the progressive decrease in the Al_2O_3/SiO_2 ratio of the melt, largely resulting from fractionation of plagioclase.

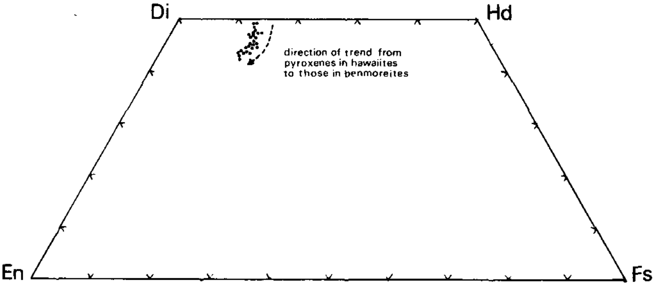
Ca shows a steady decrease in the clinopyroxenes from the hawaiites (around 22.5 % CaO) to the benmoreites (around 20.5 % CaO). This trend correlates well with the variation in the Ca content of

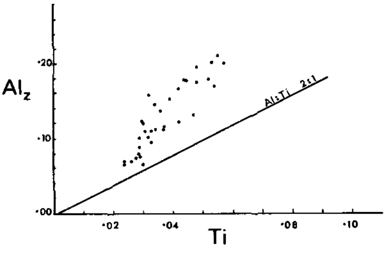
TABLE I. *A selection of microprobe analyses of clinopyroxene phenocrysts from Etnean trachybasaltic lavas. A complete set of analyses is available from the authors on request*

Pyroxene phenocrysts in	Hawaiites		Basic mugearites		Mugearites		Benmoreites	
SiO_2	47.91	47.40	50.69	50.03	50.48	51.87	50.91	51.57
Al_2O_3	5.02	5.86	2.98	3.43	3.98	2.24	2.54	2.01
TiO_2	1.82	1.85	1.04	1.16	1.52	1.06	1.04	0.85
FeO	7.80	7.59	8.50	8.16	8.54	8.00	8.07	8.07
MgO	12.76	12.63	14.11	13.46	13.66	14.56	14.54	14.97
CaO	22.67	22.78	21.60	21.91	21.25	20.92	20.89	20.62
MnO	0.16	0.15	0.24	0.20	0.33	0.37	0.48	0.45
Na_2O	0.51	0.56	0.43	0.50	0.58	0.41	0.49	0.50
Total	98.65	98.82	99.59	98.86	100.34	99.43	98.96	99.04
			Formulae on the basis of six oxygens					
Si	1.821	1.798	1.899	1.889	1.877	1.935	1.914	1.934
Al_z	0.179	0.202	0.101	0.111	0.123	0.065	0.086	0.066
Al_y	0.045	0.060	0.031	0.042	0.051	0.034	0.027	0.023
Ti	0.052	0.053	0.029	0.033	0.042	0.030	0.029	0.024
Fe	0.248	0.241	0.266	0.258	0.266	0.250	0.254	0.253
Mn	0.005	0.005	0.008	0.006	0.010	0.012	0.015	0.014
Mg	0.723	0.714	0.788	0.758	0.757	0.810	0.815	0.837
Ca	0.923	0.926	0.867	0.887	0.846	0.836	0.842	0.829
Na	0.038	0.041	0.031	0.037	0.042	0.030	0.036	0.036
	2.03	2.04	2.02	2.02	2.01	2.00	2.02	2.02
Fe/Mg	0.35	0.34	0.34	0.34	0.36	0.31	0.31	0.30

the lavas. Because of this steady trend, and also because Ca is relatively unaffected by sector zoning, the Ca content makes a good differentiation index for the pyroxenes.

As can be seen in fig. 3*a* the variation for Fe in these pyroxenes is unusual in that there is no marked Fe-enrichment. It appears that there is slight enrichment in the Fe content of the pyroxenes from the hawaiites to the basic mugearites, but for pyroxenes from the basic mugearites to the benmoreites there is a slight drop in the Fe content. The Mg content of these pyroxenes also shows an unusual trend with increasing Mg from the hawaiites to the benmoreites (fig. 3*b*). There is an antipathetic relationship between the progressive decrease in Ca and the increase in Mg, suggesting that Mg^{2+} may be substituting for Ca^{2+} in clinopyroxenes crystallizing from the more evolved melts.



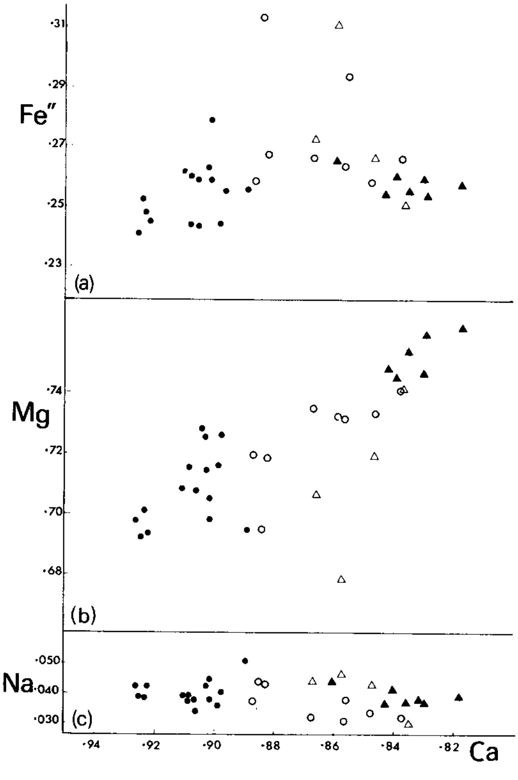


FIGS. 1 and 2. FIG. 1 (*left*). Compositional variation of pyroxene phenocrysts plotted on the pyroxene quadrilateral. FIG. 2 (*right*). Plot of Al_z against Ti calculated on the basis of six oxygens.

The Fe/Mg ratio of the clinopyroxenes, therefore, decreases as the Fe/Mg ratio of the melt progressively increases with differentiation. It is suggested that this antipathetic relationship reflects the competition of different crystallizing phases for the Fe and Mg in the melt. In the more basic melts clinopyroxene will be competing with olivine for the available Mg, whereas in the more evolved magmas clinopyroxene is the only phase likely to incorporate Mg in appreciable amounts. As well as the Fe/Mg ratio of the melt increasing with differentiation, the Fe^{3+}/Fe^{2+} ratio of the liquid is also likely to increase. With fractionation the magma becomes progressively enriched in alkalis and will also fall in temperature. According to Carmichael *et al.* (1974, p. 282) both these factors tend to increase the Fe^{3+}/Fe^{2+} ratio of the melt. This is borne out by the Fe_2O_3/FeO ratios of the lavas which show a general increase from the hawaiites to the benmoreites. Such an increase in the Fe^{3+}/Fe^{2+} ratio of the melt will favour the crystallization of magnetite, thereby depleting the amount of Fe available for the crystallizing pyroxenes.

Na shows little chemical variation in these clinopyroxenes (fig. 3*c*) and shows no direct relationship with the variation of Na in the whole-rock chemistry. Though the lavas show alkali enrichment this is not reflected in the chemistry of the pyroxenes. It is likely that any increase in Na in the melt will favour crystallization of a more sodic plagioclase and this is borne out by the petrography of the rocks. It is unlikely that Na will become an important component in the pyroxene chemistry unless there is insufficient Al available in the melt to form feldspar, that is until peralkaline conditions are achieved.

The Mn content of the clinopyroxenes shows a general increase with fractionation, again probably reflecting the decrease in available Fe.



pyroxene phenocrysts in hawaiites •, basic mugearites ○, mugearites △, benmoreites ▲

FIG. 3. Plot of atomic proportions of (*a*) Fe^{2+}, (*b*) Mg, and (*c*) Na against Ca for pyroxene phenocrysts from the trachybasaltic lavas.

Trace element chemistry

An augite phenocryst from one of the hawaiite lavas was separated and analysed for certain trace elements by atomic absorption technique. Transition metals generally are enriched in the augite relative to whole-rock composition, none of the transition metals considered exceeds a concentration of 0.1 % in the rock composition. The latter, although not identical to the composition of the melt from which the phenocrysts were crystallizing, can be used as a guide to the composition of the melt. The results (Table II) provide some information on the partitioning of these elements between the augite and the melt plus the other crystallizing phases.

Cr is strongly enriched in the clinopyroxene. This is to be expected as Cr^{3+}, with its high crystal-field

TABLE II. *Trace element concentrations of olivine and augite phenocrysts from a hawaiite lava*

	1	2	3
Sr	938	264	288
Ni	57	849	353
Co	70	130	200
Zn	90	158	83
Cr	69	140	848
Cu	58	50	40

Values quoted in ppm
1 whole rock composition
2 olivine phenocryst
3 augite phenocryst

stabilization energy (CFSE) in octahedral coordination, will be readily admitted into the clinopyroxene $M1$ site (Campbell and Borley, 1974). The alumina-rich nature of the trachybasaltic magma may favour the incorporation of Cr^{3+} in the pyroxene with the possible substitution $Si_z + M_y^{2+} \rightleftharpoons Al_z^{3+} + Cr_y^{3+}$.

Ni^{2+}, despite its high CFSE in octahedral coordination, is less strongly enriched in the augite than in the olivine. This is probably because the augite octahedral sites are more distorted than those in the olivine structure.

Co is enriched in the augite but not as markedly as are Ni or Cr. Co^{2+} gains positive CFSE in octahedral coordination but not as strongly as Ni^{2+} or Cr^{3+} (Curtis, 1964).

There is no enrichment of Cu in the augite relative to the whole rock. Cu^{2+} is stabilized by the Jahn-Teller effect in distorted sites and Burns (1970) suggests that Cu^{2+} might be stabilized in the clinopyroxene $M2$ site. This is not observed in the augites and might be explained by Cu^{2+} being also stabilized in the more deformable sites in the silicate melt. The exact nature of cation coordination in silicate melts, however, is not fully known (Henderson, 1979).

Zn^{2+}, having a full orbital of d electrons, receives no CFSE in octahedral coordination and there is in fact no enrichment of Zn in the augite.

Sr^{2+}, as expected from its large ionic radius, is not readily accepted into the clinopyroxene lattice.

Chemical zoning in the clinopyroxene phenocrysts

A detailed examination was carried out on the chemical zoning of the phenocrysts from one of the hawaiite lavas (Table III).

Cryptic zoning. Microprobe spot analyses and

TABLE III. *Microprobe spot analyses of the sectors within a clinopyroxene phenocryst from a hawaiite lava*

	{11$\bar{1}$} sector				Prism sectors					
	L	D	L	D	D	L	D	L	D	L
SiO_2	50.31	49.43	50.20	50.13	48.23	48.70	48.58	48.14	48.26	49.52
Al_2O_3	3.11	3.89	3.56	3.61	4.86	4.34	4.82	4.96	5.05	4.19
TiO_2	1.09	1.26	1.06	1.08	1.68	1.38	1.49	1.56	1.54	1.19
FeO	8.11	8.33	7.79	7.75	8.79	8.21	8.28	8.18	8.19	7.80
MgO	13.76	13.32	13.90	13.79	12.68	13.25	13.06	13.00	12.95	13.45
CaO	22.28	22.34	22.66	22.56	22.23	22.34	22.50	22.34	22.26	22.36
MnO	0.24	0.30	0.26	0.28	0.36	0.04	0.04	0.56	0.68	1.01
Na_2O	0.53	0.56	0.49	0.46	0.60	0.52	0.52	0.51	0.50	0.48
	99.43	99.43	99.92	99.66	99.43	98.78	99.29	99.25	99.43	100.00
	Formulae based on six oxygens									
Si	1.891	1.863	1.877	1.878	1.825	1.847	1.834	1.822	1.823	1.856
Al_z	0.109	0.137	0.123	0.122	0.175	0.153	0.166	0.178	0.177	0.144
Al_y	0.029	0.036	0.034	0.037	0.042	0.041	0.048	0.043	0.048	0.041
Ti	0.031	0.036	0.030	0.030	0.048	0.039	0.042	0.044	0.044	0.034
Fe	0.255	0.263	0.244	0.243	0.278	0.260	0.261	0.259	0.259	0.244
Mn	0.008	0.010	0.008	0.009	0.012	0.001	0.001	0.018	0.022	0.032
Mg	0.771	0.748	0.774	0.770	0.715	0.749	0.735	0.733	0.729	0.751
Ca	0.897	0.902	0.908	0.906	0.901	0.908	0.910	0.906	0.901	0.898
Na	0.039	0.041	0.036	0.033	0.044	0.038	0.038	0.037	0.037	0.035
	2.03	2.04	2.03	2.03	2.04	2.04	2.04	2.04	2.04	2.04
Fe/Mg	0.34	0.35	0.31	0.31	0.39	0.35	0.35	0.36	0.36	0.32

L represents a light oscillatory zone and D a dark oscillatory zone (see fig. 4).

Mineral analyses performed on the Cambridge Instruments Microscan 5 at University College London using wavelength dispersion. Accelerating voltage 20 kV, standards native elements for Ti and Mn and BM minerals for other elements; Mason, Frost, Reed correction program.

scan traces within any one sector of a phenocryst showed there to be no appreciable chemical variation from core to rim.

Oscillatory zoning. Oscillatory zoning is generally well developed in the outer half of these phenocrysts and is readily distinguished optically (fig. 4). This zoning is reflected in the chemistry by variation of Si, Al, Ti, and Mg. In this oscillatory chemical variation, Si and Mg vary antipathetically with Al and Ti. Oscillatory zoning has been described by Augustithus (1976) in zoned augites from an Ethiopian basaltic lava which show a somewhat different chemical variation in Mg, Fe, and Ti.

Downes (1974) considers that the oscillatory zoning in Etnean augites is controlled by the interaction of crystal growth and ionic diffusion in the melt, in a manner similar to that proposed by Bottinga *et al.* (1966) for oscillatory-zoned plagioclases. This is a likely mechanism, it being difficult to envisage a process whereby a short-period cyclic variation in the composition of the melt could be achieved giving rise to oscillatory zoning. It is possible, however, that the oscillatory zoning could be due to rhythmic variation in the pressure of the subvolcanic conduit giving rise to a periodic variation in the conditions of crystallization. As yet there is little information available concerning the sensitivity of the concentrations of Al, Si, Ti, and Mg in clinopyroxenes to variations in pressure at shallow depths.

Sector zoning. Sector zoning is well developed in the clinopyroxene phenocrysts. In thin section the sectors are readily apparent as areas of coherent birefringence and extinction. The sectors can be regarded as pyramids with their apices at the centre of the crystal and with their bases represented by crystal faces. In augites showing 'hour-glass' structure prism sectors of the forms $\{100\}$, $\{110\}$, and $\{010\}$ and basal sectors $\{11\bar{1}\}$ are commonly developed (Leung, 1974). Downes (1974) carried out a detailed study of zoning in single, whole calcic-augites from M. Rossi, Etna, and recognized the principal basal sector $\{11\bar{1}\}$ and the three prism sectors.

As part of the present work a detailed chemical study was carried out on a large clinopyroxene phenocryst which showed well-developed sector zoning (fig. 4). Microprobe analysis showed the basal $\{11\bar{1}\}$ sector to be chemically distinct from the prism sectors. Analyses were made in both the pale and dark bands (when viewed under crossed polars) so as to overcome the problem of chemical variation within a sector due to oscillatory zoning. In thin section it was difficult in many cases to distinguish between the $\{100\}$, $\{110\}$, and $\{010\}$ sectors and these are collectively referred to as prism sectors. Downes in his detailed study with crystallographic control showed there to be little difference between the prism sectors.

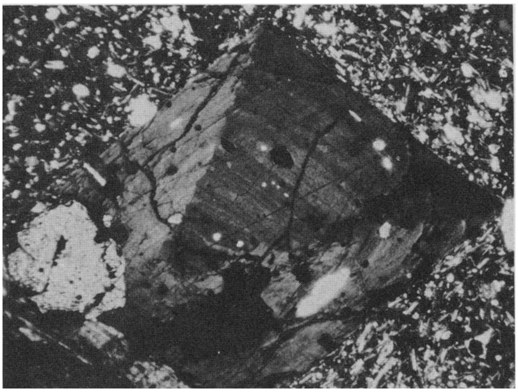


FIG. 4. Sector zoned clinopyroxene phenocryst on which a detailed chemical study was carried out. (Augite crystal about 1.5 mm in width.)

The basal $\{11\bar{1}\}$ sector is enriched in Si relative to the prism sectors with an average cation content (on the basis of six oxygens) of 1.88 in comparison to 1.84 for the two prism sectors. As is to be expected from the distribution of Si the basal sector is depleted in Al_z and Ti relative to the prism sectors. The basal sector has a higher concentration of Mg but a somewhat lower value of Fe than the prism sectors. Ca and Na show no apparent variation between the sectors. These chemical variations between the sectors, with Si and Mg enriched and Ti, Al, and Fe depleted in the basal $\{11\bar{1}\}$ sector relative to the $\{100\}$, $\{110\}$, and $\{010\}$ prism sectors are in accord with studies of other examples of sector zoning in terrestial augites, e.g. Hollister and Gancarz (1971), Wass (1973), Leung (1974), and Harkins and Hollister (1977).

Various mechanisms have been proposed for the development of growth sectors in clinopyroxenes. Strong (1969) considers that the marked chemical disparity between sectors in hour-glass zoning may be a result of the various sectors growing at different stages in the crystallization of the melt. Quench studies have shown that dendritic growth is common in the early stages of crystal growth of pyroxenes. Strong proposes that subsequent infilling of crystal dendrites may give rise to the sector zoning. In the Etnean augites, however, the growth bands cut through the different sectors indicating simultaneous growth.

Leung (1974) suggests that sector zoning in augites is related to differential growth rate and preferential uptake of certain elements with respect to different crystallographic directions. This gives rise to localized disequilibrium in the melt adjacent to faces as the crystal grows at a greater rate than ionic diffusion can occur through the liquid. A similar mechanism is outlined by Downes (1974), with different rates of growth of the various faces being the controlling influence in the development of sector zoning in Etnean augites.

Nakamura (1973) and Dowty (1976) stress the importance of the crystal structure presented by each of the growing faces in controlling the chemical variation of the sectors. Dowty proposes that each face will grow by the accumulation of an adsorption layer; this adsorption layer is likely to be closer in composition to the melt than to the crystal. With rapid growth this adsorption layer may be incorporated metastably into the crystal. This mechanism, according to Dowty (1976), involving the adsorption of cations into partially completed sites, proto-sites, can account for the enrichment of Al and Ti into the prism sectors.

The main difficulty for the mechanisms for sector growth outlined above is that they assume the silicate melt to have no structure. Almost certainly there is some development of SiO_3 polymers in silicate liquids. These SiO_3 polymers in the melt will readily link to the pyroxene chain structure favouring rapid growth in the *c* crystallographic direction. It is considered that the $\{11\bar{1}\}$ sectors, therefore, grew too rapidly to maintain equilibrium with the melt. There is some evidence to support this proposition: the $\{11\bar{1}\}$ sectors are richer in SiO_2 (about 50 wt%) than augites in hawaiites from Hawaii (about 48 wt%). Under equilibrium conditions one might expect the Hawaiian pyroxenes to be richer in SiO_2 than their Etnean counterparts as the hawaiite lavas from Hawaii have a lower Al_2O_3/SiO_2 ratio. It is proposed, therefore, that the rapid growth of the Etna pyroxenes by ready attachment of SiO_3 polymers gave rise to $\{11\bar{1}\}$ sectors, enriched in Si, which grew out of equilibrium with the melt. The prism sectors on the other hand, which grew less rapidly, more closely maintained equilibrium conditions.

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REFERENCES

Augustithus (S. S.), 1976. In *International congress on thermal waters, geothermal energy and vulcanism of the Mediterranean area. 3. Proceedings on vulcanism*, pp. 1–11.

Bottinga (Y.), Kudo (A.), and Weill (D.), 1966. *Am. Mineral.* **51**, 792–806.

Burns (R. G.), 1970. *Mineralogical applications of crystal field theory.* Cambridge, Cambridge University Press.

Campbell (I. H.) and Borley (G. D.), 1974. *Contrib. Mineral. Petrol.* **47**, 281–97.

Carmichael (I. S. E.), Turner (F. J.), and Verhoogen (J.), 1974. *Igneous Petrology.* New York, McGraw-Hill.

Curtis (C. D.), 1964. *Geochim. Cosmochim. Acta.* **28**, 389–403.

Deer (W. A.), Howie (R. A.), and Zussman (J.), 1978. *Rock-forming minerals. 2a. Single chain silicates.* London, Longmans.

Downes (M. J.), 1974. *Contrib. Mineral. Petrol.* **47**, 187–96.

Dowty (E.), 1976. *Am. Mineral.* **61**, 460–9.

Duncan (A. M.), 1978. *Geol. Mag.* **115**, 273–85.

Fodor (R. V.), Keil (K.), and Bunch (T. E.), 1975. *Contrib. Mineral. Petrol.* **50**, 173–95.

Harkins (E.) and Hollister (L. S.), 1977. *Am. Mineral.* **62**, 390–4.

Henderson (P.), 1979. *Mineral. Mag.* **43**, 399–404.

Hollister (L. S.) and Gancarz (A. J.), 1971. *Am. Mineral.* **56**, 959–79.

Le Bas (M. J.), 1962. *Am. J. Sci.* **260**, 267–88.

Leung (I. S.), 1974. *Am. Mineral.* **59**, 127–38.

Nakamura (Y.), 1973. Ibid., **58**, 986–90.

Scott (P. W.), 1976. *Mineral. Mag.* **40**, 805–16.

Strong (D. F.), 1969. Ibid., **37**, 472–79.

Wass (S. Y.), 1973. Ibid., **39**, 133–44.

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