

# Carbonates of the magnesite–siderite series from four carbonatite complexes

H. A. BUCKLEY AND A. R. WOOLLEY

Department of Mineralogy, British Museum (Natural History), Cromwell Road, London SW7 5BD

## Abstract

Carbonates of the magnesite–siderite series have been found and analysed in carbonatites from the Lueshe, Newania, Kangankunde, and Chipman Lake complexes. This series has been represented until now only by a few X-ray identifications of magnesite and three published analyses of siderite and breunnerite (magnesian siderite). Most of the siderite identified in carbonatites in the past has proved to be ankerite, but the new data define the complete solid-solution series from magnesite to siderite. They occur together with dolomite and ankerite and in one rock with calcite. The magnesites, ferroan magnesites and some magnesian siderites may be metasomatic/hydrothermal in origin but magnesian siderite from Chipman Lake appears to have crystallized in the two-phase calcite + siderite field in the subsolidus  $\text{CaCO}_3\text{--MgCO}_3\text{--FeCO}_3$  system. Textural evidence in Newania carbonatites indicates that ferroan magnesite, which co-exists with ankerite, is a primary liquidus phase and it is proposed that the Newania carbonatite evolved directly from a Ca-poor, Mg-rich carbonatitic liquid generated by partial melting of phlogopite–carbonate peridotite in the mantle at pressures >32 kbar.

**KEYWORDS:** carbonate, carbonatite complexes, magnesite, siderite, breunnerite.

## Introduction

MAGNESITE and siderite are relatively rare in carbonatites and no analyses of the former have been found in the literature. Siderite described from a number of occurrences, e.g. Chilwa Island (Garson and Campbell Smith, 1958) and Gronnedal-Ika (Emeleus, 1964), has subsequently proved to be ankerite. Siderite analyses are quoted from Iron Hill (Nash, 1972) and from an unnamed locality in the USSR (Samoilov, 1984), while an analysis of breunnerite (magnesian siderite) from Sallanlatva, USSR, is quoted by Kapustin (1980). These analyses, however, seem to represent the total published chemical data for the series in carbonatites.

During a general study of the rock-forming carbonates (Ca–Mg–Fe carbonates) of carbonatites, members of the magnesite–siderite series have been encountered in four complexes, in two of them for the first time. The new data indicate that the complete series from magnesite to siderite is represented in carbonatites.

## Methods

Analyses were made on polished thin sections using a Hitachi S2500 scanning electron micros-

cope and a Link Analytical AN10/55S energy-dispersive analysis system, operated at standard conditions of 15 kv and 1 nA current on a vanadium calibration standard.

## Nomenclature

In the discussion that follows the boundary between dolomite and ankerite is taken at an Fe:Mg value of 1:4 (Deer *et al.*, 1962). The term 'breunnerite' is sometimes used for magnesite with significant iron, particularly in the USSR, but is ill-defined and not an IMA approved term. For convenience, therefore, the magnesite–siderite series has been subdivided at Mg:Fe ratios of 0.75, 0.5 and 0.25 the divisions being referred to as magnesite, ferroan magnesite, magnesian siderite, and siderite.

## Material analysed and results

*Lueshe, Zaire.* Lueshe is a complex of carbonatites, including dolomitic and calcitic varieties, and cancrinite syenite, situated at the northern end of the western branch of the East African Rift system (Maravic and Morteani, 1980). Of five samples of carbonatite investigated, one [BM

Table 1. Selected analyses of carbonates from Lueshe, Newania, Kangankunde and Chipman Lake carbonatites

	Lueshe -----				Chipman Lake --		Newania, 83/172			
	1	2	3	4	5	6	7	8	9	10
	dol	dol	mag	Femag	cc	ank	Mgsid	ank	sid	Mgsid
FeO	1.39	5.99	10.70	19.00	0.69	7.92	40.56	13.12	51.21	34.64
MnO	0.43	0.89	1.20	2.12	0.27	0.31	1.56	0.94	0.47	0.79
MgO	18.94	16.10	34.88	28.80	0.22	15.78	12.47	12.02	5.15	19.37
CaO	28.51	27.52	1.10	1.80	55.81	28.89	2.07	26.72	0.18	0.81
SrO	1.21	0.53	0	0	0	0.35	0.20	0.99	0	0
Total	50.48	51.03	47.88	51.72	56.99	53.25	56.86	53.79	57.01	55.61
FeCO <sub>3</sub>	1.94	8.57	14.41	26.13	0.95	10.84	61.98	19.08	84.48	49.34
MgCO <sub>3</sub>	47.10	40.97	83.71	70.71	0.54	38.50	33.96	31.15	15.14	49.18
CaCO <sub>3</sub>	50.96	50.46	1.88	3.16	98.51	50.66	4.05	49.76	0.38	1.48
	Newania, 16NE		Kangankunde, 59			-----		Kangankunde, 78		
	11	12	13	14	15	16	17	18	19	20
	ank	Femag	dol	ank	Femag	Femag	cc	ank	ank	Mgsid
FeO	12.05	31.18	0.77	7.19	20.00	29.19	0	5.01	7.51	29.70
MnO	1.17	1.87	3.55	1.48	1.13	5.34	0	2.25	3.27	10.66
MgO	13.54	21.58	20.61	15.12	29.44	19.00	1.14	15.94	14.09	14.50
CaO	27.21	0.65	29.42	28.26	1.34	0.83	55.20	27.40	27.58	0.35
SrO	0.94	0	0.81	0.87	0	0	0	0.53	0	0
Total	54.91	55.28	55.16	52.92	51.91	54.36	55.34	51.13	52.45	55.21
FeCO <sub>3</sub>	16.96	44.24	1.02	10.22	26.96	45.53	0.00	10.29	11.05	53.04
MgCO <sub>3</sub>	33.97	54.58	48.85	38.31	70.73	52.82	2.79	40.12	36.95	46.16
CaCO <sub>3</sub>	49.07	1.18	50.13	51.47	2.31	1.66	97.21	49.58	52.00	0.80

cc, calcite; dol, dolomite; ank, ankerite; mag, magnesite;  
Femag, ferroan magnesite; Mgsid, magnesian siderite;  
sid, siderite

1986,P22(12)] proved to contain ferroan magnesite. In thin section this rock is a coarse, dolomitic carbonatite in which the ferroan magnesite forms small areas of higher relief and finer grain in the enclosing dolomite. These areas are sometimes vein-like and occasionally envelop larger dolomite grains. It is probable that the ferroan magnesite is later than the dolomite, but the petrography is ambiguous.

The large crystals proved to vary from dolomite to ankerite and the finer-grained material to be ferroan magnesite. Selected analyses are given in Table 1 and the results plotted in terms of CaCO<sub>3</sub>, MgCO<sub>3</sub>, and FeCO<sub>3</sub> on Fig. 1A. Meyer and Bethune (1958, Table II, no. 10) gave an analysis of a carbonatite from Lueshe described as "Rauhagite a 90% de magnesite"; unfortunately, they furnish no petrographic or mineralogical description. The bulk rock composition is plotted on Fig. 1A and falls close to the MgCO<sub>3</sub> vertex, confirming that it must contain a high proportion of magnesite, although of a more magnesian composition than that analysed during this study.

*Newania, India.* The Newania intrusion is a single inclined sheet some 250 m thick comprising interdigitating zones of dolomitic and ankeritic carbonatite (Viladkar and Wimmenauer, 1986), the latter intruding and metasomatizing the for-

mer. We were kindly given a suite of carbonatite specimens from Newania by Dr M. J. Le Bas, four of which proved to contain rare siderite-magnesian siderite. We were also loaned a polished section of Newania carbonatite (NE16) by Dr J. Keller, which had already been analysed (Hornig, 1988) and which contains ankerite plus magnesian siderite. The data obtained from NE16 form two compact clusters one of ankerite, with two slightly more iron-rich compositions, and one of ferroan magnesite (Fig. 1A)..

The Le Bas material containing magnesite-siderite is of two distinct textural types. In one (specimen 83/172) the magnesite-siderite forms rare, stout crystals up to 0.5 mm across which may be subhedral (Fig. 2A) or rounded. These grains show some marginal alteration to iron oxides, but they appear to be primary and are interpreted as having crystallized at approximately the same time as the surrounding ankerite. Although no zoning is apparent there is a considerable range of Mg:Fe ratios (Fig. 1A) in the magnesian siderite-siderite compositional range. In the second textural type magnesite-siderite is very fine-grained and in complex intergrowth with what may be a mixture of iron oxides and carbonate. However, high-quality analyses of this material could not be obtained, so it is not plotted in Fig. 1A.

*Kangankunde, Malawi.* The intrusive rocks of the Kangankunde complex, like Newania, comprise various types of carbonatite with no con-sanguineous igneous silicate rocks (Garson, 1965). The carbonatites are generally iron-rich, the main rock-forming carbonates being of the dolomite-ankerite series. Magnesite-siderite series minerals have been found in two rocks. In one rock [BM 1962,73(59)] ferroan magnesite forms subhedral grains which are surrounded by a zone of ferroan dolomite-ankerite. This can be interpreted either as early growth of ferroan magnesite followed by dolomite-ankerite, or possibly as replacement of the former by the latter. As is apparent from Fig. 1B there is a broad range of Mg:Fe ratios in both carbonate series.

The second rock [BM 1962,73(78)] contains calcite, dolomite, ankerite and ferroan magnesite-magnesian siderite. The calcite and dolomite form complex intergrowths and this textural relationship, together with the relatively large amount of Mg dissolved in the calcite, suggests that these were the first, and highest temperature, carbonates to crystallize. It is likely that the dolomites containing excess Ca (Fig. 1B), although they appear to be homogeneous, in fact contain fine intergrowths of calcite. There is no textural evidence bearing on the order of crystallization of

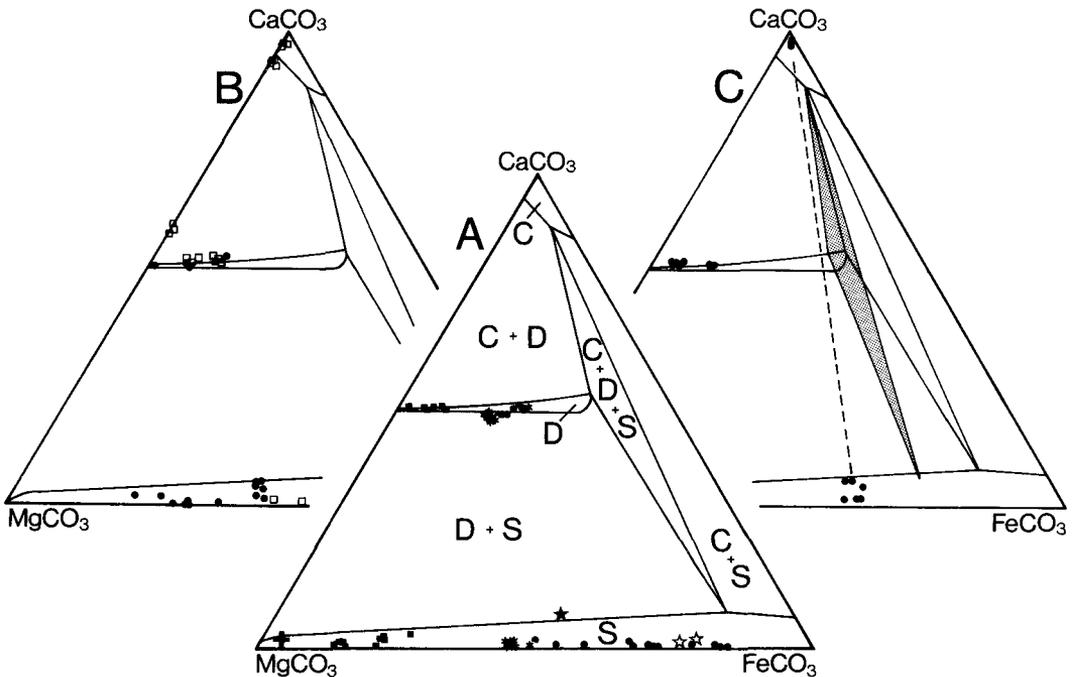


FIG. 1. Plots of carbonate compositions from carbonatites containing carbonates of the siderite–magnesite series in the system  $\text{CaCO}_3$ – $\text{MgCO}_3$ – $\text{FeCO}_3$ . The field boundaries are for the subsolidus system at  $450^\circ\text{C}$  taken from Rosenberg (1967) with the three-phase field at  $400^\circ\text{C}$  (shaded area) also shown on Fig. 1C. FIG. 1A. Carbonates from the Lueshe carbonatite, Zaire (BM1986, P22(12)—squares) and Newania, India (83/172—circles, and NE16—asterisks). The cross is a magnesite rauhaugite from Lueshe (Meyer and Bethune, 1958, Table II, no. 10). The filled star is a breunnerite from Sallanlatva, USSR (Kapustin, 1980), the more Fe-rich open star a siderite from Iron Hill, USA (Nash, 1972), and the second open star a siderite from a carbonatite complex in the USSR (Samoilov, 1984). C—calcite solid solution; D—dolomite solid solution; S—siderite–magnesite solid solution. FIG. 1B. Carbonates from the Kangankunde carbonatite, Malawi (BM1962, 73(59)—circles, and BM1962, 73(78)—open squares). FIG. 1C. Carbonates from rock 33, Chipman Lake, Canada. For details of dashed line see text.

the ankerite and ferroan magnesite–magnesian siderite (Fig. 1B).

*Chipman Lake, Canada.* The Chipman Lake occurrence comprises a series of carbonatite dykes with broad fenite aureoles (Sage, 1985). The carbonates analysed define a complete series from dolomite, through ferroan dolomite to ankerite, with rather less calcite. In one sample (specimen 33) the principal carbonate is dolomite–ankerite but with some small areas consisting of magnesian siderite within calcite grains (Fig. 2B). Analyses of the three carbonate phases are depicted in Fig. 1C. Evidence from other Chipman Lake samples implies that the ferroan dolomite evolves to ankerite, but the relationship of the calcite and magnesian siderite suggests either that the two phases crystallized together, or that they were generated by the breakdown of an iron-rich ankerite.

### Sr and Mn

The average values for Mn and Sr in calcite, dolomite–ankerite and magnesite–siderite for the six carbonatites described above are given in Table 2. Sr is strongly partitioned into dolomite–ankerite and very low, often below detection, in the magnesite–siderite series. It is noteworthy that in the two rocks with calcite, Kangankunde 1962,73(78) and Chipman Lake, Sr is high in calcite from the former but absent from the latter. In the Kangankunde rock the calcite was probably an early crystallizing phase, and so could take up Sr preferentially from the melt. The Chipman Lake calcite, however, was a very late phase and the melt had presumably become depleted in Sr.

With one exception, Mn is preferentially partitioned into the magnesite–siderite series carbonates (Table 2). In the Newania rock 83/172 the

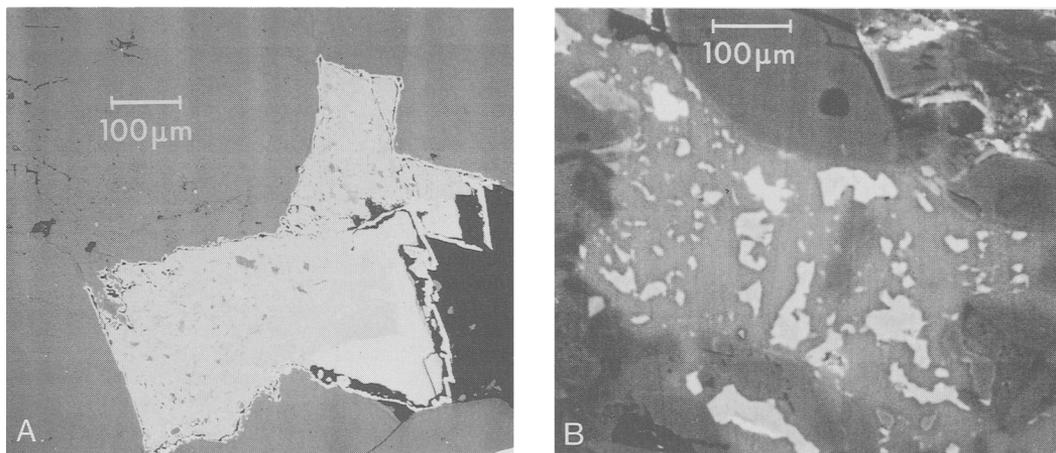


FIG. 2. Back-scattered image photographs showing textural relationships of carbonates of the magnesite-siderite series. *A.* Subhedral/euhedral crystals of siderite-magnesian siderite surrounded by ankerite; rock 83/172, Newania. *B.* Small areas of magnesian siderite (white) in calcite; rock 33, Chipman Lake.

Table 2. Average values of Mn and Sr in carbonates

		no of anal.	weight % Mn	Sr
Lueshe (1968, P22(12))	Dolomite-ankerite	5	0.70	0.80
	Magnesite-siderite	9	0.87	bd
Newania (NE16)	Dolomite-ankerite	14	0.98	0.83
	Magnesite-siderite	16	1.86	0.03
Newania (83/172)	Dolomite-ankerite	3	0.96	0.64
	Magnesite-siderite	5	0.58	bd
Kangankunde (1962, 73(59))	Dolomite-ankerite	8	1.82	0.67
	Magnesite-siderite	13	4.17	0.08
Kangankunde (1962, 73(78))	Calcite	4	bd	0.45
	Dolomite-ankerite	15	2.32	0.69
Chipman Lake (33)	Magnesite-siderite	2	10.43	bd
	Calcite	3	0.54	bd
	Dolomite-ankerite	9	0.19	0.38
	Magnesite-siderite	6	1.51	0.03

bd - below detection limit

reverse holds. The Kangankunde dolomite-ankerite and magnesite-siderite carbonates are noteworthy for their high Mn contents, rock 1962,73(78) containing >10% by weight MnO in the ferroan magnesite-magnesian siderite. In contrast, the early calcite of this rock is quite free of Mn. However, the late calcite of the Chipman Lake carbonatite contains much more Mn than the earlier crystallizing dolomite-ankerite, presumably indicating a concentration of Mn in the last liquid.

### Discussion

The subsolidus relationships in the system  $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$  at 450°C as determined by Rosenberg (1967) are indicated on Fig. 1A-C. The fields of magnesite-siderite and dolomite-an-

kerite solid solution are indicated, the area lying between being a two-phase field. Rosenberg also showed that there is a three-phase field with vertices at calcite, iron-rich ankerite and siderite, as indicated. Up to, but no more than, about 70 mol. %  $\text{CaFe}(\text{CO}_3)_2$  is soluble in dolomite (Goldsmith, 1983), but we have found no ankerites in carbonatites that are so iron-rich, about 50 mol. % generally being the limit. This is compatible with the position of the three-phase field identified by Rosenberg (1967) at 400°C, which, in comparison with the three-phase field at 450°C, is displaced towards more magnesian compositions (shaded area on Fig. 1C).

The Chipman Lake data can be explained in terms of the subsolidus system. The earliest phase to crystallize was dolomite which, with falling temperature, evolved towards ankerite. The co-existing calcite and magnesian siderite of Chipman Lake indicates that the final composition lay in the two-phase calcite + magnesian siderite field, which is limited on the magnesium side by the three-phase calcite + ankerite + siderite field. However, Rosenberg (1967) only determined the three-phase field at 450 and 400°C (Fig. 1C), but, as the dashed tie-line between the Chipman Lake calcite and magnesian siderite indicates, it is probable that at lower temperatures the two-phase field extends to even more magnesian compositions.

The Newania rock NE16, containing ankerite and ferroan magnesite showing little compositional range, and 83/172, with stout siderite-magnesian siderite grains but of a broad range of Mg:Fe

ratios, are both considered to be primary magmatic rocks. Experimental work (Goldsmith and Heard, 1961) has shown that in the system  $\text{CaCO}_3\text{-MgCO}_3$  there are solvi between calcite-dolomite and dolomite-magnesite, which, if the solvi persist when iron is added to the system, would preclude a melt lying above the  $\text{CaMg}(\text{CO}_3)_2\text{-CaFe}(\text{CO}_3)_2$  join in the  $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$  system evolving to a composition below the join. Thus the two Newania rocks in which ankerite and magnesite-siderite carbonates appear to have co-precipitated probably represent melts which have bulk compositions lying below the  $\text{CaMg}(\text{CO}_3)_2\text{-CaFe}(\text{CO}_3)_2$  join in the  $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$  system. The evolution of the Newania and Chipman Lake magnesite-siderite-bearing carbonatites are, therefore, different in detail, but both appear to represent magmatic assemblages.

Although one of the Kangankunde specimens contains a little calcite, both are dominated by carbonates of the dolomite-ankerite series, but with significant ferroan magnesite and minor magnesian siderite. Like the Newania rocks, therefore, they probably have an overall carbonate composition lying below the  $\text{CaMg}(\text{CO}_3)_2\text{-CaFe}(\text{CO}_3)_2$  join in the  $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$  system. However, there are no clear textural criteria to indicate whether the magnesite-siderite is a primary magmatic phase, and so could be either late hydrothermal or metasomatic.

Apart from being more magnesian, the Lueshe data are similar to those of Kangankunde. However, the petrography indicates that the ferroan magnesite in this rock is likely to be a late phase developed along cracks and veins and thus possibly of metasomatic/hydrothermal origin. It is not clear why such a de-calcification reaction should take place, but with the present limited evidence we are not persuaded that the ferroan magnesite in the Lueshe carbonatites, like the ferroan magnesite-magnesian siderite of Kangankunde, is a primary magmatic phase.

The presence of magnesian siderite in the Chipman Lake carbonatite was explained above in terms of the subsolidus  $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$  system, and the Lueshe and Kangankunde magnesite-siderite carbonates may be of metasomatic/hydrothermal origin. However, the Newania rocks with co-existing ankerite-ferroan magnesite and magnesian siderite demand overall compositions lying below the  $\text{CaMg}(\text{CO}_3)_2\text{-CaFe}(\text{CO}_3)_2$  join. Experimental work at 10 kbar on the system  $\text{CaCO}_3\text{-MgCO}_3$  (Byrnes and Wyllie, 1981) indicates that at high temperatures dolomite breaks down to periclase + liquid + vapour, while at 27 kbar (Irving and Wyllie, 1975; Byrnes and Wyl-

lie, 1981) before complete melting a field of liquid + magnesite solid solution extends from dolomite to magnesite compositions. Eggler (1989) points out that near-solidus melts formed from phlogopite-carbonate peridotite are predicted from work on simple systems to be carbonatitic. Thus the work of Brey *et al.* (1983) and Olafsson and Eggler (1983) show that with increasing pressure phlogopite-carbonate peridotite produces liquids of more magnesian compositions and that the carbonate mineralogy changes at about 32 kbar from dolomite to magnesite. Partial melting of a phlogopite-carbonate peridotite at pressures > 32 kbar is, therefore, capable of producing a carbonatitic melt from which magnesite would crystallize as a primary phase. Clearly the Newania ferroan magnesite-ankerite carbonatite could have evolved from such a melt, implying that it was generated directly in the mantle.

The discovery in spinel lherzolite xenoliths from Spitsbergen by Amundsen (1987) of evidence of three quenched liquids, of which one is carbonatitic and consists of co-existing dolomite and magnesite, is a further indication that dolomite-magnesite liquids are present at mantle depths. Amundsen's (1987) observations appear to indicate that the carbonatitic liquid is immiscible with associated silicate liquids, but whether or not liquid immiscibility is involved, the experimental and observational data coincide in indicating that Ca-poor, Mg-rich carbonatitic liquids are stable at mantle temperatures and pressures. From this it is proposed that the Newania ferroan magnesite-ankerite carbonatite evolved directly from such liquids.

#### Acknowledgements

We are grateful to Dr M. J. Le Bas for kindly giving us a suite of carbonatites from Newania, and to Dr I. Hornig who, through Dr J. Keller, lent us a polished section of carbonatite from the same complex. G. C. Jones wrote a computer program for recalculation of the carbonate analyses. Valerie Jones drafted the figures. We much appreciate useful comments on the paper from Dr A. L. Graham, Dr P. Henderson, Dr D. D. Hogarth and Dr M. J. Le Bas. Dr T. Andersen, as a referee, also made many helpful comments that were much appreciated, although he does not necessarily concur with all our conclusions.

#### References

- Amundsen, H. E. F. (1987) Evidence for liquid immiscibility in the upper mantle. *Nature, London*, **327**, 692-5.
- Brey, G., Brice, W. R., Ellis, D. J., Green, D. H., Harris, K. L. and Ryabchikov, I. D. (1983) Pyroxene-carbonate reactions in the upper mantle. *Earth Planet. Sci. Lett.* **62**, 63-74.

- Byrnes, A. P. and Wyllie, P. J. (1981) Subsolidus and melting relations for the join  $\text{CaCO}_3\text{-MgCO}_3$  at 10 kbar. *Geochim. Cosmochim. Acta*, **45**, 321-8.
- Deer, W. A., Howie, R. A. and Zussman, J. (1962) *Rock-forming minerals*, 5. *Non-silicates*, Longmans, London, 371 pp.
- Eggler, D. H. (1989) Carbonatites, primary melts, and mantle dynamics. In *Carbonatites: genesis and evolution* (Bell, K., ed.) 561-79. Unwin Hyman, London.
- Emeleus, C. H. (1964) The Gronnedal-Ika alkaline complex, South Greenland. The structure and geological history of the complex. *Meddel. om Gronland*, **172** (3), 1-75.
- Garson, M. S. (1965) Carbonatite and agglomerate vents in the western Shire Valley. *Mem. Geol. Surv. Malawi*, **3**, 167 pp.
- and Smith, W. Campbell (1958) Chilwa Island. *Ibid.* **1**, 1-127.
- Goldsmith, J. R. (1983) Phase relations of rhombohedral carbonates. In *Carbonates: mineralogy and chemistry* (Reeder, R. J., ed.) *Reviews in Mineralogy*, **11**. Min. Soc. Am., 49-76.
- and Heard, H. C. (1961) Subsolidus phase relations in the system  $\text{CaCO}_3\text{-MgCO}_3$ . *J. Geol.* **69**, 45-74.
- Hornig, I. (1988) *Spurenelementuntersuchungen an Karbonatiten mit Hilfe der ICP-Atomemissionsspektroskopie*. Doctoral Dissertation, Albert-Ludwigs-Universität, Freiburg i.Br. 238 pp.
- Irving, A. J. and Wyllie, P. J. (1975) Subsolidus and melting relations for calcite, magnesite and the join  $\text{CaCO}_3\text{-MgCO}_3$  to 36 kb. *Geochim. Cosmochim. Acta*, **39**, 35-53.
- Kapustin, Yu. L. (1980) *Mineralogy of carbonatites*. Amerind Publishing, New Delhi, 259 pp.
- Maravic, H. V. and Morteani, G. (1980) Petrology and geochemistry of the carbonatite and syenite complex of Lueshe (N. E. Zaire). *Lithos*, **13**, 159-70.
- Meyer, A. and Bethune, P. de (1958) La carbonatite Lueshe (Kivu). *Bull. Serv. Geol. Congo Belge*, **8** (5), 1-19 and 1-12.
- Nash, W. P. (1972) Mineralogy and petrology of the Iron Hill carbonatite complex, Colorado. *Bull. Geol. Soc. Am.* **83**, 1361-82.
- Olafsson, M. and Eggler, D. H. (1983) Phase relations of amphibole, amphibole-carbonate, and phlogopite-carbonate peridotite: petrologic constraints on the asthenosphere. *Earth Planet. Sci. Lett.* **64**, 305-15.
- Rosenberg, P. E. (1967) Subsolidus relations in the system  $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$  between 350° and 550°C. *Am. Mineral.* **52**, 787-96.
- Sage, R. P. (1985) Geology and carbonate-alkalic rock complexes of Ontario: Chipman Lake area, Districts of Thunder Bay and Cochrane. *Study. Ont. Geol. Surv.* **44**, 1-40.
- Samoilov, V. S. (1984) *Geochemistry of carbonatites*. Moskva: Izdvo Nauka.
- Viladkar, S. G. and Wimmenauer, W. (1986) Mineralogy and geochemistry of the Newania carbonatite-fenite complex, Rajasthan, India. *Neues Jahrb. Mineral. Abh.* **156**, 1-21.