

High-pressure, synthetic loweringite–davidite and its rare earth element geochemistry

T. H. GREEN AND N. J. PEARSON

School of Earth Sciences, Macquarie University, North Ryde, NSW 2113, Australia

Abstract

Loweringite–davidite members of the crichtonite group were synthesized at high pressure and temperature (7.5 kbar, 1000–1050 °C) from a melt of TiO₂ and rare earth element (REE) enriched basaltic andesite composition. Four sets of partition coefficients for La, Sm, Ho, Lu and Sr (analogue for Eu²⁺) were obtained. These show that light and heavy REE are readily accommodated, but the intermediate REE are discriminated against in the loweringite–davidite structure. This confirms the previously proposed two sites (*A* and *M*) for REE substitution in the crichtonite group. Additional experiments verified the stability of REE-rich crichtonite group minerals to 20 kbar, 1300 °C and 30 kbar, 1000 °C, and indicate that this phase may be an important accessory repository for the light and heavy REE in the upper mantle.

KEYWORDS: loweringite, davidite, crichtonite group, rare earth element geochemistry.

Introduction

LOWERINGITE–DAVIDITE members of the crichtonite group have been recorded as accessory phases in cumulates from layered intrusions (Campbell and Kelly, 1978) and K, Ba, Ca and REE-containing crichtonite group minerals occur in kimberlites (Jones *et al.*, 1982; Haggerty, 1983). The latter occurrences in rocks of deep-seated origin, together with the documented close-packed structure of the mineral series (Grey *et al.*, 1976; Gatehouse *et al.*, 1978, 1979), suggest that it may be stable under upper-mantle conditions. Thus members of the crichtonite group may be important hosts for incompatible elements such as the REE, as well as Sr, Pb, U, K and Ba in the upper mantle.

As part of a wider investigation of the solubility of Ti-rich phases in common magmas, and the partitioning relationships of the REE between these phases and co-existing silicate liquid, loweringite–davidite was identified and analysed in four runs on a quenched melt of a TiO₂, REE-enriched basaltic andesite composition at 7.5 kbar, 1000–1050 °C. This paper documents these synthetic compositions, and also the first determinations of partition coefficients (*D*) for La, Sm, Ho, Lu and Sr between loweringite–davidite and silicate liquid. These data are then compared with selected chondritic normalized REE patterns published for natural crichtonite group minerals (Campbell and Kelly, 1978; Haggerty, 1983; Foord *et al.*, 1984, and references

therein). Also an experiment on a REE-enriched sphene composition (Green and Pearson, 1986) produced loweringite–davidite, as well as sphene and rutile, at 7.5 kbar and 900 °C.

Additional runs were carried out on a model loweringite–davidite composition to confirm the stability of this phase at high pressure (*P*) and temperature (*T*) and to determine any broad *P,T*-dependent changes in the loweringite–davidite solid solution. All the compositional data provide new information on the extent of REE–Ca solid solution in the crichtonite mineral group. However, U was not a component in the synthetic systems, but is regarded as characteristic of natural davidite compositions (Campbell and Kelly, 1978). Thus the synthetic compositions cannot be equated precisely to natural davidites.

Experimental procedure

The various starting compositions used in this study are presented in Table 1. The basaltic andesite was a natural rock from Tonga (Ewart, 1976), to which was added TiO₂ and a rare earth element-enriched glass. The mix was then melted and quenched to a glass, twice, with fine grinding in between. The synthetic sphene and loweringite–davidite were prepared from analytical reagent grade chemicals (major element oxides) or specpure oxides (REE and Sr) fired together at 850 °C for

Table 1. Starting compositions used in the experimental work, and details of REE glass components added to the basaltic andesite (either 15 or 20 wt. % of this glass was added).

	basaltic andesite + 10% TiO ₂	REE ^a glass	REE-rich sphene	Davidite
SiO ₂	48.68	50	27.4	
TiO ₂	10.50		30.7	66.0
Al ₂ O ₃	15.98	12	3.1	1.8
FeO _{TOT}	8.84		1.1	14.3 ⁺
MnO	0.17		-	-
MgO	3.62		0.1	2.5
CaO	10.03	5	21.4	1.8
Na ₂ O	1.60	4	-	-
K ₂ O	0.50	4	-	-
P ₂ O ₅	0.07		-	-
SrO		5.0	-	0.7
La ₂ O ₃		5.0	0.6	5.0
Sm ₂ O ₃		5.0	4.5	1.0
Ho ₂ O ₃		5.0	6.9	2.7
Lu ₂ O ₃		5.0	4.2	4.2

⁺ denotes Fe present as Fe₂O₃

24 hours. The fired mixes were then used as the starting compositions for two series of high-pressure experiments.

The high-pressure experiments were carried out in a piston-cylinder apparatus, using pressure cells and techniques described elsewhere (Green and Pearson, 1985). Nominal pressures using a piston-in procedure were corrected by -10% (Green *et al.*, 1966). Temperatures were measured with a Pt/Pt 10% Rh thermocouple, uncorrected for any effect of pressure on the e.m.f. Temperatures are

believed accurate to $\pm 15^\circ\text{C}$, allowing for $\pm 5^\circ\text{C}$ variation about the set point and $\pm 10^\circ\text{C}$ uncertainty due to temperature gradient within the graphite furnace. Run times for these synthesis experiments are given in Table 2. At the conclusion of a run, the sample was crushed, examined optically and then fragments mounted in resin and polished for electron microprobe analysis.

Analytical procedure

An Etec autoprober was used for the microprobe analysis, using operating conditions and procedures outlined in Watson and Green (1981) and Green and Pearson (1985). Where possible a large number of analyses of each phase was obtained and averages determined, because of the relatively low count rates for the REE at the 15 kV accelerating voltage used. This was chosen as a compromise, to allow simultaneous analysis of other major elements at the same time as the REE, and to allow the smallest possible crystals, or glass areas, to be analysed without interference from neighbouring phases.

Results

Analyses of all crichtonite group compositions obtained from high-pressure experiments on the three different starting compositions are given in Table 2. Structural formulae, calculated on the

Table 2. Synthetic Davidites analysed in various high-pressure, high-temperature experimental runs. Compositions: Runs 942, 987X were on basaltic andesite + 10% TiO₂ + 15% REE glass, runs 987X, 1033 were on basaltic andesite + 10% TiO₂ + 20% REE glass (with Cr₂O₃ contamination); run 1010 was on a model REE-rich sphene composition; runs 1051-1053 were on a model Davidite composition (see Table 1 for starting compositions). Abbreviations: P = pressure, T = temperature, t = time, n = number of analyses; "phases" refers to those coexisting with Davidite - sph - sphene, gl = glass, ilm = ilmenite, r = rutile. Bracketed values are 2 standard errors of the mean value. Cr-rich and Cr-poor major element Davidite analyses for Runs 987X and 1013 are given, as well as the average data. (*for 987X Sr and REE only are averaged). Fe analysed as FeO, but calculated to Fe₂O₃ for structural formulae, except for the synthetic Davidite, where the analysed value is given as wt. % Fe₂O₃.

Run No.	942	987X	987Y	1033	1010	1051	1052	1053	Synthetic Davidite compos.			
P(kb)	7.5	7.5	7.5	7.5	7.5	30	20	20				
T(°C)	1000	1000	1000	1050	900	1000	1300	1000				
t(hrs)	6	6	6	3	24	12.75	1	30				
H ₂ O(wt.%)	5	5	5	5	5	3	-	-				
n	15	1	12*	1	14	1	10	10				
Phases	sph,gl	sph,ilm,gl	sph,ilm,gl	r,gl	sph,r	r						
TiO ₂	66.85(.17)	64.70	61.78	65.40(.41)	64.86	55.41	60.5(1.90)	62.21(3.60)	57.43(.73)	64.44(.54)	64.26(.35)	66.0
Al ₂ O ₃	0.95(.03)	2.02	2.26	1.98(.04)	2.11	2.65	2.08(.06)	1.06(.19)	2.42(.40)	2.04(.23)	1.77(.06)	1.8
Cr ₂ O ₃	-	0.23	6.19	-	0.89	11.17	7.07(1.72)	-	-	-	-	-
FeO _{TOTAL}	13.21(.08)	12.93	11.10	12.98(.06)	12.18	11.29	10.41(.50)	16.81(.57)	17.63(1.06)	14.14(.38)	15.12(.19)	14.3
MnO	0.12(.01)	0.13	0.12	0.12(.01)	0.12	0.19	0.15(.01)	-	-	-	-	-
MgO	2.45(.01)	2.66	2.23	2.64(.02)	2.25	2.21	1.97(.08)	0.49(.07)	3.98(.74)	3.18(.08)	2.74(.07)	2.5
CaO	1.93(.04)	1.54	1.15	1.85(.04)	1.80	1.38	1.63(.08)	2.31(.76)	0.49(.08)	1.10(.04)	1.17(.12)	1.8
Na ₂ O	0.94(.02)	0.11	0.05	-	0.10	0.07	-	-	-	-	-	-
SrO	0.68(.11)	0.76(.08)	-	0.67(.07)	1.02	0.99	0.89(.14)	-	1.12(.11)	1.07(.07)	0.99(.11)	0.7
La ₂ O ₃	4.09(.08)	5.27(.14)	-	4.83(.10)	4.08	3.44	4.48(.28)	5.21(1.12)	6.51(.22)	5.60(.12)	5.35(.23)	5.0
Sm ₂ O ₃	1.14(.05)	0.88(.17)	-	0.94(.03)	1.17	-	0.63(.15)	0.91(.18)	0.60(.05)	0.78(.04)	1.03(.05)	1.0
Ho ₂ O ₃	2.80(.06)	2.72(.04)	-	2.48(.06)	3.86	3.16	3.51(.12)	3.39(.45)	3.34(.17)	2.94(.07)	3.14(.19)	2.7
Lu ₂ O ₃	3.58(.07)	4.63(.07)	-	4.02(.11)	3.68	3.43	4.35(.27)	5.44(.23)	5.61(.16)	5.08(.10)	4.78(.10)	4.2
	97.84		97.91	98.11	95.39	97.15	97.63	99.13	100.37	100.35	100.0	
Number of atoms on the basis of 38 oxygens												
Ti	14.613	14.193	13.583	14.312	14.264	12.584	13.530	14.000	12.850	13.967	13.949	14.380
Al	0.325	0.694	0.779	0.679	0.727	0.943	0.729	0.374	0.849	0.693	0.602	0.615
Cr	-	0.053	1.431	-	0.206	2.667	1.662	-	-	-	-	-
Fe ³⁺	3.178	3.121	2.686	3.127	2.949	2.822	2.562	4.163	4.341	3.372	3.612	3.117
Mn	0.030	0.032	0.030	0.030	0.030	0.049	0.040	-	-	-	-	-
Mg	1.062	1.157	0.972	1.145	0.981	0.995	0.873	0.219	1.765	1.366	1.179	1.080
Ca	0.601	0.481	0.360	0.577	0.564	0.447	0.519	0.741	0.156	0.340	0.362	0.559
Na	0.023	0.062	0.028	-	0.057	0.041	-	-	-	-	-	-
Sr	0.115	0.129	0.129	0.113	0.173	0.173	0.153	-	0.193	0.179	0.166	0.118
La	0.438	0.567	0.568	0.518	0.440	0.383	0.491	0.575	0.714	0.595	0.569	0.534
Sm	0.121	0.094	0.094	0.100	0.125	-	0.069	0.100	0.065	0.082	0.109	0.106
Ho	0.259	0.252	0.253	0.229	0.359	0.303	0.332	0.323	0.316	0.289	0.288	0.249
Lu	0.314	0.408	0.409	0.353	0.325	0.313	0.391	0.492	0.504	0.442	0.417	0.367
	21.08	21.24	21.32	21.18	21.20	21.72	21.35	20.99	21.75	21.31	21.25	21.12

basis of 38 oxygen atoms and assuming all the iron is present as Fe^{3+} (cf. Gatehouse *et al.*, 1978; Campbell and Kelly, 1978). However, Foord *et al.* (1984) note the uncertainty surrounding the $\text{FeO}/\text{Fe}_2\text{O}_3$ ratio in loveringite-davidite, and the consequent uncertainty in the sum of the cations in structural formulae determinations. The effect of increasing FeO at the expense of Fe_2O_3 would be to increase the number of cations placed in the M position, thus giving cation totals closer to the general formula $AM_{21}O_{38}$ than recorded in Table 2. In this general formula A = large cations (such as Ca, light *REE*, Sr) and M = small cations (mainly Ti, Fe^{3+} and to a lesser extent Al, Cr, Mg, Fe^{2+} and heavy *REE* = Ho, Lu).

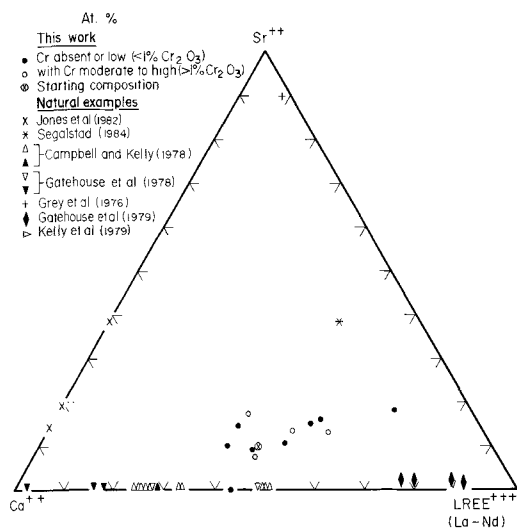


FIG. 1. End member, atomic % ternary diagram for crichtonite (Sr)-loveringite(Ca)-davidite (*LREE*) solid solutions, comparing documented, natural compositions with synthetic compositions obtained at high pressure and temperature.

A plot of these results on a crichtonite (Sr)-loveringite (Ca)-davidite (*REE*) end-member diagram (Fig. 1) shows that the synthetic compositions are essentially loveringite-davidite solid solution, with a subordinate crichtonite component, and range from near the loveringite-davidite compositional boundary to the dominantly davidite boundary. The distinction between loveringite and davidite is based on the ratio $\text{Ca}/\text{U} + \text{LREE}$ (> 1 for loveringite and < 1 for davidite). This follows the proposal of Campbell and Kelly (1978).

A plot of the sum of the small cations ($\text{FeO}_{\text{TOTAL}} + \text{MgO}$) versus TiO_2 (cf. Haggerty *et al.*,

1983; Haggerty, 1983) (Fig. 2) illustrates that the synthetic loveringite-davidites fall within a general crichtonite group field which, in terms of TiO_2 , lies between ilmenite at lower TiO_2 , and armalcolite and then rutile at higher TiO_2 .

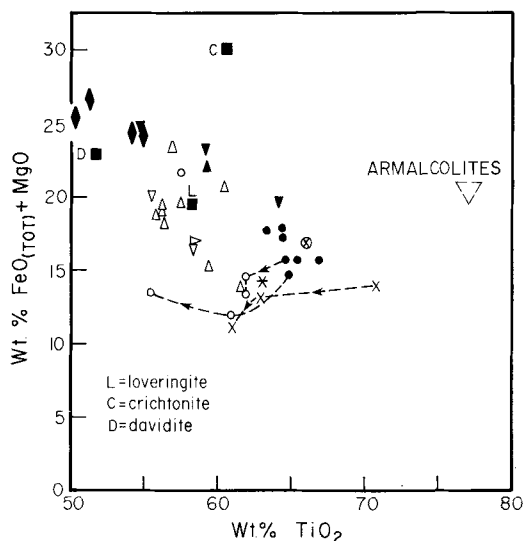


FIG. 2. Ti, Fe and Mg distributions for crichtonite group minerals, compared with armalcolite. Symbols as for Fig. 1.

Basaltic andesite + TiO_2 composition. The loveringite-davidite solid solutions synthesized from this composition form two compositional groups, depending on the presence or absence of Cr. Accidental Cr contamination apparently occurred in the preparation of the basaltic andesite + 10% TiO_2 + 20% *REE* glass composition. This produced loveringite-davidite with a highly variable Cr_2O_3 content (from 0.2 to 6.2 wt. % in run 987x and from 0.9 to 11.2 wt. % in run 1033—see Table 1). The increased Cr_2O_3 content is mainly at the expense of TiO_2 (Fig. 2). Fig. 1 also shows that Cr-bearing compositions fall in the davidite field at 1000 °C, but at 1050 °C are in the loveringite field. The loveringite-davidite from Cr-free runs at similar physical conditions (runs 942, 987Y) plot in the loveringite field, near the boundary between loveringite-davidite.

REE-enriched sphene composition. This contained no Sr or Cr and the crichtonite group phase produced falls marginally into the loveringite field with, apart from the absence of Sr, overall similarity to the loveringite produced from runs 942 and 987Y.

Synthetic loveringite-davidite composition. The starting composition plots at the loveringite-davidite join (Fig. 1), but the high-pressure run products from this composition plot well within the davidite field (Fig. 1, Table 2). The two runs at 20 kbar, 1000°C or 1300°C show relatively little compositional difference with change in temperature; however, the 1000°C 30 kbar run product is significantly different from the 20 kbar composition, with higher REE, Mg, Fe and lower TiO₂ content and marked displacement towards the davidite composition for the 30 kbar compared with 20 kbar results.

Table 3. Compositions of glasses coexisting with davidite. Abbreviations and run details as for Table 2. Differences from 100% give approximate indication of water content.

Run No. n	942 15	987X 15	987Y 15	1033 18
SiO ₂	50.14(.14)	50.53(.24)	51.36(.22)	47.33(.08)
TiO ₂	4.24(.04)	3.27(.03)	3.54(.11)	6.26(.05)
Al ₂ O ₃	15.22(.09)	15.69(.04)	15.93(.07)	14.00(.05)
Fe _{TOTAL}	7.53(.04)	7.08(.11)	6.86(.12)	7.39(.05)
MnO	0.11(.01)	0.12(.01)	0.12(.01)	0.13(.01)
MgO	3.15(.02)	2.88(.03)	3.06(.02)	2.86(.02)
CaO	8.42(.07)	7.40(.08)	8.16(.07)	8.40(.05)
Na ₂ O	2.07(.01)	2.28(.01)	2.02(.01)	2.08(.01)
K ₂ O	1.11(.01)	1.32(.01)	1.07(.01)	1.18(.01)
F ₂ O ₅	—	0.17(.03)	0.19(.03)	0.18(.01)
SiO	0.67(.09)	1.08(.04)	0.70(.05)	1.01(.05)
La ₂ O ₃	0.40(.05)	0.71(.06)	0.44(.03)	0.85(.05)
Sm ₂ O ₃	0.53(.04)	0.54(.04)	0.43(.03)	0.92(.04)
Ho ₂ O ₃	0.57(.05)	0.63(.04)	0.43(.04)	1.27(.05)
Lu ₂ O ₃	0.51(.04)	0.77(.04)	0.51(.04)	1.20(.07)
	94.67	94.27	94.82	95.06

REE partitioning. Compositions of quenched glasses coexisting with loveringite-davidite in the basaltic andesite + TiO₂ composition are given in Table 3, and the partition coefficients (*D*) for La, Sm, Ho and Lu, and Sr (as an analogue for Eu²⁺) are plotted in Fig. 3). This clearly shows that loveringite-davidite readily accommodates both light and heavy REE (La and Lu respectively), but discriminates against the middle REE (Sm), and also Sr (or Eu²⁺).

Discussion

Comparison is made in Fig. 1 of the synthetic high-pressure loveringite-davidite with documented natural examples of members of the crichtonite-loveringite-davidite solid solution series. This shows that in terms of Ca-LREE substitution only some of the synthetic compositions (942, 987Y, 1033) overlap with natural loveringite-davidites reported by Campbell and Kelly (1978) and Gatehouse *et al.* (1978), while others (987X, 1051-1053) fall in a compositional gap between the loveringite-davidite just referred to, and davidites (Gatehouse *et al.*, 1978, 1979). This points to a complete solid

solution between the loveringite and davidite members of the series. Additionally, the Sr component confirms significant solid solution towards the Sr end-member, covering a field on Fig. 1 not represented by known natural examples. Finally, in this overall compositional comparison, the absence of U from the synthetic system limits closer compositional comparison of the synthetic davidite with natural davidite, where U is regarded as an essential constituent (e.g. Campbell and Kelly, 1978).

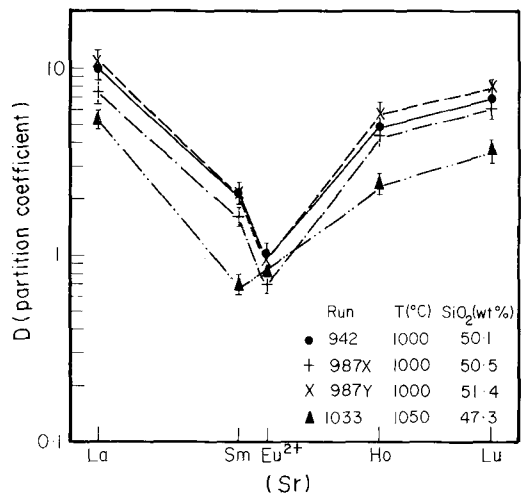


FIG. 3. Partition coefficients (*D*) for La, Sm, Ho and Lu and Sr²⁺ (as an analogue for Eu²⁺) distribution between synthetic loveringite-davidite, and coexisting silicate liquid.

Comparison of the small cation content of synthetic and natural loveringite-davidite is given in Fig. 2. The synthetic examples have lower (FeO_{TOTAL} + MgO) and higher TiO₂ than most of the natural compositions, but are still clearly different from armalcolites.

The marked downward V-shaped pattern for the partition coefficients for the REE (Fig. 3) mimics the chondrite-normalized pattern for the REE distribution in natural loveringite and davidite (Campbell and Kelly, 1978) and clearly confirms the suggestion (Gatehouse *et al.*, 1978; Campbell and Kelly, 1978; Foord *et al.*, 1984) that the REE substitute into two distinctly different sites in the crystal lattice of crichtonite group minerals. Thus the light REE enter the *A* site, along with Ca, while the heavy REE enter the *M* site. The relatively low partition coefficient for Sr is surprising in view of the existence of the crichtonite (Sr) end member in the solid solution, and the observation that Sr

readily enters the *A* site of the davidite structure (Campbell and Kelly, 1978). The present results suggest that Sr enters this site less readily than both Ca and the light *REE*. *REE* are essential structural constituents of the loveringite-davidite solid solution, and so the partition coefficients between mineral and coexisting silicate liquid will be dependent on their concentration in the melt (Hanson and Langmuir, 1978). Thus the partition coefficients determined in these artificially *REE*-enriched liquids cannot be applied directly to natural rocks, where the *REE* content is over an order of magnitude lower. Natural *D* values will be much higher, but the overall pattern should remain the same in the natural systems.

The highly varied Cr-content of the loveringite-davidite from the Cr-contaminated composition (where this contamination of the bulk composition was < 0.1% Cr₂O₃) indicates that Cr partitions strongly into loveringite-davidite, and lends support to the view that Cr concentration may have an influence on increasing the stability of this mineral group (Campbell and Kelly, 1978).

Conclusions

The synthesis of loveringite-davidite solution from three different starting compositions at high pressure and temperature confirms its stability under upper-mantle conditions, and at magmatic temperatures. Thus loveringite-davidite may act as an important host for *REE* and other large-ion lithophile (LIL) elements in the mantle, and may crystallize from LIL-enriched melts or fluids saturated in a Ti-rich phase. This is also indicated by the presence of crichtonite-group minerals in kimberlites (Haggerty, 1983). The determination of a V-downward pattern for the *REE* partition coefficients supports the proposal that these elements are accommodated in two different sites in

the loveringite-davidite lattice (a larger site for La and a smaller site for Lu).

Acknowledgements

This research has been supported by funds from the Australian Research Grants Scheme (E79/15170) and from Macquarie University Research Grants. Drs I. Campbell and S. O'Reilly kindly read the manuscript and gave constructive comment.

References

- Campbell, I. H., and Kelly, P. R. (1978) *Mineral. Mag.* **42**, 187-93.
- Ewart, A. E. (1976) *Contrib. Mineral. Petrol.* **58**, 1-21.
- Foord, E. E., Sharp, W. N., and Adams, J. W. (1984) *Mineral. Mag.* **48**, 97-106.
- Gatehouse, B. M., Grey, I. E., Campbell, I. H., and Kelly, P. R. (1978) *Am. Mineral.* **63**, 28-36.
- and Kelly, P. R. (1979) *Ibid.* **64**, 1010-17.
- Green, T. H., and Pearson, N. J. (1985) *Contrib. Mineral. Petrol.* **91**, 24-36.
- (1986) *Chem. Geol.* **54**, 185-201.
- Ringwood, A. E., and Major, A. (1966) *J. Geophys. Res.* **71**, 3589-94.
- Grey, I. E., Lloyd, D. J., and White, J. S. (1976) *Am. Mineral.* **61**, 1203-12.
- Haggerty, S. E. (1983) *Geochim. Cosmochim. Acta*, **47**, 1833-54.
- Smyth, J. R., Erlank, A. J., Rickard, R. S., and Danchin, R. V. (1983) *Am. Mineral.* **68**, 494-505.
- Hanson, G. N., and Langmuir, C. H. (1978) *Geochim. Cosmochim. Acta*, **42**, 725-41.
- Jones, A. P., Smith, J. V., and Dawson, J. B. (1982) *J. Geol.* **90**, 435-53.
- Kelly, P. R., Campbell, I. H., Grey, I. E., and Gatehouse, B. M. (1979) *Can. Mineral.* **17**, 635-8.
- Segalstad, T. V. (1984) *Am. Mineral.* **69**, 388-90.
- Watson, E. B., and Green, T. H. (1981) *Earth Planet. Sci. Lett.* **56**, 405-21.

[Manuscript received 27 January 1986;
revised 21 April 1986]