

Isotopic disequilibrium in clinopyroxenes from nephelinitic lavas, Napak volcano, eastern Uganda

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ABSTRACT

Pyroxene phenocrysts from nephelinites associated with the Tertiary carbonatite-nephelinite Napak volcano are not in isotopic equilibrium with their host rocks and reveal a complicated evolutionary history that involved fractional crystallization of a melt undergoing continuous isotopic change. Intrasample pyroxene populations have different isotopic compositions and are interpreted as earlier formed pyroxenes that failed to isotopically equilibrate with the host liquids and that were later scavenged by ascending melts. The Napak data show that the pyroxenes can be effective in monitoring isotopic shifts that occur during magma evolution.

INTRODUCTION

Included among the eruptive centers of the East African Rift Valley system is a series of carbonatite-nephelinite volcanoes in eastern Uganda and Kenya with ages ranging from 32 to 15 Ma (Baker et al., 1971; Cahen et al., 1984). One such center is the deeply dissected Napak volcano, which contains mammalian fossil remains of early Miocene age (Bishop, 1958). K-Ar whole-rock and mineral dates from Napak tuffs and lava flows (Bishop et al., 1969) range from 30 to 7 Ma.

The Napak volcano consists of a carbonatite-ijolite central plug flanked by interlayered agglomerates, tuffs, and silica-undersaturated lava flows that overlie quartzofeldspathic gneissic and granulitic basement. Pyroclastic rocks form 97% of Napak, and the remaining 3% consists of silica-undersaturated lava flows, mostly nephelinitic in composition (King, 1949). Two groups of nephelinites, olivine-free and olivine-bearing, are present at Napak, and Mg numbers for both groups are between 61 and 80 (Simonetti and Bell, unpublished), characteristic of primary mantle melts (Roeder and Emslie, 1970).

Experimental studies have shown that primary nephelinite melts are consistent with melting of an amphibole peridotite at pressures of 20 to 25 kbar (Olafsson and Eggler, 1983; Eggler, 1989) or with small (<5%) degrees of partial melting of a carbonated peridotite or pyrolite at high pressures (Brey and Green, 1977; Brey, 1978; Olafsson and Eggler, 1983; Wallace and Green, 1988). The isotope ratios of nephelinites can, therefore, provide valuable insights into the chemical nature and evolution of the subcontinental lithosphere.

Previously published Nd and Sr isotopic results from East African carbonatites and nephelinites are quite variable and have been

mainly attributed to the mixing of isotopically distinct mantle components. Nd and Sr isotopic data from recent East African carbonatite complexes (Bell and Blenkinsop, 1987) define a Nd-Sr isotopic array, termed the East African carbonatite line (EACL). The similarity of the slope of this carbonatite line to the "Lo-Nd" array of Hart et al. (1986), suggests that the line may represent a mixture of HIMU (high U/Pb mantle) and EM I (enriched mantle I) mantle components (Bell and Blenkinsop, 1987), the two end members of the "Lo-Nd" array. In addition, Pb isotopic results so far obtained from East

African carbonatites define a line (Grünenfelder et al., 1986) with a slope similar to the oceanic regression line (Tatsumoto, 1978), and the data have been interpreted as the result of mantle mixing (Grünenfelder et al., 1986).

ISOTOPIC RESULTS

The isotopic data from six Napak phenocryst separates and their host rocks are given in Table 1. Analytical procedures for Nd and Sr isotope analysis were similar to those described in Bell and Blenkinsop (1987). Hand-picked pyroxene phenocrysts were washed

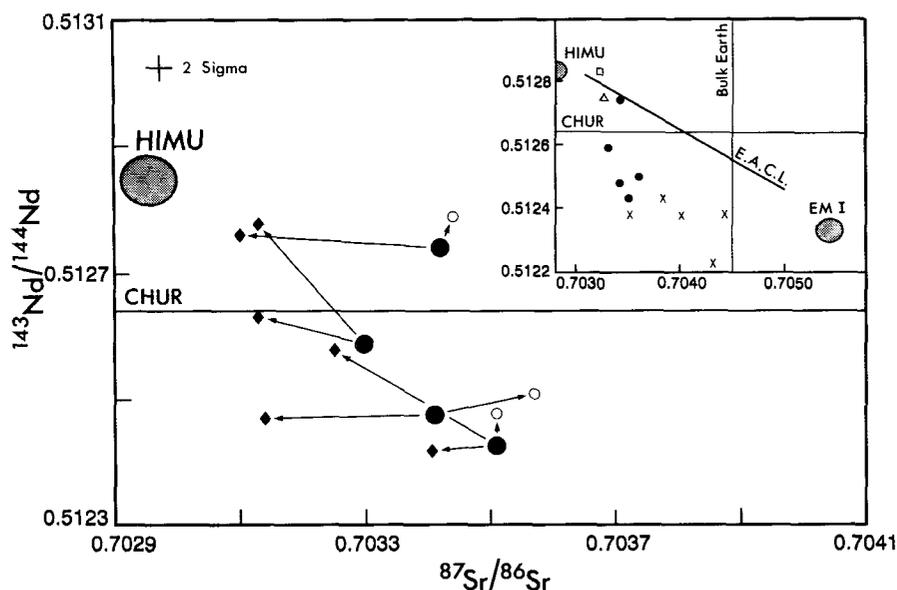


Figure 1. Plot of $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. E.A.C.L. = East African carbonatite line (Bell and Blenkinsop, 1987). Solid circles = olivine-bearing nephelinite whole-rock data; solid diamonds = clinopyroxenes; open circles = leachates. Tie lines join pyroxenes with corresponding whole rock analysis. HIMU (high U/Pb mantle) and EM I (enriched mantle I) data from Hart (1988). Inset shows whole-rock data: solid circles = olivine-bearing nephelinites; Xs = olivine-free nephelinites; square = carbonatites (two samples); triangle = melilitite nephelinite. Age-corrected Nd and Sr isotopic ratios for whole-rock nephelinites (Simonetti and Bell, unpublished) show negligible decrease (<0.0001) in present-day ratios.

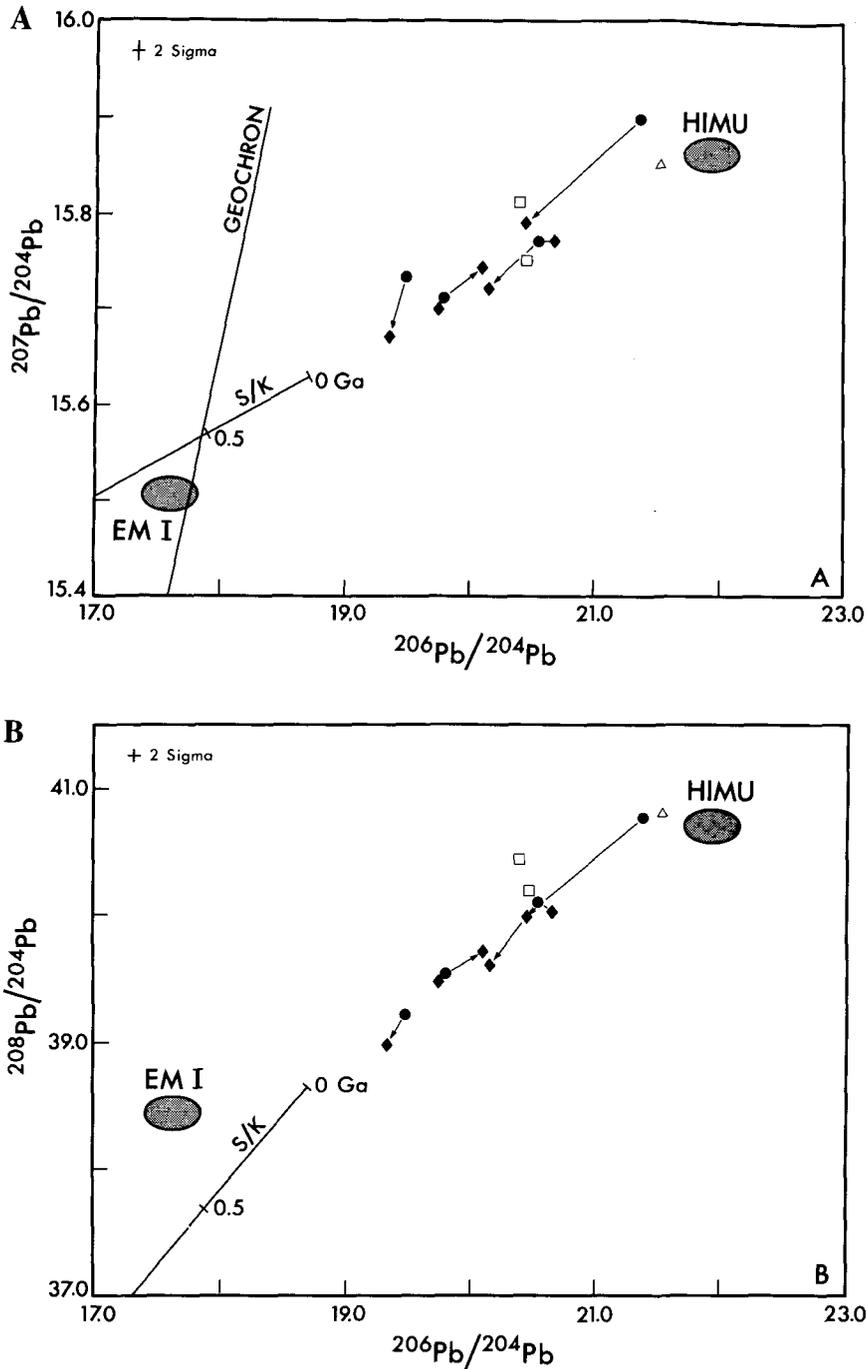


Figure 2. A: Plot of $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$. B: Plot of $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$. Symbols as in Figure 1. Age-corrected Pb isotopic ratios (Simonetti and Bell, unpublished) show negligible decrease (within analytical uncertainty) of present-day ratios.

for ~30 min in an ultrasonic cleaner with acetone, ultrapure water, 2 N HCl and then 1 N HBr. Pyroxenes from two of the samples, NP 100 and NP 112, could be divided into light and dark fractions. Pb was separated in HBr and HCl by using two-column anion ion-exchange techniques. Details are given in Kwon (1986). Pb samples were run on single Re filament using silica gel and phosphoric acid.

Shown in Figure 1 are the Nd and Sr isotopic data from six Napak diopside pheno-

cryst separates (made up of at least 40 grains) and associated olivine-bearing nephelinites. The inset shows Nd and Sr isotopic ratios from all of the analyzed whole-rock nephelinites and carbonatites (Simonetti and Bell, unpublished). Figure 2 shows Pb isotope data from pyroxenes and associated whole rocks.

As can be seen from Table 1, (1) most pyroxenes have Pb and Sr isotopic ratios that are lower than those of their host lavas, (2) the Nd, Pb, and Sr isotopic ratios of some

pyroxenes and whole rocks differ from sample to sample, (3) different pyroxene populations from the same sample have different Nd and Pb isotopic ratios, and (4) the Pb isotope ratios from both whole rock and pyroxenes define linear arrays (see Fig. 2).

The most significant feature to emerge from these isotopic data is that the pyroxene phenocrysts are clearly out of isotopic equilibrium with their host lavas. Few examples of isotopic disequilibrium among mineral phases from volcanic rocks are detailed in the literature. The study by Geist et al. (1988) is one such example.

DISCUSSION

The isotopic differences between the clinopyroxene phenocrysts and their host liquids can be explained in several different ways, including (1) fluid interaction with olivine-bearing nephelinites under subsolidus conditions, (2) entrapment of xenocrysts from a mantle source, and (3) transportation of cognate crystals, formed during melt contamination, by isotopically more contaminated liquids.

It may be possible to attribute the differences in the whole-rock and pyroxene Sr isotopic compositions to ground-water interaction. Alteration of mineral phases, particularly nepheline, by ground water could increase the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios but leave the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios relatively unchanged. In an attempt to evaluate ground-water interaction, leachates were obtained from three whole-rock nephelinites by using dilute HCl and HF. The leachates yielded isotopic ratios that are generally similar to those of the whole-rock data (Fig. 1), and from this we conclude that the lavas have retained their original isotopic ratios. Subsidiary alteration appears to have played a minor role, if any, in the isotopic evolution of the Napak nephelinites. This is also supported by petrographic observations of the nephelinite samples.

The Napak clinopyroxenes could also be considered mantle xenocrysts, derived from a metasomatized spinel lherzolite mantle characterized by a high $\text{CO}_2/(\text{CO}_2 + \text{H}_2\text{O})$ ratio (Brey and Green, 1977; Brey, 1978; Olafsson and Eggler, 1983; Wallace and Green, 1988). Studies from some lherzolite nodules (Menzies and Murthy, 1980a, 1980b; Cohen et al., 1984) show that isotopic disequilibrium can exist between coexisting minerals and that some of the data fall within the lower left quadrant (Menzies and Murthy, 1980a) of the Nd-Sr plot, similar to the isotopic ratios from Napak.

Most pyroxene phenocryst compositions from the olivine-bearing nephelinites are inconsistent with a xenocrystic origin. Average compositions of some phenocrysts,

given in Table 2, are similar to supposed magmatic diopsides from other complexes of alkaline affinity (Le Bas, 1987), including Phalaborwa (Eriksson, 1989). Also, they differ chemically (higher Al, total Fe, and Ti contents and lower Mg) from Cr-bearing diopsides from East Africa thought to be mantle xenocrysts (Le Bas, 1987; Cohen et al., 1984). Although the light pyroxene fractions from samples NP 100 and NP 112 (Table 2) have Cr₂O₃ and MgO contents similar to Cr-bearing diopsides, all of the analyzed pyroxenes show a continuous chemical variation that includes a decrease in Mg number with decrease in Cr and a decrease in Cr

coupled with an increase in Al₂O₃. Chemical variations both within and among individual pyroxene grains (e.g., negative correlations between Fe and Mg) and appropriate positive correlations in Pearce element-ratio diagrams (e.g., 2CaO/TiO₂ vs. SiO₂/TiO₂; Pearce, 1990) of the whole-rock data (Simonetti and Bell, unpublished), along with textural features, such as oscillatory, normal, and complex zoning, suggest that the pyroxenes from Napak crystallized from a mafic magma and are not crystals scavenged from a peridotitic mantle.

In a separate paper (Simonetti and Bell, unpublished), the variation of the whole-

rock Nd and Sr isotope ratios from Napak has been attributed to an assimilation-fractional crystallization process (De Paolo, 1981) involving a primary nephelinite magma (generated from a predominantly HIMU source). The whole-rock Nd and Sr isotope data from Napak (Fig. 1, inset) define a hyperbola, which contrasts with the linear distribution of nephelinite data from other carbonatite-nephelinite centers, such as Oldoinyo Lengai (Bell and J. B. Dawson, unpublished) and Shombole (Bell and Peterson, 1991). The upper end of the hyperbola is anchored well inside the depleted quadrant by the isotopic data from two carbonatites and two nephelinites.

The isotopic variations of the clinopyroxene phenocrysts from the olivine-bearing nephelinites are best interpreted as the result of open-system magma behavior coupled with fractional crystallization. The reasons for this are twofold. First, the pyroxene phenocrysts are clearly out of equilibrium with the melt. Reaction rims of diopsidic composition (depleted in Mg but enriched in Fe relative to the cores) around many of the pyroxene phenocrysts, the presence of irregularly shaped and embayed grains, and complex internal zoning as seen by backscattered-electron images (see Fig. 3) support our interpretation that the pyroxenes precipitated from a melt that was undergoing continuous chemical change. Second, the different isotopic ratios from the two pyrox-

TABLE 1. CLINOPYROXENE AND ASSOCIATED WHOLE-ROCK Nd, Pb, AND Sr ISOTOPIC DATA

Sample	Type	¹⁴³ Nd	⁸⁷ Sr	²⁰⁶ Pb	²⁰⁷ Pb	²⁰⁸ Pb
		¹⁴⁴ Nd	⁸⁶ Sr	²⁰⁴ Pb	²⁰⁴ Pb	²⁰⁴ Pb
TL 973	Cpx	0.51276	0.70310	20.46	15.79	40.00
TL 973	Whole rock	0.51274	0.70342	21.37	15.89	40.78
NP 100	Dark cpx	0.51263	0.70313	20.14	15.72	39.61
NP 100	Light cpx	0.51278	0.70313	20.66	15.77	40.04
NP 100	Whole rock	0.51259	0.70330	20.53	15.77	40.10
NP 101	Cpx	0.51247	0.70314	19.34	15.67	38.99
NP 101	Whole rock	0.51248	0.70342	19.48	15.73	39.21
NP 112	Dark cpx	0.51242	0.70340	19.75	15.70	39.47
NP 112	Light cpx	0.51258	0.70325	20.09	15.74	39.72
NP 112	Whole rock	0.51243	0.70351	19.78	15.71	39.56

Note: Isotope results normalized to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 and ⁸⁶Sr/⁸⁶Sr = 0.1194. NBS 987 Sr standard = 0.71025 ± 0.00002; La Jolla Nd standard = 0.51186 ± 0.00002; and BCR-1 ¹⁴³Nd/¹⁴⁴Nd = 0.51266 ± 0.00002. Uncertainties are given at the 2 σ level. Reproducibility for Pb ratios is 0.1%. An average fractionation factor of 0.1% per mass unit was applied to all measured Pb ratios on the basis of the average analysis of NBS 982. On the basis of average daughter/parent ratios for pyroxenes (Cohen et al., 1984; Davies and Lloyd, 1991) and the relatively young age of the lavas, the clinopyroxene Nd, Pb, and Sr isotopic ratios are considered to be close to initial. Cpx = clinopyroxene.

TABLE 2. NAPAK CLINOPYROXENE AVERAGE COMPOSITIONS

	TL 973	NP 101	NP 100 DARK	NP 100 LIGHT	NP 112 DARK	NP 112 LIGHT
No. of analyses:	8*	8*	15	15	18	18
SiO ₂	50.47	50.78	51.53	53.60	50.09	53.11
TiO ₂	1.27	1.17	0.93	0.40	1.30	0.44
Al ₂ O ₃	3.39	3.36	3.00	1.19	3.80	1.20
Cr ₂ O ₃	0.16	0.30	0.19	0.58	0.12	0.81
FeO _{total}	6.25	6.28	5.48	3.28	6.94	3.28
MnO	0.07	0.51	0.02	0.03	0.02	0.02
MgO	14.46	14.67	15.27	17.42	14.24	17.04
CaO	22.21	21.82	22.30	22.45	22.24	22.30
Na ₂ O	0.67	0.65	0.92	0.79	0.95	0.72
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00
Total	98.95	99.54	99.64	99.74	99.70	98.92
Di	0.82	0.76	0.85	0.92	0.84	0.90
Hd	0.13	0.19	0.07	0.03	0.09	0.05
Ac	0.05	0.04	0.07	0.05	0.07	0.05

Note: Clinopyroxene microprobe analyses were determined using a Cambridge Microscan 5 EDS system. Thirty-five grains were analyzed. Uncertainties: major oxides, 2% of the quoted value; minor oxides, <5 wt% (5%), <1 wt% (10%). Compositions are expressed as molecular end-members Di (Mg cation proportions), Hd (Fe²⁺ + Mn cation proportions) and Ac (Na cation proportions).

*Core analyses.

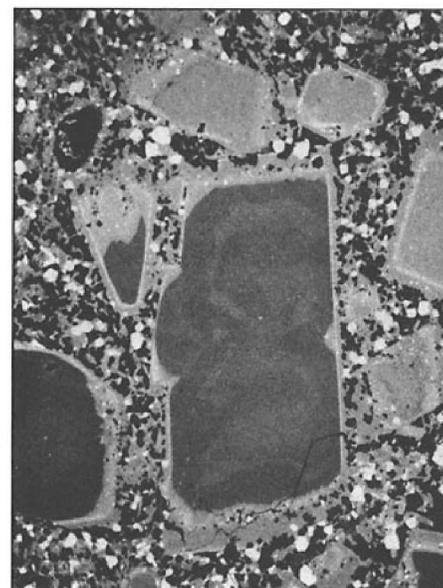


Figure 3. Backscattered electron image of sample NP 112 showing pyroxene phenocrysts. Note embayed crystals, reaction rims and complex internal zoning. Large phenocryst in center belongs to light colored fraction. Pyroxenes in this one section cover complete range of chemical compositions shown by Napak pyroxenes. Field of view is ~2.7 mm.

ene populations from each of the two samples NP 100 and NP 112 show that the minerals did not precipitate out of the melts that transported them to the surface. Furthermore, the pyroxenes did not have sufficient time to reequilibrate with their enclosing melts. The isotopic data from the clinopyroxene populations are consistent with mixing different generations of cognate crystals that crystallized from a melt undergoing progressive contamination.

The large range in Pb isotope ratios from the clinopyroxenes and associated whole-rock nephelinites from Napak alone is similar to that shown by all the Pb isotopic data so far collected from other East African carbonatite centers (Allègre et al., 1979; Grünenfelder et al., 1986). The slope, about 0.10, of the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ linear array from Napak (Fig. 2A) is similar to that shown by data from the East African carbonatite complexes (Grünenfelder et al., 1986), the oceanic regression line (Tatsumoto, 1978), and a Pb isotopic array defined by clinopyroxenes from mantle xenoliths from western Uganda (Davies and Lloyd, 1991).

The Pb isotopic data from Napak can be explained in several different ways. Included among these are the mixing of mantle components, possibly HIMU and EM I (Fig. 2), in different proportions. A second alternative involves the mixing of two isotopically distinct mantle melts, but the continuous variations in the chemical compositions of the pyroxenes would argue against this. A case can also be made for lower crustal involvement since Nd and Sr isotope ratios from mafic granulite xenoliths found in the nearby Lashaine tuff cone, Tanzania (Cohen et al., 1984), fall in the lower left quadrant of Figure 1. The Pb isotope ratios, however, are only partly consistent with this model.

CONCLUSIONS

The isotopic results from the Napak clinopyroxene phenocrysts indicate a complex crystallization history for the parent Napak magma. Although the melt was undergoing fractional crystallization and isotopic change, the pyroxenes failed to equilibrate isotopically with their host liquids as the liquid changed its isotopic composition. The data from Napak illustrate that clinopyroxenes may preserve the isotopic ratios that characterized the melt at the time of their crystallization. These clinopyroxenes were then transported by more evolved liquids during magma migration to the surface. This study reveals the importance of mineral isotopic analyses in understanding the melt dynamics associated with one volcano and cautions against using only whole-rock isotopic

data to evaluate the detailed magmatic history of a single eruptive center.

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