

## The trace element content and petrogenesis of kimberlites in Riley County, Kansas, U. S. A.<sup>1</sup>

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### Abstract

Kimberlites and associated xenoliths, carbonate veins, and interstitial carbonate material from Riley County, Kansas have been analyzed for certain trace elements and Fe using neutron activation. The non-micaceous kimberlites (Bala and Randolph No. 1) are higher in the incompatible elements (REE, Ba, Th, Hf, and Ta) compared to the micaceous kimberlites (Stockdale and Leonardville.) Contamination due to the numerous crustal xenoliths and interstitial carbonate material has probably been small. The xenoliths and interstitial carbonate would generally tend to dilute slightly the trace element concentrations of the kimberlites. The trace element contents (except perhaps the LREE and Th) of the kimberlites can be explained by slightly different degrees of incipient partial melting of average upper mantle peridotite containing about 56% olivine, 33% orthopyroxene, 5% clinopyroxene, and 6% garnet. Significant fractional crystallization of pyroxene, olivine, or garnet is precluded in the kimberlite melt since the compatible element contents (Co, Cr, and Sc) are quite high and similar to values expected by direct melting of peridotite. However, the LREE and Th contents of the kimberlite are somewhat higher than predicted by direct melting of peridotite possibly the result of volatile transport of these elements in H<sub>2</sub>O- and CO<sub>2</sub>-rich fluids. Alternatively, a more LREE- and Th-rich source than used in average peridotite in the above melting model may account for the enrichment of these elements in the kimberlites.

None of the carbonate material (veins, xenoliths, and kimberlite groundmass) appears to be igneous carbonate. Rather, it appears to be the result of varied amounts of secondary or hydrothermal (H<sub>2</sub>O- and CO<sub>2</sub>-rich fluids) activity. The relative importance of these processes cannot be evaluated with the present data.

### Introduction

The petrology, major element contents, and strontium isotopic compositions of the six kimberlites of probable Late Cretaceous age in Riley County, Kansas have been studied extensively by Brookins and his students (*e.g.*, Brookins, 1967, 1970a, 1970b; Brookins and Naeser, 1971). This study focuses on how certain trace elements may be used to determine the petrogenesis of these kimberlites.

Current models for the formation of kimberlites based on mineralogy, major and trace element contents, isotopic data, and experimental petrology indicate that kimberlites form by small degrees of

melting of upper mantle peridotite at depth in excess of 100 km (*e.g.*, Wedepohl and Muramatsu, 1979; Wyllie, 1979; Egglar and Wendlandt, 1979; Cullers and Graf, 1982a). This study demonstrates that the trace element distribution of the Riley County, Kansas kimberlites are consistent with a simple model of their formation by incipient melting of garnet peridotite followed by possible volatile transport of the LREE (light rare-earth elements) and Th in CO<sub>2</sub>- and H<sub>2</sub>O-rich fluids.

The kimberlites are crowded with xenoliths, mostly of crustal rocks. Several of these xenoliths were analyzed to evaluate the possible effects of contamination on the trace element characteristics of the kimberlites. Samples of the carbonate material found in these kimberlites were analyzed. This material does not appear to be igneous carbonate, but probably represents either secondary or hydrothermal veins.

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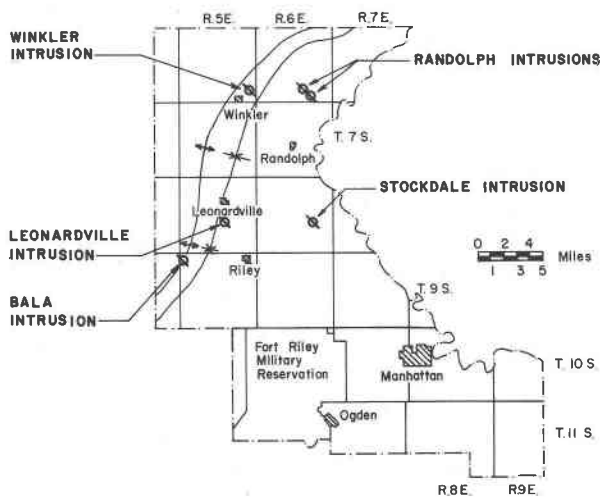


Fig. 1. The location of the kimberlites in Riley County, Kansas.

### Location

The six known kimberlites are located in Riley County in northern and eastern Kansas, U. S. A. (Fig. 1). They are intruded into lower Permian sedimentary rocks along a synclinal-anticlinal axis.

### Experimental

Samples obtained from the surface were the freshest possible samples. In addition, cores of the Bala and Leonardville kimberlites were also analyzed. Few xenoliths were included in the whole rocks of analyzed kimberlites, but it was impossible to avoid some xenolith contamination since they were so abundant in all but our Bala core. Xenoliths have also been analyzed separately to give some feeling as to how significantly they may contaminate the kimberlites.

The experimental procedure for the trace element analyses was adopted from methods of Gordon *et al.* (1968) and Jacobs *et al.* (1977). Typical precision obtained by us on standard rocks is summarized in Cullers *et al.* (1979).

### Mineralogy and petrography

The mineralogy and petrology of these kimberlites have been summarized in most detail by Brookins (1970). The following section summarizes mostly the petrography and isotopic geochemistry done by Brookins. His petrography is consistent with the results we obtained. Brief petrographic descriptions of our samples are included in the appendix.

The kimberlites are porphyritic with phenocrysts of olivine and smaller amounts of pyroxene, magnetite, ilmenite, pyrope, and/or phlogopite. Most olivine and pyroxene phenocrysts are altered extensively to serpentine or calcite, and many have a reaction rim of serpentine or chlorite. The phenocrysts occur in a very fine-grained, panidiomorphic matrix of mainly serpentine and calcite. Other minor minerals such as perovskite, zircon, ilmenite, magnetite, and chromite, may also occur in the matrix.

Most of the kimberlites are crowded with altered shale or carbonate xenoliths. In addition, the Stockdale kimberlite has a wide range of igneous and metamorphic xenoliths from the crust and upper mantle.

Numerous calcite veins cross-cut the kimberlites. Post-emplacment veins have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7079–0.7093 similar to the Permian limestones in the area. These veins are clearly secondary. Other veins have lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7028–0.7044 similar to igneous carbonate or hydrothermal veins. The groundmass carbonate contains intermediate Sr isotopic compositions between the two extremes and must be a mixture of primary and secondary carbonate.

Brookins (1970) distinguishes two groups of kimberlites: micaceous ( $\leq 15\%$  phlogopite) and lamprophyric (non-micaceous). The Stockdale, Leonardville, and Winkler kimberlites are micaceous kimberlites. The micaceous kimberlites contain more pyrope and ilmenite than the non-micaceous types. The non-micaceous kimberlites are the Bala, Randolph No. 1, and Randolph No. 2 kimberlites; they contain no more than traces of phlogopite. Pyrope is rare in non-micaceous types, and is found only in the groundmass. Ilmenite grains are smaller in the non-micaceous kimberlites than in the micaceous kimberlites.

### Major elements

Compared to the other basic rocks like basalts, the Riley County kimberlites are higher in MgO (20–25%), CaO (13–19%), H<sub>2</sub>O (8–10%), and CO<sub>2</sub> (9–12%) and lower in SiO<sub>2</sub> (21–24%), Al<sub>2</sub>O<sub>3</sub> (2–5%), K<sub>2</sub>O (0.02–0.30%) and Na<sub>2</sub>O (0.04–0.5%) (Brookins, 1970; Wedepohl and Muramatsu, 1979). These kimberlites are similar to basalts in Fe<sub>2</sub>O<sub>3</sub> (6.5–7.4%). Compared to the average of other kimberlites, the Riley County kimberlites are lower in SiO<sub>2</sub> and K<sub>2</sub>O and higher in CaO and CO<sub>2</sub> (Brookins, 1970; Wedepohl and Muramatsu, 1979). The CaO

and CO<sub>2</sub> contents of these kimberlites are fairly high compared to other kimberlites because of the large amount of calcite. These kimberlites may be low in the alkalis because of extensive alteration. Alteration is unaffected by depth in the intrusion; major and trace element analyses and the petrography in cores are nearly identical to those at the surface (Brookins, 1970; also this paper).

### Results

The trace element and Fe contents of the analyzed kimberlites, inclusions, and veins are given in Table 1. Compared to basalts (even alkali basalts), kimberlites are enriched in LREE, Ba, Th, Hf, and Ta and depleted in Co and Sc (Wedepohl and Muramatsu, 1979).

The average trace element and Fe contents of these kimberlites are compared to the average of all kimberlites in Table 2. In general, Ba and Ta in the Riley County kimberlites are very much enriched over the average of all kimberlites. Other elements are variously enriched or depleted in these kimberlites compared to the average. The non-micaceous kimberlites (Bala and Randolph No. 1) have significantly different trace element contents compared to the micaceous kimberlites (Stockdale and Leonardville). The non-micaceous kimberlites are significantly higher in REE (rare-earth elements), Ba, Th, Hf, Sc, and Ta compared to the micaceous kimberlites and to the average of kimberlites (except Hf in the latter). The two groups of kimberlites have about the same Co and Cr. The Co and Cr contents of the kimberlites are also similar to the average of all kimberlites.

The Leonardville and Bala kimberlites have been analyzed in some detail since considerable fresh core was available. Except for Ba, there seems to be no systematic variation in trace elements with depth. The lowest Ba occurs in the bottom two samples in both the Leonardville and Bala kimberlites.

The REE contents of the Bala kimberlite, inclusions, and veins are shown in Figure 2. The REE content of the samples are as follows: kimberlite > inclusions > veins. The LREE and Th of the Bala kimberlite are the highest of the kimberlites reported in this study. Also the carbonate-shale inclusions in this kimberlite have the highest LREE and Th contents compared to corresponding material in the other kimberlites. The LREE are also high but the Th contents are low in carbonate veins from the

Bala kimberlite compared to such veins in the Stockdale kimberlite.

The other non-micaceous kimberlite analyzed, Randolph No. 1, is somewhat lower in Th and LREE than the Bala kimberlite, but it is higher in Ba, Hf, and Ta. No carbonate veins and no inclusions have been analyzed in the Randolph No. 1 kimberlite.

As with the other kimberlites, the REE content of the Leonardville kimberlite is greater than that of the inclusions (Fig. 3). The Leonardville kimberlite has the highest LREE, Ba, Th, and Hf of the micaceous kimberlites (Table 2; Figs. 3 and 4). Both micaceous kimberlites are similar to one another in the content of all other analyzed elements. The element contents in the inclusions in these micaceous kimberlites are lower in all analyzed elements than inclusions in the Bala kimberlite.

The REE content of the Stockdale kimberlite is greater than that of the altered shale inclusions which are in turn greater than that of the carbonate veins (Fig. 4). This order of REE abundance is the same as for the Bala kimberlite.

### Discussion

#### *Carbonate-shale xenoliths*

The carbonate-shale xenoliths in the Leonardville and Stockdale kimberlites have lower trace element contents than the corresponding kimberlite (Fig. 5). This is also true in carbonate-shale xenoliths relative to kimberlite for all elements but Yb, Lu, Ba, and Hf in the Bala kimberlite. Thus, contamination by xenoliths should act to dilute most elements slightly in the whole rock. The values for most elements should be slightly higher in unaltered kimberlite. Nevertheless, we avoided large xenoliths in our sampling of Leonardville, Stockdale, and Randolph No. 1 kimberlites. There were few visible xenoliths in our Bala sample. Thus, we believe that most element contents were not significantly affected by xenolith contamination in the whole rock analyses.

#### *Melting models*

Most models of kimberlite petrogenesis focus on their formation by a very small percentage of melting of upper mantle peridotite at depths in excess of 100 km. Trace elements can be used to model this process if a reasonable mineralogy of the source, trace element content of the source, and percent melting can be assumed, and if it is known how the

Table 1. The trace element and Fe contents of the Riley County kimberlites

	La	Ce	Sm	Eu	Tb	Yb	Lu	$\Sigma$ REE <sup>1</sup>	Eu/Sm	La/Lu <sup>2</sup>	Ba	Th	Hf	Ta	Co	Sc	Fe <sub>2</sub> O <sub>3</sub> <sup>%</sup>	Cr	%Nb <sub>2</sub> O	
<u>Bala Kimberlite</u>																				
19.5 feet core	301	529	18.5	5.2	1.19	1.38	0.30	1056	0.28	104	6300	44	5.4	24	75	20.5	9.99	1110	0.09	
27.9 feet core	301	537	18.5	4.9	1.09	1.45	0.34	1070	0.26	91	6210	46	4.9	25	69	20.1	10.0	1080	0.08	
50.7 feet core	298	502	17.5	4.1	0.97	1.27	0.28	1014	0.23	110	5820	42	5.3	23	63	19.0	9.7	1010	0.22	
75.3 feet core	314	534	18.9	5.05	1.24	1.23	0.30	1091	0.27	108	6180	41	5.0	23	64	20	9.4	1080	0.10	
94 feet core	293	508	18.1	4.6	0.98	1.03	0.27	1023	0.25	112	6820	45	4.2	26	66	19.3	9.6	1110	0.20	
113 feet core	297	504	17.3	3.86	1.05	1.23	0.15	1023	0.22	205	4350	40	4.5	--	54	17.4	8.5	1100	0.072	
137.8 feet core	309	500	19.5	4.20	0.96	1.10	0.16	1034	0.22	200	4490	48	4.4	--	62	18.9	9.3	1200	0.093	
CO <sub>3</sub> -rich shale inclusion	154	231	8.44	1.96	--	3.03	0.50	502	0.23	32	17,200	13	20	5.7	39	7.0	3.5	111	0.11%	
CO <sub>3</sub> -shale inclusion less CO <sub>3</sub> (22%) <sup>3</sup>	147	220	8.6	1.94	1.0	3.3	0.62	481	0.23	25	24,000	17	28	6.6	27	9.1	4.8	107	0.03%	
Carbonate vein	58.5	71	1.19	0.32	-0.048	--	<0.0037	151	0.27	--	17,350	<0.04	<0.1	--	<0.5	0.2	0.17	<8	0.14	
Carbonate vein	54.8	65	1.14	0.33	--	--	139	0.23	0.23	--	14,400	<0.03	<0.04	--	0.7	0.2	0.16	11	0.12	
Kimberlite (‡)+ carbonate vein	185	257	10.0	2.43	0.52	0.66	0.055	557	0.24	348	13,320	22	1.9	14.8	32	9.3	4.86	580	0.13	
<u>Randolph No. 1 Kimberlite</u>																				
Surface-1	231	397	15.5	3.90	0.92	1.55	0.22	807	0.25	109	---	--	5.9	33	58	21.4	10.7	1020	0.07	
Surface-2	230	364	15.0	3.54	0.88	--	0.23	766	0.24	103	6760	27	--	--	--	--	--	--	--	
<u>Leonardville Kimberlite</u>																				
Surface	178	235	12.2	3.3	0.86	1.26	0.20	541	0.27	92	5830	26	3.9	26	72	15.2	6.7	1110	0.07	
22 feet core	156	262	11.8	2.74	0.77	-0.8	0.19	550	0.23	85	4860	23	3.6	26	62	14.5	6.6	1250	--	
68 feet core	161	256	10.4	3.08	0.79	-0.63	0.14	538	0.20	119	4770	20	2.9	14	68	12.8	10.1	1000	0.12	
120 feet core	150	251	10.9	3.16	0.83	0.99	0.15	525	0.29	103	4100	20	3.4	15	73	12.9	6.9	930	0.13	
213 feet core	129	219	9.91	2.66	0.71	0.7	0.14	458	0.27	95	2900	18	3.1	15	63	12.4	7.3	920	0.11	
273 feet core	140	235	10.3	2.58	0.74	0.73	0.16	492	0.25	90	2510	19	3.0	10	75	11.2	6.6	--	0.11	
CO <sub>3</sub> -shale inclusion	27.9	35.9	1.79	0.41	-0.15	-0.30	-0.08	84	0.23	36	350	2.6	0.90	-0.8	19	4.1	2.0	33	0.29	
CO <sub>3</sub> -shale less carbonate (33%) <sup>3</sup>	10.2	18.8	1.16	0.32	-0.19	-0.29	-0.07	42	0.28	15	240	3.9	1.4	1.1	13	5.9	3.1	35	0.35	
80-100 mesh; 273 feet core	122	240	9.6	2.50	0.74	0.73	0.19	477	0.26	66	3010	19	3.3	11	77	12.1	7.1	970	0.10	
80-100 mesh; 273 feet core less carbonate (17%) <sup>3</sup>	113	226	9.8	2.52	0.65	0.79	0.19	451	0.26	61	3100	21	3.6	13	75	13.5	8.2	1040	0.09	
Stockdale Kimberlite Surface	89.2	133	7.08	1.82	0.55	0.97	0.13	296	0.26	71	---	--	--	--	--	--	--	--	--	
	83.7	148	6.4	1.76	0.50	0.80	0.13	307	0.28	67	2500	10.2	2.7	20	79	10.4	8.52	1310	0.07	
	95.0	145	6.75	1.66	0.44	0.70	0.11	314	0.25	89	2800	13.7	2.5	19.4	79.4	10.6	7.18	986	0.11	
CO <sub>3</sub> -shale inclusion	28.5	37.9	1.29	0.34	0.12	0.32	0.074	83	0.26	40	1000	3.2	0.65	0.17	11.9	3.11	1.68	35.7	0.055	
CO <sub>3</sub> veins	15.8	17.6	0.55	0.12	--	0.04	0.01	41	0.22	163	300	0.37	--	12.6	22.5	0.38	0.36	6	0.043	
	4.0	5.1	0.47	0.074	--	0.33	0.084	14	0.16	5	--	0.61	0.48	0.10	11.5	3.1	0.63	68	0.050	
	10.6	12.2	0.58	0.12	--	0.17	0.017	30	0.21	64	4400	0.66	0.21	0.07	3.4	0.68	1.07	7.7	0.034	

1 - The  $\Sigma$ REE include estimates of all the REE concentrations estimated from chondrite-normalized curves (Y not included).

2 - These are chondrite-normalized La/Lu ratios.

3 - A very fine powder of these samples was placed in 0.3M acetic acid and washed to remove the carbonate.

Table 2. Average Trace element and Fe contents of Riley County kimberlites compared to the average contents of kimberlites (<sup>1</sup>Wedepohl and Muramatsu, 1979; values in ppm except where indicated)

Average in Kimberlites <sup>1</sup>	non-micaceous			micaceous	
	Average Bala Kimberlite (7 samples)	Average Randolph No. 1 Kimberlite (1 or 2 samples)	Average Leonardville Kimberlite (6 samples)	Average Stockdale Kimberlite (2 or 3 samples)	
La	150	231	152	89	
Ce	200	381	243	142	
Sm	13	15.3	10.9	6.7	
Eu	3.0	3.7	2.9	1.75	
Tb	1.0	0.90	0.78	0.50	
Yb	1.2	1.55	0.85	0.82	
Lu	0.16	0.23	0.16	0.12	
Ba	1000	6760	4160	2650	
Th	16	27	21	12	
Hf	7	5.9	3.3	2.6	
Ta	9	33	18	20	
Co	77	58	69	79	
Sc	15	21	13	10.5	
Fe <sub>2</sub> O <sub>3</sub> (%)	10.2	10.7	7.4	7.9	
Cr	1110	1020	1040	1150	
Na <sub>2</sub> O(%)	0.27	0.07	0.11	0.09	

trace elements partition between the source and melt (e.g., Shaw, 1970). The problems involved with these assumptions will not be elaborated on here in detail as they have been discussed in great detail in many other papers (e.g., Haskin, 1982; Cullers and Graf, 1982a and b).

First, a D. C. (distribution coefficient) needs to be defined. A D.C. is defined as the equilibrium concentration of a trace element in a mineral relative to its concentration in a melt. The D. C. values used in this study for mineral-basic melt pairs are summarized in the appendix along with the corresponding references. We have used D. C.'s which are at the low end of all measured ranges for these mineral-melt pairs. This results in an upper limit for the trace element contents in the melt. One problem is that the listed D. C.'s are usually obtained at low pressure, and we are not certain if the D.C.'s change at the high pressure needed to form kimberlites. Also these are the D. C. for minerals relative to basaltic melts instead of kimberlitic melt.

Upper mantle peridotite with 56% olivine, 33% orthopyroxene, 5% clinopyroxene, and 6% garnet with a trace element content of average peridotite (Wedepohl and Muramatsu, 1979) is assumed to undergo a small percentage of equilibrium melting.

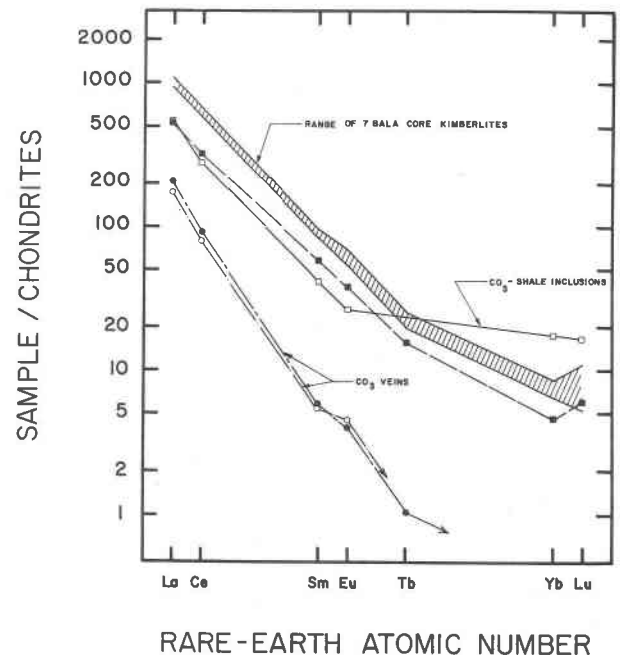


Fig. 2. The REE content of the Bala kimberlite, inclusions (xenoliths), and veins normalized to chondrites (values of Haskin et al., 1968) (Range of kimberlite, cross-hatch lines; kimberlite with carbonate vein, solid square and dashed line; carbonate-shale inclusion, open square and solid line; carbonate veins, circles and dash-dot or long dash-short dash line).

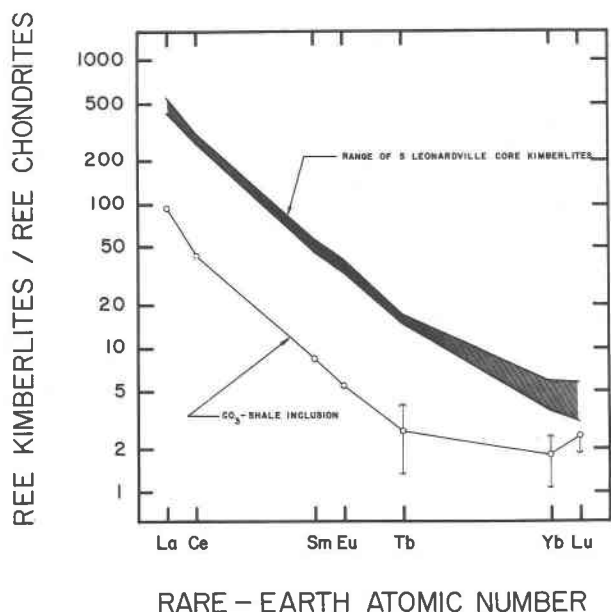


Fig. 3. The REE content of the Leonardville kimberlite and carbonate-shale inclusions normalized to chondrites (range of kimberlite, cross-hatch lines; carbonate-shale inclusion, open circles).

This model is consistent with models proposed by many others for the formation of basic and ultrabasic rocks enriched in the incompatible elements (*e.g.*, Gast, 1968; Kay and Gast, 1973; Cullers and Medaris, 1977; Mitchell and Brunfelt, 1974). The incompatible elements with low *D.C.*'s for peridotite relative to kimberlite melt will concentrate in the melt (LREE, Ba, Th, Hf, and Ta). The compatible elements with high *D.C.*'s for peridotite relative to kimberlite melt will concentrate in the peridotite (Co, Cr). Sc has a *D.C.* close to one for this system so it should partition equally between peridotite and kimberlite melt.

The predicted trace element contents of the melt assuming 0.5% equilibrium melting of average peridotite are compared to the Bala (example of a non-micaceous kimberlite) and Leonardville (micaceous) kimberlites in Figure 6. Note the trace element contents in this figure are normalized to the average peridotite of Wedepohl and Muramatsu so enrichment or depletion of an element in the melt relative to the source rock can easily be noted. We believe this model is supported by the data since there is good agreement for most elements between the predictions and observations. In addition, the non-micaceous kimberlites have higher contents of the incompatible elements than the micaceous kim-

berlites, and all kimberlites have similar concentrations of the compatible elements. These differences and similarities are precisely what is to be expected if small differences in partial melting at small degrees of melting are producing the variations in trace element content of the melt. The incompatible elements are expected to decrease with increased melting (especially in the range of 0.5% to several percent melting) so presumably the non-micaceous kimberlites may represent a smaller degree of melting than the micaceous kimberlites. The compatible elements are insensitive to the degree of melting in this range of melting and should have about the same concentration in the melt as long as the source is homogeneous in these trace element contents.

Even though predictions and observations for most elements agree well in the above model, the predicted values for the LREE and Th are too low compared to the observed values in any of the kimberlites. We do not believe this difference between observed and predicted values for these elements negates the model considering the many assumptions involved. For example, inappropriate *D.C.*'s may have been used for these elements due to differences in composition or pressure between

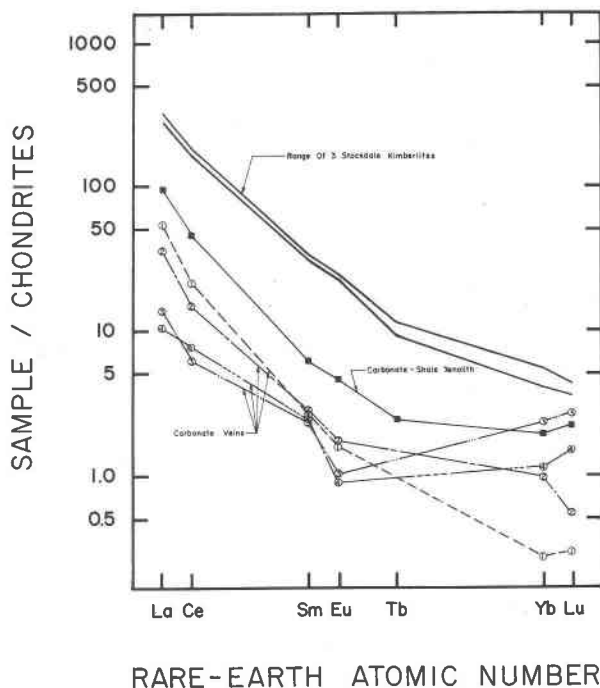


Fig. 4. The REE content of the Stockdale kimberlite, carbonate-shale inclusions, and carbonate veins (range of kimberlite, cross-hatch lines; carbonate-shale inclusions, open circle; carbonate veins, closed circle).

the peridotite-kimberlite melt system at high pressure and the mineral-basaltic melt system at low pressure in which the D. C.'s were measured. Indeed, Th D. C.'s are not even well established at low pressure. Also the LREE and Th contents of the peridotite source may have been higher than that used in this model. Nixon *et al.* (1981), for example, report mantle xenoliths that are much more enriched in the incompatible elements (especially the LREE) used in the above model. Melting of these enriched xenoliths could still generate the range of trace element contents of the Riley County kimberlites using D. C. values that are not as low as those used in the above model. Finally, there may be other processes, as discussed below, affecting the REE and Th contents in kimberlites.

High pressure fractional crystallization of eclogite has been used to explain increased LREE contents in kimberlite melts over that predicted in partial melting models (*e.g.*, Mitchell and Brunfelt, 1974). Large amounts of fractional crystallization of garnet and clinopyroxene from kimberlite could produce the higher REE and Th contents of kimberlite over those predicted in the melting model. This model, however, would result in increased amounts

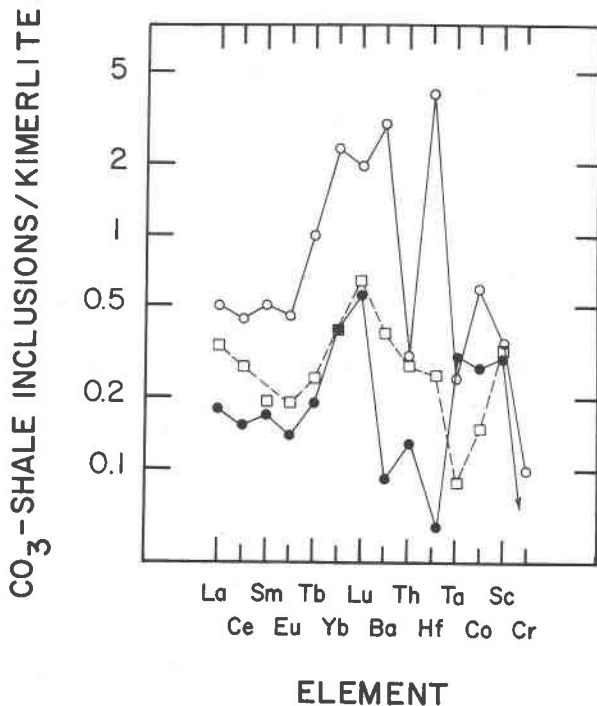


Fig. 5. The element content of carbonate-shale inclusions relative to their corresponding kimberlite (Bala, open circles; Leonardville, solid circles; Stockdale, solid square).

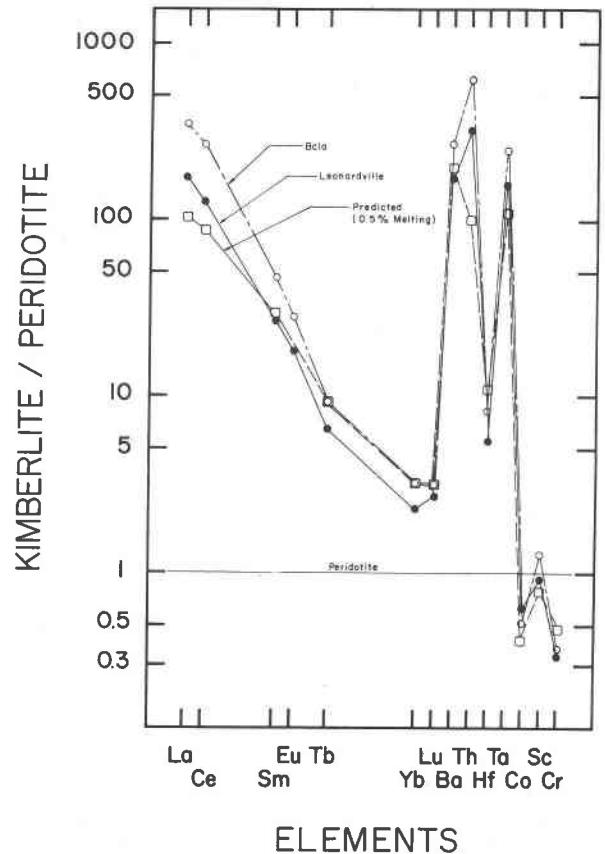


Fig. 6. The element content of Bala (solid circle) and Leonardville (open circle) kimberlites are normalized to average peridotite. Also plotted is the predicted element content of a melt produced by 0.5% equilibrium melting of peridotite with olivine/orthopyroxene/clinopyroxene/garnet = 56/33/5/6.

of the incompatible elements (Ba, Th, Ta, Hf) and dramatic decreases in the compatible elements (Co, Cr, Sc, and probably the heavy REE) over those observed in the kimberlites. The decrease expected for the compatible elements is the main reason the fractional crystallization model must be rejected.

Crustal contamination has also been suggested as not having a significant effect on the trace element contents in this study. Minimal contamination by crustal rocks is also supported by the very low  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{Al}_2\text{O}_3$ , and strontium isotopic contents of the kimberlites (Brookins, 1970).

Kimberlites contain abundant volatiles, and volatile transport of the LREE and Th in  $\text{CO}_2$ - and  $\text{H}_2\text{O}$ -rich fluids may be a viable mechanism to explain the high LREE and Th contents in kimberlites (*e.g.*, Fesq *et al.*, 1974). No experimental work has been done on Th, but recent experimental studies support the mobility of the REE in  $\text{CO}_2$ - and  $\text{H}_2\text{O}$ -rich

fluids if the mass of these fluids is large enough (Mysen, 1979; Wendlandt and Harrison, 1979). For example, the LREE become soluble in H<sub>2</sub>O-rich fluids relative to silicate solids and melts at mantle pressure. The LREE could concentrate in a large mass of H<sub>2</sub>O in contact with a moving kimberlite melt. At lower pressure, the LREE are less soluble in the H<sub>2</sub>O-rich fluid relative to silicate melt (Cullers *et al.*, 1973; Mysen, 1979) so the LREE might concentrate back into the kimberlite melts as they rise.

Thus, we believe the trace element content of these kimberlites can be explained by a very small percentage of melting of garnet peridotite with a trace element content similar to Wedepohl and Muramatsu's average peridotite followed by possible volatile transport of the LREE and Th. Alternatively, a peridotite source more enriched in the LREE and Th than that used above could partially melt and produce the range of trace element contents of the Riley County kimberlites. Crustal contamination or fractional crystallization is not believed to be a major process in affecting these trace element contents during the formation of the Riley County kimberlites.

#### *Formation of the carbonate veins and dispersed carbonate*

Brookins (1970) distinguishes post-emplacment (secondary) veins with high Sr isotopic ratios and

low Sr contents similar to the limestone country rock and pre-emplacment veins (primary) with low Sr isotopic ratios and high Sr contents more similar to igneous carbonate (*i.e.*, carbonate formed from carbonate melts) in the Riley County kimberlites. The carbonate in the groundmass of the kimberlite has intermediate values between the two extremes and this carbonate appears to be a mixture of igneous and sedimentary carbonates.

The data for the trace elements in the carbonate material in this study may be considered preliminary since we plan to do more detailed work on this material. The data for the carbonate fractions are compared to average primary carbonatites, replacement carbonatites, and limestones in Table 3. Average carbonatite is very much more enriched in all elements compared to average limestone. Yet there is quite a difference in the degree of enrichment of these elements in the carbonate fractions of these kimberlites. None of the carbonate fractions appear to be all igneous carbonate or sedimentary carbonate. The Bala veins are very enriched in the LREE and Ba contents similar to carbonatite, but they are significantly depleted in heavy REE, Th, Co, Sc, and Cr contents compared to carbonatite. The Stockdale veins have lower LREE and Ba contents and have higher Co contents than the Bala veins. Other elements are similar in veins of the two kimberlites. This suggests these veins are not igneous carbonate. They could, for example, be second-

Table 3. Trace element contents of carbonate fractions in veins, inclusions, and groundmass of Riley County kimberlites compared to average limestones and carbonatites (ppm)

	La	Lu	Ba	Th	Hf	Ta	Co	Sc	Cr
Bala veins	56	<0.0037	15,900	<0.04	<0.1	--	<0.7	0.23	11
Stockdale veins	4-15.8	0.01-0.08	300-4400	0.37-0.66	0.21-0.48	0.07-12.6	3.4-22.5	0.38-3.1	6-68
From carbonate- <sup>1</sup> shale inclusions	64-178	0.1-0.75	~0-570	~0	~0	0.2-2.5	32-79	~0-0.4	29-125
From Leonardville kimberlite- groundmass	166	0.19	2,570	5	1.8	1.2	87	~0	630
Carbonatite-primary <sup>2</sup>	600	0.5	15,000	1,500			17	10	48
Carbonatite <sup>2</sup> replacement	480	2.5	5,300	130			33	25	470
Limestone <sup>2</sup>	1	0.2	10	1.7	0.3	0.0?	0.1	1	11

1 - These are inferred values based upon mass balance calculations knowing the fraction of carbonate relative to non-carbonate fraction and knowing the concentration of the elements before and after dissolution in 0.3M acetic acid. The quantity of trace elements leached from the kimberlite could not be checked directly, but the trace element contents of a variety of layer silicates did not change before and after using this technique.

2 - Average values given are from many sources but the main ones are Rösler and Lange (1972), Armbrustmacher (1979), Cullers and Graf (1981).



ary veins in which the LREE and Ba were more mobil than the other elements so the LREE and Ba became enriched in the carbonate veins over average limestone concentrations. Alternatively, these veins might be hydrothermal, but not enough is known about the behavior of these elements in hydrothermal veins to evaluate this possibility (Cullers and Graf, 1982b). Determination of the Sr isotopic compositions of these veins should distinguish between these two possibilities.

Even the carbonate material from the carbonate-rich shale inclusions is not clearly sedimentary. The Ba, Th, Hf, Ta, and Sc contents of the carbonate in these inclusions are similar to limestones, but the LREE, Co, and Cr contents are quite high compared to those of limestones.

Finally, the carbonate material from the groundmass of the kimberlite is also neither clearly igneous or clearly sedimentary, but it must result from a complex mixture of processes. The REE, Ba, Co, and Cr contents are similar to carbonatite, but the Th and Sc contents are similar to average limestone. This is consistent with Brookins' (1970) previously discussed interpretation that the Sr contents and Sr isotopic compositions of this material results from mixed primary and secondary processes. Also if the carbonate material from the groundmass is not clearly igneous, it should be considered as a contaminant for the trace elements in the kimberlite. The Co content of the carbonate groundmass is about the same as that of the kimberlite although all other elements are variously depleted in the groundmass relative to kimberlite. Thus, the groundmass carbonate like the carbonate-shale xenoliths should tend to dilute slightly the kimberlite in most trace elements.

*Note added in proof:*

The Randolph No. 2 Kimberlite has recently been analyzed, and it has a similar trace element content to the other non-micaceous kimberlites. Thus, it presumably formed in a similar fashion as the non-micaceous kimberlites. Samples at Winkler crater have not been analyzed since they are highly altered.

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#### **Appendix 1. Brief petrographic descriptions of the rocks analyzed in this study**

**Bala Kimberlite.** This porphyritic rock contains up to 30 percent phenocrysts (up to 2 mm) of olivine and pyroxene (altered to serpentine, calcite, and magnetite) and a few phenocrysts of pyrope. The groundmass contains fine-grained serpentine and lesser calcite, opaque oxides, and hematite. The veins are composed of nearly all calcite. There are few xenoliths in the rocks analyzed.

**Randolph No. 1. Kimberlite.** This is a porphyritic rock containing 25 percent phenocrysts (up to 2 mm) of predominately olivine and pyroxene altered to serpentine, calcite, hematite, and black oxides. The phenocrysts occur in a very fine-grained groundmass of lizardite, calcite, and iron oxyhydroxides. There are few xenoliths in the rocks analyzed.

**Leonardville Kimberlite.** This porphyritic rock contains up to 30 percent phenocrysts (up to 5 mm) of olivine and pyroxene (altered to calcite, serpentine, or magnetite) and a few phenocrysts of pyrope, phlogopite, and magnetite. The fine-grained matrix is composed of serpentine of varied grain size with lesser phlogopite, opaque oxides, calcite, and garnet. There are up to 10 percent xenoliths of shale with finely disseminated calcite.

**Stockdale Kimberlite.** This porphyritic rock contains about 20 percent phenocrysts (up to 2 mm) of olivine (altered to serpentine), pyroxene (altered to serpentine), and phlogopite in a fine-grained matrix

of lizardite with minor calcite and black oxides. About 20 percent of the rock is composed of altered xenoliths (dunite, eclogite, phyllite, shales) of varied size and shape. The rock is brecciated and

riddled with calcite veinlets. The veins analyzed are composed primarily of calcite although the sample that has 4.0 ppm La has about 30 percent serpentine in addition to calcite.

Appendix 2. D.C. used in the modeling during the melting of peridotite to produce kimberlite melt.<sup>1</sup>

	La	Ce	Sm	Eu	Yb	Lu	Ba	Hf	Th	Co	Sc	Cr
Olivine	0.001	0.001	0.002	0.002	0.002	0.002	0.001	0.1	0.01*	3	0.3	2
Orthopyroxene	0.002	0.003	0.010	0.013	0.05	0.06	0.001	0.03	0.01*	2	1.2	1.8
Clinopyroxene	0.10	0.12	0.26	0.30	0.28	0.28	0.001	0.07	0.013	2	3	5
Garnet	0.02	0.02	0.22	0.32	4.0	4.5	0.002	0.03	--	0.3	10	2

<sup>1</sup> - Many sources were surveyed to obtain these D.C.'s, and the lowest values available tended to be used for the modeling. The references listed below had at least one value close to the values of the above D.C.'s: Paster et al., 1974; Philpotts and Schnetzler, 1970; Frey et al., 1974; Henderson and Dale, 1969-70; Muir et al., 1964; Gunn, 1971; Onuma et al., 1968; Duke, 1976; Leeman and Scheidegger, 1977; Haskin and Korotev, 1977; Schreiber and Haskin, 1976; Hart and Brooks, 1974; Griffin and Murthy, 1969; Baker et al., 1977; Irving and Frey, 1977; Cox et al., 1979.

\* - These values are not established. The D.C.'s should be considerably less than one.