Mororó, E.A.A., et al., 2024, Rare earth element transport and mineralization linked to fluids from carbonatite systems: Geology, <u>https://doi.org/10.1130/G51531.1</u>

Supplemental Material

Data, results, calculations, methods, experimental details, sampling, and petrography.

SUPPLEMENTAL MATERIAL

METHODS

Raman spectroscopy

Raman spectroscopy was conducted on both the rock-forming minerals in studied rock and on the quartz-hosted fluid inclusions at the Faculty of Science Research and Instrument Core Facility of Eötvös University, Budapest (ELTE FS-RICF), using a confocal HORIBA Labram HR (high resolution) 800 spectrometer with Nd-YAG laser ($\lambda = 532.07$ nm) excitation, 600 to 1800 grooves/mm optical grating, 50–100 µm confocal hole, 3–200 seconds acquisition time with at least 2 accumulations, and a 100× objective (numerical aperture 0.9). The laser spot size (lateral) was 1.2 µm, with depth resolution of 1.7 µm (using a 50 µm confocal hole and 100× objective) and spectral resolution of 1.12 cm⁻¹ at 1398.02 cm⁻¹ (full width at half maximum of one neon line). Laser power were 130 mW at the source and ~50 mW at the sample surface. Data evaluation (background fitting and peak fitting using the Gaussian–Lorentzian sum profiles) was carried out using LabSpec v6.5.1 software. The databases of Frezzotti et al. (2012) and RRUFF (rruff.info) were used for the comparison and identification of fluid components. Raman spectroscopy had multiple applications on this study, as listed below:

Spot analyses of host minerals as well as daughter minerals were conducted at room temperature, in the 100 cm⁻¹ to 1500 cm⁻¹ and 2800 cm⁻¹ to 4000 cm⁻¹ spectral ranges. The main bands of interest were: v₁-CO₃ of nahcolite / REE-bearing natrite solid solution (natrite_{ss}, 1048 cm⁻¹ / 1078 cm⁻¹), v₁-SO₄ of thenardite / arcanite (994 cm⁻¹ / 983 cm⁻¹), CO₂ Fermi diad (~1285 cm⁻¹ and ~1388 cm⁻¹, slightly changes along with the density, Rosso and Bodnar, 1995). Every measurement in natrite_{ss} contained v₁-SO₄

bands at approximately 998 cm⁻¹. Spectral range between 2800 cm⁻¹ and 4000 cm⁻¹ was used for the H_2O -related bands of hydrated phases and dissolved H_2O in CO_2 .

- Raman X-Y-Z (3D) imaging of representative fluid inclusions was carried out with a 0.5 μm horizontal X-Y step size and a 0.75 μm to 1.0 μm vertical separation between Z planes (3 to 5 planes per inclusion). Bulk fluid composition was calculated, at room-T, based on area proportions and density of each individual daughter phase. CO₂ density was estimated based on the Fermi diad Δ (using the equation developed by Fall et al., 2011). REE-bearing natrite_{ss} was considered analogous in composition to OL gregoryite phenocrysts (Mitchell and Kamenetsky, 2012).
- 3) Raman-combined microthermometric data from quartz-hosted fluid inclusion were collected using a Linkam THMS 600 heating-cooling stage and a Linkam TS1200 heating stage. An Olympus BXFM free-space microscope was used to monitor the visible phase-changes during the stepwise heating experiments. The measurements started at 25 °C, which is below the CO₂ critical temperature (30.98 °C; Span and Wagner, 1996) and the quartz-hosted inclusions were heated at a rate of 15°C/min to a maximum temperature of 900 °C. Stepwise heating was paused for the necessary duration to obtain Raman spectra from the fluid inclusions, and measurements were performed on multiple parts of the inclusion to observe phase changes and homogenization.

Focused Ion Beam - Scanning Electron Microscopy – Energy-Dispersive X-ray Spectroscopy (FIB-SEM-EDS)

FIB-SEM-EDS analysis was performed using a FEI QUANTA 3D FIB-SEM equipped with both secondary (SE) and backscattered electron (BSE) detectors with an SSD Apollo XP

spectrometer (EDS) at ELTE FS-RICF on two selected representative quartz-hosted fluid inclusions (OL24 and OL26), which were previously Raman-mapped. Electron beam analysis was performed with 20 kV accelerating voltage, 240 pA currents and 50s to 100s counting time. Slicing was done in 0.2 μ m increment and EDS spectra was collected for each slicing step on each exposed phase (OL24 n=103, OL26 n=97). Based on the collected EDS spectra, phases were identified using the EDAX ZAF standardless quantification algorithm of the Genesis software, their volume was calculated and their 3D disposition modeled using the RECONSTRUCT software. Daughter phase volume proportions were used to calculate bulk fluid composition, at room-T, based on the density of each individual daughter phase (Table S2). REE-bearing natrite_{ss} was considered analogous in composition to OL gregoryite phenocrysts (Mitchell and Kamenetsky, 2012). Among the mineral phases identified (REE-bearing natrite_{ss}, nahcoline, halite, sylvite, thenardite, arcanite) only REE-bearing natrite_{ss} is likely to contain significant amounts of REE. REE-bearing natrite_{ss} can be analogue to burbankite [(Na,Ca)₃(Sr,Ba,Ce)₃(CO₃)₅], accepting Sr, Ba and REE substitution while nahcolite, halite, sylvite, thenardite and arcanite are unlikely to accept similar substitutions.

Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS)

Fluid inclusions (n = 15) within double polished quartz grains (> 30 μ m thick) were analyzed using a NWR 193 HE laser ablation system coupled with an Agilent 8900 triplequadrupole mass spectrometer at the University of Geneva, Department of Earth Sciences. Samples were ablated with a He carrier gas flux of 0.82 to 0.87 L min⁻¹, pulse repetition rate of 8 Hz to 10 Hz, using spot sizes of 20 μ m to 40 μ m and laser fluence of 7.1 J cm⁻². Data processing, utilizing SILLS software, considered silicon as matrix-only tracer. Minimum sodium concentration (12 wt% Na) used as internal standard was obtained from previous FIB-SEM (Table S2) measurements. It should be noted that among the daughter minerals inside the fluid inclusions, not only halite but also nahcolite (NaHCO₃) and natrite solid solution [(Na₂,K₂,Ca)(CO₃)] contain sodium. Total sodium was obtained from all these minerals (Table S1 and S2).

Sampling and petrography

Characteristic rock samples (n = 5) were collected from OL combeite-wollastonite nephelinite tuff, nearby the volcano summit (Fig. S1). The rocks are rounded and greenish, 6-10 cm large xenoliths showing porphyritic texture and consisting of two distinct parts: roughly parallel oriented metamorphic relict crystals/minerals and an igneous matrix/groundmass (Fig. S2 A and B). Relict crystals are quartz (100 μ m – 0.3 cm) and anorthoclase relict-feldspar (200 μ m – 0.4 cm), which are completely surrounded and encrusted by groundmass crystals (Fig. S2 C and D). Mineral phases in the groundmass are titanite (30-150 μ m), clinopyroxene (20-100 μ m), and oligoclase groundmass-feldspar (20-100 μ m). Peralkaline rhyolitic glass fills the space between groundmass crystals.

Fluid inclusions were studied in detail in sample L14E. Fluid inclusions are abundant in relict crystals, but completely absent in groundmass crystals (Fig. S2 E). Secondary fluid inclusions occur as intergranular trails (Fig. S2 F), varying in size from <1 µm to 50 µm and are negative-crystal shaped to ellipsoidal (Fig. 1A). They present solid-liquid-vapor (S-L-V) phases at room temperature with vapor bubbles comprising approximately 80% of their volume (Fig. 1B). No melt inclusions have been found in relict crystals.

Although silicon fluoride species have been linked to quartz formation in some carbonatites (Huang et al., 2023), this mechanism does not seem to have played a significant role in our sample, as quartz contains secondary fluid inclusions, which means that this mineral did not crystallize from the trapped fluid. The absence of fluid inclusions on groundmass crystals suggest they are not coeval to quartz and relict-feldspar. The slightly oriented relict crystals (Fig. S2 B) indicate

metamorphic origin, explaining the compositional contrast between anorthoclase relict-feldspar and oligoclase groundmass-feldspar. Replacement of anorthoclase relict-feldspar by oligoclase groundmass-feldspar and dissolution features in quartz indicate that the metamorphic relicts were not in equilibrium with a, likely, silica-undersaturated peralkaline melt. The reaction between silica-undersaturated peralkaline melt and a metamorphic xenolith, generating the oligoclase+aegirine+titanite+glass groundmass, must have been similar to magmatic skarn formation (Xu et al., 2023), with the metamorphic xenolith undergoing desilification.



Fig. S1. A – Sample collection site showing the studied volcanic bombs embayed in nephelinite tuff. B – Sample collection site, outcrop. C – Geological map of Oldoinyo Lengai, after Klaudius and Keller (2006), and sample collection site.



Fig. S2. Photomicrographs and backscattered electron images (BSE) showing the characteristic petrographic features of the studied samples. A – Macroscopic appearance of a xenolith fragment from OL with highlighted outer tuff rim. B – Distribution of quartz and relict-feldspar on a thin section (highlighted by orange ellipses). C, D – Details of groundmass phases

(titanite, clinopyroxene, feldspar and glass) and microvesicles (void, now filled with glue) surrounding the relict feldspar (BSE image). \mathbf{E} – Representative image on the groundmass. \mathbf{F} – Quartz-hosted fluid inclusions enclosed along trails (unpolarized light). qtz – quartz, fsp – feldspar, r-fsp – relict-feldspar, cpx – clinopyroxene, gl – peralkaline rhyolitic glass, FIs – fluid inclusion.

Phase identification and Raman-combined microthermometry experiments

Solid phases within the fluid inclusion (daughter minerals) were identified based on their Raman spectra at room temperature (25 °C) as: nahcolite (v₁ at 1047 cm⁻¹), natrite_{ss} (v₁ at 1079 cm⁻¹) ¹), CO₂ liquid and CO₂ vapor (Fermi diad at 1285 and 1388 cm⁻¹) (Fig. S3). Raman inactive minerals, halite and sylvite, were identified during FIB-SEM-EDS experiments only. On Ramancombined microthermometry experiments nahcolite dissociation (2 NaHCO₃ \rightarrow Na₂CO₃ + CO₂ + H₂O) occurs below 200 °C, marked by the disappearance of nahcolite v_1 bands, and appearance of O-H overlapping stretching vibrations from 3600 cm⁻¹ to 3700 cm⁻¹ (Figs. S4 and S5) together with the increasing intensity of natrite_{ss} v_1 bands at 1079 cm⁻¹ (Fig. S5). The formation of an alkali carbonate fluid phase (molten natritess) at approximately 400 °C is marked by the band broadening simultaneously with an abrupt shift of REE-bearing natrite_{ss} v_1 bands to lower wavelengths (Fig. S5). In parallel, no O-H bands were observed before nahcolite dissociation, from room temperature to ~ 200 °C one phase CO₂ coexists with nahcolite and natrite_{ss} (Fig. S4). Following nahcolite dissociation, the presence of a H₂O-rich fluid phase is observed at 200 °C. Progressive dissolution of H₂O into the CO₂-rich fluid phase occurs above 200 °C (Fig. S4). Homogenization of CO₂-rich and H₂O-rich fluid phases into a single phase takes place between 400 °C and 500 °C (Fig. S4), as expected based on fluid inclusion bulk NaCl content (Table S2). After the H₂O dissolution into CO₂, two phases were present within the fluid inclusions: 1/ a sulfate-bearing alkali carbonate fluid phase (molten natritess), 2/ a CO₂-H₂O fluid phase. Upon heating, resulting from the increased

mutual solubility, the composition of the two phases (molten natrite_{ss} and CO₂-H₂O fluid phase) gradually converged to each other, forming an homogeneous alkali carbonate fluid phase (Fig. S4-S6). At 600 °C, no significant spectral variations occurred in any part of the inclusions.



Fig. S3. Representative Raman spectra of solid phases within quartz-hosted fluid inclusions at room temperature. Spectral window set between 600 cm⁻¹ and 1300 cm⁻¹. Black curves – Raman spectra of solid phases within the inclusion. Grey curve – host quartz measurement. $SO_4 v_1 - SO_4^{2-}$ on REE-bearing natrite_{ss}. Host mineral and fluid inclusion solid phases measurements taken with the same parameters (optical grating, confocal hole, acquisition time, accumulations).



Fig. S4. Representative results on Raman-combined microthermometry measurements on the studied fluid inclusions. 2800 cm⁻¹ to 4000 cm⁻¹ spectral range, from 35 °C to 500 °C. No H-O Raman bands are present at 35 °C.



Fig. S5. Representative results on Raman-combined microthermometry measurements on the studied fluid inclusions, from 150 °C to 600 °C. Grey curve – measurements focusing on CO_2 -rich and CO_2 +H₂O homogeneous fluid phases in the fluid inclusion. Black curve – measurements focusing on solid (150 °C) and alkali-carbonate fluid phases in the studied fluid inclusions. natrite_{ss} - natrite solid solution.



Fig. S6. Schematic figure displaying the phase assemblages at different temperatures of the fluid based on Raman-combined microthermometric measurements on the studied fluid inclusions displaying observed Raman-active phase transitions, from 25 °C to 700 °C. natrite_{ss} - natrite solid solution.

Phase proportions and bulk fluid composition

Raman spectroscopy determined the bulk fluid composition to be (in wt%, Table S1): 16.6 to $30.18 \text{ Na}_2\text{O}$, $0.67 \text{ to } 2.31 \text{ K}_2\text{O}$, 1.06 to 3.66 CaO, <0.84 MgO, $0.75 \text{ to } 3.08 \text{ SO}_3$, $13.71 \text{ to } 26.24 \text{ CO}_2$ as carbonate, $32.70 \text{ to } 63.03 \text{ CO}_2$ as vapor, $2.05 \text{ to } 6.2 \text{ H}_2\text{O}$. FIB-SEM-EDS allowed us to determine volume proportions of the Raman inactive phases found (halite and sylvite). However, when considering an inclusion measured by both methods the total volume of solids did not vary greatly, only their composition (Inclusion OL26, Table S1 and S2).

Table S1. Fluid phase composition calculated based on Raman imaging at room temperature. Nahcolite considered as Na-endmember, REE-bearing natrite_{ss} considered as compositionally equivalent to OL gregoryite phenocrysts (Mitchell and Kamenetsky, 2012). CO₂ density calculated based on Fermi diad delta (Fall et al., 2011). CO₂ (l) - CO₂ as carbonate. CO₂ (u₁) - CO₂ vapor from nahcolite dissociation. CO₂ (u₂) – CO₂ vapor at room temperature.

	Fluid phase composition (sample L14E)								
	02	04	05	07	26				
		v	olume %						
CO ₂	76.14	64.55	61.21	81.47	87.62				
ahcolite	7.36	29.18	20.53	9.44	6.69				
llfate	-	-	-	0.99	0.43				
EE-bearing natrite _{ss}	16.50	6.27	18.27	8.10	5.26				
olomite	-	-	-	-	-				
otal	100.0	100.0	100.0	100.0	100.0				
		v	Veight %						
O ₂	31.41	27.81	22.69	47.02	57.39				
ahcolite	19.17	57.90	38.22	25.09	21.53				
ılfate	-	-	-	3.16	1.66				
EE-bearing natrite _{ss}	49.41	14.29	39.09	24.74	19.43				
olomite	-	-	-	-	-				
tal	100.00	100.00	100.00	100.00	100.00				
	20.30	20.18	22.36	15.42	12.34				
₂ density (g/cm ³)	0.35	0.48	0.44	0.48	0.45				
		Oxio	le weight %						
₂ O	27.39	27.24	30.18	20.81	16.66				
0	2.31	0.67	1.83	1.16	0.91				
0	3.66	1.06	2.90	1.83	1.44				
gO	-	-	-	-	-				
)3	2.60	0.75	2.06	3.08	1.96				
O2 (as carbonate)	25.54	21.10	26.24	16.84	13.71				
2 (as vapor)	31.41	27.81	22.69	47.02	57.39				
(from nahcolite)	5.02	15.17	10.01	6.57	5.64				
0	2.05	6.20	4.09	2.69	2.31				
otal	100.0	100.0	100.0	100.0	100.0				

Table S2. Fluid phase composition calculated based on FIB-SEM-EDS. Nahcolite considered as Na-endmember, REE-bearing natrite_{ss} considered as compositionally equivalent to OL gregoryite phenocrysts (Mitchell and Kamenetsky, 2012). CO₂ density calculated based on Fermi diad delta (Fall et al., 2011). CO₂ (l) - CO₂ as carbonate. CO₂ (ν 1) - CO₂ vapor from nahcolite dissociation. CO₂ (ν 2) – CO₂ vapor at room temperature.

Fluid phase composition (sample L14E)									
	OL24	OL26							
	Volum	1e %							
CO ₂	91.21	92.76							
Nahcolite	5.67	2.04							
REE-bearing natrite _{ss}	2.27	1.95							
Halite	0.85	2.90							
Sylvite	-	0.35							
Total	100.0	100.0							
	Weigh	nt %							
CO ₂	62.02	67.07							
Nahcolite	23.64	9.06							
REE-bearing natrite _{ss}	10.89	9.93							
Halite	3.45	12.57							
Sylvite	-	1.37							
Total	100.00	100.00							
Na	14.01	12.06							
CO ₂ density (g/cm ³)	0.36	0.36							
	Weight %								
Na ₂ O	13.20	7.43							
NaCl	3.45	12.57							
K ₂ O	0.51	0.46							
KCl	-	1.37							
CaO	0.81	0.74							
MgO	-	-							
SO ₃	0,57	0.52							
CO ₂ (as carbonate)	10.71	6.50							
CO ₂ (as vapor)	62.02	67.07							
CO ₂ (from nahcolite)	6.19	2.37							
H ₂ O	2.53	0.97							
Total	100.0	100.0							

Fluid trace element content

The studied fluid inclusions show enrichment in Ba, Sr, Th, U and LREE (Table S3, Fig. S7): 0.2 to 2.6 Ba wt%, 0.8 to 2.9 Sr wt%, 500 to 3416 La ppm, 701 to 3809 Ce ppm, 39 to 314 Pr ppm, 115 to 1133 Nd ppm, 26 to 180 Sm ppm, < 46 Eu ppm, < 98 Gd ppm, < 16 Tb ppm, < 13 Ho ppm, < 329 Y ppm, < 24 Yb ppm, < 1 Lu ppm. These fluids are comparatively less enriched in Li, Nb, Ta, Zr, Hf, Ti, Sc and Cu: < 490 Li ppm, < 753 Nb ppm, < 10 Ta ppm, < 2868 Zr ppm, < 63 Hf ppm, < 8063 Ti ppm, < 1047 Sc ppm, < 181 Cu ppm. The host quartz is trace element poor (Table S4).

Table S3. Fluid inclusion's trace element content (n=15, in ppm) based on LA-ICP-MS measurements. Elements proportions based on sodium concentration (12 wt%). Silicon used as matrix-only tracer.

Fluid inclusion's trace element content (sample L14E)									
Measurement	28b04	28b07	28b09	28b11a	28b11b	28b11c	28b14	28a09	
Rb	185	169	151	108	< 118	127	315	305	
Th	34	87	49	26	21	25	46	77	
U	80	64	40	56	74	49	52	83	
Ba	11849	6812	14425	13891	8983	18585	10546	14129	
Nb	271	29	81	122	143	94	147	22	
Ta	< 0.8	< 6.3	< 5.7	< 5.1	< 12	< 9.6	< 1.3	< 5.2	
La	1203	606	923	1952	1354	2382	699	1544	
Ce	1919	729	1331	2485	1899	2812	933	2118	
Pb	228	129	< 49	77	< 109	169	172	145	
Pr	188	39	100	153	150	143	56	151	
Nd	544	224	226	735	447	950	203	450	
Sr	20349	8111	19339	17624	10435	24111	10820	9952	
Zr	371	146	84	197	285	81	171	285	
Hf	< 2.7	< 22	< 20	< 18	< 43	< 33	17	< 18	
Sm	46	< 39	40	107	145	89	< 8.5	86	
Eu	25	< 10	< 9.5	< 8.5	< 20	< 15	< 2.2	< 8.7	
Gd	27	< 39	< 36	38	< 79	< 60	21	< 32	
Ti	3732	< 1157	8063	3788	< 1498	5223	3595	< 1703	
Tb	10	7.6	< 4.7	< 4.2	< 10	< 7.9	3.2	< 4.3	
Но	7.8	< 6.0	< 5.4	7.2	< 11	< 9.1	7.6	7.4	
Y	211	33	61	108	87	98	52	133	
Yb	13	< 26	< 24	< 42	< 80	< 64	< 8.8	< 22	
Lu	< 1.3	< 5.9	< 5.4	< 4.8	< 11	< 9.1	< 1.2	< 4.9	
Total REE	3987	1607	2621	5480	3997	6377	1926	4359	

Table S3, continued. Fluid inclusion's trace element content (n=15, in ppm) based on LA-ICP-MS measurements. Elements proportions based on minimum sodium concentration (12 wt%) from FIB-SEM-EDS measurements. Silicon used as matrix-only tracer.

Fluid inclusion's trace element content (sample L14E)									
Measurement	28c06	28c08a	28c08b	28c09	29c18a	29c18b	29c19		
Rb	391	334	244	282	270	< 132	278		
Th	568	59	65	106	537	122	146		
U	84	123	65	90	87	103	86		
Ba	19087	12502	14404	15608	17216	26575	19695		
Nb	114	364	68	30	754	210	146		
Ta	10	< 2.8	< 2.0	< 4.1	6.6	< 9.4	2.0		
La	1372	500	713	1785	2668	2577	2788		
Ce	2469	824	1147	2492	3809	3010	3036		
Pb	271	296	224	120	286	469	118		
Pr	152	56	65	204	315	254	241		
Nd	340	225	267	451	1134	779	741		
Sr	29768	14643	12979	11696	19777	28435	19964		
Zr	110	371	482	< 4.1	565	402	223		
Hf	< 8.2	< 9.8	< 4.6	< 14	7.2	< 32	5.3		
Sm	63	26	50	86	121	< 59	86		
Eu	23	< 4.7	18	< 6.7	27	46	15		
Gd	43	52	31	37	66	85	38		
Ti	2682	< 1426	6950	< 1189	4968	3977	1061		
Tb	7.2	< 2.3	< 1.1	5.0	6.5	17	2.5		
Но	4.9	8.0	2.8	8.6	12	13	3.7		
Y	105	115	72	152	329	106	98		
Yb	14	< 18	< 5.6	< 17	24	< 39	7.5		
Lu	< 2.2	< 2.6	< 1.2	< 3.8	1.1	< 8.8	< 0.5		
Total REE	4493	1693	2295	5070	8186	6782	6960		



Fig. S7. Chondrite-normalized (Sun and McDonough, 1989) diagram showing the normalized REE distribution of the studied fluid inclusions from a carbonatite system, determined in situ by LA-ICP-MS.

Table S4. Host quartz trace element content (n=12, in ppm) based on LA-ICP-MS measurements. Elements proportions based on major oxides (SiO₂, TiO₂, Al2O₃, FeO^T, MnO, MgO, CaO, Na₂O, K₂O, and P₂O) equal to 100 wt%.

Host quartz's trace element content (sample L14E)												
Measurement	28a09	28b04	28b07	28b09	28b11	28b14	28c06	28c08	28c08	28c09	28c18	28c19
Rb	<0.2	< 0.02	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	<0.1	< 0.1
Th	0.1	< 0.002	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04
U	0.1	< 0.002	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.04	< 0.04
Ba	1.6	< 0.02	<0.4	< 0.3	<0.3	<0.3	< 0.3	<0.3	< 0.3	<0.3	<0.5	<0.4
Nb	0.2	0	< 0.06	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.06	< 0.06
Та	< 0.05	< 0.002	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.04	< 0.04	< 0.04
La	0.2	0	< 0.04	< 0.04	< 0.04	< 0.03	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.05
Ce	0.3	0	< 0.04	< 0.04	< 0.04	< 0.03	< 0.04	< 0.04	< 0.04	< 0.03	< 0.04	< 0.04
Pb	<0.2	< 0.03	< 0.1	< 0.1	<0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Pr	< 0.05	< 0.001	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.03	< 0.03	< 0.03
Nd	< 0.2	< 0.01	<0.2	<0.2	< 0.1	< 0.2	< 0.2	<0.2	< 0.2	<0.2	<0.2	<0.2
Sr	1	0.1	< 0.08	< 0.08	< 0.07	< 0.06	< 0.06	< 0.07	< 0.07	< 0.08	< 0.08	< 0.09
Zr	0.3	< 0.006	< 0.09	< 0.1	< 0.01	< 0.09	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Hf	<0.2	< 0.007	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Sm	<0.3	< 0.01	< 0.2	<0.2	<0.2	< 0.2	<0.2	<0.2	<0.2	< 0.2	<0.2	< 0.2
Eu	< 0.08	< 0.003	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.06	< 0.06
Gd	<0.3	< 0.01	< 0.2	<0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	<0.2	< 0.2
Ti	13	8.2	8	8.1	8.2	8.1	5.9	5.9	5.9	5.9	12	12
Tb	< 0.04	< 0.001	< 0.03	< 0.03	< 0.02	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Но	< 0.04	< 0.002	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03
Y	< 0.06	< 0.005	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.07	< 0.05
Yb	< 0.2	< 0.008	< 0.1	< 0.1	< 0.1	< 0.1	<0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Lu	< 0.04	< 0.002	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03

REFERENCES CITED

Fall, A., Tattitch, B., and Bodnar, R.J., 2011, Combined microthermometric and Raman spectroscopic technique to determine the salinity of H₂O-CO₂-NaCl fluid inclusions based on clathrate melting: Geochimica et Cosmochimica Acta, v. 75, p. 951–964, https://doi.org/10.1016/j.gca.2010.11.021.

Guilong, M., Meier, D.L., Allan, M.M., Heinrich, C.A., and Yardley, B.W.D., 2008, APPENDIX A6: SILLS: A MATLAB-BASED PROGRAM FOR THE REDUCTION OF LASER ABLATION ICP–MS DATA OF HOMOGENEOUS MATERIALS AND INCLUSIONS: https://ethz.ch/content/dam/ethz/specialinterest/erdw/geopetro/mineralsystems-

dam/documents/MAC_SC_40_Sills_description.pdf (accessed May 2023).

- Huang, Y., Liu, Q., Liu, F., Li, X., Liu, Y., Tang, G., Fan, H., Li, X., Li, Q., 2023, Large Si isotope fractionation reveals formation mechanism of quartz in silicon-poor carbonatite: Geology, v. 51: p. 1038–1042, https://doi.org/10.1130/G51314.1.
- Mitchell, R.H., and Kamenetsky, V.S., 2012, Trace element geochemistry of nyerereite and gregoryite phenocrysts from natrocarbonatite lava, Oldoinyo Lengai, Tanzania:
 Implications for magma mixing: Lithos, v. 152, p. 56–65, https://doi.org/10.1016/j.lithos.2012.01.022.
- Span, R., and Wagner, W., 1996, A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa: Journal of Physical and Chemical Reference Data, v. 25, p. 1509–1596, https://doi.org/10.1063/1.555991.

Sun, S.-s., and McDonough, W.F., 1989, Chemical and isotopic systematics of oceanic basalts:

implications for mantle composition and processes: Geology Society Special Publications, v. 42, p. 313–345, https://doi.org/10.1144/GSL.SP.1989.042.01.19.

Xu, X., Szmihelsky, M., Yan, J., Xie, Q., Steele-MacInnis, M., 2023, Melt inclusion evidence for limestone assimilation, calc-silicate melts, and "magmatic skarn": Geology, v. 51, p. 491–495, https://doi.org/10.1130/G50893.1.