Partitioning of REE between calcite and carbonatitic melt containing P, S, Si at 900-650 °C and 100 MPa

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Abstract

Many carbonatites host deposits of REE and HFSE, and fractional crystallization might be a potentially powerful mechanism controlling magma enrichment by these metals to economically significant values. At present, information about the control of fractional crystallization by partition coefficients of ore-forming elements at magmatic stage is incomplete. Here we present an experimental study of REE partitioning between carbonatite melt and calcite in the system $\text{CaCO}_3\text{-Na}_2\text{CO}_3$ with varying amounts of P_2O_5 , F, Cl, SiO_2 , SO_3 at 650–900°C and 100 MPa using cold-seal pressure vessels and LA-ICP-MS. The presence of phosphorus in the system generally increases the distribution coefficients but its effect decreases with increasing concentration. The influence of temperature is great: at 900 – 770°C $D_{\text{REE}} \geq 1$, while at lower temperatures the values are below unity. Silicon also promotes the fractionation of REE into calcite, while sulfur contributes to the retention of REE in the melt. Our results imply that calcite may impose significant control upon REE fractionation at the early stages of crystallization of carbonatite magma and can be a closest proxy for monitoring the REE content in initial melt.

Introduction

Carbonatites are rare carbonate-dominated mantle-derived rocks that, in some cases, host economically significant deposits of REE, Nb, Zr, which are important for modern high-tech and “green” industry. More than 527 carbonatite occurrences have been recorded in the world so far [1]. However, only about 30 mineralized carbonatites host economic resources of REE and Nb [2, 3]. The scientific and practical interest in carbonatites is great, but the processes of carbonatite formation and ore-grade enrichments of Nb and REE are far from being fully understood. Contemporary models of carbonatite petrogenesis fall into three major groups:

- (1) primary origin of carbonatitic magmas by partial melting of a carbonated mantle source [4–15];
- (2) derivative origin from an homogeneous alkaline silicate magma by silicate-carbonate liquid immiscibility [16, 17];
- (3) derivative origin by extensive fractional crystallization of a carbonated silicate parental liquid [18, 19].

Identification of the exact process (or processes) responsible for the formation of carbonatitic magmas is hampered by widespread Na–K metasomatism (finitization) associated with carbonatites, which manifests the loss of alkalis and volatiles from their parental magmas [20]. In addition, many, if not most, intrusive carbonatites are cumulates, dominated by calcite or dolomite, differing in composition from their parental magma [21] and often affected by extensive textural and chemical re-equilibration after emplacement [22].

As seen from experimental works [14, 23–25], direct smelting from the mantle source and silicate-carbonate immiscibility are unable to provide concentration of REE to economically significant levels. Immiscibility experiments in various silicate–carbonate systems have demonstrated that Pb, Nb, Th, U and most of the REE preferentially partition into the silicate liquid, whereas Sr, Ba and F partition into the conjugate liquid carbonate phase [23, 24, 26]. This pattern of element partitioning is inconsistent with a high content of primary LREE- and HFSE-rich minerals in carbonatites: fluorapatite, fluorcarbonates, monazite, pyrochlore, etc. Thus, another evolutionary mechanism is needed for the enrichment of carbonatitic magmas in REE and HFSE, and fractional crystallization might be powerful driver for it.

The majority of experimental estimates of the partition coefficients for REE have been obtained for the main rock-forming minerals (olivine, pyroxene, garnet, amphibole and biotite), and some accessory minerals (such as rutile, apatite, perovskite, and baddeleyite) at P–T conditions of the upper mantle [25, 27–37]. Experimental constraints on REE partitioning in carbonatitic magmas at crustal pressures are sparse. Because of low crystallization temperature and low viscosity of carbonatitic magmas, fractional crystallization can proceed in them up to shallow depths and control the distribution of REE and HFSE, leading to the formation of a deposit or a barren carbonatite body. Therefore, it is important to assess the effect of fractional crystallization at crustal conditions and to identify the influencing factors.

Carbonate minerals are the principal constituents of intrusive carbonatites: their content ranges from 50 modal %, which is accepted as a nominal threshold for this rock type [38], to well over 90 % in some varieties interpreted as cumulates [21]. Considering the high propensity of calcite to various postmagmatic changes, plasticity and recrystallization, observed trace element contents may be far from the original magmatic pattern. Hence, experimental modelling of trace element distribution between calcite and carbonatite melt at magmatic conditions is important.

Additional ligands such as F^- , OH^- , Cl^- , SO_4^{2-} and PO_4^{3-} are likely to have strong effects upon the REE partitioning. In our previous work [39] we carried out a pilot series of experiments to obtain distribution coefficients for REE and HFSE between calcite, fluorite and nominally dry carbonatitic melts in synthetic compositions with CaO at 37–54 wt.%, Na_2O 7–24 wt.%, F 5–9 wt.%, P_2O_5 between 0 and 9.5 wt.% at 650–900°C and 100 MPa. The distribution coefficients for individual REE in calcite in that study did not exceed 0.1 and in fluorite they were below 0.25. Total REE concentrations in calcites were at about 500–700 ppm. Such concentrations are normal for primary igneous calcites in carbonatites [40]. However, there are described primary igneous calcites with REE contents at 1400–2000 ppm (e.g., the Aley complex, Canada [40]). This study was aimed at a more detailed assessment of the effects of melt composition, and especially the concentrations of P_2O_5 , SiO_2 and SO_3 components on the REE distribution between calcite and melt at 900 – 650°C and 100 MPa.

Results

Carbonatite melts in all the experiments quenched as aggregates of fine-grained dendritic crystals with abundant fluid bubbles probably dominated by CO_2 (Fig. 1, 2; Table 2, 3). In phosphate-bearing samples, quenched melt is full of needle-shaped crystals of quench Ca-phosphate, presumably apatite (Fig. 1a; 2a, b, c). In experiments with SiO_2 fine crystals of wollastonite and Zr-Hf-silicate (zircon-hafnon) are also formed (Fig. 2d; Table 2). Oxides of HFSE and REE in all samples form aggregates of fine crystals with complex composition (baddeleyite, perovskite-lueshite solid solutions and crystals of pyrochlore supergroup)

(Fig. 2a, b, c). The crystals are few microns in size and are not suitable for representative analyzes by microprobe or LA-ICP-MS. Rounded, irregularly shaped, drop-like fluorite crystals are formed in samples with high content of F (Fig. 2a; Table 2).

Table 2
Experimental conditions and run products.

Run #	Mixture	Temperature, °C	Duration, hours	Phases
1	NCFP-7	760	26	Melt, fluid, calcite
2	NCFP-8	900 – 850	20	Melt, fluid, calcite
3	NCFP-9	900 – 650	141	Melt, fluid, calcite, fluorite, baddeleyite, pyrochlore
4	NCP-1	900 – 830	44	Melt, calcite, baddeleyite
5	NCPS-1	900 – 830	25	Melt, fluid, calcite
6	NCP-1	820 – 770	55	Melt, fluid, calcite, REE and HFSE oxides
7	NCPSi-1	820 – 770	55	Melt, fluid, calcite, wollastonite, zircon-hafnon
8	NCPS-1	820 – 770	55	Melt, fluid, calcite, baddeleyite, pyrochlore
9	NCP-2	820 – 770	64	Melt, fluid, calcite, Hf-oxide, REE and HFSE oxide
10	NCPSi-2	820 – 770	64	Melt, fluid, calcite, wollastonite, zircon-hafnon
11	NCPS-2	820 – 770	64	Melt, fluid, calcite, REE and HFSE oxides
12	NCPSi-3	900 – 760	52	Melt, fluid, calcite, wollastonite

Table 3
Major composition of run products (in wt.%).

Run #	Mixture	Phase	Na ₂ O	CaO	SiO ₂	P ₂ O ₅	SO ₃	F	Cl	(Cl + F ₂)=O	Total
1	NCFP-1	Melt (3)	12 (2)	48 (2)	-	12 (3)	-	9.7 (9)	-	4.10	77.00
		Calcite (5)	0.06 (3)	57 (1)	-	-	-	-	-	-	57.06
2	NCFP-3	Melt (6)	6 (1)	54 (1)	-	11 (2)	-	11 (1)	-	4.50	77.00
		Calcite (4)	0.09 (3)	56.1 (0)	-	-	-	-	-	-	56.20
3	NCFP-4	Melt (19)	20 (2)	35.9 (4)	-	0.6 (1)	-	10.4 (2)	-	-	67.00
		Calcite (16)	-	54.5 (3)	-	-	-	-	-	-	54.60
4	NCP-1	Fluorite (17)	-	71.6 (4)	-	1 (1)	-	48.4 (7)	-	20.40	100.00
		Melt (9)	20.5 (17)	35.9 (4)	-	0.6 (1)	-	10.4 (2)	-	-	67.40
		Calcite (10)	-	53.4 (6)	-	-	-	-	-	-	53.40
5	NCPS-1	Melt (12)	20 (2)	35 (2)	-	6 (4)	0.8 (3)	0.63 (9)	0.3 (2)	0.40	62.86
		Calcite (7)	-	54 (0)	-	-	-	-	-	-	54.00
6	NCP-1	Melt (9)	22.2 (7)	32 (1)	-	6 (1)	-	0.66 (7)	0.42 (8)	0.47	60.81
		Calcite (11)	-	54 (0)	-	-	-	-	-	-	54.00
7	NCPSi-1	Melt (2)	23 (2)	31 (2)	2 (3)	2 (2)	-	0.6 (4)	0.4 (1)	0.43	58.82
		Calcite (7)	-	54 (0)	-	-	-	-	-	-	54.00
8	NCPS-1	Melt (17)	23 (2)	31 (2)	-	4 (4)	1 (0)	0.66 (8)	0.17 (2)	0.36	59.92
		Calcite (8)	-	53.3 (5)	-	-	-	-	-	-	53.30
9	NCP-3	Melt (10)	25.6 (9)	30.6 (9)	-	3 (2)	-	-	0.18 (1)	0.08	58.92
		Calcite (8)	0.4 (3)	54.7 (2)	-	-	-	-	-	-	55.10
10	NCPSi-3	Melt (11)	21 (3)	30.7 (7)	1.9 (6)	-	-	-	0.03 (4)	0.01	53.99
		Calcite (4)	-	54.6 (3)	-	-	-	-	-	-	54.60
11	NCPS-3	Melt (16)	25 (2)	31 (2)	-	3 (4)	0.7 (1)	0.45 (1)	0.07 (2)	0.22	58.97
		Calcite (9)	0.27 (6)	54.6 (7)	-	-	-	-	-	-	54.80
12	NCPSi-4										
		Melt (8)	26 (2)	29.8 (4)	-	2 (3)	-	-	0.06 (0)	0.03	56.97
		Calcite (6)	-	53.7 (4)	-	-	-	-	-	-	53.70

The numbers in the parentheses next to the phase name indicates the number of analyzes. The numbers in the parentheses next to the analyzes are the standard deviation and reported as the least unit cited. For example, 55.50 (64) should be read as 55.50 ± 0.64 wt.%.

Calcite has various morphology: rhombohedral or prismatic (Fig. 1a; 2a), amorphous (Fig. 1b), needle-like (Fig. 1d, f) and tabular rounded crystals (laths) up to 250 micrometers in most experiments (Fig. 1c, e; 2 c), which are typical for early generations of calcite in carbonatites [44]. The amount of calcite crystals in some samples is so high that they form a crystal mush at the bottom of the samples (Fig. 1c, e). Calcite major element composition is close to that of stoichiometric Ca carbonate (Table 3).

Trace elements composition of the run products given in Table 4. Partition coefficients calculated according to the Nernst formula as mass ratios of element content in a crystalline phase to its content in the melt: $D_{\text{Element}} = C^{\text{Crystal}} / C^{\text{Melt}}$ (Table 5). D_{Sr} is > 1 for all samples (Fig. 3). In all experiments $D_{\text{Sr}} > D_{\text{REE}}$, except NCPSi mixtures. Almost all D_{REE} plots show a positive Eu and Y anomalies. In general, the slope of the D_{REE} plots is positive, with the exception of NCPSi samples, what is apparently associated with active fractionation of HREE into wollastonite.

Table 4
Trace element composition of run products (in ppm).

Run #	Mixture	Phase	Sr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Y	Er	Tm	Yb	Lu
1	NCFP-1	Melt (5)	450 (24)	183 (10)	155 (9)	160 (10)	153 (8)	178 (7)	155 (8)	161 (10)	155 (7)	165 (11)	173 (8)	156 (8)	172 (7)	172 (7)	177 (10)	163 (11)
		Calcite (5)	741 (24)	95 (10)	94 (9)	121 (10)	118 (8)	144 (7)	145 (8)	138 (10)	138 (7)	160 (11)	166 (8)	122 (8)	174 (7)	184 (7)	208 (10)	192 (11)
2	NCFP-3	Melt (5)	426 (9)	132 (4)	120 (6)	137 (10)	126 (6)	134 (7)	135 (4)	132 (7)	126 (5)	135 (8)	135 (5)	129 (2)	136 (7)	138 (3)	175 (12)	128 (3)
		Calcite (3)	708 (6)	103 (5)	101 (6)	122 (8)	121 (9)	143 (7)	181 (6)	142 (7)	143 (9)	157 (11)	161 (8)	129 (2)	168 (10)	176 (12)	215 (10)	178 (2)
3	NCFP-4	Melt (5)	703 (60)	618 (51)	389 (13)	427 (13)	444 (29)	435 (34)	499 (40)	453 (34)	438 (27)	438 (20)	665 (62)	474 (43)	443 (11)	471 (14)	535 (24)	552 (34)
		Calcite (5)	520 (73)	85 (44)	79 (38)	90 (42)	95 (44)	95 (37)	123 (43)	96 (37)	97 (32)	102 (30)	110 (29)	83 (20)	110 (28)	115 (27)	119 (25)	123 (22)
		Fluorite (3)	195 (47)	bdl	bdl	11 (11)	9 (3)	29 (11)	33 (1)	55 (25)	51 (22)	56 (22)	109 (79)	152 (94)	46 (26)	85 (65)	48 (13)	55 (24)
		Ca-phosphate (1)	581	116	103	114	116	118	154	129	128	132	141	85	134	136	139	134
4	NCP-1	Melt (9)	126 (18)	274 (29)	225 (29)	261 (54)	285 (59)	282 (52)	289 (48)	268 (47)	258 (51)	247 (51)	253 (35)	268 (41)	260 (11)	286 (47)	308 (63)	314 (62)
		Calcite (5)	150 (28)	248 (40)	196 (22)	232 (10)	265 (25)	279 (34)	292 (56)	296 (57)	277 (52)	270 (48)	292 (52)	281 (32)	303 (64)	336 (84)	318 (32)	343 (31)
5	NCPS-1	Melt (5)	80 (3)	169 (6)	161 (8)	179 (8)	191 (6)	204 (10)	197 (9)	201 (9)	196 (8)	193 (9)	188 (9)	176 (10)	183 (9)	182 (11)	186 (14)	182 (12)
		Calcite (5)	180 (21)	262 (42)	214 (39)	233 (30)	238 (27)	226 (26)	264 (38)	216 (29)	203 (21)	207 (28)	193 (19)	190 (22)	189 (24)	185 (20)	193 (30)	200 (27)
6	NCP-1	Melt (5)	109 (4)	268 (19)	219 (14)	244 (16)	257 (14)	262 (13)	263 (14)	265 (18)	260 (15)	262 (14)	262 (15)	253 (15)	252 (13)	256 (16)	275 (21)	277 (18)
		Calcite (5)	137 (6)	147 (28)	132 (28)	148 (32)	166 (33)	172 (42)	196 (36)	185 (46)	181 (49)	184 (51)	182 (48)	184 (45)	182 (50)	186 (54)	205 (70)	211 (62)
7	NCPSi-1	Melt (3)	124 (15)	210 (47)	167 (24)	202 (28)	221 (17)	240 (56)	234 (28)	243 (26)	224 (32)	212 (27)	225 (40)	222 (38)	226 (37)	235 (45)	266 (62)	272 (62)
		Calcite (3)	156 (4)	125 (2)	84 (1)	86 (1)	82 (1)	71 (1)	78 (2)	70 (2)	65 (0)	66 (1)	69 (2)	72 (1)	65 (0)	64 (1)	65 (1)	67 (1)
8	NCPS-1	Melt (5)	87 (2)	204 (11)	178 (10)	199 (9)	208 (7)	220 (10)	223 (9)	222 (8)	218 (10)	215 (10)	219 (11)	201 (12)	208 (13)	206 (17)	214 (21)	219 (26)
		Calcite (5)	119 (8)	147 (14)	122 (12)	139 (12)	153 (15)	155 (15)	173 (13)	167 (17)	163 (17)	164 (16)	176 (17)	166 (15)	167 (17)	167 (15)	175 (17)	183 (18)
9	NCP-3	Melt (5)	67 (8)	27 (6)	21 (4)	24 (4)	27 (4)	29 (4)	28 (4)	27 (4)	26 (6)	26 (6)	25 (5)	23 (5)	23 (5)	23 (5)	24 (5)	24 (5)
		Calcite (5)	78 (8)	24 (6)	20 (4)	22 (5)	27 (6)	29 (6)	31 (6)	29 (6)	26 (5)	26 (5)	26 (5)	25 (6)	23 (4)	24 (4)	25 (5)	26 (6)
10	NCPSi-3	Melt (5)	57 (6)	17 (2)	14 (1)	16 (0)	17 (0)	17 (2)	21 (4)	21 (7)	21 (9)	20 (12)	21 (13)	24 (15)	20 (14)	21 (16)	21 (17)	26 (26)
		Calcite (4)	136 (14)	35 (2)	26 (0)	28 (0)	27 (1)	27 (1)	31 (1)	28 (0)	25 (1)	21 (0)	20 (1)	25 (2)	17 (1)	15 (1)	15 (2)	15 (2)
11	NCPS-3	Melt (5)	69 (1)	27 (2)	20 (1)	24 (1)	27 (1)	27 (1)	27 (1)	26 (1)	27 (1)	26 (1)	27 (1)	25 (1)	25 (1)	24 (1)	26 (1)	26 (0)
		Calcite (5)	89 (18)	29 (12)	23 (9)	27 (12)	31 (14)	33 (14)	33 (11)	34 (15)	32 (12)	32 (11)	33 (11)	30 (8)	31 (10)	28 (8)	32 (10)	33 (8)
12	NCPSi-4	Melt (5)	46 (2)	107 (8)	92 (6)	106 (8)	116 (8)	117 (13)	136 (10)	112 (18)	105 (19)	96 (19)	95 (24)	87 (22)	83 (26)	81 (32)	77 (32)	73 (37)
		Calcite (5)	73 (5)	200 (17)	154 (12)	163 (12)	169 (10)	152 (7)	168 (12)	150 (10)	138 (6)	132 (6)	129 (5)	126 (2)	114 (5)	111 (5)	110 (5)	108 (6)

The numbers in the parentheses next to the phase name indicates the number of analyzes. The numbers in the parentheses next to the analyzes are the standard deviation and reported as the least unit cited. For example, 182 (48) should be read as 182 ± 48 ppm.

Table 5
Calcite-melt partition coefficients of trace elements.

Element	1		2		3		4		5		6		7		8		9		10
	NCFP-7		NCFP-8		NCFP-9		NCP-1		NCPS-1		NCP-1		NCPSi-1		NCPS-1		NCP-2		NC
	D _{REE}	σ	D _{REE}	σ	D _{REE}	σ	D _{REE}	σ	D _{REE}	σ	D _{REE}	σ	D _{REE}	σ	D _{REE}	σ	D _{REE}	σ	D _{RI}
Sr	1.65	0.07	1.66	0.04	0.77	0.04	1.25	0.15	2.42	0.11	1.23	0.05	2.33	0.30	1.37	0.12	1.16	0.19	2.3
La	0.52	0.11	0.78	0.04	0.09	0.01	0.79	0.08	1.72	0.10	0.55	0.05	4.70	1.13	0.71	0.07	0.90	0.32	2.1
Ce	0.61	0.11	0.84	0.06	0.14	0.01	0.89	0.07	1.49	0.08	0.60	0.04	3.95	0.81	0.67	0.07	0.92	0.26	1.8
Pr	0.76	0.09	0.89	0.09	0.15	0.01	1.00	0.08	1.42	0.09	0.61	0.05	3.64	0.65	0.69	0.08	0.94	0.26	1.7
Nd	0.77	0.06	0.96	0.08	0.15	0.02	1.02	0.10	1.35	0.05	0.64	0.03	3.07	0.49	0.72	0.07	1.00	0.26	1.6
Sm	0.81	0.16	1.07	0.08	0.17	0.02	1.06	0.10	1.21	0.08	0.66	0.05	2.48	0.37	0.70	0.07	1.00	0.25	1.5
Eu	0.94	0.09	1.34	0.06	0.19	0.02	0.99	0.08	1.50	0.10	0.75	0.05	2.79	0.39	0.76	0.04	1.10	0.25	1.4
Gd	0.85	0.16	1.08	0.08	0.16	0.02	1.00	0.06	1.18	0.06	0.70	0.05	2.61	0.40	0.74	0.08	1.07	0.28	1.3
Tb	0.89	0.06	1.13	0.08	0.18	0.01	0.91	0.08	1.10	0.09	0.70	0.06	2.53	0.54	0.74	0.07	1.00	0.29	1.1
Dy	0.97	0.15	1.16	0.11	0.19	0.01	0.92	0.07	1.15	0.13	0.70	0.08	2.48	0.57	0.76	0.07	0.98	0.29	1.0
Ho	0.96	0.15	1.20	0.07	0.13	0.01	1.03	0.12	1.08	0.09	0.69	0.06	2.78	0.61	0.80	0.07	1.04	0.30	0.9
Y	0.78	0.09	1.00	0.03	0.15	0.02	1.05	0.15	1.14	0.15	0.73	0.09	3.18	0.66	0.83	0.08	1.10	0.33	1.0
Er	1.01	0.18	1.24	0.10	0.21	0.01	1.20	0.29	1.11	0.10	0.72	0.06	2.84	0.68	0.81	0.08	1.01	0.29	0.8
Tm	1.07	0.07	1.28	0.09	0.21	0.02	1.38	0.42	1.08	0.10	0.73	0.07	2.79	0.60	0.81	0.08	1.06	0.30	0.7
Yb	1.18	0.07	1.23	0.10	0.20	0.02	1.20	0.16	1.14	0.12	0.74	0.08	2.74	0.56	0.82	0.09	1.04	0.30	0.7
Lu	1.18	0.14	1.39	0.04	0.20	0.02	1.22	0.19	1.17	0.13	0.76	0.08	2.82	0.62	0.85	0.11	1.08	0.33	0.5
σ - the standard deviation																			

D_{REE} of calcites, published in our previous work [39], are close to zero: 0.02–0.04 in NCF samples and 0.04–0.1 in sample with NCFP-6. In experiments with the NCFP mixtures, presented in this work, the averages of D_{REE} are much higher: 0.1–0.2 and 0.52–1.39 (Fig. 3a). The averages of D_{REE} in NCP samples vary in 0.55–1.4, but taking into account the error for each individual element, it is almost the same (Fig. 3b). In experiments with the highest temperatures the highest D_{REE} are observed for both mixtures.

NCPSi samples demonstrate highest D_{REE} with large variations (Fig. 3c). #7 NCPSi-1 sample demonstrates the highest D_{REE} among them, while D_{REE} of #10 NCPSi-2 and #12 NCPSi-3 is almost equal. This is probably directly related to the content of SiO₂ and P₂O₅ of the samples.

The graphs of D_{REE} of NCPS samples are almost flat, with a slight positive slope. The average D_{LREE} in #5 NCPS-1 vary in 1.2–1.7 with strong Eu anomaly, while the coefficients of other elements is about 1.2 and almost equal with #11 NCPS-2.

Discussion

Factors influencing the partitioning of REE into calcite in carbonatite systems

As seen from natural carbonatite samples, the early generations of calcites are characterized by increased content of cations, which size doesn't allow stoichiometrically replace Ca²⁺ at crustal conditions: Mg, Sr, Ba are most abundant among them [44, 46]. Sometimes it leads to the formation of Ca-Ba-Sr "protocarbonates", unstable and decaying into calcite and baritocalcite in the form of a solid solution. With the progressive crystallization of calcite, the content of these cations decreases and the trend is replaced by an increased content of Mn and Fe. Consequently, elevated temperatures favor the entry of cations, whose size precludes their unlimited substitution for Ca²⁺. Along with these cations, REEs can also enter the structure of calcite, which is also noted in natural samples: for example, the correlation between Ba and Pb and LREE in early calcites of the Aley complex (Canada) [40, 44].

The strong effect of temperature is confirmed by our experiments: in most experiments D_{REE} >1 in high temperatures (900 – 820°C), while at other temperatures it's about unity or lower [39].

As follows from a comparison of these experiments and the previous ones [39], the presence of phosphorus is another (and possibly key) positive factor for the fractionation of REE into calcite in carbonatite systems with a high Na₂O content, but it is difficult to make an unambiguous conclusion between its content and the value of D_{REE}. Another powerful driver for increasing D_{REE} is SiO₂. Sulfur, on the contrary, promotes the dissolution (retention) of REE in the melt. To evaluate the net effect of these and other parameters (such as F, Cl), additional experiments are required.

Calcite As A Monitor Of Ree

Our new data show that at some stage in the evolution of carbonatite magma, with a combination of certain factors, calcite in carbonatites can retain a significant gross REE budget of whole carbonatite and may be a closest proxy for estimation of initial REE content in the melt. For example, at high temperatures, in local areas of a carbonatite body, or when there is a lack of material for fractionation of early traditional mineral concentrators of a large amount of REE (such as apatite, monazite, etc.) even at low concentration of REE in the melt.

Given the high susceptibility of calcite to postmagmatic changes, plasticity and recrystallization, this creates the possibility of releasing from calcite large bulk amounts of REE, Sr and Ba and their subsequent redeposition as a result of interaction with later melts or solutions or as a result of metamorphism. According to various estimates [40, 44], such processes can occur at shallow depths already at temperatures of 400–600 and even 730°C, which can lead to active loss of REE by calcite, overprinting his textures, and transfer and redeposition of REE far from it due to weakening of the carbonatite body by porous fluids. These events can also be aggravated by recrystallization of calcite during plastic deformation under a stress conditions.

Indeed, patterns of such phenomena occur, for example, in calcites from Afrikanda and Murun carbonatites (Russia) and Bearpaw Mts (USA) [44]: diffusion-induced zoning in primary calcite involving a decrease in Mn, Sr, Ba and REE along grain boundaries and fractures; the Sr and REE released from calcite are precipitated interstitially as strontianite, baritocalcite, Ba-Sr-Ca-carbonates, barite, burbankite and ancylite.

Stability Of Zircon And Hfse In Carbonatitic Systems

Gervasoni et al. [45] conducted experiments upon stability of baddeleyite and zircon at 0.7 GPa and 1200°C in the system with CaO 18–39 wt.%, Na₂O 2–9 wt.%, ZrO₂ 8–14 wt.%, MgO 1–2 wt.%, SiO₂ 0–45 wt.% and H₂O 1–2 wt.%. In these experiments, zircon appears at (CaO + MgO + Na₂O)/SiO₂ = 0.5–1.4 in the system. At 2.8–11.1, only baddeleyite is stable. In our experiments, zircon formed at shallower conditions, lower amounts of ZrO₂ and HfO, and lower activity of silica: (Ca + Na₂O)/SiO₂ = 13.24 and 22.45.

Gervasoni et al. [45] also consider the issue of the stability of zircons in carbonatite melts. They conducted an experiment on the solubility of zircon in haplocarbonatite melts with 0 and 17 wt.% SiO₂. In the experiment without SiO₂, zircon decomposed into a siliceous melt and baddeleyite, and at 17 wt% it slightly melted and recrystallized. Based on their experiments, Gervasoni et al. concludes that zircons in carbonatite magmas with SiO₂ < 20 wt.% cannot survive. Therefore, one should be careful with the dating of zircons from carbonatites, since they may be xenogenic and do not reflect the real time of intrusion of carbonatite magma.

It seems to us that the range between 0 and 17 wt.% of is quite drastic SiO₂, especially since a small amount of silica is almost always presented in natural carbonatites. From our experiments, it follows that zircons can crystallize from carbonatite magmas even with small proportions of SiO₂ to other components and in shallower environments.

Methods

Experimental mixtures were composed of reagent-grade CaCO₃, Na₂CO₃, Ca₃(PO₄)₂, CaF₂, Na₂Si₂O₅ and Na₂SO₄ and doped with mixtures of trace elements: Zr, Hf, Nb, Ta, Ti, Sr, W, Mo (HFSE mixture) and all REE, including Sr and Y (REE mixture) (Table 1). Both mixtures of trace elements were composed of equal weight proportions of reagent-grade CeF₂, SrCO₃ and pure oxides of other individual elements. Pure reagents were dried at 180°C overnight, mixed under acetone in agate mortar and dried again. The mixtures of NCFP type are direct analogues of our mixtures, used in previous work [39]. About 45–55 mg of the starting mixtures were put in gold capsules and sealed by arc-welding in the flow of Ar.

Table 1
Nominal major and trace compositions of starting mixtures (in wt%).

Components, wt. %	NCFP-7	NCFP-8	NCFP-9	NCP-1	NCP-2	NCPSi-1	NCPSi-2	NCPSi-3	NCPS-1	NCPS-2
SiO ₂	-	-	-	-	-	4.84	2.90	2.90	-	-
CaO	40.72	47.31	53.14	47.14	45.55	42.43	42.82	42.82	45.06	43.53
Na ₂ O	18.57	11.37	5.78	20.31	21.64	21.68	22.38	21.89	21.34	22.61
F	10.12	9.19	10.62	0.03	0.01	0.02	0.01	0.01	0.02	0.01
Cl	-	-	-	0.02	0.01	0.02	0.01	0.01	0.02	0.01
SO ₃	-	-	-	-	-	-	-	-	2.50	2.50
P ₂ O ₅	9.15	9.15	9.15	5.33	2.65	4.80	2.49	2.49	5.10	2.54
REE	0.40	0.40	0.40	0.50	0.05	0.45	0.05	0.47	0.48	0.05
HFSE	0.40	0.40	0.40	0.03	0.05	0.02	0.05	0.05	0.02	0.05
CO ₂	20.65	22.18	20.51	26.64	30.03	25.73	29.29	29.36	25.46	28.70
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
(CaO + Na ₂ O)/SiO ₂						13.24	22.45	22.28		
CaO/SiO						8.77	14.74	14.74		

Experiments were performed at pressure of 100 MPa and over temperature interval of 650–900°C in rapid-quench cold-seal pressure vessels at the German Research Centre for Geosciences (GFZ Potsdam). A detailed description of this type of the vessels described in [41]. The autoclaves at GFZ Potsdam are made of the Ni–Cr alloy Vakumelt ATS 290-G (ThyssenKrupp AG). Oxygen fugacity was not controlled, but believed to have been close to that of the Ni–NiO equilibrium, buffered by oxidation reactions of water, used as pressure medium, and the Ni–Cr alloy of the autoclave. Temperature measured by external Ni–CrNi thermocouple, calibrated against the melting temperature of gold. Temperature measurements are corrected for a temperature gradient inside the autoclaves, which was measured using a second inner thermocouple during the initial calibration of the vessels. The external thermocouple has an error of approximately $\pm 1^\circ\text{C}$, and the total error of temperature measurements, including the uncertainties due to the temperature gradients, is estimated to be $\pm 5^\circ\text{C}$. Pressure is measured by transducers, and results were checked against a pressure gauge. The transducers and gauge are factory calibrated and have an accuracy of better than ± 0.1 MPa. Run times varied from 20 to 141 hours. In experiments with decreasing temperature, the temperature lowered gradually, with decrease of 5–7°C in every 1–1.5 hour. Samples were kept for at least 10 hours at the final temperature before quenching. The quenching of the experimental samples in such apparatus is isobaric and less than a second.

After the experiments, samples were mounted in epoxy resin and polished with diamond polishing pastes without water to avoid dissolution of alkalis. Major components of the run products were analyzed using Cameca SX-50 and SX-100 electron microprobes in the GFZ Potsdam and energy-dispersive spectrometry (EDS) in combination with back-scattered electron imaging (BSE) using a MIRA 3 LMU SEM (TESCAN Ltd.) equipped with an INCA Energy 450 XMax 80 microanalysis system (Oxford Instruments Ltd.) in the Analytical Center for multi-elemental and isotope research SB RAS (Novosibirsk, Russia).

Microprobe analyses were performed in WDS mode with a 10 nA beam current and accelerating voltage of 15 kV. Counting time for F (analyzed with TAP crystal) was 40 s. For all other elements it was set to 20 s on peak and 10 s on background. These parameters are benign to avoid any damage to carbonates or melt. The following synthetic and natural standards were used for the calibration: wollastonite (Ca), albite and jadeite (Na), apatite (P), LiF (F). Quenched melts were analyzed with a defocused beam (beam diameter of 20–40 μm). At least five point analyses were performed on each phase to obtain statistically representative averages.

For EDS analyses the samples were coated with a 25 μm conductive carbon coating. EDS analyses were made at low vacuum of 60–80 Pa, an accelerating voltage of 20 kV, a probe current of 1 nA, and accumulation time of 20 s. The simple compounds and metals were used as reference samples for most of the elements: SiO₂ (Si-K α and O-K α), diopside (Ca-K α), albite (Na-K α), Ca₂P₂O₇ (P-K α), BaF₂ (F-K α), pyrite (S-K α), SrF₂ (Sr-K α) and various (LREE)PO₄ (LREE-L α). Correction for matrix effects was made by the XPP algorithm, implemented in the software of the microanalysis system. Metallic Co served for quantitative optimization (normalization to probe current and energy calibration of the spectrometer).

Trace elements were measured by LA-ICP-QQQ-MS applying a Geolas Compex Pro 193 nm excimer laser coupled to a Thermo iCAP TQ mass spectrometer in the GFZ Potsdam. Analytical conditions comprised a spot size of 24 μm , repetition rate of 8 Hz, and laser energy density of 5 J cm⁻². NIST SRM 610 was used as external standard and Ca as derived from EPMA as internal standard. BCR-2G was analyzed as known-unknown for accuracy control and trace element concentrations are in agreement with published data at < 10% 2 σ RSD. Each analysis comprised 20 s background, 40 s ablation and 20 s wash-out. Data was processed using the trace elements IS data reduction scheme [42] in iolite 3.63 [43].

Declarations

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Author contributions

D.A.C. developed the idea of the paper, conducted the experiments, collected and interpreted the analytical data, wrote and designed the original manuscript; C.W.-U. collected the analytical data and reviewed the original manuscript.

Competing interests

The author declare no competing interests

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Figures

Figure 1

Morphology of calcites formed in experiments: (a) #3 NCFP-9; (b) #4 NCP-1; (c) #6 NCP-1; (d) #7 NCPSi-1; (e) #8 NCPS-1; (f) #10 NCPSi-3.

Figure 2

Textures of the experimental samples: (a) #3 NCFP-9; (b) #4 NCP-1; (c) #6 NCP-1; (d) #7 NCPSi-1.

Figure 3

The average partition coefficients of REE with the standard deviation as error bars for calcites.