



Trace element partitioning between perovskite and kimberlite to carbonatite melt: New experimental constraints



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ABSTRACT

We present experimentally determined trace element partition coefficients (D) between perovskite (CaTiO_3) and several different silicate and carbonate melt compositions. Our data indicate that perovskite is able to strongly fractionate trace elements during the evolution of SiO_2 -undersaturated magmas. In silicate magmas, perovskite efficiently fractionates Zr and Hf from Nb and Ta, with D_{Zr} and D_{Hf} coefficients below and D_{Nb} and D_{Ta} , significantly above unity, respectively. All trace element partition coefficients between perovskite and the diverse silicate melts, which primarily differ in their CaO and SiO_2 contents, are fairly similar within propagated uncertainties. We find that D perovskite/silicate melt for the high field strength elements is much lower than corresponding perovskite/carbonate melt partition coefficients for the same elements. Another key difference between perovskite/melt trace element partitioning in silicate and carbonate systems is the relative behavior of U and Th. Whereas all silicate system experiments show that $D_{\text{Th}} > D_{\text{U}}$, the relationship is different in the carbonatite experiment. This implies that perovskite may fractionate U and Th in silicate magmas whereas perovskite cannot fractionate U and Th in carbonate magmas. The Th/U ratio of magmatic perovskite may, therefore, provide a tool for a better understanding of the evolution of hybrid carbonate-silicate magmatic systems.

The rare earth elements (REE) show similar perovskite/melt partitioning in the silicate and carbonate systems investigated. Our data indicate that the REE are highly compatible in perovskite in both silicate and carbonatite compositions, which explains the high rare earth element concentrations in naturally occurring magmatic perovskites. In particular, our new trace element partition coefficients help to better understand and to quantify the strong control of perovskite on the bulk REE budget of kimberlites and related rocks.

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1. Introduction

Understanding trace element behavior in magmatic systems requires a thorough understanding of the partitioning of trace elements between minerals and melts. Previous studies have focused on the trace element partitioning between major rock forming minerals and melts (Green, 1994), and relatively few partition coefficients are available for accessory phases such as rutile, ilmenite, apatite, or perovskite (e.g., Nagasawa et al., 1980; Kennedy et al., 1994; Corgne and Wood, 2002; Klemme and Dalpe, 2003; Klemme and Meyer, 2003; Corgne and Wood, 2005; Klemme et al., 2005; Prowatke and Klemme, 2005; Klemme et al., 2006). The phases mentioned above typically do not play an important role during the fractionation of basaltic magmas, but they certainly exert strong control on the trace element distribution in alkaline, kimberlite, and

carbonatite magmatic systems where they occur throughout the crystallization sequence and reach abundance levels commonly exceeding 5 vol.%, i.e., they can be minor rock forming constituents (Mitchell, 1986; Tappe et al., 2004; Tappe et al., 2009; Malarkey et al., 2010; Chen and Simonetti, 2013–this issue).

In this study we focus on CaTiO_3 -perovskite, which is a common phase in silica-undersaturated alkaline (Veksler and Teptev, 1990; Dawson, 1994; Tappe et al., 2005; Rosenthal et al., 2009), kimberlite (Mitchell, 1986; Chakhmouradian and Mitchell, 2000; Malarkey et al., 2010; Rao et al., 2011; Tappe et al., 2011) and, more rarely, carbonatite magmas (Chakhmouradian and Mitchell, 1997; Chakhmouradian, 2006; Cox and Wilton, 2006). Although perovskites from different alkaline and kimberlite varieties appear to be close to CaTiO_3 end-member composition (Mitchell, 1995; Chakhmouradian and Mitchell, 2000; Tappe et al., 2006), perovskites from carbonatites show relatively large compositional diversity, in particular in terms of their REE and Nb contents (Lupini et al., 1992; Platt, 1994; Viladkar and Subramanian, 1995; Mitchell, 2002; Chakhmouradian, 2006; Reguir et al., 2010). Whether this behavior is due to the typically elevated REE and Nb concentrations of carbonate-rich magmas, or simply a function of distinctly different perovskite/melt trace element partitioning between silicate and carbonate magmatic

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systems, will be addressed during the discussion of our new experimental results.

Corgne and Wood (2002, 2005) investigated the partitioning of trace elements at varying P–T conditions in the system $\text{SiO}_2\text{--CaO--TiO}_2 \pm \text{Al}_2\text{O}_3$. Their data suggest that pressure and temperature have only minor influence on the partitioning of trace elements between CaTiO_3 and silicate melts. However, they observed a change in the partitioning behavior with varying CaO contents of the melt, suggesting that melt composition has a strong effect on trace element partitioning (Kohn and Schofield, 1994; Klemme, 2004; Klemme et al., 2005; Prowatke and Klemme, 2005, 2006a,b; Schmidt et al., 2006; Evans et al., 2008). The objective of our study is to extend the database to more natural bulk compositions, and to evaluate the applicability of simple system partition coefficients to more complex silicate and carbonate melt compositions. Therefore, we initially determined perovskite/melt trace element partition coefficients in a simple system following Corgne and Wood (2005) and compared these data with our results from a more complex $\text{H}_2\text{O-}$ and CO_2 -bearing silicate system, the average near-primary kimberlite composition (Becker and Le Roex, 2006). In addition, we performed an experiment in a simplified carbonatitic system, which enables us to present the first perovskite/carbonatite melt trace element partitioning data.

2. Starting material and methods

2.1. Starting mixtures and experimental approach

To ensure the nucleation and growth of perovskite to a reasonable size and, thus, enabling in situ analysis by laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS), the starting materials were super-saturated in CaO and TiO_2 . In order to avoid possible experimental problems related to iron-loss, the compositions were all iron-free. Mix 1 is a composition in the system $\text{SiO}_2\text{--CaO--TiO}_2$, whereas Mix 2 is more complex in the system $\text{SiO}_2\text{--CaO--TiO}_2\text{--MgO--K}_2\text{O--Al}_2\text{O}_3$. All compositions were prepared from analytical grade oxides, hydroxides, and carbonates (Table 1), which were ground in an agate mortar under ethanol. For the high-pressure partitioning experiments in a kimberlitic system, the composition of our starting material (MixBeyK1) was guided by an average near-primary kimberlite composition from southern Africa (Becker and Le Roex, 2006). Furthermore, a model carbonatite composition was prepared in the system $\text{CaCO}_3\text{--TiO}_2$ (SKHDCMB2). The choice of this rather simple composition was made after our reconnaissance experiments in more complex carbonate systems yielded only small perovskite crystals (<15 μm), which were impossible to analyze by our LA-ICP-MS set-up.

Mix 1 and Mix 2 were heated in air from 800 °C to 1000 °C with a ramp of 150 °C/h. They were then held at 1000 °C for 3 h in order to ensure complete decarbonation. Subsequently, the mixtures were heated to temperatures well above the liquidus, quenched, and again

ground to fine powders. MixBeyK1 was decarbonated in the same manner, but $\text{Mg}(\text{OH})_2$ and CaCO_3 were added at a later stage as sources of H_2O and CO_2 , respectively. For the carbonatite starting material SKHDCMB2, CaCO_3 and TiO_2 were mixed in the appropriate ratios. All starting materials were doped with a trace element solution containing the following elements in 2% HNO_3 solution: Li, Sr, Ba, Sc, Zr, Nb, La, Ce, Pr, Sm, Gd, Lu, Y, Hf, Ta, Pb, U, and Th. This solution was prepared from 1000 $\mu\text{g/g}$ ICP-AES standard solutions. The doped starting materials were dried and denitrified in a laboratory-type drying cabinet at 110 °C overnight.

The 1-atmosphere experiments with Mix 1 and Mix 2 as starting materials were carried out in two different gas-mixing furnaces under air. The temperature was monitored and controlled with a Type B thermocouple ($\text{Pt}_{70}\text{Rh}_{30}\text{--Pt}_{94}\text{Rh}_6$). The runtime varied between 18 and 66 h (see Table 2 for details). After quenching of the experimental charges, the samples were embedded in epoxy resin and polished using a series of diamond pastes.

The high-pressure experiments were performed in an end-loaded piston cylinder apparatus (Boyd and England, 1960) at 1.5 GPa (Table 2). This pressure is representative for the uppermost mantle where the first phenocrysts of alkaline magmas are thought to crystallize (Mitchell, 1986). The samples were enclosed in a 2 mm O.D. platinum capsule. The pressure assemblies consisted of a 1/2 inch talc-Pyrex tube, and a 6 mm diameter graphite heater. Cavities were filled with crushable alumina ceramics. The temperature was monitored by $\text{W}_{97}\text{Re}_3\text{--W}_{75}\text{Re}_{25}$ thermocouples. A friction correction of -13% was applied which was calibrated for this particular assembly on the quartz-coesite transition (Bose and Ganguly, 1995) and the $\text{MgCr}_2\text{O}_4 + \text{SiO}_2 = \text{MgSiO}_3 + \text{Cr}_2\text{O}_3$ reaction (Klemme and O'Neill, 1997). Run durations varied between 5 and 8 h. Based on our pressure calibration, the quoted pressures are estimated to be accurate within 0.1 GPa (Table 2).

2.2. Analytical methods

Run products were examined qualitatively using a JEOL 6610LV scanning electron microscope with EDX system. Major element analyses were performed with a 4-spectrometer JEOL JXA 8900 electron microprobe at the University of Münster using an acceleration voltage of 15 kV. Mineral phases were analyzed using a focused beam current of 15 nA. Counting times were 20 s on the peak and 10 s on the background. Glasses and quenched melts were analyzed with a $\sim 10 \mu\text{m}$ defocused beam and counting times were 5 s on the peak and 2.5 s on the background to minimize loss of volatile elements. Matrix-matched minerals were used as reference materials. Additionally, a set of well-characterized secondary standards was measured together with the unknowns to monitor external precision and accuracy (Klemme et al., 2008).

Seventeen trace elements were analyzed using a LA-ICP-MS system at the University of Münster that consisted of an Element 2 (ThermoFisher) SF-ICP-MS connected to a 193 nm ArF excimer laser ablation system (UP193HE, New Wave Research). Laser repetition

Table 1
Starting material compositions (wt.%).

	Mix 1	Mix 2	MixBeyK1	SKHDCMB2
SiO_2	17.5	25	28	
TiO_2	54	20	11.2	27.5
CaO	28.5	15	17	40.6
Al_2O_3		2.5	2.7	
MgO		20	26	
NiO			0.1	
Na_2O				
K_2O		2.0	1.0	
H_2O			8	
CO_2			6	31.9

Table 2
Experimental run conditions.

Run no.	P	T/°C	Run duration/h	Starting material	Phases present
MCB1_1	1 atm	1100	28	Mix 2	ol, pv, melt
MCB1_2	1 atm	1300	66	Mix 2	ol, pv, melt
RPER2_1	1 atm	1200	18	Mix 2	ol, pv, tnt, melt
RPER2_2	1 atm	1300	18	Mix 2	ol, pv, melt
RPER1_2	1 atm	1350	18	Mix 1	pv, melt
RPER2_3	1 atm	1450	18	Mix 1	ol, melt
PC513	1.5 GPa	1200	8	MixBeyK1	pv, ol, melt
PC520	1.5 GPa	1300	5	SKHDCMB2	pv, melt

ol = olivine, pv = perovskite, tnt = titanite (sphene), melt = quenched melt. Note that the experiments MCB1_1 and RPER2_3 were not analyzed for trace elements as they contained only very small (MCB1_1) or no perovskite crystals.

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