# TRACE ELEMENT SOLUBILITY AND REACTION KINETICS IN THE CAS-SYSTEM

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# INTRODUCTION

A new locality of lower mantle inclusion bearing diamonds has been described recently from the Kankan district of Guinea (Stachel et al., 2000). Besides majoritic garnet and ferropericlase there are two new minerals: Ca-Si-titanite coexisting with larnite, and a CaSiO<sub>3</sub> phase with walstromite structure (Joswig et al., 1999). From experiments (Gasparik et al., 1994) it is known that Ca-Si-perovskite disproportionates to larnite and Si-titanite phase at pressures below ~12 GPa at 1200°C. These two phases recombine to Cawalstromite at pressures below ~10 GPa (Fig. 1). One inclusion from Kankan consisted of larnite and Sititanite separated by a small zone of CaSiO<sub>3</sub> (presumably with walstromite structure). More often CaSiO<sub>3</sub> inclusions are found as an amorphous phase, possibly indicating a former Ca-perovskite. An understanding of the reaction kinetics in the CaO-SiO<sub>2</sub> system could help to reconstruct diamond ascent paths. A series of isothermal retrograde multi-anvil



**Figure 1**: Temperature vs. Depth diagram showing the stability fields of Ca-silicate-phases. Green arrows represent experimental conditions of different isothermal runs.

experiments were performed insitu at the Daresbury Synchrotron, which allow the determination of fundamental kinetic parameters. Such data are essential for reconstructing the ascent history of the host diamond.

To determine the depth from which these inclusions originated, we also investigated the maximum solubility of REE in Ca-silicates. We conducted a series of experiments with belt and multi-anvil apparatuses at pressures from 3.0 GPa to 15 GPa and temperatures from 1200°C to 1500°C. REE contents in the walstromite and perovskite structures coexisting with a Ca-REE-silicate phase Ca(Ca,La,Gd,Lu)  $_2$ Si<sub>2</sub>O<sub>8</sub> were determined. A further series of experiments was conducted to determine the maximum solubility of K and P in Ca-walstromite coexisting with an apatite phase. These elements are of interest because of their high concentrations observed in the Ca-silicate inclusions from Kankan (Stachel et al, 2000).

## METHODS

#### **REACTION KINETICS EXPERIMENTS**

The experiments were conducted in a Walker-type multi-anvil press which is installed on beamline 16.4. at the Daresbury synchrotron. This press is designed to allow insitu energy dispersive X-Ray diffraction (EDXRD). The three Germanium solid state detectors were calibrated using the method by Walker et al., 2000. A new pressure cell design was developed which allows insitu observation up to pressures of 15 GPa and temperatures in exess of 1600°C. Run pressures were calculated from the change of the lattice parameters of the MgO internal pressure standard (Fig 2). The temperature was controlled within  $\pm$  5 °C using a S-type thermocouple (and D-type for high T).

The starting material for the kinetic study was  $Ca SiO_3$  gel loaded into a MgO/Cr<sub>2</sub>O<sub>3</sub>- cell with a LaCrO<sub>3</sub> heater in "fin to fin"-orientation (Fig. 2). The sample was first brought to pressure and then heated to 1200°C. After the formation of Ca-perovskite the pressure was reduced at a constant rate into the larnite + Si-titanite stability field. The reaction rate was determined by collecting diffraction spectra every 180 seconds. Reaction at the sample-standard-interface was limited to  $< 50 \ \mu m$  over a 24 h period and this area was avoided during meassurement. A Re sleeve prevented reaction with the surrounding MgO in the pressure cell.



**Figure 2**: Experimental setup using white synchrotron radiation: data from MgO pressure standard and sample were collected by moving the whole multi-anvil press relative to the detector system.

#### TRACE ELEMENT SOLUBILITY EXPERIMENTS

Experiments up to 5 GPa pressure were conducted in a belt apparatus using CaF2 single-crystal pressure media and graphite heaters. Experiments above 5 GPa were performed in a Walker-type multi-anvil press using 14 mm MgO octahedra, rhenium foil heaters and pyrophyllite gaskets. The starting material was prepared from element oxides and carbonates for the REE-series and from gels for the K and P runs (Table 1). For the REE runs La, Gd, Lu were added as a light, middle and heavy REE, respectively. These three elements were added as hydrated carbonates, which released a CO<sub>2</sub>/H<sub>2</sub>O fluid during the experiment. This fluid served as a flux to better achieve equilibrium. For the second series of experiments Mix2 (Table 1) was CaSiO<sub>3</sub> gel with K and P added as potassiumdihydrogenphosphate. Starting material was fineground and sealed in Pt capsules without excess water. The experiment was loaded to the run pressure and subsequently heated at a rate of 50°C/min. Run durations were 72-96 h. Experiments were quenched by switching off the electric power. The capsules were cut and polished for electron microprobe analysis.

# Table 1: composition of the starting materials (weight % oxide)

Mix1(REE)	Mix2(K,P)
	7.72
43.34	44.57
4.54	
4.90	
5.25	
1.52	
40.45	41.60
	5.12
	0.98
100.00	99.99
	Mix1(REE) 43.34 4.54 4.90 5.25 1.52 40.45  100.00

### **RESULTS AND DISCUSSION**

#### **KINETICS**

First results of retrograde high pressure experiments performed at 1200°C indicate that the disproportionation reaction of Ca-perovskite to larnite + Si-titanite proceeds at an order of magnitude faster than the recombinition to walstromite. This confirms what was deduced before from the natural diamond inclusions (Stachel et al. 2000):

Further phases were found as seperate inclusions in the same diamond which indicate that the touching paragenesis of larnite and Si-titanite was originally  $CaSiO_3$  in perovskite structure. On uprise the dispropotionation reaction went to completion whereas the subsequent reaction to combine the two phases to Ca-walstromite remained incomplete. This is consistent with our observation that this reaction is proceeding at a much slower rate than the disproportionation reaction. This "frozen" state of the Ca-walstromite formation is the key to reconstruct the ascent history of the host diamond.

The ongoing work at different temperatures will allow to deduce fundamental parameters (activation energy) and to model the ascent path of the mantle domain hosting the diamonds.

#### **REE-SOLUBILITY**

The solibility of the trace elements investigated was determined by EMS analysis. Since a REE-rich phase coexists with  $CaSiO_3$  and melt (Fig. 3), the REE-data represent the maximu m solubility in Ca-walstromite. Table 2 shows some of the analytical data at upper mantle conditions.



**Figure 3** BSE image of run product KW323 (4.0 GPa, 1200°C): Ca-walstromite (dark grey) coexisting with melt (light grey) and a REE phase (white hexagonal crystals)

# Table 2: maximum solubility (mol % of cations) of REE in Ca-walstromite

	4.0 Gpa 1200°C	6.0 GPa 1300°C
Si	50,21	50,48
Ca	49,45	49,15
AI	0,05	0,04
La	0,02	0,02
Gd	0,10	0,12
Lu	0,16	0,20

#### K AND P SOLUBILITY

The run products from this experimental series yielded Ca-walstromite coexisting with melt and an apatite phase, a buffer phase for the solubility of phosphorus. On a molar basis potassium in Ca-walstromite exeeds the value for P by a facor of ~3 (Fig. 5). Charge balance must then occur via vacancies which is in contrast to the findings from natural inclusions in diamond. There, K and P occur in a one to one ratio, which suggests solution as a KPO<sub>3</sub>-component (with K<sup>+</sup> replacing Ca<sup>2+</sup> and P<sup>5+</sup> replacing Si<sup>4+</sup>).



Figure 5: K and P solibility in Ca-walstromite



**Figure 4**: BSE image of run product #1241 (5 GPa, 1400°C): Ca-walstromite (isometric crystals) coexisting with an apatite phase (light prismatic crystals) within melt.

# REFERENCES

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