

## Experimental melting of peridotites in the presence of CO<sub>2</sub> and H<sub>2</sub>O at 40 – 60 kbar

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Partial melting of peridotites containing both CO<sub>2</sub> and H<sub>2</sub>O in the pressure range 4.0-6.0 GPa (120-190km) is important for explaining the origin of kimberlites, ultramafic lamprophyres, and possibly carbonatites, kamafugites and alkaline picrites, but is currently very poorly constrained with experiments. Incipient melts of peridotite may be seen at the surface of the Earth as igneous rocks, but may also be important for the production of melts that lead to metasomatic reactions in the cratonic mantle lithosphere, and for producing ultramafic veins that play an important role in the genesis of alkaline igneous rocks. Previous experiments at 3-10 GPa on CO<sub>2</sub>-bearing but dry compositions indicate that a wide temperature interval of low-degree melting occurs directly above the solidus in which melt compositions increase in SiO<sub>2</sub> content from carbonatitic (>6wt%) to "kimberlitic" (20-35 wt%) with increasing temperature (Dalton & Presnall, 1998a,b; Dasgupta & Hirschmann 2007; Brey et al., 2008). In water-bearing conditions, a field for carbonatite melts is well defined at 2-3 GPa (Wallace and Green, 1988), but has not been constrained at higher pressures. Here, we present major and trace element compositions of incipient melts at 5 GPa, corresponding to the pressure of interest for many cratonic CO<sub>2</sub>-bearing alkaline rocks. The CO<sub>2</sub> and H<sub>2</sub>O contents are similar to those used by Wallace and Green (1988).

### Experimental methods

We have conducted experiments on three peridotite compositions (Table 1): (i) MP: (MORB-Pyrolite) with CO<sub>2</sub> and H<sub>2</sub>O added as hydroxides and carbonates in a sintered oxide mix; (ii) HP (Hawaiian Pyrolite) characterized by higher TiO<sub>2</sub> than MORB-Pyrolite. 40%

olivine was "extracted" from the Hawaiian Pyrolite composition: this was originally intended as a convenience for the optical identification of minerals in run products, but serves here to increase the abundance of volatiles and fertile components, thus increasing the amount of melt for analysis whilst maintaining saturation in peridotite minerals; (iii) HPK (Hawaiian Pyrolite with added K) to investigate the effects of phlogopite on incipient melting of peridotite. All three compositions contained 0.5 wt% of a mixture of trace elements in concentrations ranging from approximately 50-150 ppm.

We used Au<sub>80</sub>Pd<sub>20</sub> capsules which do not remove Fe from the samples, and ran experiments for durations of 48-96 hours in a piston-cylinder apparatus at the Research School of Earth Sciences in Canberra.

Table 1: Compositions of starting mixtures

	MP	HP	HPK
SiO <sub>2</sub>	43.39	45.87	45.17
TiO <sub>2</sub>	0.16	1.13	1.11
Al <sub>2</sub> O <sub>3</sub>	4.24	5.66	5.57
FeO	7.32	8.44	8.31
MgO	37.4	27.58	27.16
CaO	3.28	4.92	4.85
Na <sub>2</sub> O	0.39	0.91	0.90
K <sub>2</sub> O	0.19	0.21	1.74
Cr <sub>2</sub> O <sub>3</sub>	0.44	0.69	0.68
MnO	0.11	0.12	0.12
NiO	0.25	0.12	0.12
CO <sub>2</sub>	2.0	3.2	3.2
H <sub>2</sub> O	0.4	0.63	0.63
Trace elements	0.5	0.5	0.5
Mg#	90.1	85.4	85.4

### Results and melt compositions

Low degrees of melting occur in all three compositions at 1180°C, which is >60°C above the solidus. Melts do not quench to

glasses but are found as fine-grained aggregates of quenched silicate and carbonate minerals up to several micrometres across. Analyses were possible where melt collected in pools along cracks or at the boundary between samples and metal capsule. Major element analyses (Table 2) are averages of numerous EDS scans of areas between 8x5 and 15x12 micrometers. Olivine, orthopyroxene, clinopyroxene and garnet are stable in all experiments, Mg-ilmenite occurs in HP and HPK due to the higher TiO<sub>2</sub> content, and additionally phlogopite coexists with melt in HPK.

**Table 2: Melt compositions at 5 GPa and 1180°C**

	MP	HP	HPK
SiO <sub>2</sub>	5.19	7.46	13.15
TiO <sub>2</sub>	0.08	0.91	2.60
Al <sub>2</sub> O <sub>3</sub>	1.43	1.41	1.93
FeO	5.92	7.28	5.54
MgO	16.07	15.25	10.03
CaO	23.85	23.97	10.78
Na <sub>2</sub> O	0.36	1.69	3.30
K <sub>2</sub> O	0.37	0.54	13.74
Sum	53.27	58.51	61.07
Mg#	82.9	78.9	76.3

Melts have carbonatitic compositions broadly similar to those seen in the CMAS-CO<sub>2</sub> system at 5 GPa (Dalton & Presnall, 1998b) and in natural systems at slightly higher pressures (Dasgupta & Hirschmann, 2007; Brey et al., 2008). Ca/(Ca+Mg) values of 0.52-0.53 for MP and HP are similar to the CMAS data despite the extra components in the compositions studied here. The HPK value of 0.43 is also considerably higher than most 6 GPa melts described by Brey et al. (2008).

The most remarkable difference to previous experiments is the enrichment of potassium in carbonate-rich melts. This is accentuated in the HPK melt which contains between 10 and 14 wt% of each of SiO<sub>2</sub>, MgO, CaO and K<sub>2</sub>O. This indicates that where phlogopite is present during melting of CO<sub>2</sub>-bearing peridotite, it makes a much greater contribution to the melt than the carbonate-dominated melting reactions that have been identified in previous experiments at 5-6 GPa, none of which have contained water (Dalton

& Presnall, 1998a,b; Dasgupta & Hirschmann, 2007; Brey et al., 2008). High alkali contents in carbonatitic melts were found by Wallace and Green (1988) at 2-3 GPa, but these were characterized by Na-enrichment in conditions where amphibole, and not phlogopite, was the stable hydrous phase. Nevertheless, K<sub>2</sub>O contents in carbonatite melts were more than twice those in the bulk composition. The potassic carbonatite melts found in the HPK experiment may be crucial in explaining mica-bearing carbonate-rich igneous rocks such as ultramafic lamprophyres (Tappe et al., 2006).

### Trace elements in partial melts

Trace element analyses (Laser-ICP-MS) are averages from several ablation holes between 12 and 25 micrometers diameter.

**Table 3: Trace element enrichment factors melts at 5 GPa and 1180°C**

	MP	HP	HPK
Sc	6.2	5.7	2.9
V	10.8	9.6	4.8
Cr	2.3	3.0	1.0
Mn	2.6	1.8	1.3
Co	7.0	2.7	2.2
Ni	3.5	0.34	0.49
Cu	0.29	0.30	0.08
Zn	1.7	0.86	0.55
Ga	10.0	3.0	3.1
Rb	16.4	15.6	3.0
Sr	7.5	6.4	5.4
Y	9.3	7.2	4.9
Nb	10.0	9.0	5.7
Cs	9.6	6.0	1.9
Ba	7.9	5.4	6.8
La	16.5	9.9	10.7
Ce	12.0	6.5	6.2
Pr	14.3	9.8	8.8
Sm	11.4	9.0	7.9
Eu	15.0	9.0	8.5
Gd	10.0	7.6	6.7
Dy	9.4	6.9	5.3
Ho	9.5	7.1	4.9
Er	8.1	6.0	3.9
Tm	7.8	5.5	3.5
Yb	7.5	5.7	3.4
Lu	7.8	5.5	3.2
Hf	5.1	4.9	3.1
Ta	5.0	7.4	5.2
U	17.4	18.8	12.3

Results are given in Table 3 as enrichment factors rather than element concentrations (mostly between 200 and 2000 ppm) because of the strongly non-natural ratios in the trace element mix. The enrichment factors express ratios of concentration in melt to concentration in the bulk composition (starting mix), and so represent a rough indication of trace element patterns on rock-normalized diagrams.

Trace element concentrations in carbonatitic melts have been presented for H<sub>2</sub>O-free experiments at 6 GPa by Brey et al. (2008). Our results agree with theirs in several important aspects. Firstly, near-solidus carbonatitic melts will not be able to strongly fractionate rare earth elements: the enrichment factors for LREE are only 2-3 times higher than for HREE, and there is no strong enrichment in LREE as in many natural carbonate-rich igneous rocks. The high field strength elements do not behave differently to other incompatible elements, showing significant enrichment in partial melts. This means that high Zr/Hf and low Ti/Eu often inferred to be typical for metasomatism of peridotites by carbonatite melts (Yaxley et al., 1991; Rudnick et al., 1993) are not characteristic of the original melts themselves. The same is true for Y/Ho (Bühn & Rankin, 1999), which show identical enrichment factors of 5-9.

Our Sc and V data agree with those of Brey et al. (2008), showing unexpectedly high enrichment factors. The lowest factors are for Cu, probably because of alloying with the AuPd capsules. The enrichment factors for Rb and Cs are 3-5x higher in the MP and HP experiments than in the HPK experiments, reflecting the control of these two elements by phlogopite in HPK.

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