

# A universal concept of melting in mantle upwellings: all deep melts are born kimberlitic

Max. W Schmidt, Andrea Giuliani, Nadezdha Paneva

*Dep. Earth Sciences, ETH, 8092 Zurich, Switzerland*

max.schmidt@erdw.ethz.ch

## Introduction - C and H availability in the asthenosphere

Small degree melting in the deep Earth is very much governed by the availability of volatile components as the hydrous or carbonated solids of mantle rocks are several hundred degrees lower than the dry solidus. Yet, volatiles are not easily available away from subduction zones, where slab-delivered H<sub>2</sub>O and minor CO<sub>2</sub> control mantle melting. This is because the asthenospheric mantle is at temperatures above the thermal stability of known hydrate or carbonate mantle minerals, which hence cannot deliver H or C. Consequently, more complex mechanisms are required to form CO<sub>2</sub>+H<sub>2</sub>O bearing melts such as kimberlites, ultramafic lamprophyres or alkaline basanites, for which radiogenic isotopes demonstrate a source in the convecting asthenosphere.

Rather than carbonates and hydrates, the sources of C in the deep asthenosphere are diamond or metal alloys while H is stored in nominally anhydrous minerals (NAMs). In mantle upwellings, majoritic garnet decompression causes shedding of its majorite component concomitantly with its quite large Fe<sup>III</sup>-content, a reaction that completes around 8-6 GPa (Rohrbach et al. 2007). The ferric Fe reacts with elemental carbon according to  $\text{Fe}^{\text{III}}_{\text{majorite}} + \text{C}^0 = \text{CO}_2 + \text{Fe}^{\text{II}}_{\text{olivine, opx}}$  transforming a diamond and/or alloy saturated mantle into a CO<sub>2</sub>-bearing one. At this point the CO<sub>2</sub>-bearing solidus applies instead of the dry one, and carbonated silicate melts form (Rohrbach & Schmidt, 2011). These low degree melts then acquire H through partitioning with the nominally anhydrous minerals. With a partition coefficient  $D^{\text{peridotite/melt}}$  of ca. 0.005-0.007 (Hirschmann et al. 2009) and H contents of 100-300 ppm, the resulting melts contain in the order of 2-5 wt% H<sub>2</sub>O. These latter values should be independent of degree of melting (as long as at a few percent or less – (Hirschmann et al. 2009).

The aim of this work is to investigate, which kind of melts occur at the redox front, at realistic CO<sub>2</sub>, H<sub>2</sub>O and incompatible element concentrations. To approximate this goal, we equilibrate erupted primitive melts, corrected for volatiles, at redox front conditions.

## Experimental strategy

In our experiments we equilibrate a wide range of mantle-derived melts related to mantle upwellings, i.e. mid-ocean ridge basalts, alkaline basalts (Hawaii), alkaline basanites (Cape Verdes), and kimberlites with lherzolitic mantle at 7 GPa at adiabatic and super-adiabatic temperatures of 1450 and 1630 °C. In these experiments the surface melts are forced to equilibrate with the four (lherzolite) mantle minerals at 7 GPa using an iterative experimental protocol.

The original primitive surface melt is doped with variable amounts of CO<sub>2</sub> and H<sub>2</sub>O: for CO<sub>2</sub> this is 1 wt% for MORBs as in the Atlantic “popping rocks”, 5 wt% for alkali-basalts and -basanites as derived from melt inclusions, and 5-15 wt% for kimberlitic melts. Starting H<sub>2</sub>O-contents of 1-2 wt% are used, targeting the expected H<sub>2</sub>O content from partitioning with NAMS in the source. Iterations are run such that the original surface melt is reacted with a 4-phase peridotite at 7 GPa, which invariably leads to the loss of either one

of the pyroxenes and/or olivine, the melt composition is then measured, and the new composition again run with a 4-phase peridotite. Between 3 and 8 iterations then render a four-phase mantle assemblage including olivine, garnet and the two pyroxenes in equilibrium with a carbonated silicate melt.

### **Melting at the redox front – 7 GPa**

As the principal result, in each case, that is for MORB, alkaline mafic and kimberlitic melts, saturation with the four mantle phases at 7 GPa and 1450 °C invariably yields a kimberlitic melt. Carbonatitic melts were never encountered, simply because the temperature and pressure dependent SiO<sub>2</sub>-solubility in carbonated melts in equilibrium with olivine + orthopyroxene is >20 wt% at 7 GPa at adiabatic temperature (1450 °C). Instead our 7 GPa melts have 25-30 wt% SiO<sub>2</sub>, uniformly ~2 wt% Al<sub>2</sub>O<sub>3</sub>, 17-22 wt% MgO, 9-15 wt% CaO and 5-8 wt% Na<sub>2</sub>O+K<sub>2</sub>O. Total volatile contents are 14-23 wt%. These melts are hence all of kimberlitic nature. Their relatively uniform chemistry is explained by Si and Fe+Mg buffering by olivine + orthopyroxene (for a given CO<sub>2</sub>), the Ca:(Mg+Fe) ratio by buffering with clinopyroxene and orthopyroxene, and the low Al-content by garnet-pyroxene equilibrium. One can then rationalize Na-contents as determined by partitioning with clinopyroxene, and H-contents as determined by partitioning with olivine + pyroxenes, essentially leaving K, Ti and P behaving as incompatible elements and at least in part governed by mantle heterogeneities.

### **A universal concept of deep mantle melting**

From these experiments, we formulate a universal concept for the formation and subsequent diversification of mantle melts. At the redox front, roughly corresponding to the metal saturation depth (~250-300 km, Rohrbach & Schmidt, 2011), where C<sup>0</sup> oxidizes to CO<sub>2</sub>, all deep mantle melts start out kimberlitic. When rising, these melts evolve to (i) higher degrees of melting, (ii) become less influenced by fusible mantle heterogeneities, (iii) exhibit lesser concentrations of volatiles and incompatible elements, but (iv) with ongoing decompression higher SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents. Conceptually, full equilibration is maintained during porous flow in the asthenosphere, hence equilibrium with the 4 mantle phases maintained. Such equilibrium also governs Na and H behavior, which will follow a pressure-dependent partitioning between the melt and pyroxenes+olivine, hence will not be governed by a supposed general incompatibility and hence not depend on the degree of melting (at values of a few percent).

Chemical separation from the mantle may then occur as deep as the asthenosphere-lithosphere boundary above which channeled or fracture flow is possible. In those cases where the lithosphere commences just above the C→CO<sub>2</sub> redox-front (~250 km or 8 GPa), kimberlitic melts issue directly. Lithospheric thicknesses of ~150 km lead to melilitites or similar melts and then to progressively less silica-undersaturated melts up to alkali basalts. Finally, at lower pressures the additional voluminous dry melting near mid-ocean ridges generates more tholeiitic and finally MORB-type melts.

The indistinguishable radiogenic isotope systematics of kimberlites, intracontinental sodic basalts and ocean-island basalts (OIB) is entirely consistent with this scenario, whereas the substantially higher melting degrees associated with MORB result in more geochemically-depleted isotopic signatures. Regardless, irrespective of whether the erupted melts are kimberlites, alkaline ocean island or mid-ocean ridge basalts, the first melts generated in mantle upwellings are kimberlitic.

### **The lithospheric contribution to kimberlitic melts**

It have been previously postulated that kimberlites may form in the carbonated lithosphere, which is in clear contradiction with existing isotopic evidence (Giuliani et al. 2023). Furthermore, such a hypothesis has two major conceptual issues: the origin of CO<sub>2</sub> and the heat budget. Carbonated lithosphere may only exist to temperatures of the carbonated peridotite solidus, at which carbonate minerals melts out, i.e. 1100 °C at 2.1 GPa (corresponding to the carbonate “ledge”) and 1200 °C at 5.5 GPa (corresponding to the intersection of the dolomite stability with the coldest cratonic geotherm ever observed). Considering any carbonated

lithosphere that undergoes some heating, carbonatite melts form at the solidus and, due their low viscosity and wetting angles, rise immediately (Hammouda and Laporte, 2000), such that no carbonate would be left at higher temperature. At the same time, the adiabatic cooling of carbonate melts is 35-45 °C/GPa (calculated from thermodynamic data), which is the same slope as the carbonated solidus. At best, carbonatite melts hence could creep along their solidus, if not immediately solidifying through exchange of heat or through reaction with their surrounding peridotite wall rocks, but not overheat. This signifies that kimberlitic melts cannot form in carbonated lithosphere, as kimberlite melts require 200 °C higher than the carbonated peridotite solidus (e.g., Gudfinnsson & Presnall, 2005). We hence posit that the lithosphere contributes solid material for reaction and assimilation, but not a melt component in kimberlites. At the same time, Si-contents of kimberlitic melts can only decrease within the lithosphere: Any low degree melt in the mantle has Si-contents buffered by olivine+opx and assimilation of lithospheric material decreases temperatures and hence Si-solubility. Further, assimilation of opx is endothermic and will further cool the kimberlitic melt.

## Conclusion

Our experiments show that when CO<sub>2</sub> becomes available in the mantle through redox exchange with iron (at ~7-8 GPa), the adiabatic temperatures are such that kimberlitic melts result. At this point, solid state upwellings become melt-bearing, and these melts remain in equilibrium with their surrounding peridotite when rising through porous flow, as characteristic for the asthenosphere. When arriving at the lithosphere-asthenosphere boundary, these melts may infiltrate in channels and then quickly ascend towards the surface with some interaction with lithospheric wall rocks – as widely recognised for kimberlites. In any case, the deepest observable melt chemistry should correspond to the depth of the uppermost asthenosphere, a concept that has been previously postulated (Mitchell, 2005; Humphreys & Niu 2009). Furthermore, this is true for adiabatic as well as superadiabatic upwellings, such that for any upwelling, whether of lesser intensity or leading to mid-ocean ridges, such kimberlitic melts will occur first. With decreasing pressure of melt extraction and hence increasing melting degree, the originally kimberlitic melts become progressively richer in Si and lower in CO<sub>2</sub> and alkalis, yielding a diverse range of asthenospheric melts which are further slightly to moderately modified in the lithosphere.

## References

- Dasgupta R, Hirschmann MM (2006) Melting in the Earth's deep upper mantle caused by carbon dioxide. *Nature* 440: 659–662
- Giuliani A, Schmidt MW, Torsvik TH, Fedortschuk Y (2023) Genesis and evolution of kimberlites. *Nature Rev Earth Environ* 4: 738-753
- Gudfinnsson GH, Presnall DC (2005) Continuous Gradations among Primary Carbonatitic, Kimberlitic, Melilititic, Basaltic, Picritic, and Komatiitic Melts in Equilibrium with Garnet Lherzolite at 3–8 GPa. *J Petrol*, 46: 1645-1659
- Hammouda T, Laporte D (2000) Ultrafast mantle impregnation by carbonatite melts. *Geol* 28: 283–85
- Hirschmann MM, Tenner T, Aubaud C, Withers AC (2009) Dehydration melting of nominally anhydrous mantle: The primacy of partitioning. *Phys Earth Planet Inter* 176: 54–68
- Mitchell RH (2005) Carbonatites and carbonatites and carbonatites. *Can Mineral* 43: 2049–2068
- Humphreys ER, Niu Y (2009) On the composition of ocean island basalts (OIB): The effect of lithospheric thickness variation and mantle metasomatism. *Lithos* 112: 118-136
- Rohrbach A, Ballhaus C, Golla-Schneider U, Ulmer P, Kamenetsky VS, Kuzmin DV (2007) Metal saturation in the upper mantle. *Nature* 449: 456-448
- Rohrbach A, Schmidt MW (2011) Redox freezing and melting in the Earth's deep mantle resulting from carbon-iron redox coupling. *Nature* 472: 209–12