Melting of sediments in the deep mantle produces saline fluid inclusions in diamonds

Michael W. Förster1*, Stephen F. Foley1, Horst R. Marschall2, Olivier Alard1,3, Stephan Buhre4

Diamonds growing in the Earth’s mantle often trap inclusions of fluids that are highly saline in composition. These fluids are thought to emerge from deep in subduction zones and may also be involved in the generation of some of the kimberlite magmas. However, the source of these fluids and the mechanism of their transport into the mantle lithosphere are unresolved. Here, we present experimental results showing that alkali chlorides are stable solid phases in the mantle lithosphere below 110 km. These alkali chlorides are formed by the reaction of subducted marine sediments with peridotite and show identical K/Na ratios to fluid inclusions in diamond. At temperatures >1100°C and low pressures, the chlorides are unstable; here, potassium is accommodated in mica and melt. The reaction of subducted sediments with peridotite explains the occurrence of Mg carbonates and the highly saline fluids found in diamonds and in chlorine-enriched kimberlite magmas.

INTRODUCTION
The lithospheric mantle beneath the cratons (1) contains a complex record of geochemical depletion by ancient melting events that are overprinted by later refertilization by infiltrating liquids (2, 3). Fast-growing fibrous diamonds, and less often, gem-quality diamonds (4), trap and preserve fluids that are present during their formation, providing insights into the chemical environment of diamond formation (5, 6). The encapsulated fluids may be highly saline, with K/Na ratios (by mass) of 1:1 to 9:1, siliceous, or low- or high-Mg carbonatitic in composition (2, 7–9). However, the source of these exotic fluids within the lithospheric mantle has remained ambiguous (4, 7, 8). Weiss et al. (2) argue that the saline component in diamond micro-inclusions originates from subducted seawater in altered oceanic crust, but the mechanism of fluid transport and the fractionation of K from Na remain enigmatic.

Diamonds (10) are transported to the surface by kimberlites, which are rapidly emplaced magmas with exotic H2O- and CO2-rich compositions and whose origin is still a matter of debate (11–14). Melting experiments on peridotite with H2O and CO2 can explain the carbonate component in kimberlites but cannot reproduce the high K/Na unless the starting composition is preenriched in K2O (15). The most recent models explain kimberlites as hot (>1400°C) melts of peridotite (16, 17), whereas other authors argue for cooler primary melts from a carbonated peridotite and Na carbonatite chloride compositions with low emplacement temperatures (<800°C) (18). The models that advocate primary kimberlite magmas similar to carbonatites suggest that kimberlitic melts are similar to the high-Mg saline, carbonatic micro-inclusions in diamonds (18, 19). However, the micro-inclusions show higher contents of alkalis, even when compared to the most alkaline kimberlite, Udachnaya-East (18), and highly saline fluids may play only a restricted role in shaping the source of many kimberlites. The Udachnaya-East kimberlite is also globally prominent because of its abundant chlorite phases and may have been formed from an unusual chloride-rich source (18). In addition to fluid inclusions, diamonds contain mineral inclusions, with compositions indicative of the rock type in which they formed (7, 9). These include olivine, chromite, orthopyroxene, clinopyroxene, and garnet sourced from mantle peridotites, as well as omphacite, a characteristic phase of eclogite, which results from basalt or gabbro being metamorphosed at high pressures (20).

In this study, we conducted two types of experiments: a melting experiment on marine sediments and reaction experiments using a two-layer arrangement in which marine sediment and a geochemically depleted peridotite (dunite) were loaded as distinct blocks in single experimental capsules. Experiments were conducted at 3 to 6 GPa and 800° to 1100°C, corresponding to a depth of 100 to 200 km in the mantle (table S1). Generally, subducted crustal rocks have solidus temperatures as low as 675°C, which depend on pressure and particularly on volatile contents (21–23). The experiments were all conducted above the solidus of the marine sedimentary rock, while the experiment at 3 GPa/800°C is close to the solidus, as indicated by the small melt fraction of ~10% (fig. S1). In subduction zones, slab-surface temperatures vary strongly with age, speed, and angle of subduction (24). Hence, the deep subduction of sediments to cratonic mantle depths is most probable in the case of an old cold slab. Because substantial element transport from subducted sediments to the mantle wedge only occurs above the solidus (22), sediment subduction to the deep mantle is feasible in a cold slab. The experiments presented here trace this scenario, simulating the reaction of sediments that melt only after rapid subduction to a depth of >100 km.

RESULTS
Here, we present the results of an experimental study that simulates the reaction of subducted marine sediments with mantle peridotite at pressures corresponding to the mid-cratic to lower cratonic lithosphere. The results shed light on the origin of exotic diamond fluid compositions. All reaction experiments resulted in a reaction zone situated between the two rock types, whereby the former sediment layer that recrystallized to garnet and clinopyroxene (Fig. 1, A and B); these reaction zones contain Na-K chlorides in experiments at pressures...
at and above 4 GPa (Fig. 1, A, C, and D, and figs. S1 to S4). Most of the analyzed chlorides contain 5 to 15 weight % (wt %) Na and 30 to 45 wt % K, with K/Na ratios between 2:1 and 9:1 (by mass; Fig. 2). In contrast, all reaction experiments at 3 GPa and the higher temperature experiment at 4 GPa/1100°C, as well as the sediment melting experiment at 4 GPa/1000°C, are devoid of chlorides. In these experiments, potassium and sodium are contained in phengite, Mg-rich mica (phlogopite), and melt (Fig. 1, B, E, and F). The melts are silica rich (>55 wt % SiO2), containing 0.2 to 0.4 wt % chlorine and exhibiting K/Na ratios of 3:1 to 7:1. However, melt and mica do not account for all chlorine in the starting sediment composition, just as the low abundance of Na-K chlorides of ~0.5% does not contain all Na and K in mica- and melt-free experiments. Mass balance calculations show that the experiments contain a Cl, F–enriched fluid phase depleted in K at <4 GPa and >1000°C, whereas fluids in equilibrium with Na-K chlorides are Cl, F–depleted and enriched in Na and K (Supplementary Materials). Light element analysis of the sedimentary starting material shows C, H, and N mass fractions of 8.2 ± 0.1, 1.8 ± 0.2, and 0.35 ± 0.01 wt %, respectively, which are sourced from carbonate, clay minerals, and organic material. The loss on ignition of 15.3 wt % gives an oxygen mass fraction of ~6.9 wt % by subtracting carbon, hydrogen, and nitrogen and addition of oxygen from SO3 and Fe2O3 reduction (table S2). The breakdown of carbonate, clay, and organic material would thus produce a mixed H2O ± H2 ± CO2 ± CO ± CH4 fluid, the speciation of which depends strongly on pressure, temperature, and oxygen fugacity. Given carbon saturation, the decomposition of the sediment follows the reaction: CH4 + H2O = 3 H2 + CO (25). Because equilibrium constants are undetermined for the experimental pressure range, the measured mass fractions of 8.2 wt % C, 1.8 wt % H, and 6.9 wt % O will fall within a range for each species at the beginning of the reaction: 4.0 to 5.3 wt % CH4, 9.7 to 12.0 wt % CO, 0 to 1.5 wt % H2O, 0 to 0.5 wt % H2. Because of the graphite inner capsule, which provides excess C, the C species change during the experiments. The graphite inner capsule also buffers the oxygen fugacity at C-CO2, and the equilibrium 2 CO = C + CO2 leads to CO2 formation at all relevant thermobaric conditions (26). At T < 1000°C, CO2 reacts with olivine to form magnesite and orthopyroxene: Mg2SiO4 + CO2 = MgCO3 + MgSiO3.

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Fig. 1. Backscattered electron images of experimental charges. Locations of images (A) to (D) from sediment-peridotite reaction experiments are schematically shown in capsule on the left. (A, C, and D) Reaction experiments at 5 GPa/1000°C with superimposed energy-dispersive x-ray maps of chlorine [green in (C) and (D)]. The sediment half of two-layer experiments recrystallized to garnet and clinopyroxene (Cpx), whereas orthopyroxene (Opx), magnesite (Mgs), and Na-K chlorides formed at the leading edge of the reaction zone against the peridotite. (B) Peridotite layer in the reaction experiment at 3 GPa/900°C contained phlogopite (Phl) behind the magnesite + orthopyroxene zone, and Na-K chlorides were absent. (E and F) Sediment melting experiment (no peridotite included) at 4 GPa/1000°C showing silicate melt (E) in equilibrium with garnet (Gt), coesite (Coe), and Mg calcite (Mg-Cc) shown in (F). Scale bars, 100 µm (A and B) and 20 µm (C to F).

Fig. 2. K/Na ratios of experimental chlorides and saline micro-inclusions in diamonds. Most saline micro-inclusions (orange diamonds) (2, 7, 30) have a K/Na ratio between 1:1 and 9:1, similar to the ratios found in the experimental Na-K chlorides of this study (gray diamonds). Full analyses of chlorides are given in tables S9 to S12.
which is in accordance with the presence of <7 wt % magnesite in the reaction zones (fig. S1).

Besides magnesite, the reaction zone in all experiments at <1100°C is also enriched in clinopyroxene (Fig. 1, A and B). These clinopyroxenes exhibit a gradual change in composition from high Na$_2$O (~5 wt %) and Al$_2$O$_3$ (~10 wt %) in the former sedimentary rock to low Na$_2$O (~0.6 wt %) and Al$_2$O$_3$ (~3 wt %) in the peridotite (fig. S5A). Micas also fall into two groups based on their Al and Ti contents: Those from experiments at 1000° to 1100°C contain 13 to 16 wt % Al$_2$O$_3$ and 1 to 2 wt % TiO$_2$, whereas in experiments at lower temperatures they contain lower Al$_2$O$_3$ (8 to 13 wt %) and TiO$_2$ (0.5 to 1 wt %) (fig. S5B).

**DISCUSSION**

If the fluids found as micro-inclusions in diamond ultimately originated from seawater in subducting sediments, then a process that very efficiently fractionates Na$^+$ from K$^+$ is required to explain their high K/Na ratios of 1:1 to 9:1. Weiss et al. (2) postulated that Na$^+$ is consumed during low-temperature alteration of seafloor basalts and that K/Na is increased further by the formation of Cl$^-$-rich phengite. Our experimental results show that the fractionation of Na$^+$ from K$^+$ can also occur at high pressures in liquids that originate from the reaction between subducted marine sediments and peridotite; this is in accordance with previous results that show a gradual increase of K/Na in fluids and melts with pressure and temperature (22). The Na-K chlorides formed only in reaction experiments conducted at 4 to 6 GPa and <1100°C, giving way to Cl-bearing mica and silicate melt at lower pressure and higher temperature (Fig. 3). The restriction of chlorides to the reaction experiments (they do not occur in the melting experiment on the sedimentary rocks) shows that these phases are only stable in an ultramafic, high-pressure environment (fig. S1). The euhedral appearance of cubic chloride crystals is indicative of equilibrium growth from highly saline fluids rather than forming as a quench phase (Fig. 1D), which would result in a mix of interlocking crystals at random angles, as seen in many high-pressure experiments (14). While the capsule setup in this study does not allow for direct measurement of the fluid composition, the mass balance calculation estimates K/Na of the fluid to be 4.5 ± 3.6 (Supplementary Materials), which is within the average K/Na of 7.3 ± 5.9 of the Na-K chlorides. The fluid has to be enriched in K because Na is sequestered in abundant, coexisting Na-rich clinopyroxene and K is absent in any other phase than the Na-K chlorides in the reaction experiments at 4 to 6 GPa (fig. S1). Because the Na-K chlorides only account for ~20% of the total mass fraction of K in the experiments, a K/Na-rich fluid has to be present during the crystallization of the chlorides. It also has to be emphasized that all chloride-bearing experiments are devoid of any hydrous phase. It is thus likely that the process of chloride formation is restricted to a reducing environment and a shift in fluid species, which consumes H$_2$O following the reactions: CH$_4$ + H$_2$O = 3 H$_2$ + CO and 2 CO = C + CO$_2$. The reaction also produces C, because the removal of CO$_2$ shifts the equilibrium on the product side of the second equation. The coexistence of elemental C with CO$_2$ and magnesite has been previously observed in diamond inclusions (27). Thus, the sequestration of CO$_2$ in magnesite is related to the consumption of CH$_4$ + H$_2$O until H$_2$O is exhausted. Hence, Na-K chlorides form by precipitation from an oversaturated solution: Na/K$^+$aq + Cl$^-$aq = (Na,K)Cl.

The crystallization of Na-K chlorides is induced by the reducing conditions in the inner graphite capsule, and any experimental buffer material at fO$_2$ (oxygen fugacity) equal to or below CCO will lead to chloride formation. In contrast, at any fO$_2$ above CCO, H$_2$O will not be exhausted and Na, K, and Cl stay in solution to form the known highly saline fluids. Given the low fO$_2$ that is needed for chloride precipitation, magnesite and H$_2$ may be expected to react: MgCO$_3$ + H$_2$ = Mg(OH)$_2$ + CO. However, the process of carbonate reduction is known to be kinetically slow, especially at high pressure (28, 29). Because the dehydration of the fluid is only observed in reaction experiments at >3 GPa, the sequence leading to chloride precipitation has to be as follows: (i) melting of the sediment and reaction with dunite; (ii) total consumption of the melt phase by anhydrous phases (garnet and pyroxene) as evident from mass balance calculations (figs. S1 and S2), which drives all H$_2$O into a fluid phase; and (iii) dehydration of the fluid by reaction of H$_2$O to H$_2$ and precipitation of chloride from a fluid saturated in K, Na, and Cl. If fO$_2$ is above CCO, then Na-K chlorides will not precipitate but instead will be dissolved in highly saline hydrous fluids. The absence of hydrous crystalline phases such as mica in all chloride-bearing metasomes (brown) is in accordance with the presence of <7 wt % magnesite in the reaction zones (fig. S1).

The K/Na ratios of the chlorides (1:2 to 9:1) largely overlap with those of saline fluids included in diamonds (1:1 to 9:1; Fig. 2). The Cl/(Na + K) of Na-K chlorides give 1.03 ± 0.44, which is comparable to the values of 1.05 ± 0.36 measured for saline fluids. However, the fluid micro-inclusions in diamond show lower total mass fractions of Na$^+$ and K$^+$ (2, 7, 30), and thus may represent diluted equivalents of the chlorides (i.e., they are closer to the origin in Fig. 2). Silicate melts in experiments at 3 GPa attain K/Na ratios of 3:1 to 7:1, indicating that the process of Na separation and K enrichment in the melt is equal to the processes that lead to high K/Na chlorides. All reaction experiments...
contain clinopyroxene, which shows an increase in Na and Al across
the reaction zone from the peridotite toward the sediment (fig. S5A).
We argue that the enrichment of K/Na in melts and chlorides is caused
by the contemporaneous crystallization of Na-Al–rich clinopyroxene
in the former sedimentary rock, transforming it to a Na-enriched
residue with low K/Na ratios. Similar clinopyroxenes rich in Na and
Al are found in natural mantle xenoliths that occur in kimberlites
such as Udachnaya-East (31). These sodic, aluminous clinopyroxenes
are of metasomatic origin and are geochemically distinct from pe-
didotite clinopyroxenes (fig. S5A). In the 3-GPa experiments, clinopy-
roxene coexists with mica, which is also comparable to mica found
in the metasomatic Udachnaya-East xenoliths (fig. S5B) (31).

The formation of Mg carbonates, and of chlorides with high K/Na,
demonstrates that the reaction between sediment and peridotite
may cause a type of mantle metasomatism that is vital for the forma-
tion of some diamonds. The compositions of saline micro-inclusions
in diamonds are distributed between four end-members: a Na-K chloride-
richened composition, low- and high-Mg carbonaticitic, and silicic
compositions (Fig. 4). Weiss et al. (2) interpret this suite to repres-
ent mixing of highly saline fluids from the subducting slab with
carbonated peridotite and eclogite. From our experimental obser-
vations, we argue that the carbonate is also derived from the sedi-
ment and forms by the reaction of CO2-bearing saline fluids with
mantle peridotite. This process consumes CO2, which is incorpo-
rated into Mg carbonate (magnesite) that grows at the expense of
olivine at the reaction front (Fig. 1, A and B). Because magnesite is the
only observed carbonate phase within the peridotite, the metasoma-
tically overprinted mantle would preferentially produce high-Mg
carbonatitic melt if remelted at a later stage. In a natural setting, dia-
monds would grow during the reaction that produces the magnesite
and enclose fluids from various stages of this interaction. If “most
diamonds were created equal” (4), then it would follow that the re-
action between sedimentary rocks and peridotite during subduction
is a main mechanism for the formation of lithospheric diamonds and
mantle carbonates.

The high mobility of saline fluids provides an effective mecha-
nism to metasomatize the cratonic lithosphere. Na-K chlorides and
carbonates are widely distributed in the reaction zone and the pe-
didotite in the experiments, whereas the growth of mica in halide-free
experiments is restricted to the reaction zone (Fig. 1B). This demon-
strates that Na-K chlorides and carbonates crystallized from highly
mobile fluids. Our experimental delineation of alkali chloride sta-
bility restricts this to depths greater than approximately 120 km,
spreading to shallower depths where temperatures are lowest. Fluo-
rids that move far from their source are strongly depleted in all
major elements except for the highly fluid-soluble alkalis and mag-
nesium, because only magnesite and chlorides are observed within
the peridotite layer (Fig. 1, A, C, and D). This means that radiogenic
isotope and geochemical signatures of the sediment probably
remain sequestered in clinopyroxene in the reaction zone. Hence,
if Sr and Eu are mostly retained in clinopyroxene, then the fluid
that progresses into the peridotite should have gradually flatter
positive Sr and Eu anomalies as well as evolving to lower 87Sr/86Sr
ratios (2).

Fig. 4. Ternary diagram of experimental phase compositions compared to diamond inclusions. Composition of saline and silicic diamond micro-inclusions (orange
diamonds) (2, 7, 9, 30) and omphacite mineral inclusions in diamonds (red circles) (2) compared to clinopyroxenes (light gray diamonds), orthopyroxenes (pink triangles),
olivines (green diamonds), magnesite (olive diamonds), and Na-K chlorides (gray triangles) from this study. The “carbonated peridotite” field represents various mixtures
of Mg carbonate (magnesite) and silicates. Saline micro-inclusions are mixtures between the Na-K chloride and carbonated peridotite (green arrow). The source for proto-
kimberlitic melts of Udachnaya-East (black squares) (40) is enriched in Na and K relative to carbonated peridotite and trends toward bulk kimberlite composition (pink
stars) (44) by assimilating pyroxenes, as indicated by the pink arrow.
The change of style of metasomatic overprinting in the depleted peridotite from highly saline fluids and chlorides at ≥4 GPa to melt infiltration and mica formation below 4 GPa has further consequences for the cratonic mantle: Fluids that rise to mantle levels shallower than the stability of Na-K chlorides will stall and crystallize mica, as evident from reaction experiments at 3 GPa (Fig. 3). The depth at which these highly saline fluids stall is characteristic for the seismic mid-lithosphere discontinuity, a zone of low seismic velocities that is widespread in the continental lithospheric mantle, and is found intermittently beneath all continents at a depth of 80 to 100 km. The mid-lithosphere discontinuity has been suggested to be related to the occurrence of hydrous assemblages (32, 33), which is consistent with the formation of mica in our experiments.

Kimberlite magmas are generally considered to originate from partial melting of a carbonated peridotite source (34, 35). The occurrence of Na-rich mineral and fluid inclusions in olivine phenocrysts in kimberlites (36–38) is consistent with the presence of primary Na-Ca carbonate melts. The loss of sodium is thought to occur after emplacement by rapid weathering of the kimberlite matrix (18, 39). The Udachnaya-East kimberlite is a very fresh chlorine-rich kimberlite that has been used to propose that Cl-rich carbonate may be a common protokimberlitic composition (18, 39). Our experimental observation of Na-K chlorides coexisting with carbonate in the reaction zone between sedimentary rock and peridotite may thus be directly relevant for the source of some kimberlites. Melting experiments on chloride-rich Udachnaya-East kimberlites (40) at 4.5 to 6.5 GPa/1000°C to 1100°C within the carbonated peridotite stability field have produced melts close to the composition of diamond micro-inclusions of high-Mg carbonatitic composition (Fig. 4) (19). Hence, our experiments provide evidence that the reaction between sediment-derived melts and mantle peridotite at >120 km can produce the same fluids that are trapped in diamonds. These fluids precipitate chlorides as a direct result of migrating into the strongly reduced environment of the lower cratonic mantle, producing sources that may later melt to form exotic chloride-bearing alkaline kimberlites such as those found at Udachnaya-East.

**MATERIALS AND METHODS**

The sediment sample used as a starting material in the experiments was acquired from the International Ocean Discovery Project (ODP 161-976 B 18 X3 105-106.5) and is a carbonate-bearing (<10%) siliciclastic marine sediment (table S1) similar to global subducting sediment composition (41) but with higher contents of carbonate. For the depleted peridotite, we used a clinopyroxene-bearing dunite (sample ZD11–53) containing olivine (>97%), spinel (~2%), and clinopyroxene (<1%) from the Zedang ophiolite (south Tibet, China), which occurs as a lens-shaped body within harzburgite (table S2). The dunite was chosen because it represents the most depleted end-member of peridotites that are present within the lithospheric mantle. Furthermore, all metasomatic phases that grow during the experiment are easy to recognize and cannot be confused with phases that are already present in less depleted peridotite. Both samples were ground to powders in an agate mortar. Experiments were carried out using a piston cylinder apparatus at the University of Mainz at 3 GPa and a belt apparatus at Goethe Universität Frankfurt at 4 to 6 GPa. Sediment and peridotite powders were placed as separate layers in an inner carbon capsule, which controls P02 via the C + CO equilibrium. The inner carbon capsule was sealed in an outer platinum capsule. For the piston cylinder experiments, the experimental assembly consisted of a pressure cell made of Al2O3 spacers, a graphite furnace, B-type thermocouple, and a CaF2 spacer outside the capsule. For belt apparatus experiments, most of the materials were similar to piston-cylinder experiments, but the spacer and capsule holder consisted of natural polycrystalline calcium fluoride. All cell assemblies were first pressurized and subsequently heated at a rate of 50°C/min. Thermobaric conditions were kept constant for 2 to 14 days. At the end of each experiment, charges were quenched by switching off the heating. Quench times to temperatures below 500°C were approximately 6 s for the piston-cylinder runs and 8 s for the belt runs. Major element compositions of phases in experimental run products were acquired using a JEOL JXA 8200 SuperProbe electron-probe microanalyzer equipped with five wavelength dispersive spectrometers at the University of Mainz, Germany. Micas, silicates, and glasses were analyzed with an accelerating voltage of 15 kV and a beam current of 12 nA. Peak counting times were 20 to 30 s for melts and minerals. The beam diameter was set to 2 µm. Element maps and semiquantitative energy-dispersive x-ray analysis were performed using a nanoScience Instruments Phenom XL benchtop electron microscope. Three aliquots of the sediment were analyzed for H, C, and N in an automated vario EL cube elemental analyzer (Elementar, Langenselbold, Germany) using the method described by Le Huong et al. (42). Analyses of SDO-1 (U.S. Geological Survey reference material—shale) yielded H = 1.57 ± 0.14 wt %, C = 9.11 ± 0.01 wt %, and N = 0.36 ± 0.01 wt %, within error of the GeoReM (http://georem.mpch-mainz.gwdg.de/) (43) compiled values for H and C (H = 1.34 wt %; C = 9.95 wt %).

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/5/eaau2620/DC1

**Fig. S1.** Modal proportions of phases in the reaction experiments and the melting experiment.

**Fig. S2.** K/Na and Cl/F in mica, melt, fluid, and solid halide phases (chlorides + fluorides).

**Fig. S3.** Chloride map of 5 GPa/1000°C experiment.

**Fig. S4.** Backscattered electron image of the 6 GPa/1100°C experiment showing an unpolished capsule half.

**Fig. S5.** Composition of silicate phases in reaction experiments.

**Table S1.** Phase relations of experiments.

**Table S2.** Starting materials.

**Table S3.** Reaction experiment (3 GPa/800°C).

**Table S4.** Reaction experiment (3 GPa/850°C).

**Table S5.** Reaction experiment (3 GPa/900°C).

**Table S6.** Reaction experiment (3 GPa/1000°C).

**Table S7.** Reaction experiment (4 GPa/900°C).

**Table S8.** Sediment melting (4 GPa/1000°C).

**Table S9.** Reaction experiment (4 GPa/1000°C).

**Table S10.** Reaction experiment (4 GPa/1100°C).

**Table S11.** Reaction experiment (5 GPa/1000°C).

**Table S12.** Reaction experiment (6 GPa/1100°C).

**Table S13.** Reaction experiment (6 GPa/1000°C).

**Table S14.** Mass balance of 3 GPa/800°C reaction experiment.

**Table S15.** Mass balance of 3 GPa/850°C reaction experiment.

**Table S16.** Mass balance of 3 GPa/900°C reaction experiment.

**Table S17.** Mass balance of 3 GPa/1000°C reaction experiment.

**Table S18.** Mass balance of 4 GPa/1100°C reaction experiment.

**Reference (45)**

**REFERENCES AND NOTES**

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ACKNOWLEDGMENTS: We acknowledge the Macquarie University Faculty of Science and Engineering Microscope Facility (MQOSE MF) for access to its instrumentation and support from its staff. We thank T. Kautz (Goethe-Universität Frankfurt) for assistance with beamline experiments. We acknowledge D. Jacob and B. Griffin for proofreading this manuscript. We also thank O. Navon and Y. Weiss for reviewing and improving the final version of this paper. This is contribution 1331 from the ARC Centre of Excellence for Core to Crust Function of the Earth’s Lithosphere (C2CE). The work was supported by the Australian Research Council (DP150100437) and by grants from the Swedish Research Council (grant 621-2016-0059) and the European Research Council (grant 715662 to A.D.B.). We thank O. Jablonsky for discussions and comments on the manuscript.

Funding: The work was supported by the Australian Research Council (DP150100437) and by grants from the Swedish Research Council (grant 621-2016-0059) and the European Research Council (grant 715662 to A.D.B.). We thank O. Jablonsky for discussions and comments on the manuscript.

Citation: Förster, W., S. F. Foley, H. R. Marschall, O. Alard, S. Buhre, Melting experiments of kimberlites in the deep mantle: High pressure contents in mantle melts. Science, 364, 939–942 (2019).
Supplementary Materials for

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Michael W. Förster*, Stephen F. Foley, Horst R. Marschall, Olivier Alard, Stephan Buhre

*Corresponding author. Email: michael.forster@mq.edu.au

Published 29 May 2019, *Sci. Adv.* 5, eaau2620 (2019)

DOI: 10.1126/sciadv.aau2620

The PDF file includes:

- Fig. S1. Modal proportions of phases in the reaction experiments and the melting experiment.
- Fig. S2. K/Na and Cl/F in mica, melt, fluid, and solid halide phases (chlorides + fluorides).
- Fig. S3. Chloride map of 5 GPa/1000°C experiment.
- Fig. S4. Backscattered electron image of the 6 GPa/1100°C experiment showing an unpolished capsule half.
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Other Supplementary Material for this manuscript includes the following:

(available at advances.sciencemag.org/cgi/content/full/5/5/eaau2620/DC1)

- Table S2 (Microsoft Excel Format). Starting materials.
- Table S3 (Microsoft Excel Format). Reaction experiment (3 GPa/800°C).
- Table S4 (Microsoft Excel Format). Reaction experiment (3 GPa/850°C).
- Table S5 (Microsoft Excel Format). Reaction experiment (3 GPa/900°C).
- Table S6 (Microsoft Excel Format). Reaction experiment (3 GPa/1000°C).
- Table S7 (Microsoft Excel Format). Reaction experiment (4 GPa/900°C).
- Table S8 (Microsoft Excel Format). Sediment melting (4 GPa/1000°C).
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- Table S10 (Microsoft Excel Format). Reaction experiment (4 GPa/1100°C).
- Table S11 (Microsoft Excel Format). Reaction experiment (5 GPa/1000°C).
- Table S12 (Microsoft Excel Format). Reaction experiment (6 GPa/1100°C).
- Table S13 (Microsoft Excel Format). Mass balance of 3 GPa/800°C reaction experiment.
- Table S14 (Microsoft Excel Format). Mass balance of 3 GPa/850°C reaction experiment.
- Table S15 (Microsoft Excel Format). Mass balance of 3 GPa/1000°C reaction experiment.
Table S16 (Microsoft Excel Format). Mass balance of 4 GPa/1100°C reaction experiment.
Table S17 (Microsoft Excel Format). Mass balance of 4 GPa/1000°C sediment melting experiment.
Table S18 (Microsoft Excel Format). Mass balance of 5 GPa/1000°C reaction experiment.
Supplementary Materials

Mass balance calculations

To determine the modal phase proportions, the bulk composition of the contents of the experimental capsule has to correspond to the equations:

Sediment + Dunite = Mineral(s) + (Melt), for the reaction experiments, and

Sediment = Mineral(s) + Melt for the melting experiment.

Here, "sediment" and "dunite" refer to the amounts that are involved in the reaction, as opposed to the amounts originally included in the capsule at the start of the experiments. Since the composition of the fluid phase cannot be determined in our experiments, it is not part of the equation. However, we can estimate the fluid composition by subtracting the modal proportions of the measured phases from the bulk composition. The mass balance calculation is iterative; the left side of the equation has to match the proportions of the phases on the right side of the equation. With increase in pressure and temperature, the sediment increasingly reacts with dunite to a maximum where 50% sediment reacts with 50% dunite (fig. S1; tables S13 to S18). The proportion of dunite involved in the reaction on the educt side of the equation is determined by the composition of the product: a high proportion of reacted dunite leads to low mass fractions of oxides such as CaO and Al₂O₃ (which are absent in the dunite) but greatly increased MgO within the reacted products strongly increases. The least-squares best fit of the mass balance calculation is taken to correspond to the best solution for the amount of sediment and dunite involved in the reaction. The increase of the proportion of dunite involved in the reaction, and thus addition of more MgO from the dunite to the sediment layer, leads to a high modal proportion of garnet and pyroxene at the expense of melt and mica. This is clearly seen when the sediment melting experiment is compared
with the reaction experiments: without the addition of MgO from the dunite, the sediment melting experiment lacks pyroxene and shows a higher melt fraction.

The chloride-bearing experiments show the highest contents of garnet (25%) and pyroxenes (47% Opx, 17% Cpx) and are distinguished from chloride-free experiments by the absence of hydrous phases such as melt and mica. In contrast, the sediment melting experiment is devoid of chlorides and pyroxenes and contains the highest mass fraction of melt (65%). The main difference between this and the reaction experiment is its low MgO (1.5% in the melt), which inhibits the crystallization of pyroxene and therefore the melt is not consumed, but remains as the most abundant phase. The correlation of oxide species (+Cl, F) on both sides of the equation gives the coefficient of determination ($R^2$). All mass balance calculations (table S13-S18) achieve an $R^2$ of >0.99 and each oxide species of the balanced reaction phases resembles that of the starting condition within ~15% deviation except for Na$_2$O, K$_2$O, Cl, and F, which are interpreted to be accommodated in a fluid phase, and FeO (which could have been lost to the metal outer capsule during the experiment). While the fluid contains other elements, they cannot be confidently estimated since the mass balanced compositions are within <15% deviation from the starting composition. The resulting calculated fluid phase for experiments containing mica and melt shows high Cl/F and low K/Na which respectively increase and decrease with increasing pressure and temperature. This contrasts with chloride-bearing experiments, which contain fluids with high K/Na, while Cl and F are depleted (fig. S2).
Fig. S1. Modal proportions of phases in the reaction experiments and the melting experiment. From 3-5 GPa and 800-1100°C, the sedimentary rock reacts with an increasing amount of peridotite (3 GPa: 800°C – 15 %, 850°C – 25 %, 1000°C – 30 %; 4 GPa/1100°C – 40 %; 5 GPa/1000°C – 50 %) which leads to an increase in modal pyroxene and garnet in place of mica and melt. The sediment melting experiment contains the highest melt fraction and is devoid of phases such as pyroxenes that are characteristic for the reaction experiments. Unlike the reaction experiments it did not contain peridotite and therefore remains depleted in MgO, inhibiting pyroxene crystallization.
Fig. S2. K/Na and Cl/F in mica, melt, fluid, and solid halide phases (chlorides + fluorides). The ratio of Cl/F in mica and melt decreases with increasing pressure and temperature, while K/Na increases. In contrast, the fluid shows high Cl/F and low K/Na in the presence of melt and mica, while fluids in chloride-bearing experiments are depleted in halogens and show high K/Na.
Supporting information of preparation and measurement of Na-K chlorides

Here we present additional information that demonstrates the authenticity of Na-K chlorides forming a stable phases at 4-6 GPa:

1. All experiments from 3-6 GPa used the same starting materials and capsule materials. Mount preparation was identical for all samples, which were cut using a Struers low-speed saw with water-free cutting fluid and polished using water-free Struers DP-Suspension A.

2. The unpolished sample (fig. S4) contains Na-K chlorides.

3. Chlorides are distributed interstitially within the crystal assemblage (Fig. 1 C,D, fig. S3,S4) and are accompanied by subsidiary amounts of other halides such as Ca-fluoride (fig. S4).

4. Quantitative EPMA and semi-quantitative EDX measurements and maps show that chlorides crystallized as NaCl-KCl solid solution with K/Na of 1-9 (Fig. 2), which requires a minimum crystallization temperature of T >500 °C at ambient pressure (45). The idiomorphic appearance of Na-K chlorides in this study shows that they crystallized, slowly at high T rather than during quenching after the experiments (Fig. 1, fig. S3, S4).

5. K/Na ratios of Na-K chlorides are similar to those in silicate melts of experiments at 3 GPa. The separation of Na from K thus followed the same mechanism by crystallizing Na-rich clinopyroxene (fig. S5A).

6. Chloride-bearing experiments are devoid of silicate melt and hydrous phases that accommodated K and Cl in reaction and melting experiments at 3 GPa and 4 GPa.
### Table S1. Phase relations of experiments.

| #  | Composition                  | T [°C] | P [GPa] | % Melt | Phases formed by reaction                                      | Duration [d] |
|----|------------------------------|--------|---------|--------|----------------------------------------------------------------|--------------|
| 1  | Sediment                     | 1000   | 4       | ~70    | Gt + Coes + Mg-Cc + Ky + silicate melt                         | 3            |
| 2  | Sediment/Peridotite Reaction | 800    | 3       | ~10    | Phl + Cpx + Opx + Mg-Cc + Gt + silicate melt                   | 6            |
| 3  | Sediment/Peridotite Reaction | 850    | 3       | ~15    | Phl + Mgs + Cpx + Opx + Gt + silicate melt                     | 13           |
| 4  | Sediment/Peridotite Reaction | 900    | 3       | ~20    | Phl + Mgs + Cpx + Opx + Gt + silicate melt                     | 14           |
| 5  | Sediment/Peridotite Reaction | 1000   | 3       | ~40    | Phl + Cpx + Opx + Gt + silicate melt                           | 4            |
| 6  | Sediment/Peridotite Reaction | 900    | 4       | 0      | Cpx + Opx + Mgs + Gt + Na-K chloride                            | 2            |
| 7  | Sediment/Peridotite Reaction | 1000   | 4       | 0      | Cpx + Opx + Mgs + Gt + Na-K chloride                            | 3            |
| 8  | Sediment/Peridotite Reaction | 1100   | 4       | ~25    | Phl + Gt + Opx + silicate melt                                 | 3            |
| 9  | Sediment/Peridotite Reaction | 1000   | 5       | 0      | Cpx + Opx + Mgs + Gt + Na-K chloride                            | 3            |
| 10 | Sediment/Peridotite Reaction | 1100   | 6       | 0      | Cpx + Opx + Mgs + Gt + Na-K chloride                            | 3            |
**Fig. S3. Chloride map of 5 GPa/1000°C experiment.** EDX map of chlorine (green) is superimposed on a backscattered electron image of chlorides (white, bottom right) at the inner carbon capsule wall next to garnet crystals of the reaction zone.
Fig. S4. Backscattered electron image of the 6 GPa/1100°C experiment showing an unpolished capsule half. The image shows the reaction zone with silicate phases (garnet and pyroxene), with the corresponding EDX spectra for Na-K chlorides (bottom) and Ca-fluoride (top).
Fig. S5. Composition of silicate phases in reaction experiments. A) Clinopyroxenes from experiments at 3-6 GPa (grey diamonds) show a transition in Na$_2$O (5 to 0.2 wt%) and Al$_2$O$_3$ (12 to 2 wt%), gradual decreasing across the reaction zone towards the peridotite layer. Mantle xenoliths from the Udachnaya-East pipe contain two types of clinopyroxenes, an Al-rich (low-T) metasomatic and an Al-poor (high-T) peridotite suite (blue diamonds) (31). Omphacite inclusions in diamonds (red circles) (2) are similar to the Na-Al-rich clinopyroxene in the experiments. B) Phlogopites from experiments at 3-4 GPa (grey squares) form a low-temperature group (800-900 °C) with low Ti and Al, and a high-temperature group (1000-1100 °C) with high Ti and Al. Udachnaya-East mantle xenoliths (blue squares) (20) contain phlogopites similar to the low-T group. Full analyses of silicates are found in tables S3-S11.
Melting of sediments in the deep mantle produces saline fluid inclusions in diamonds
Michael W. Förster, Stephen F. Foley, Horst R. Marschall, Olivier Alard and Stephan Buhre

Sci Adv 5 (5), eaau2620.
DOI: 10.1126/sciadv.aau2620

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