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Supplementary Materials for

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

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The PDF file includes:

Other Supplementary Material for this manuscript includes the following:

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

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 Al_2O_3 (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_2O, K_2O, 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).
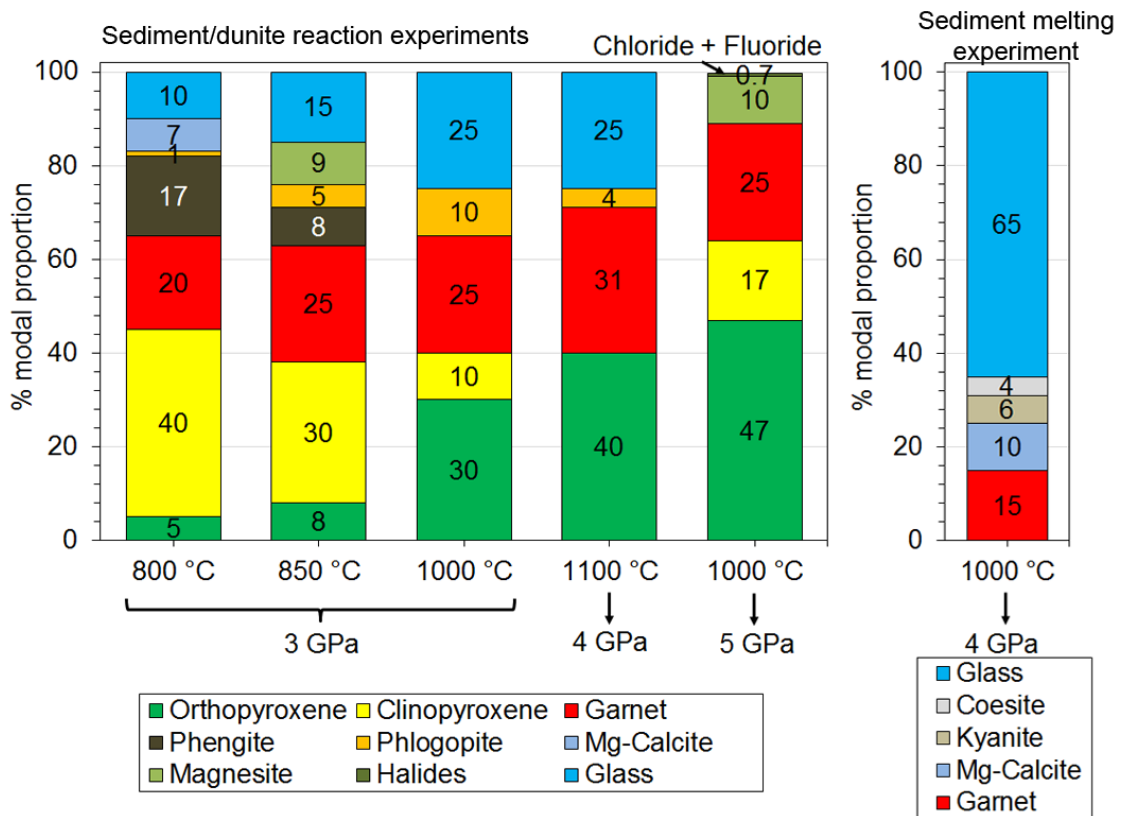
Fig. S1. Modal proportions of phases in the reaction experiments and the melting experiment. From 3-5 GPa and 800-1100°C, the sedimentary rock reacts with an increasing amount of peridotite (3 GPa: 800°C – 15 %, 850°C – 25 %, 1000°C – 30 %; 4 GPa/1100°C – 40 %; 5 GPa/1000°C – 50 %) which leads to an 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.
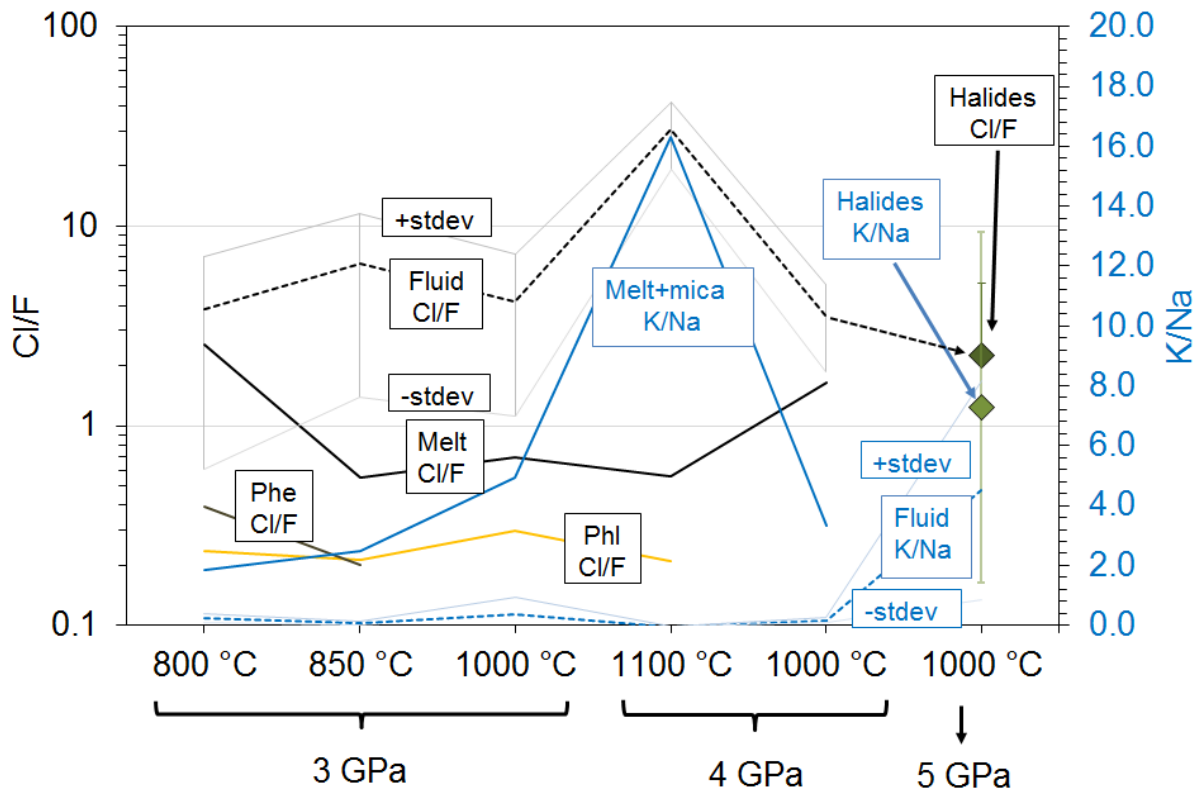
Fig. S2. K/Na and Cl/F in mica, melt, fluid, and solid halide phases (chlorides + fluorides). The ratio of Cl/F in mica and melt decreases with increasing pressure and temperature, while K/Na increases. In contrast, the fluid shows high Cl/F and low K/Na in the presence of melt and mica, while fluids 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
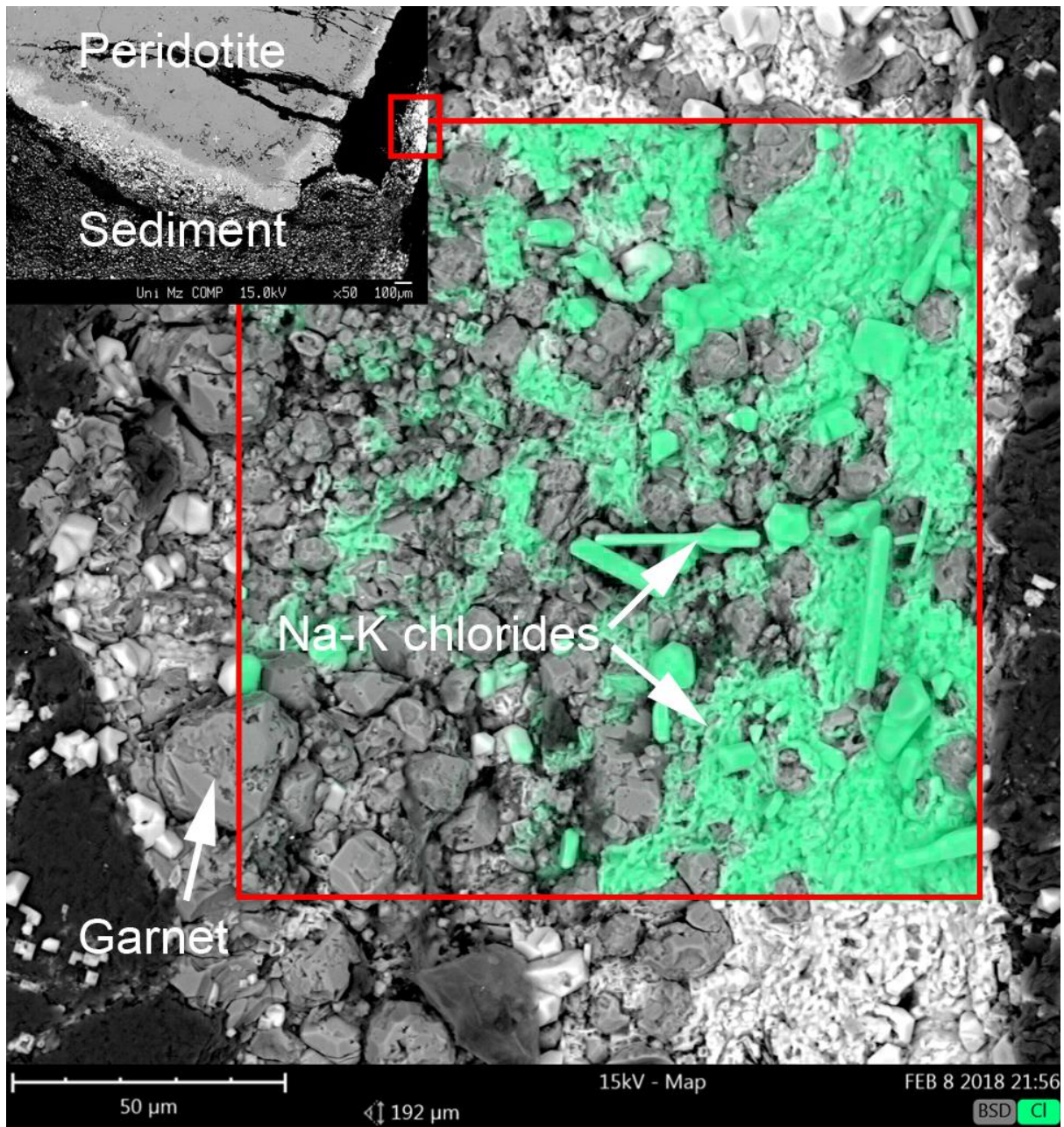
Fig. S3. Chloride map of 5 GPa/1000°C experiment. EDX map of chlorine (green) is superimposed on a backscattered electron image of chlorides (white, bottom right) at the inner carbon capsule wall next to garnet crystals of the reaction zone.
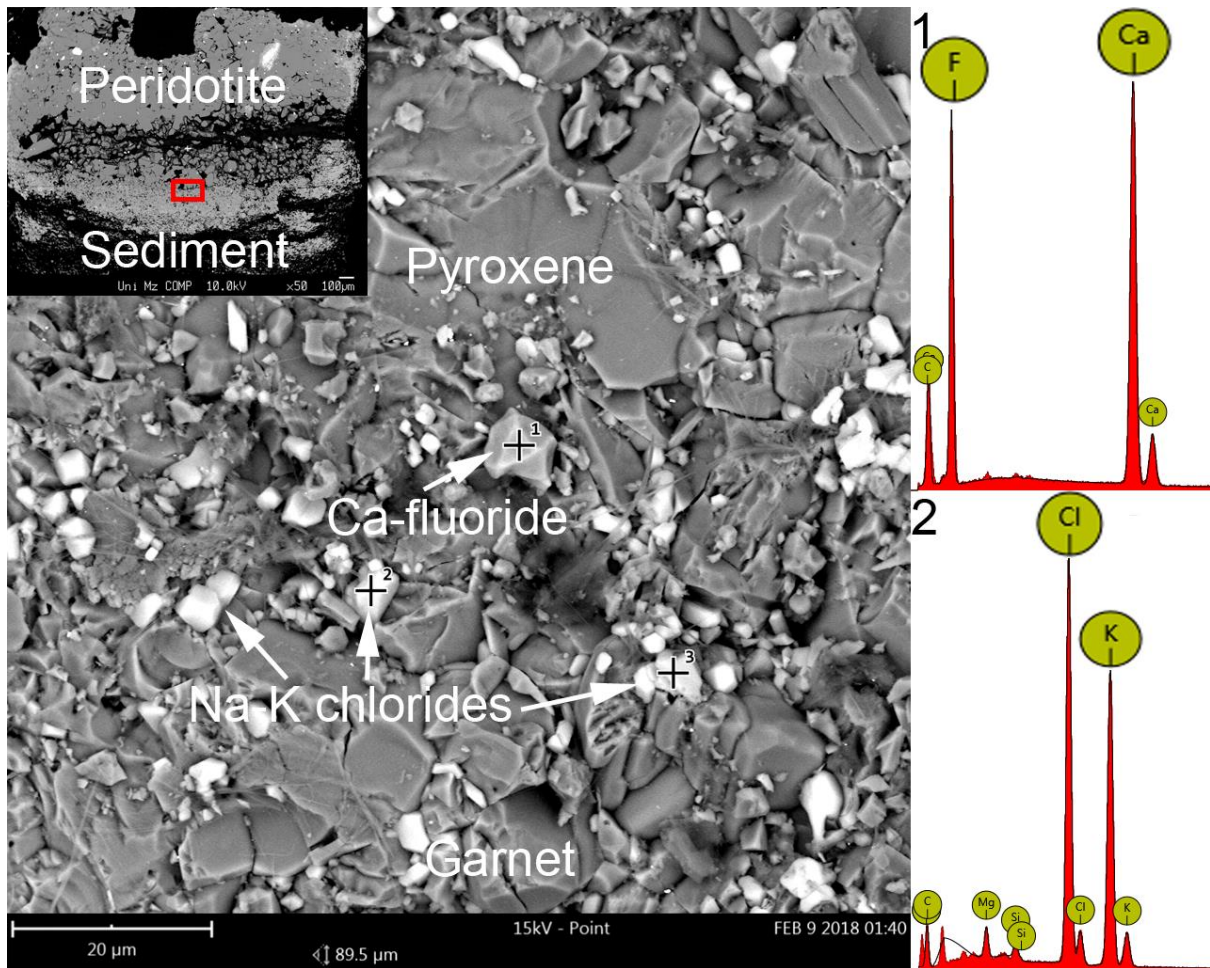
Fig. S4. Backscattered electron image of the 6 GPa/1100°C experiment showing an unpolished capsule half. The image shows the reaction zone with silicate phases (garnet and pyroxene), with the corresponding EDX spectra for Na-K chlorides (bottom) and Ca-fluoride (top).
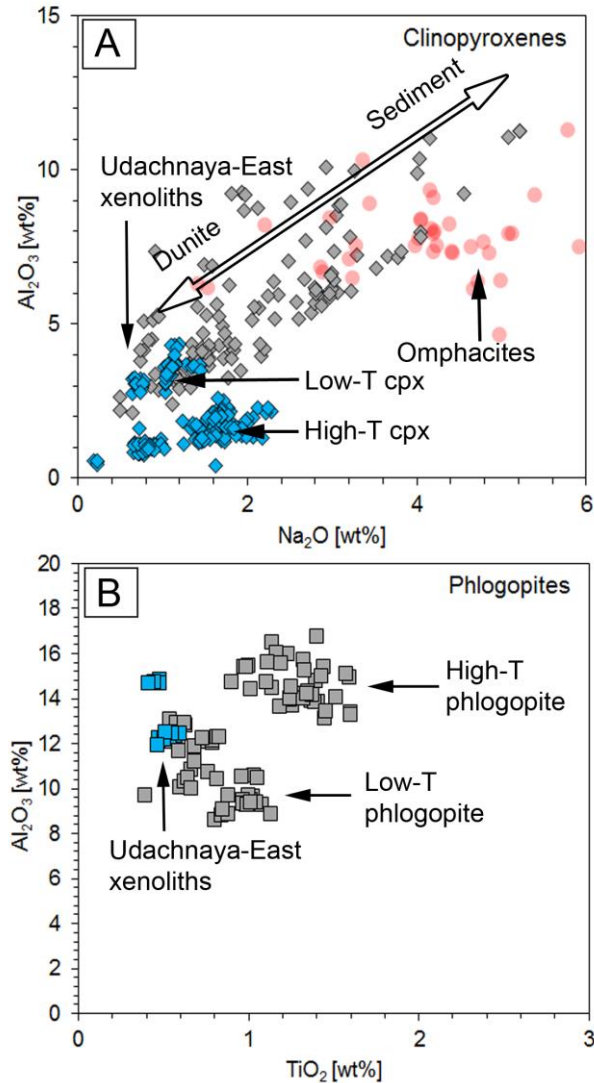
Fig. S5. Composition of silicate phases in reaction experiments. A) Clinopyroxenes from experiments at 3-6 GPa (grey diamonds) show a transition in Na_2O (5 to 0.2 wt%) and Al_2O_3 (12 to 2 wt%), gradual decreasing across the reaction zone towards the peridotite layer. Mantle xenoliths from the Udachnaya-East 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.