From Slab to Mantle: Phengite's Role in Deep Earth Fluorine and Chlorine Delivery

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Subduction zones play a crucial role in the deep Earth cycling of volatiles like fluorine (F) and chlorine (Cl), yet the mechanisms governing their transport to deep mantle remain poorly understood. Here we investigate the high-pressure stability and breakdown behavior of phengite, a major hydrous phase in subducted lithologies, with a focus on its role as a carrier of F and Cl using high-pressure experiments. Experiments were performed at 5-11 GPa and 900-1200°C, using starting materials with average altered oceanic crust containing 0.33 wt.% F and 0.21 wt.% Cl, and 1.2 wt.% water. Results show that phengite remains stable at 850-1050°C and 5 to 11 GPa, coexisting with an assemblage of garnet, clinopyroxene, coesite/stishovite, rutile, and minor amounts of apatite and titanite establishing phengite as the dominant host for both F and Cl under sub-arc conditions. At 11 GPa and 900°C, phengite breaks down into K-hollandite and KMgF₃, accompanying with the Cl release. In warm to hot subduction zone, phengite undergoes dehydration melting between 950 and 1200°C, releasing Cl into the silicate melts, while some F may be retained in residual garnet. In contrast, in cold subduction zones, phengite stability extends to ~10 GPa before transforming into Khollandite and KMgF3 at 11 GPa and 900°C. This transition releases nearly all Cl into a fluid phase, with no melt present. Notably, the presence of F extends phengite's stability. Our results indicate that phengite can effectively transport substantial quantities of F and Cl to depths up to ~330 km (~11 GPa). The breakdown of phengite, either by melting (in warm/hot subduction) or through phase transition (in cold subduction), generates Cl-enriched fluids or silicate melts. These melts/fluids may serve as potential precursors to the halides/saline highdensity fluids (HDFs) observed as inclusions in cratonic diamonds. Furthermore, we estimate global F and Cl subduction fluxes beyond the arc via phengite: ~2.06×10¹²g F/yr and $\sim 4.44 \times 10^{10}$ g Cl/yr in warm subduction zones (up to ~ 330 km), and ~2.20×10¹²g F/yr and ~9.61×10¹⁰g Cl/yr in cold subduction zones (up to ~ 300 km).

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