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Volatiles in subductions zones: reducing the deficit

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Studies of volatile budgets in convergent margins show that more volatiles are subducted than are returned to the surface at volcanic arcs. The deficit, D, expressed as the ratio of annual volatile mass degassed to mass subducted, ranges from <0.1 for S, through $\sim$0.2-0.3 for H_2O, B, N, Cl, to $\sim$0.6 for CO_2. $D<1$ holds for all volatiles even after accounting for mid-ocean ridges, ocean-island basalts, and diffuse degassing on volcano flanks. This deficit has been used to calculate long-term volatile enrichment of the mantle or mediation of Earth's volatile budget by extraterrestrial supply. However, such calculations ignore potential loss to the deep, subvolcanic crust. Hydrologic modeling and experimental data on the solubility of volatile-bearing minerals suggest that an actively metamorphosing suprasubduction-zone crustal column can accommodate sufficient subduction-derived volatiles to erase the "deficit."

Volatiles are liberated from the slab and transported to the mantle wedge by slab devolatilization. Recent experimental results on calcite and anhydrite solubility in H_2O-NaCl fluids demonstrate high solubilities in slab-derived fluids at high P (Caciagli and Manning, 2003; Newton and Manning, 2002, 2005), leading to volatile enrichment of the source region for arc magmas. Significant volatile loss from arc magmas may begin upon ponding at the base of the crust, or upon deep saturation with a multicomponent fluid phase, as suggested by H_2O-CO_2-S-Cl rich melt inclusions in numerous systems. In tectonically active regions, the crustal column is permeable to fluid at all depths (Manning and Ingebritsen, 1999). For example, crustal permeability during metamorphism is sufficient to transport not only fluids produced within the crust, but also the entire deficit in subducted H_2O ($\sim$7x10^{14} g/yr; Ingebritsen and Manning, 2002), assuming delivery by degassing of magma ponded at the base of the crust. This H_2O is only 2% of the total metamorphic fluid flux calculated for global arc crust. Other volatiles may be carried by this fluid or lost to minerals precipitated along its path. The solubility of calcite and anhydrite in $H_2O \pm NaCl$ decrease significantly as fluid moves upward in the crust, leading to precipitation and volatile sequestration in the crust. For example, calcite solubility in H_2O increases by nearly 10^4 times from 1-20 kbar at 600 ˚C (Caciagli and Manning, 2003), yielding a strong potential for CO_2 sequestration in the crust as $CaCO_3$. This simple model is supported by isotopic evidence (O, C, Sr, He) for a volumetrically small but real involvement of mantle-equilibrated fluids in many metamorphic systems. Mediation of the terrestrial volatile budget by a crustal-scale fluid system in arc crust reduces the apparent deficit in volatiles returned from the mantle in subduction zones.

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