Exosphere H_2O/Ce, CO_2/Nb, and CO_2/Ba and Deep Earth Volatile Cycles

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The legacy of Erik Hauri includes innovative analytical and conceptual advances to understanding of mantle volatile reservoirs and to global volatile cycling. One facet of this legacy was application of previously identified and new "canonical" ratios between volatiles and refractory trace elements, which behave similarly during partial melting. Observed differences in such ratios illuminate differentiation processes apart from melting which have established Earth's principal volatile reservoirs. Studies of oceanic basalts suggest variations in these ratios such as H_2O/Ce, CO_2/Ba, and CO_2/Nb that may trace subduction-associated recycling to the deep mantle. Greater variations are seen when these ratios are compared between the mantle and the exosphere, defined as all those reservoirs above the Moho, including the crust, oceans, sediments, hydrosphere, and atmosphere. The H_2O/Ce of the exosphere is 1540±360, much greater than the span seen in oceanic basalts (50-350). This reflects preferential deep subduction of Ce relative to H_2O and/or primordial establishment of the oceans. The CO_2/Ba and CO_2/Nb ratios of the exosphere are 40±14 and 1620±730, which are, respectively, significantly lower than and greater than values typical of oceanic basalts (100±20, 810±220, respectively). Thus, time-averaged deep recycling of C has been intermediate between those of Nb and Ba. But to accumulate all the Ba in the continents without any Ba return to the mantle, >35% of the outgassed C must have returned. Either there was no large surface C reservoir accompanying the earliest oceans, meaning C was somehow retained in the interior during early mantle outgassing, or the return of C to the mantle has been even more efficient than the bracket provided by CO_2/Ba, stemming from an early episode of C burial or from C return through geologic time. Observed H_2O/Ce and CO_2/Ba ratios of oceanic basalts suggest bulk mantle H_2O and C concentrations of 290±80 and 110±40 µg/g, assuming that there are not significant hidden mantle reservoirs. Thus, the mantle contains 0.75±0.2 exospheres ("oceans") of H_2O but 4.2±2 exospheres of C. Unless C was formerly more compatible than H_2O during partial melting, models for deep Earth volatile cycling must acknowledge that C return to the mantle via subduction has been more efficient than deep recycling of H_2O.