Short magma residence times for Kilauea Volcano based on high-precision Pb isotope ratios

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We present new high-precision Pb isotopic analyses of 46 historical Kilauea summit lavas (1823-2008). These data are used here to investigate the architecture of Kilauea's summit magma storage reservoir and the characteristics of the volcano's mantle source region. These lavas exhibit a temporal trend characterized by low $^{206}Pb/^{204}Pb$ ratios in 1823, a gradual increase to a maximum in 1921, an abrupt drop to relatively constant intermediate values from 1923 to 1959, and a rapid decrease to 2008. These variations indicate that Kilauea's summit reservoir is being supplied by rapidly changing parental magma compositions derived from a mantle source that is heterogeneous on a small scale. At least three components are required to explain two distinct mixing arrays on a plot of $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$, where the 19th century lavas have a low $^{206}Pb/^{204}Pb$ at a given $^{208}Pb/^{204}Pb$ compared to the 20th century lavas. Analyses of multiple lavas from several individual eruptions reveal small but significant differences in $^{206}Pb/^{204}Pb$ ratios (~0.01-0.03). For example, the extra-caldera lavas from Aug. 1971 and Jul. 1974 display significantly lower Pb isotope ratios and higher MgO contents (10 wt. %) than the intra-caldera lavas (MgO ~7-8 wt. %) from the same eruption. These distinctions appear to be spatially delineated by the rim of the volcano's summit caldera. From 1971 to 1982, the $^{206}Pb/^{204}Pb$ ratios of the lavas define two separate decreasing temporal trends. Intra-caldera lavas from 1971, 1974, 1975, Apr. 1982 and the lower MgO lavas from Sep. 1982 have consistently higher $^{206}Pb/^{204}Pb$ ratios at a given time (compared to the extra-caldera lavas and the higher MgO lavas from Sep. 1982). Magma residence-time modeling of the high $^{206}Pb/^{204}Pb$ (low MgO) and low $^{206}Pb/^{204}Pb$ (high MgO) trends suggest that the intra- and extra-caldera lavas are being supplied from two distinct magma bodies, each with a volume of ~0.2 km^3. This volume estimate is more precise and much smaller than previous estimates of a single, ~2-3 km^3 magma body based on trace element ratios. Overall, these observations suggest that Kilauea's summit reservoir has a small volume that efficiently transfers the changing compositional signals of the mantle-derived parental magmas.

The calcite–water interface and its interactions with selenium IV and VI

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Due to the reactivity of its surface, calcite may play an important role for the retention of contaminants in soils, lacustrine-, marine- and aquifer environments.

Selenium is on the one hand an important nutrient. On the other hand, if a certain concentration limit is exceeded, it is toxic. The chemical toxicity is highest for the oxidized selenium IV and VI species. These are also the species expected to be the most mobile in soils and aquifers. Selenium-79, is a long lived nuclear fission product formed in nuclear power plants. It is of special concern, as it is expected be able to diffuse through the technical and geological barrier systems around nuclear waste disposals and increase the radiotoxicity of groundwater in adjacent aquifers.

At calcite equilibrium conditions, tetravalent selenium shows only very weak adsorption at the calcite surface. At pH below 9, K_D values are about 0.001. Above pH 9 no adsorption is observed. In situ grazing incidence EXAFS measurements at the calcite(104) face show no contribution to the selenium(IV) spectra that could be assigned to the calcite surface. If the calcite saturation index is increased selenium(IV) starts coprecipitating with calcite. The ordering of the coprecipitated selenite ($Se(IV)O_3^{2-}$) ions corresponding to the orientation of the calcite carbonate ions becomes visible in polarization dependent grazing incidence XANES spectra. Coprecipitation of selenite with calcite is quantified in mixed flow reactor (MFR) experiments at steady state and low supersaturation (SI~0.8) conditions. Homogeneous partition coefficients range from 1 to 10. EXAFS spectra measured on selenite doped calcite from MFR experiments show that selenite is structurally incorporated into calcite onto a slightly distorted carbonate lattice site.

Selenium(VI) shows a slightly stronger adsorption to the calcite surface. Grazing incidence EXAFS spectra, measured in situ at the calcite(104) face, show clear contributions that can be assigned to two Ca^{2+} neighbours from the calcite surface, at about 3.5 Å distance. There are two non-equivalent adsorption sites at the calcite(104) face that could explain this result. The GIXAFS data however, cannot be used to distinguish between the two.

Coprecipitation of selenium(VI) with calcite in MFR experiments was below detection limit.