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$^{238}U/^{235}U$ fractionation in high temperature environments

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^{238}U and ^{235}U, the two long-lived isotopes of uranium, are known to fractionate from each other in a variety of environments. $^{238}U/^{235}U$ fractionations impart measurable signatures that can be used to infer oxidation states and reaction pathways. Most studies have focused on low-temperature environments such as the seafloor, sediments, and ore-forming fluids. However, it has also been proposed that $^{238}U/^{235}U$ measurements could provide information on high-temperature igneous and metamorphic processes, particularly where the average oxidation state of uranium differs between coexisting phases. The present reconnaissance study uses electronic structure models to estimate equilibrium $^{238}U/^{235}U$ fractionations in several silicate, oxide, and hydroxide minerals representing the U(IV), and U(V), and U(VI) oxidation states. Zircon substituted with either U(IV) or U(V) is also modeled for comparison. Subtle, but potentially measurable $^{238}U/^{235}U$ fractionation of up to ~0.5‰ at 1000K is predicted between the studied phases. Estimated fractionations are mainly controlled by the oxidation state of uranium in each phase, with $^{238}U/^{235}U$ systematically higher in U(IV) species, whereas U(V) and U(VI) species are roughly similar to each other. Uranyl-type U(VI) species with a well-defined UO_2^{2+} structural unit are predicted to have slightly higher $^{238}U/^{235}U$ than uranate-type U(VI) species lacking short U-O bonds (~0.1‰ at 1000 K). The nuclear field shift is the dominant driver of equilibrium fractionation at high temperatures, typically with a small opposing mass-dependent component of fractionation. The dominance of nuclear field shift fractionation increases at higher igneous temperatures, even as overall fractionations become weaker. The results suggest that useful $^{238}U/^{235}U$ signatures are most likely to be found when coexisting phases have distinct average oxidation states of uranium, for example U(IV) in titanite vs. U(V) in zircon or melt.