Evaporation-induced 'anomalous' isotope fractionation factors do not require high gas pressures

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Evaporation induced isotope fractionation factors of various elements (Mg, Si, O, K, Cd, Hg etc..) are commonly scaled using an ad-hoc mixture of equilibrium and kinetic fractionations. In this case, the contribution of an equilibrium fraction is possible owing to high gas pressure that allows some sort of isotope re-equilibration.

This hypothesis predicts that evaporation experiments performed under vacuum should display the pure kinetic-fractionation factor endmember: this is, to very few exceptions, never the case.

Using a series of four independent published in-vacuo experimental studies for which the system is actually over-constrained, we can model the observed isotope compositions of evaporated product with an unprecedented level of accuracy (including so-called mass-independent fractionations of O, Si, Cd, Hg). The isotope compositions can be explained if a significant fraction (typically 10-30%) actually evaporates under conditions corresponding to equilibrium (i.e. even under full vacuum).

Among several implications, we point that the physics of evaporation as commonly modelled using the so-called Graham's law is inappropriate. Similarly, any model scaling the fractionation factor(s) to pressure in the evaporating medium is erroneous. Available data actually suggests a very limited role of gas pressure upon fractionation factors, the equilibrium fraction rather reflecting gardening at the evaporating surface rather than isotope re-equilibration.