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It's not air: what we can learn from Ar-Kr-Xe isotopes in volcanic gases at the per mil level and below

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The noble gas composition of mantle-derived gases holds important information about the origin of Earth's volatiles and their cycling between reservoirs in the Earth system. The heavy noble gases (Ar, Kr, Xe) together contain a large number of primordial (i.e., from Earth's accretion) and secondary (e.g., radiogenic) isotopes, making them useful tracers of sources and processes related to Earth's volatile evolution. CO_2-rich hydrothermal systems (e.g., bubbling hot springs) are ubiquitous throughout the world, in principle offering an opportunity to explore heavy noble gas signals associated with various mantle sources. In practice, however, measurements of Ar-Kr-Xe isotopes in hydrothermal systems often resemble air (with the exception of radiogenic ^{40}Ar) at the precision of traditional noble gas mass spectrometers, except for in a handful of exceptional magmatic degassing sites (e.g., Eifel, Germany [1] or Bravo-Dome, USA [2]).

At finer resolution, do these isotope ratios still resemble air? What can we learn about physical transport processes from fractionation at the per mil level and below? And can we improve physical corrections for fractionation to robustly detect small, yet potentially significant mantle heavy noble gas anomalies throughout hydrothermal systems worldwide?

We will present recent progress on a new analytical technique for the collection [1], purification, and dynamic isotope-ratio mass spectrometric analysis [3] of Ar-Kr-Xe isotopes in large volumes of hydrothermal gas. Our new approach allows for robust measurements at the 0.01 per mil level, and we have now applied it to samples from hydrothermal systems in Chile, Bolivia, New Zealand, Yellowstone, Eifel, California, Iceland, Kenya, Djibouti, and Costa Rica in the past two years. We will share findings of coherent physical fractionation of groundwater-derived Ar, Kr, and Xe isotopes that mix with deep mantle-derived and crustal noble gases in the subsurface [4]. With these new constraints on physical fractionation, we will present several case studies demonstrating how this new technique opens the door to exploring the spatial variability of both geological noble gas source signals and physical transport processes.

[1] Bekaert et al. (2019), *EPSL*.
[2] Holland & Ballentine (2006) *Nature*
[3] Seltzer and Bekaert (2022), *IJMS*.
[4] Bekaert et al. (in-review), *Science Advances*.