Fractionation of stable isotopes in organic contaminants by volatilization and sorption

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The assessment of degradation of organic contaminants in groundwater plumes by measuring compound-specific ratios of stable carbon and hydrogen isotopes is increasingly used in practice, but relies on the assumption that phase transfer processes do not create any significant isotope fractionation. The aims of our studies were to find quantitative arguments for or against the validity of this assumption.

Volatilization experiments with artificial kerosene were performed at a field site and in a laboratory column and yielded both significant enrichment of ^{13}C in hydrocarbon vapors [1]. A quantitative explanation was given based on the faster diffusion of isotopic light contaminants through soil to the atmosphere. The isotopic evolution of a volatilizing source can be modelled analytically or numerically.

Previous studies on the fractionation of stable isotopes by equilibrium sorption by other authors have shown that the effects are very close to detection limits by actual mass spectrometers, but may nevertheless be significant at the field scale. We propose thus an indirect method to quantify fractionation by sorption. Linear free energy relationships (LFERs) were established which relate stable carbon and hydrogen isotope enrichment factors for equilibrium sorption to equilibrium vapor-liquid enrichment factors for alkanes, monoaromatic hydrocarbons, and chloroethenes. These LFERs predict that isotopic light compounds sorb more strongly than their heavy counterparts. The effect is very small for ^{13}C, and larger for ^{2}H. Some values predicted by LFER agree well to values measured experimentally in sorption experiments with perdeuterated compounds on soils. It is concluded that 1) volatilization creates isotopic enrichment in remaining contaminant pools, and 2) sorption can create isotopic enrichment at plume fronts, but only for hydrogen isotopes and for compounds that sorb strongly.

[1] Höhener, P.. Bouchard, D.. Hunkeler, D. In *Advances in Subsurface Pollution of Porous Media. Indicators, Processes and Modelling*. Candela, L.. Vadillo, I.. Elorza, F. J., eds.. CRC Press, Taylor and Francis Group: Boca Raton, 2008, pp 123-135.

Primordial krypton in the terrestrial mantle is not solar

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Noble gases are key tracers for the origin of volatiles in the terrestrial planets and of interaction between mantle reservoirs and the atmosphere. The general consensus is that material accreting in the solar nebula and nebula gases from the Sun itself were incorporated into the Earth, providing a starting point for models of planetary evolution. Recent noble gas data from magmatic CO_2 natural gases have proved to be an additional and invaluable resource when investigating noble gases from the mantle. Of particular note is the Bravo Dome natural CO_2 gas field which shows clear Xe isotopic anomalies over air and very similar values to those observed in MORB [1,2], although the specific source of this primitive component was not resolvable due to the limited precision of the single collector instrument employed. We have returned to the Bravo Dome suite to measure Kr and Xe isotopes with a multicollector instrument which permits much improved precision. Kr isotope data show a clear non-air signature which trends towards average carbonaceous chondrite (AVCC) Kr, compatible with Xe isotope data. These results require that there is no solar heavy noble gases in the mantle and the most likely source of Earth's primitive Kr and Xe is the same as that which contributed noble gases to the primitive meteorites. Further implications of an AVCC rather than solar mantle include the need for a hidden Xe reservoir and the prohibition of mantle outgassing of Kr to form the atmosphere.

[1] Caffee *et al*. (1999) *Science* **285**, 2115-2118. [2] Holland and Ballentine (2006) *Nature*, **441**, 186-191.