

## Excess air in groundwater as a proxy for paleo-humidity

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The concentrations of dissolved noble gases in groundwater usually exceed the atmospheric solubility equilibrium. The equilibrium component provides information on paleotemperatures via the temperature dependent solubilities. The excess component (“excess air”) might reflect other environmental conditions – in particular humidity – during groundwater recharge.

Excess air originates from air bubbles that are trapped in the quasi-saturated soil zone, i.e. the zone affected by periodic fluctuations of the groundwater table. Contrary to previous assumptions, this “entrapped air” is usually not completely dissolved. Instead, a new equilibrium between partially dissolved bubbles and groundwater is reached. Model calculations as well as laboratory experiments show that the size of the resulting gas excesses, e.g. the relative Ne excess  $\Delta\text{Ne}$ , is directly linked to the hydrostatic pressure on the entrapped gas bubbles.

The hydrostatic pressure in the quasi-saturated zone depends on the amplitude of water table fluctuations, which in turn reflects the intensity and variability of recharge. As a result,  $\Delta\text{Ne}$  is expected to be linked to the climate variable precipitation. This link appears to be particularly strong in semi-arid climate zones, where precipitation and recharge exhibit large seasonal and inter-annual fluctuations.

For example, in groundwater from the Continental Terminal aquifers of Niger, we found correlated variations of stable isotope ratios, excess air ( $\Delta\text{Ne}$ ), and noble gas temperature (NGT) over the past 40 kyr. Compared to modern samples from the top aquifer, the late Pleistocene to mid Holocene samples from the deeper aquifers show depleted stable isotopes, higher values of  $\Delta\text{Ne}$ , and lower NGTs.

These observations consistently indicate recharge during more humid periods. In such periods with more intense rainfall, stable isotopes were depleted due to the amount effect,  $\Delta\text{Ne}$  was increased due to larger water table fluctuations, and NGTs were lowered by a reduction of the difference between soil and air temperature due to increased vegetation. In the case of Niger, it appears that excess air reflects groundwater recharge intensity, whereas NGT does not directly indicate atmospheric temperature.

## Experimental Constraints on Core Formation

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Over the past several years numerous high-pressure experimental studies have placed important constraints on the physics and chemistry of planetary core formation. For the Earth, core formation appears to have occurred within a deep magma ocean.

Dihedral angle measurements of metal/silicate wetting experiments show that core melt segregation from a solid silicate mantle, under static compression, is inefficient and excess metal would be stranded in the mantle. Efficient metal segregation, consistent with the observed upper mantle, may require significant silicate melting where liquid metal sinks to the core by rainfall. Experiments on wetting of perovskite suggest that percolation of metal melt is significantly more efficient in the lower mantle.

Moderately siderophile elements Ni and Co have metal/silicate partition coefficients that decrease with pressure and converge to a value consistent with the average Ni/Co of the Earth's upper mantle. This convergence of Ni and Co partition coefficients occurs in the range 28-35 GPa (750-900 km depth) and can be interpreted as the pressure or depth of the bottom of a magma ocean where the upper part of the mantle last equilibrated with sinking core melt.

Slightly siderophile elements V, Cr, and Mn are similarly depleted in the mantles of the Earth and Moon. New metal-silicate partitioning data for V, Cr, and Mn explain the mantle depletions by core formation at super-liquidus temperatures (>3000 C) under oxygen fugacity conditions more than two log units below the iron-wüstite buffer. The data do not require the mantle of the Moon to be derived from the Earth's mantle.

Light element metal/silicate partitioning studies show that sulfur's affinity for liquid metal increases strongly with pressure, while Si and O are highly lithophile at all experimental pressures using chondritic compositions at ~iron-wüstite buffer. Si and O content of the core should be strongly dependent on the oxygen fugacity in early Earth. Sulfur may be the dominant light element in the core if a sufficient quantity of it was sequestered in the Earth during accretion. Interestingly, the partitioning data indicate that the sulfur content of the upper mantle (250 ppm) is too high to have equilibrated with a molten outer core containing 2-10 wt% sulfur. Mass balance requires that additional sulfur be added to the upper mantle from other sources, possibly as part of a 0.2-0.6% Earth-mass late veneer.