

Kr and Xe and the origin of noble gases in the mantle and atmosphere

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We have recently reported the first primordial Kr isotopic composition to be resolved in a terrestrial sample [1]. This has a heavier isotopic composition than the atmosphere Kr and is on a mixing line between air and the average carbonaceous chondrite value (AVCC). It is quite distinct from the Solar value, which is lighter than atmosphere. We are not aware of any simple mechanism that would enable the primordial Kr now in the Earth's mantle to fractionate to form the lighter Kr now in the atmosphere. We argue that the Kr, and likely associated volatiles, now found in the atmosphere was accreted after the volatile complement of the mantle formed. The late accretion of Solar Kr but little Xe, a feature of cometary material, to a residual atmosphere containing heavily fractionated Xe would account for the current Kr and Xe composition of the atmosphere.

The mantle has an additional Ar, Kr and Xe component which is isotopically indistinguishable from the atmosphere (in isotopes unaffected by radioactive decay). The ratio of $^{36}\text{Ar}/^{84}\text{Kr}/^{130}\text{Xe}$ of this 'air' component is indistinguishable from seawater with a small excess of ^{84}Kr and ^{130}Xe attributed to marine sediment. We have argued that this is evidence for significant noble gas subduction into the convecting mantle [2]. If the limit for the $^{84}\text{Kr}/^{36}\text{Ar}$ ratio of the mantle is the seawater ratio, after correcting for the primordial component this places a limit on the primordial Kr concentration to be <25% of the total Kr. Assuming simple two component mixing between air and an unknown primordial component contributing 25% of the Kr allows us to place a limit on the primordial Kr end member composition. This is within 1 sigma of the AVCC value, reinforcing our earlier conclusions of a meteorite origin for the Earth's primordial heavy noble gases, a late cometary contribution to the atmosphere, and subduction of air dissolved in seawater into the mantle over Earth history.

[1] Holland G. Cassidy M. Ballentine C.J. (2009) *Science* **326**, 1522–1525. [2] Holland G. & Ballentine C.J. (2006) *Nature* **441**, 186–191.

Noble gas isotope insights into the geological storage of carbon

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Carbon capture and geological storage of anthropogenic CO₂ emissions remains one of the most promising options we have as a society to mitigate global warming. Whilst this can only be a decadal solution, while we transit to low carbon technologies, the safety of the carbon storage sites over a millennial timescale must be assured. This can only be achieved through multiscale studies involving laboratory tests, real time field experiments and use of natural analogues to inform models that can robustly predict the fate of CO₂ once injected into the ground.

Noble gas isotopes have a proven track record in defining the fluid environment, critical to these models. Coal field methane deposits in the San Juan basin demonstrate the ability of noble gases to peer through a multi-phase system and provide groundwater ⁴He ages [1]. Noble gases from the groundwater partition into the gas phase and quantify the volumes of water that multiphase systems have 'seen'. Again this is a critical parameter for assessing the ideal location/s for CO₂ any sequestration system. Studies of CO₂ natural gas fields provide an excellent analogue to assess the long term behaviour of CO₂ in geological reservoirs. Similar to the San Juan study we can quantify exactly how much groundwater the reservoir gas phase has been in contact with [2]. We also show how CO₂/³He ratios can be used to quantify CO₂ gas phase loss through dissolution into the groundwater in these systems. 'Solubility' trapping of CO₂ is overlooked in many models, yet can account for more than 90% of all CO₂ loss in some parts of the analogue gas fields investigated [3].

The future for noble gas studies remains promising. The most recent studies have illustrated the power of combining noble gases with stable isotope information [3, 4] while real time tracing of noble gas spiked CO₂ into sequestration targets has the potential to exploit the massive difference in noble gas diffusivity and solubility to robustly trace the effects of secondary porosity on multiphase oil/water/CO₂ systems.

[1] Zhou, Z. *et al.* (2005) *Geochim. Cosmochim. Acta* **69**, 5413–5428. [2] Gilfillan *et al.* (2008) *Geochim. Cosmochim. Acta* **72** 1174–1198. [3] Gilfillan *et al.* (2009) *Nature* **458**, 614–618. [4] Sherwood Lollar, B. & Ballentine, C.J. (2009) *Nature Geoscience* **2**, 543–547.