

## Noble gases in kimberlitic mantle xenoliths from southern Africa

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We determined the noble gas composition of peridotitic mantle xenoliths and one Cr-diopside megacryst from the kimberlite pipes of Bultfontein, Finsch and Letseng-la-Terae via the stepwise crushing method. All samples showed a highly radiogenic  $^3\text{He}/^4\text{He}$  isotope composition  $< 0.23 R_A$  ( $R_A = \text{atmospheric unit}$ ) and high concentrations of  $^4\text{He}$  (up to  $3 \cdot 10^{-4}$  ccm STP/g). The  $^3\text{He}/^4\text{He}$  and (radiogenic)  $^{40}\text{Ar}/^4\text{He}$  ratios are correlated and point to mixing between a mantle and crustal component. The  $^4\text{He}/^{40}\text{Ar}^*$  ratios range from values of 4 similar to the crustal production ratio up to highly elementally fractionated values of 200, the latter observed in the Cr-diopside megacryst. Xenon isotopes are solely atmospheric and  $^{132}\text{Xe}/^{36}\text{Ar}$  ratios correspond to an enrichment in Xe relative to Ar up to a factor of 100 relative to air ratio. Fractionation displayed in radiogenic and atmospheric element ratios is anti-correlated: The most fractionated atmospheric component is always associated with the least fractionated radiogenic component and vice versa. We also identified a clear mantle neon signal with  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios up to 11.1. The air corrected  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios of 0.06-0.09 agree with a slightly more nucleogenic composition compared with MORB values, however, the very radiogenic character of the samples implies that these values must be considered as upper limits for the mantle component. The most pronounced mantle neon signal is associated with the least fractionated radiogenic and most fractionated atmospheric element ratios, indicating that the latter is rather reflecting a depletion of the light instead enrichment of the heavier noble gases.

The generally serpentinized xenoliths indicate interaction with migrating water. This water is considered as main source of the radiogenic and atmospheric isotopes and evidences a crustal origin of these brines. Incorporation of a likely  $\text{CO}_2$ -rich mantle fluid into the xenoliths occurred prior and at much larger depth. The timing of crustal contamination remains unclear but irrespective of this we state that even small quantities of contaminating crustal brines may strongly influence the trace volatile budget of kimberlites and their xenoliths. This might also explain the highly variable and radiogenic helium isotope record reported for diamonds.

## Timing of the atmospheric oxygen evolution: Uranium transport in the Franceville series at Oklo, Gabon

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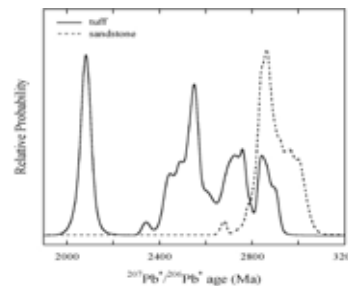
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Uranium is a good indicator of redox condition because the oxidation number of uranium changes depending on the redox conditions and uranium is only mobilized as uranyl ion ( $\text{UO}_2^{2+}$ ) under oxidizing conditions. Uraninite as detrital placers can be found in fluvial sedimentary successions older than 2.3 Ga, but is rare in younger fluvial systems than 2.3 Ga, which is strong evidence for the major increase in the atmospheric oxygen around 2.3 Ga [1]. U-Pb geochronology was applied to a syn-depositional volcanic zircon and detrital zircons in the Franceville sedimentary succession containing uranium deposits, which may allow us to improve the temporal constraints on the evolution of atmospheric oxygen deduced from the formation of its uranium and manganese deposits.



**Figure 1:** Probability density diagram of Pb-Pb ages.

Figure shows a Pb-Pb age probability density diagram of zircons from tuff and sandstone. The ages of detrital zircon in the sandstone are scattered around 3.0 to 2.7 Ga, which suggest that the FA sandstone is derived from the Archean metamorphic basement and had been deposited after 2.7 Ga. The tuff data show two major age populations from 2.8 to 2.4 Ga and around 2.1 Ga. The  $2083 \pm 9$  Ma gives the eruption age of tuff and corresponds to the lower limit of deposition age of the Franceville sediments. The detrital uranium-bearing minerals dated at 3.0-2.7 Ga had been transported under anoxic conditions before 2.1 Ga and dissolved around 2.1 Ga under oxidizing conditions. Therefore, atmospheric oxygen fugacity increased from  $< 10^{-3}$  to ca. 4 % PAL during the formation of uranium deposit at Oklo.

[1] Bekker *et al.* (2004) *Nature* **427**, 117-120.