



Constraints on Earth degassing history from the argon isotope composition of Devonian atmosphere

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The primordial and radiogenic isotopes of the noble gases combine to make them a powerful tool for determining the time and tempo of the outgassing of the Earth's interior. The outgassing history of the Earth is largely constrained from measurements of the isotopic composition of He, Ne, Ar and Xe in samples of modern mantle, crust and atmosphere. There have been few unequivocal measurement of the isotopic composition of noble gases in ancient atmosphere. We have re-visited whether ancient Ar is trapped in the ~400 Ma Rhynie chert [1]. We have analysed samples of pristine Rhynie chert using the ARGUS multi-collector mass spectrometer calibrated against the new determination of atmospheric Ar isotope ratios [2]. $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are low, with many lower than the modern air value (298.8). Importantly these are accompanied by atmospheric $^{38}\text{Ar}/^{36}\text{Ar}$ ratios indicating that the low $^{40}\text{Ar}/^{36}\text{Ar}$ are not due to mass fractionation. We conclude that the Rhynie chert has captured Devonian atmosphere-derived Ar. The data indicate that the Devonian atmosphere $^{40}\text{Ar}/^{36}\text{Ar}$ was at least 3 % lower than the modern air value. Thus the Earth's atmosphere has accumulated at least $5 \pm 0.2 \times 10^{16}$ moles of ^{40}Ar in the last 400 million years, at an average rate of $1.24 \pm 0.06 \times 10^8$ mol $^{40}\text{Ar}/\text{year}$. This overlaps the rate determined from ice cores for the last 800,000 years [3] and implies that there has been no resolvable temporal change in Earth outgassing rate since mid-Palaeozoic times. The new data require the Earth outgassed early, and suggests that pristine samples of Archaean and Proterozoic chert may prove useful as palaeo-atmosphere tracers.

[1] G. Turner, *J. Geol. Soc. London* 146, 147-154 (1989)

[2] D. Mark, F.M. Stuart, M. de Podesta, *Geochim. Cosmochim. Acta* 75, 7494-7501

[3] M. Bender et al., *Proc. Nat. Acad. Sci.* 105, 8232-8237 (2008)