Temporal variations of atmospheric helium isotopes

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The isotopic composition of the atmosphere ($^3He/^4He = 1.382 \pm 0.005 \times 10^{-6}$) is distinctly different from crustal helium ($^3He/^4He \sim 10^{-8}$). Several authors [e.g. 1, 2, 3] have proposed that the amount of excess crustal helium entering the atmosphere due to modern fossil fuel extraction may be enough to upset the balance of the helium composition in the atmosphere on a timescale short enough to detect with modern measurement techniques. Previous attempts failed to detect variations beyond the measurement precision [3, 4]. However, recent measurements by [5] from the Cape Grim Air Archive (CGAA) found a decrease of the atmospheric $^3He/^4He$ of 0.23-0.30‰ per year over the period 1978 to 2011. We will attempt to replicate these results using a high-precision helium isotope measurement system we have devised.

Air samples are collected in copper tubes which are sealed with steel clamps. Each sample is approximately 15-20 cm^3 of air which is purified all at once and then measured in 11 standard-bracketed aliquots. The amount of helium in each sample aliquot is matched to the amount in an aliquot of the standard to minimize pressure effects. Measurements are made on a Thermo Helix Split Flight Tube (SFT) multi-collector noble gas mass spectrometer. With this system we have a long-term reproducibility of sample air of 0.05% (2σ).

Our initial measurements of the $^3He/^4He$ in CGAA samples do not reproduce the results of [5]. They are consistant with no change in the helium composition over time with an upper limit (2σ) of 0.16‰ per year decrease in $^3He/^4He$. We will make further measurements of the CGAA samples.

Sample	R_{air}/R_{std} (2σ)	# analyses
CGAA 1978	1.0402 (0.0027)	3
CGAA 1979	1.0386 (0.0010)	7
CGAA 2008	1.0387 (0.0004)	4
CGAA 2011	1.0389 (0.0014)	4

[1] Oliver *et al.* (1984) *GCA* **48**, 1759-1767. [2] Pierson-Wickman *et al.* (2001) *EPSL* **194**, 165-175. [3] Sano *et al.* (2010) *GCA* **74**, 4893-4901. [4] Lupton and Evans (2004) *GRL* **31,** L13101. [5] Brennwald *et al.* (2013) *EPSL* **366**, 27-37.

Application of clumped isotope thermometry to subsurface dolostone samples

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Platform carbonates are a major hydrocarbon reservoir setting, and are often dolomitized. An important parameter in characterising these reservoirs is the palaeotemperature of the various carbonate phases during burial diagenesis. Clumped isotope analysis of CO_2 from acid digestion of carbonate phases may offer the best route to accurately and precisely determining this temperature. We apply the clumped isotope palaeothermometer to natural dolostone samples from the Northern Marion Platform (NMP, offshore NE Australia) and to dolostone samples from other subsurface locations.

Initially, five dolostone samples from the NMP collected between ~100-160 metres below sea floor (mbsf) were analysed. Petrographic analysis revealed that these samples were all pervasively dolomitized: planar-s to planar-e dolomite forms 100% of the modal mineralogy. Initial clumped isotope analysis (triplicate analyses; reaction at 90°C for 45mins; acid and non-linearity corrections applied; data transferred to universal reference frame [1]) yielded temperatures of 22 °C to 31 °C using the calibration of Ghosh *et al.* [2].

As a second step, we analysed samples from subsurface wells where independent constraints using fluid inclusion thermometry exist. By testing clumped isotope thermometry on these well-constrained natural reservoir samples, we hope to show that clumped isotope thermometry is an ideal technique to determine burial temperatures in carbonate reservoir rocks, as it overcomes some of the problems inherent in fluid inclusion and conventional $\delta^{18}O$ thermometry.

[1] Dennis *et al.* (2011) Geochim. Cosochim, Acta **75**, 7117–7131. [2] Ghosh *et al.* (2006) Geochim. Cosochim, Acta **70**, 1439–1456.

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