

## Carbonate sedimentary rocks as archive of palaeoatmospheric argon

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Solid element radiogenic isotope systems deliver robust information about the time evolution of continental crust. More difficult to reconstruct is the outgassing history of the Earth's interior. The  $^{40}\text{Ar}/^{36}\text{Ar}$ -ratio is a particularly useful isotope system that can in principle provide such information. The initial  $^{40}\text{Ar}/^{36}\text{Ar}$ -ratio of the solar system was essentially zero, but, due to decay of long-lived  $^{40}\text{K}$  (half-life 1.25 Ga), the abundance of  $^{40}\text{Ar}$  has increased since then. Today, the terrestrial atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$ -ratio is about 300, whereas the Earth's mantle exhibits large ratios of  $>25,000$ . These highly elevated values indicate an early release of primordial  $^{36}\text{Ar}$  into the atmosphere. In addition, crustal rocks contain a substantial portion of K and represent a major source of radiogenic  $^{40}\text{Ar}$ , which is partially released into the atmosphere during tectonic episodes or changes in environmental conditions (weathering, erosion). For decades, there have been attempts trying to establish palaeoatmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$ -ratios, but only two anchor points have been published so far [1,2]. In an effort to check for additional carriers that have retained ancient atmospheric argon, we have analyzed carbonates from the Neoproterozoic Transvaal basin by the stepwise crushing method. We found positive correlations between the  $^{40}\text{Ar}/^{36}\text{Ar}$ - and  $^4\text{He}/^{36}\text{Ar}$ -ratios, indicating the presence of several subcomponents: Atmosphere, *in-situ* radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$ , and a crustal component with excess  $^{40}\text{Ar}$ . In one dolomite, the data for the first 7 crushing steps are well-correlated, with an intercept  $^{40}\text{Ar}/^{36}\text{Ar}$ -ratio of  $266\pm 8$  ( $1\sigma$ ), distinctly lower than in modern air. A  $^{39}\text{Ar}$ - $^{40}\text{Ar}$  age spectrum of detrital sericite / muscovite within this rock indicates a thermal disturbance at ca. 2 Ga, likely related to the Bushveld magmatic activity. The inferred palaeoatmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$ -ratio is at the upper limit predicted by isotopic evolution models for this age, and may be still affected by minor crustal  $^{40}\text{Ar}$  contributions. Our result demonstrates the general potential of carbonate rocks as an archive of palaeoatmospheric argon.

[1] Cadogan (1977) *Nature* **268**, 38-40. [2] Pujol *et al.* (2013) *Nature* **498**, 87-92.