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Earth-atmosphere evolution based on new determination of Devonian atmosphere Ar isotopic composition

Finlay M. Stuart *, Darren F. Mark, Pierre Gandanger, Paul McConville

Isotope Geoscience Unit, Scottish Universities Environmental Research Centre, East Kilbride G75 0QF, United Kingdom

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ABSTRACT

The isotopic composition of the noble gases, in particular Ar, in samples of ancient atmosphere trapped in rocks and minerals provides the strongest constraints on the timing and rate of Earth atmosphere formation by degassing of the Earth's interior. We have re-measured the isotopic composition of argon in the Rhynie chert from northeast Scotland using a high precision mass spectrometer in an effort to provide constraints on the composition of Devonian atmosphere. Irradiated chert samples yield $^{40}Ar/^{36}Ar$ ratios that are often below the modern atmosphere value. The data define a $^{40}Ar/^{36}Ar$ value of 289.5 ± 0.4 at $K/^{36}Ar = 0$. Similarly low $^{40}Ar/^{36}Ar$ are measured in un-irradiated chert samples. The simplest explanation for the low $^{40}Ar/^{36}Ar$ is the preservation of Devonian atmosphere-derived Ar in the chert, with the intercept value in ^{40}Ar–^{39}Ar–^{36}Ar space representing an upper limit. In this case the Earth's atmosphere has accumulated only 3% ($5.1 \pm 0.4 \times 10^{16}$ mol) of the total ^{40}Ar inventory since the Devonian. The average accumulation rate of $1.27 \pm 0.09 \times 10^{8}$ mol ^{40}Ar/yr overlaps the rate over the last 800 kyr. This implies that there has been no resolvable temporal change in the outgassing rate of the Earth since the mid-Palaeozoic despite the likely episodicity of Ar degassing from the continental crust. Incorporating the new Devonian atmosphere $^{40}Ar/^{36}Ar$ into the Earth degassing model of Pujol et al. (2013) provides the most precise constraints on atmosphere formation so far. The atmosphere formed in the first ~100 Ma after initial accretion during a catastrophic degassing episode. A significant volume of ^{40}Ar did not start to accumulate in the atmosphere until after 4 Ga which implies that stable K-rich continental crust did not develop until this time.

1. Introduction

The concentration of the noble gases (He, Ne, Ar, Kr and Xe) in the main terrestrial reservoirs (mantle, crust and atmosphere) are not affected by the chemical and biological processes that govern the distribution of the reactive volatile elements. The presence of both stable and radiogenic noble gas isotopes can be used to provide temporal constraints on the outgassing history of the solid Earth and the age of the atmosphere. Consequently they have proved to be key tracers of the origin and evolution of the atmospheres of the terrestrial planets (e.g. Turcotte and Schubert, 1988).

The origin of the Earth's atmosphere has been critical in the understanding evolution of terrestrial planets. It has been recognised for many decades that the Earth's atmosphere is secondary in origin, a consequence of the outgassing of the planetary interior, rather than capture of solar nebula gases (Brown, 1949). Models of atmosphere growth are largely based on the noble gas isotope composition of the present day mantle, crust and atmosphere. The earliest models proposed that the atmosphere formed as a result of slow, continuous outgassing of the Earth's interior (Turekian, 1959). The low concentration of stable (primordial) noble gas isotopes in mantle rocks compared to primitive chondritic meteorites led to the conclusion that Earth must be strongly outgassed. Subsequent studies of Ar isotopes in Earth interior permitted the development of two-stage outgassing history; an extensive outgassing event soon after Earth accretion was followed by slow continuous degassing (Fanale, 1971; Hamano and Ozima, 1978). The early models were predicated on the assumption that the atmosphere formed by outgassing of only the crust and upper mantle where the deep mantle did not outgas significantly, and remained convectively isolated from the upper mantle (e.g. Allègre et al., 1986/87, 1996). Subsequent modelling demonstrated that the complete outgassing of an upper mantle down to the 670 km seismic discontinuity cannot provide all the ^{40}Ar in the atmosphere (e.g. Davies, 1999). The measurement non-atmospheric Ne and Ar isotope compositions in basalts from intra-plate volcanoes (e.g. Honda et al., 1993; Burnard et al., 1994) led to the recognition that the lower

* Corresponding author.
E-mail address: fin.stuart@glasgow.ac.uk (F.M. Stuart).

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mantle below 670 km cannot have remained convectively isolated for all of Earth history (e.g. Porcelli and Wasserburg, 1995; O'Nions and Tolstikhin, 1996). Recent Earth outgassing models incorporate some degree of volatile loss from the deep mantle (e.g. Gonnerman and Mukhopadyay, 2009), but the extent to which the deep Earth is degassed, and the source and location of primordial noble gases in Earth's interior remain unresolved (see discussion in Starkey et al., 2009).

While the isotopic composition of noble gases in modern terrestrial reservoirs is well established, the time-integrated rate of mass transfer between these reservoirs, as well as the rate of transfer of primordial and radiogenic volatiles, is much less well constrained (e.g. Farley et al., 1995; Stuart and Turner, 1998). The determination of the isotopic composition of noble gases in ancient atmosphere provides a first order test of the degree and rate of gas and mass transfer processes. However, the ubiquity of contaminating modern atmosphere, and the ingrowth of radiogenic isotopes in minerals after crystallisation, severely hampers the precise determination of these signals. Despite this, a low $^{40}Ar/^{36}Ar$ component appears to have been incorporated in several ancient rocks and minerals (e.g. Cadogan, 1977; Hanes et al., 1985; Rice et al., 1994; Pujol et al., 2013). These values are consistent with the incorporation and retention of ancient atmospheric Ar, although it usually relies on a correction for radiogenic ^{40}Ar ingrowth after mineral or rock formation. The difficulty in explaining systematically low $^{40}Ar/^{36}Ar$ by any other mechanism, however, indicates that it is clearly a fruitful avenue for constraining the Earth outgassing history.

The Devonian hydrothermal Rhynie chert from northeast Scotland is probably the most thoroughly studied material that may preserve an ancient atmospheric Ar signal. The first detailed study yielded an initial $^{40}Ar/^{36}Ar = 291.0 \pm 1.6$ which, it was argued, represented the value of Devonian atmosphere (Cadogan, 1977). Although this value was consistent with what would be expected for catastrophic early Earth degassing (e.g. Turner, 1989) the veracity of the measurements failed to convince some at the time (see Ozima and Podosek, 1983). Subsequent intensive study replicated the low $^{40}Ar/^{36}Ar$ (291.1 ± 0.6; Rice et al., 1994). However, as with the initial study, this work yielded no gas extraction steps with $^{40}Ar/^{36}Ar$ ratios that were unequivocally lower than the present day atmospheric value and the presence of palaeo-atmospheric Ar relied on the (not unreasonable) assumption that radiogenic ^{40}Ar was present to some degree in all gas extraction steps. High precision determinations have been made of the isotope composition of atmospheric argon trapped in samples of Antarctic ice dating back several hundred thousand years (Bender et al., 2008). These data require an average modern outgassing rate of 1.1×10^8 mol ^{40}Ar/yr. This rate is broadly consistent with, and more precise than, the long-term average calculated from the measurements of Rhynie chert. Most recently a low $^{40}Ar/^{36}Ar$ trapped in Archaean hydrothermal quartz from 3.5 Ga Pilbara craton, Western Australia (Pujol et al., 2013) has been used to place constraints on the rate of atmosphere degassing early in Earth history, which has implications for the timescale of formation of continental crust.

Several factors warrant a re-assessment of the possibility that the Rhynie chert is a repository of ancient atmospheric noble gases. Recent improvements in multi-collector noble gas mass spectrometers allows for high precision Ar isotope measurements (Mark et al., 2010). The re-determination of the Ar isotope composition of the modern atmosphere (see Mark et al., 2011a for discussion) means that fractionation in the mass spectrometer can be correctly determined, and an appropriate correction for trapped modern air can be made. Finally, a better understanding of the petrology of the Rhynie chert (e.g. Baron et al., 2004) means that potentially problematic components of the rock, e.g. detrital clay, can be avoided. Here we present new determinations of the $^{40}Ar/^{36}Ar$ of the Rhynie chert in an effort to determine isotopic composition of the Devonian atmosphere. The new value for Devonian air is incorporated into the Earth degassing model developed by Pujol et al. (2013) and is used to place constraints on the degassing history of the Earth.

2. Samples and analytical methods

Argon isotopes have been measured in mg-sized chips of irradiated and un-irradiated pristine siliceous sinter from a single specimen of Rhynie chert. Samples were selected specifically in order to avoid entrained fine-grained sediment, minimising potential issues resulting from the recoil of K-derived ^{39}Ar. We specifically targeted the siliceous sinter that developed on the surface and cooled in direct exposure to the Devonian atmosphere. Detailed descriptions of the Rhynie chert are given elsewhere (e.g. Rice et al., 1994; Baron et al., 2004). Nine samples were irradiated for 100 h in the Cd-lined nuclear reactor at McMaster, Canada. Eight of these samples were incrementally heated in 5 steps using a 50 W CO_2 laser in an attempt to selectively remove absorbed modern atmospheric Ar and release palaeo-atmospheric Ar. One sample was fused in a single step. Biotite from the Mount Dromedary monzonite (GA1550, 98.8 ± 0.5 Ma, Renne et al., 1998) was used as a neutron fluence monitor. Details of the irradiation parameters are given in the Supplementary Information. Samples were outgassed at $\sim 80\,^{\circ}C$ in a Cu laser pan for 10 days prior to analysis in order to remove adhering atmospheric Ar. The extraction, purification and analysis procedures were similar to those described in Mark et al. (2011b).

Argon isotopes were measured in 12 unirradiated chips of Rhynie chert. The gas extraction procedure and purification was identical to that applied to the irradiated chips. Five samples were incrementally heated in three steps, and seven were fused in a single step.

Argon isotope abundances and ratios were determined using a GVI ARGUS multiple-Faraday collector mass spectrometer using established laboratory procedures (Mark et al., 2010). System blanks were measured after every two measurements of unknowns. Average blank measurements for the entire run sequence were used to correct raw peak intensities. Mass discrimination (1.0059 ± 0.0009/amu) was determined by repeated measurement of air pipettes during the period of analysis (following every five analyses).

3. Results

The data from the irradiated and unirradiated samples are compiled in the Supplementary Information. Argon in the samples likely derives from four sources; modern air, Devonian air, ^{40}Ar generated from ^{40}K decay and "excess" ^{40}Ar in the hydrothermal fluids (see Rice et al., 1994 for review). These components can best be resolved using the analyses of irradiated samples. In ^{40}Ar–^{39}Ar–^{36}Ar space the data define a triangular region that appears to have a well-defined lower bound (Fig. 1). The data that plot above the lower bound may be affected by a small contribution of excess ^{40}Ar that originates in the trapped hydrothermal fluid. They are statistically insignificant. A correlation between Ca-derived ^{37}Ar and K-derived ^{39}Ar (Table S1) indicates that a Ca- and K-bearing mineral or fluid inclusion phase is present in the chert. While a trapped fluid phase is present in the Rhynie chert (Rice et al., 1994), the presence of detrital clay minerals cannot be ruled out. ^{39}Ar recoil from clays can perturb the Ar isotope systematics but there is no clear evidence of the effect in this case (Fig. 1).

Following the protocol established by earlier studies (Cadogan, 1977; Rice et al., 1994; Pujol et al., 2013) we use a conven-