Low oxygen and argon in the Neoproterozoic atmosphere implied by halite gas inclusion measurements

Laurence Y. Yeung

Department of Earth, Environmental and Planetary Sciences, Rice University, Houston, TX 77005

Abstract

Recent analyses of purportedly ancient atmospheric gases trapped in Neoproterozoic halite inclusions offer a fresh, but controversial perspective on the history of atmospheric oxygenation (Blamey et al., 2016). Those data, at face value, imply that the Tonian (815 ± 15 Ma) atmosphere contained about half the present atmospheric levels (PAL) of O_2 . Here, I reanalyze those data and argue that those samples were affected by preservation artifacts; the gases are likely contaminated with modern air and air dissolved in brines, and they may also contain signals of biogeochemical cycling within the halite inclusions. The Tonian atmosphere may instead have been low in O_2 , containing $\leq 6\%$ PAL, not $\sim 50\%$ PAL as previously suggested. The analysis also reveals a surprisingly low Tonian argon inventory, $\leq 60\%$ PAL, which, if accurate, challenges our understanding of the solid Earth's degassing history. When placed in context with other empirical estimates of paleo-atmospheric argon, the data imply a period of relatively slow atmospheric Ar accumulation in the Paleo- and Meso-Proterozoic, followed by extensive degassing in the late Neoproterozoic or early Cambrian, before returning to a relatively quiescent state by the Devonian. Still more enigmatic contaminations than the ones presented here may be relevant, but they require more extensive geochemical, petrological, and biological investigations to understand. Gases trapped in evaporites may offer important new constraints on the evolution of Earth's surface, climate, and atmosphere, but potential contaminations and other confounding factors need to be considered carefully before these records can be considered quantitative.

Submitted to *Earth and Planetary Science Letters* on X June 2017.

4,849 words

3 Figures

69 References

1 1. Introduction

2 The Neoproterozoic era was a time of great change in the Earth system. Following a period of
3 crustal thickening during the Mesoproterozoic (Taylor and McLennan, 1985; Dhuime et al., 2015), rifting,
4 metamorphism, and weathering accelerated during the breakup of Rodinia (Halverson et al., 2009; Cox et
5 al., 2016; Hawkesworth et al., 2016). Regional and global glaciation events are likely linked to these
6 tectonic events (Kirschvink, 1992; Schrag et al., 2002; Macdonald et al., 2010). Atmospheric and oceanic
7 oxygen levels experienced their second great rise (Canfield, 1998; Lyons et al., 2014). A unified picture
8 of the timing, magnitude, and interrelationships between these changes has not yet emerged, however
9 (Planavsky et al., 2014; Sperling et al., 2015; Gilleaudeau et al., 2016), due in part to limitations in proxy
10 records. Atmospheric archives offer an important perspective for these events, and while direct sampling
11 is rare, when available they can reveal a high-resolution snapshot of the atmospheric evolution amidst
12 these changes.

13 Recently, Blamey et al. (2016) reinvigorated the discussion about atmospheric records locked
14 within ancient evaporite minerals. Early work revealed preservation of O₂, but also N₂, Ar, CO₂, CH₄,
15 NH₃, and H₂S within halites of the Permian Zechstein formation (Freyer and Wagener, 1975). Unlike
16 other candidate atmospheric archives in the rock record e.g., bubbles in fossil amber (Berner and Landis,
17 1987; Cerling, 1989), halites are attractive because of their low permeability, low organic matter content,
18 abundance of fluid inclusions, and simple petrologic criteria for identifying post-depositional alteration
19 (Roedder, 1984). However, the fidelity of the gases within these archives has not been investigated.
20 Migration of gases through defects and grain boundaries for example, is difficult to diagnose. It is clear
21 from previous work that while atmospheric composition can be preserved in primary halites, some may
22 preserve gases at the sediment-water interface instead (Siemann and Ellendorff, 2001), while others still
23 may preserve dissolved gases or degradation products (Freyer, 1978). Microbes can be trapped within
24 halite as well, cycling elements within fluid inclusions for at least tens of thousands of years (Schubert et
25 al., 2009; Lowenstein et al., 2011) or perhaps even hundreds of millions of years (Vreeland et al., 2000).
26 The observation of unexpectedly high O₂ concentrations in primary Neoproterozoic bedded halites [~50%
27 PAL, 10 mol %; Blamey et al. (2016)] therefore places the reliability of these records under new
28 scrutiny.

29 Fortunately, a great number of approaches has been developed, principally from the atmospheric
30 and ice-core gas analysis field (Bender et al., 1997; Severinghaus and Battle, 2006), that can be applied in
31 principle to evaluate post-depositional processes relevant to gas preservation in ancient halites. Here, I
32 apply one such technique to reanalyze the data recently collected from Neoproterozoic (815 ± 15 Ma)
33 halites in the Officer Basin, Australia. I find evidence for modern contamination and mass-dependent gas

loss processes, as well as depositional artifacts in some samples that demand further investigation. I argue that these halites are more consistent with a low atmospheric O₂ concentration ($\leq 6\%$ PAL, ~ 1 mol %) at 815 Ma and propose several tests of this hypothesis. Surprisingly, the results also suggest that the atmospheric Ar concentration is lower than generally thought for the Neoproterozoic. If true, it indicates a more complex solid-Earth outgassing history than is captured by first-order mantle degassing models (Pujol et al., 2013; Stuart et al., 2016).

2. Methods

In the Blamey et al. (2016) study, modern halite samples were sampled from hypersaline ponds near the Mosaic mine in the U.S.A. (32°21'24" N, 103° 55' 21.75" W) and at Lake Polaris, Western Australia (31°14'11.01"S, 119°19'58.99"E). The other Phanerozoic halite samples come from the Racalmuto mine in Italy (37°15' N, 13°44' E; Messinian) and the Mengyejing Formation in China (22°42'01" N, 101°38'24" E; Cretaceous). The Neoproterozoic samples are from the Empress 1A and Lancer 1 drill cores in the Browne Formation (Officer Basin, Australia), at 1450 – 1502 m depth (Stevens and Apak, 1999; Mory and Haines, 2005 ; Spear et al., 2014). The Lancer 1 sample has been correlated geochemically with the lower Browne formation (~ 1500 m). These samples all appear to be bedded halite with primary chevron growth textures and banded fluid inclusions parallel to the growth faces showing undisturbed cubic “anticrystal” shapes. They are believed to have been precipitated in a subaerial salt pan (1478m Empress 1A sample) or a shallow lagoon environment (all other samples) (Spear, 2013). The reported Ar, O₂, and N₂ measurements for halites were originally obtained by fast-scanning quadrupole mass spectrometry of the gases released during 5 – 12 successive sample crushes. The reader is referred to Blamey et al. (2016) and Spear et al. (2014) for a full discussion.

I computed Ar/N₂ and O₂/N₂ ratios from these data and compared them to the ratios for New Mexico lab air (NMLA) reported in the same paper as $\delta\text{Ar}/\text{N}_2$ and $\delta\text{O}_2/\text{N}_2$ values, which characterize deviations from present atmospheric proportions. They are defined as $\delta\text{O}_2/\text{N}_2 = [(\text{O}_2/\text{N}_2)_{\text{sample}}/(\text{O}_2/\text{N}_2)_{\text{NMLA}} - 1]$ and $\delta\text{Ar}/\text{N}_2 = [(\text{Ar}/\text{N}_2)_{\text{sample}}/(\text{Ar}/\text{N}_2)_{\text{NMLA}} - 1]$. Alterations of the primary air composition signal, such as contamination with more recent air, radiogenic Ar production, O₂ production and consumption, mass-dependent fractionation, and N₂ production all fall on characteristic trajectories on a plot of $\delta\text{O}_2/\text{N}_2$ versus $\delta\text{Ar}/\text{N}_2$ values. I have excluded from the averages the crushes the previous authors had also excluded on the basis of the size of gas bursts and gas contents.

The O₂/N₂ and Ar/N₂ intercomparison approach assumes that atmospheric N₂ has not changed significantly since the Neoproterozoic: long-term burial of nitrogen has only been a small fraction of the

atmospheric nitrogen mass balance (<1%) during the Phanerozoic (Berner, 2006). A more recent model of N₂ over geologic time suggests that the N₂ inventory could have increased by up to several tens of percent since 1 Ga, but it is unlikely to have decreased since then (Stüeken et al., 2016; Zerkle and Mikhail, 2017). Post-depositional addition of N₂, such as denitrification or interaction with magmatic fluids rich in N₂ (Norman and Musgrave, 1994), would manifest as a N₂ excess.

3. Results

Calculation of $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values for individual halite crushes yields modern ($n = 2$), Messinian, and Cretaceous means of $103 \pm 4\%$, $91 \pm 12\%$, and $133 \pm 35\%$ (1 σ) PAL of atmospheric O₂ and $109 \pm 13\%$, $80 \pm 8\%$, and $97 \pm 9\%$ (1 σ) PAL of atmospheric Ar, respectively. These data are indistinguishable from those obtained by Blamey et al. (2016) using mole fractions. It is unclear why the Messinian halite yields an Ar inventory that is too low, but the measurement is of a single sample. Similarly, one of the modern samples yields a high Ar inventory (Lake Polaris; $118 \pm 49\%$ PAL), although its inaccuracy is largely due to two crushes with unusually low yields of gas (<1 pmol). The Cretaceous sample shows evidence for excess O₂, but the spread in individual crushes is large. The accuracy of a single sample analysis (mean of crushes) is therefore considered to be $\sim\pm 20\%$ PAL for both O₂ and Ar. The results for the Neoproterozoic halites are shown in Figs. 1 and 2.

The $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values from Empress 1A halites tend to increase downcore, with the shallowest sample (1478m) having $\delta\text{O}_2/\text{N}_2 = -0.94$ and $\delta\text{Ar}/\text{N}_2 = -0.59$ and the deepest sample (1502.2m) having $\delta\text{O}_2/\text{N}_2 = -0.41$ and $\delta\text{Ar}/\text{N}_2 = +0.07$ (Fig. 1). The time interval covering these depths is ~ 30 Myr; it exceeds the atmospheric residence time of O₂ (Bender et al., 1994; Berner, 1999; Stolper et al., 2016), but not the residence time of Ar. Atmospheric Ar increases inexorably through time (Hamano and Ozuima, 1978; Turner, 1989), which would yield in a *decrease* in Ar downcore instead. An increase in Ar downcore is thus opposite the trend expected from degassing of the solid Earth. I also note here that the Lancer 1 – 1466.3m sample, which is correlated to 1500 – 1501 m depth in the Empress 1A core using bromine concentrations (Spear, 2013), shows $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values that are significantly different from those in the 1502.2m sample ($p < 0.0008$).

Contamination by modern air and air dissolved in brine could be contributing to the measured gas concentrations. To evaluate the importance of this effect, one can inspect the trajectories for conservative mixing between the 1478m Empress 1A sample (the lowest- $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ sample) and modern air, and between the 1478m Empress 1A sample and air- and salt-saturated NaCl brines (Fig. 2). N₂ is far less soluble in brine than either Ar or O₂ (Onda et al., 1970), so contamination from dissolved air manifests as

1 a deficit in N₂, or positive excursions in $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values relative to the contemporaneous
2 atmospheric $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values.

3 The mixing curves in Fig. 2 indicate that the Neoproterozoic halite samples could contain signals
4 from atmospheric or dissolved air. All the Neoproterozoic samples lie within conservative mixing curves
5 defined by three endmembers: (1) the Empress 1A – 1478m sample, (2) air-saturated brine for
6 atmospheric composition 6% PAL O₂ and 60% PAL Ar (equal to that found in the Empress 1A – 1478m
7 sample), and (3) modern air. Both the mean $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values, as well as those of individual
8 crushes, lie within this mixing array given the analytical uncertainties (Fig. 2). Other mixing endmembers
9 could be invoked, such a brine-saturated endmember for an atmosphere of 50% PAL O₂ and 80% PAL
10 Ar, but such endmembers cannot all of the variability and would not have obvious origins. In contrast, the
11 three-endmember mixing array involving only a low-O₂/low-Ar atmosphere, NaCl brine, and the modern
12 atmosphere can explain the variability in the entire Neoproterozoic dataset. In this model, the high-O₂
13 Neoproterozoic samples would consist of 25-50% modern air. Such a contamination is possible given the
14 small size of these analyses (≤ 10 pmol total gas yield from crushes) and contaminations of similar
15 magnitude observed in other impermeable minerals (Marty et al., 2013; Pujol et al., 2013; Stuart et al.,
16 2016). No low-O₂/low-Ar procedural standards—neither capillary tubes nor synthetic halites—were
17 reported in the original Blamey et al. (2016) study.

18 The $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values of samples from below 1478m in the Empress 1A core may also
19 express mass-dependent fractionation. Two potential sources are mass-dependent fractionation in the
20 mass spectrometer and gas loss from the halites (Fig. 2). Using York's regression (York et al., 2004) and
21 the analytical 1σ errors, these samples define a best-fit slope of 0.39 ± 0.26 ($r^2 = 0.89$), indistinguishable
22 from the slope of $\sim 1/3$ expected for mass-dependent fractionation (N.B. calculated explicitly, the slope is
23 0.23 for this range in $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values). The Lancer 1 sample fits within this range as well, and
24 the regression of the combined data has an identical slope (0.34 ± 0.16 ; $r^2 = 0.88$). Knudsen diffusion
25 within this system is possible, e.g., during gas migration along grain boundaries. If gas loss follows
26 Rayleigh fractionation, however, then nearly complete gas loss between the 1497m and 1502.2m samples
27 ($\sim 94\%$) would be required to explain the wide variation in $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values. Primary chevron
28 textures and banded fluid inclusions (Spear et al., 2014; Blamey et al., 2016) argue against catastrophic
29 gas loss unless physical stresses created temporary fractures that have since healed (Roedder, 1984).
30 Diffusion of Ar via interstitial hopping, which would express size-dependent molecular fractionation
31 (Severinghaus and Battle, 2006) is too slow in halite to be important on 10^9 -year timescales [$D_0 \sim 100$
32 $\text{cm}^2 \text{s}^{-1}$, $\Delta H = 135 \text{ kJ mol}^{-1}$; (Norgett and Lidiard, 1968; Matzke et al., 1969)]: timescales for 1 m of

displacement exceed 1 Gyr, even at 200°C. Thus, while mass-dependent fractionation may be relevant, it is probably not responsible for the entirety of the correlation between $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values.

High temperatures and fracturing can result in gas loss, while recrystallization can incorporate new gases (Freyer and Wagener, 1975). Borehole temperatures in the Browne formation were measured to be 45 – 50°C (geotherm $\sim 17^\circ\text{C km}^{-1}$) during the drilling of Empress 1A. Apatite fission-track analysis of the overlying Kanpa formation (750 – 780 Ma) suggests that the Browne formation reached $>100^\circ\text{C}$ around 600 – 300 Ma, perhaps associated with the Petermann Ranges or Alice Springs orogenies (Stevens and Apak, 1999; Mory and Haines, 2005). The abundance of banded fluid inclusions suggests that these chevron halites have not been recrystallized as a result of these events. Diffusion along grain boundaries could yield correlated Ar, O_2 , and N_2 abundances for the Empress 1A samples below 1478m..

Post-depositional element cycling within the fluid inclusions by halophiles (Lowenstein et al., 2011; Davila et al., 2015; Bernau et al., 2016) cannot be ruled out. While O_2 can be ephemeral in biogeochemically active systems, the concurrent, correlated variations in Ar are more difficult to explain. A N_2 excess of $>50\%$ from halophilic denitrifiers could reproduce the apparent deficit in both O_2 and Ar observed in some of the Neoproterozoic halites, but only if the primary composition were near NMLA. Moreover, dissolved nitrogen concentrations in seawater, especially at the sea surface and prior to widespread oceanic oxygenation (Fennel et al., 2005), argue against this mechanism: Using ~ 0.1 wt % of brine in halite (Roedder, 1984), Neoproterozoic concentrations of dissolved nitrogen species would need to be tens of μM , orders of magnitude higher than those found today in the surface ocean, to yield such an excess in N_2 .

Taken together, this analysis indicates that preservation artifacts likely affected the O_2 and Ar content measured in the Neoproterozoic halites. Contamination with modern air and air dissolved in brine is the most likely; it can explain all of the variability in the data. Mass-dependent fractionation due to physical processes may be important as well. Both of these mechanisms would artificially raise the O_2 and Ar content of halite-occluded gases relative to N_2 . Consequently, among these samples, the gas contents must be considered upper limits on ancient atmospheric concentrations.

4. Discussion

4.1 Low O_2 in the Neoproterozoic

The youngest halite sample (Empress 1A – 1478m) yields an O_2 content significantly lower than observed in the other Neoproterozoic samples: it implies a $6 \pm 2\%$ PAL O_2 inventory. While Blamey et al.

(2016) argue that the low O_2 reflects growth in dysoxic bottom water, the $\delta O_2/N_2$ and $\delta Ar/N_2$ data are inconsistent with that argument. Halite growth in bottom waters leads to increased incorporation of brine, which would yield $\delta O_2/N_2$ and $\delta Ar/N_2$ values closer to the air-saturated brine endmembers shown in Fig. 2. Yet, the sample is displaced further from brine endmembers than the other samples; the sample does not contain more brine-dissolved air. Incorporation of O_2 -deficient groundwater would have a similar effect to the incorporation of brines, so it can also be ruled out. Another route to a deficit in O_2 is post-depositional O_2 consumption. Some O_2 could have been consumed after deposition if there were sufficient occluded organic matter or other reduced phase. Finally, instrumental mass fractionation, mass-dependent gas loss, and photosynthesis within the fluid inclusions (Lowenstein et al., 2011; Davila et al., 2015) would increase $\delta O_2/N_2$ values. The cause of low O_2 can thus only be explained in one of three scenarios: (1) it reflects a selective N_2 excess in the 1478m sample, but not the other samples, (2) it reflects post-depositional O_2 consumption in the 1478m sample, but much less O_2 consumption in the other samples, or (3) it reflects a less altered atmospheric signal, while the other Neoproterozoic samples incorporated O_2 after deposition.

The first scenario requires several tens of percent excess N_2 to be incorporated, presumably due to denitrification. I reject that possibility based on the excessive amount of nitrogen that would need to be part of the primary fluid inclusion (see above) and the aerobic environment inside inclusions that disfavors denitrification (Rothschild et al., 1994). The second scenario cannot be ruled out, but why none of the other Neoproterozoic halites shows a similar amount of O_2 consumption is puzzling: ephemeral salt pan environments (the depositional environment for the 1478m sample) are less likely to host a productive halophile community than perennial shallow lagoon environments, where the other Empress 1A halites were deposited (Schubert et al., 2010; Spear, 2013). They are therefore less likely to contain reduced carbon substrates for respiration, unless that carbon is allocthonous. The third scenario—a post-depositional O_2 increase—is plausible via two mechanisms. First, contamination by modern air or by contemporaneous brine-dissolved air can increase $\delta O_2/N_2$ and $\delta Ar/N_2$ values in accordance with the mixing curves in Fig. 2. Second, halophilic photoautotrophs could produce O_2 after deposition within the fluid inclusions. Incorporation of viable microbes into primary halites has been observed, primarily in perennial saline lake environments (Schubert et al., 2009, 2010; Lowenstein et al., 2011), and photosynthesis has been observed in cyanobacteria living within halite (Rothschild et al., 1994; Davila et al., 2015). Preliminary evidence suggests that microbes were indeed incorporated into some Browne formation halites (Bernau et al., 2016), but whether they are oxygenic and whether subsequent respiration would eliminate any excess O_2 produced is not known.

I therefore argue that the 1478m sample contains primary (or less altered) Neoproterozoic atmosphere. While this view remains somewhat speculative, it is the most consistent with the $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ data, low contemporaneous marine sulfate concentrations (Kah et al., 2004; Spear et al., 2014), and low contemporaneous marine phosphorus concentrations, which would limit the accumulation of O_2 in the atmosphere (Laakso and Schrag, 2014; Reinhard et al., 2017). The range in measured O_2 content in the Neoproterozoic halites is best explained as variable post-depositional contamination by modern air. One can test more definitively for this contamination by examining the relationship between $^{40}\text{Ar}/^{36}\text{Ar}$ ratios and $\text{O}_2/^{36}\text{Ar}$ ratios in these samples: ^{36}Ar is primordial and not cycled biogeochemically, so performing a similar analysis normalizing against ^{36}Ar instead of N_2 will eliminate one of the assumptions in this study. Analysis of relative amounts of CO_2 in these halites may also reveal the extent of post-depositional organic matter oxidation that could have consumed O_2 in the Empress 1A – 1478m sample. The importance of *in situ* photosynthesis on the occluded gas composition can be investigated by analyzing modern halites: The photoautotroph *Dunalliella salinas* has been routinely observed trapped within halite fluid inclusions (Rothschild et al., 1994; Schubert et al., 2009, 2010; Lowenstein et al., 2011). If photosynthesis within fluid inclusions alters the composition of gases trapped inside, then one would expect to observe O_2 excesses in those samples.

4.2 Low Ar in the Neoproterozoic

A remarkable feature of the Neoproterozoic halite archive is that nearly all samples contain a significant Ar deficit compared to modern air (Fig. 2). The lowest- $\delta\text{Ar}/\text{N}_2$ measurement, from Empress 1A – 1478m, implies an Ar inventory of $41 \pm 9\%$ PAL (1σ). The empirical uncertainty limit of $\pm 20\%$ PAL Ar suggests that the Tonian Ar inventory implied by the halite archive is likely no higher than $\sim 60\%$ PAL. Excluding the highest- $\delta\text{Ar}/\text{N}_2$ point (Empress 1A – 1502.2m)—because it is most likely to be contaminated—yields an atmospheric Ar inventory of $62 \pm 18\%$ PAL (95% confidence interval; $n = 5$). I will use this more conservative latter estimate in the quantitative discussion below.

Unlike for O_2 , changes in Ar due to biogeochemical cycling are not important. The measurements are nonetheless upper limits in part because of the potential for Ar addition via radiogenic decay of ^{40}K . There is no evidence for significant radiogenic Ar excess in these samples, however, contrary to what had been seen for other halites (Freyer and Wagener, 1975). Using an upper limit on K content of 4,000 ppm in the fluid inclusions (Spear et al., 2014) and 0.1 wt % of brine in halite (Roedder, 1984), I estimate that $\leq 4 \times 10^{-14}$ mol, or $\leq 1\%$ of the argon in these samples, would come from from radioactive decay over 815

1 Myr. The halite-derived Tonian atmospheric inventory of ~60% PAL Ar therefore appears robust in this
2 regard.

3 It is useful to compare this halite-derived Ar inventory with those from other archives covering
4 more of Earth history. Three other high-confidence determinations of ancient atmospheric argon exist in
5 the literature, and they are compared with the results of this study in Fig. 3. The best estimate comes from
6 Bender et al. (2008), who used ^{40}Ar , ^{38}Ar , and ^{36}Ar trapped in polar ice to derive the change in ^{40}Ar
7 inventory over the past 800 ka. This record implies a contemporary outgassing rate of $1.1 \pm 0.1 \times 10^8 \text{ mol}$
8 $^{40}\text{Ar yr}^{-1}$ (the total inventory today is $1.65 \times 10^{18} \text{ mol}$), which is supported by a comprehensive outgassing
9 budget and simple models based on the mass balance and heat budget of the Earth. A second higher-
10 confidence measurement comes from the exceptionally preserved Devonian Rhynie chert, which was
11 formed in a silicic hydrothermal lake (Rice et al., 2002) and believed to contain uncontaminated
12 atmospheric Ar (Cadogan, 1977; Rice et al., 1995; Stuart et al., 2016). Step-heating analyses of Ar isotope
13 ratios imply an atmospheric ^{40}Ar inventory at 404 Ma of $96.9 \pm 0.3\%$ present atmospheric level (PAL,
14 assuming ^{36}Ar has been constant); it is stated to be an upper limit. The Devonian ^{40}Ar inventory, if
15 accurate, implies a mean outgassing rate similar to the contemporary rate ($1.27 \pm 0.09 \times 10^8 \text{ mol yr}^{-1}$) over
16 the past 404 Myr. Finally, an Archaean $^{40}\text{Ar}/^{36}\text{Ar}$ ratio was estimated by Pujol et al. (2013), who analyzed
17 fluid inclusions in a 3.5 Ga hydrothermal quartz from the Dresser formation in the Pilbara craton
18 (Western Australia). They argue that the samples, which have undergone low-grade metamorphism,
19 preserve ancient atmospheric gases. If ^{36}Ar had degassed completely by 3.5 Ga, their results imply that
20 the ^{40}Ar inventory was between 48% and 71% PAL in the Archaean, depending on when the fluid
21 inclusions had formed between 3.5 Ga and 2.7 Ga. Many other examples of potential paleo-atmospheric
22 argon archives, primarily silicates, are likely contaminated with younger atmosphere or excess ^{40}Ar
23 (Martinez et al., 1984; Hanes et al., 1985; Turner, 1988; Lee, 2009)

24 The Tonian atmospheric Ar inventory derived here, if accurate, is significantly lower than the
25 inventory predicted by linearly extrapolating the Devonian outgassing rate (i.e., $93.7 \pm 0.5\%$ PAL; $p \leq$
26 0.05). Moreover, it is lower than what the most recent Ar outgassing model would predict (Fig. 3).
27 Instead, the mean measured Ar content implies that the outgassing rate between 815 – 404 Ma was 5 – 16
28 times higher than that observed since the Devonian (i.e., $7 - 21 \times 10^8 \text{ mol } ^{40}\text{Ar yr}^{-1}$). Between 2.8×10^{17}
29 and $8.7 \times 10^{17} \text{ mol } ^{40}\text{Ar}$ would need to degas in ~410 Myr, or 7 – 23% of the total amount of ^{40}Ar thought
30 to be produced over Earth's history (Zhang, 2014). These estimates require degassing fluxes at least
31 several times the radiogenic Ar that would accumulate in the crust over 1 Ga [$4 \times 10^{16} \text{ mol}$ (Porcelli and
32 Ballentine, 2002; Bender et al., 2008)], and an amount several times greater than the estimated inventory

1 of the upper, degassed mantle. In contrast, the lower, undegassed mantle is estimated to contain $\sim 10^{18}$ mol
2 ^{40}Ar (Zhang, 2014).

3 Based on the sizes of these reservoirs, the undegassed mantle reservoir would be the most likely
4 source of this radiogenic ^{40}Ar . Hotspot sources, which draw from less degassed mantle reservoirs
5 (Deschamps et al., 2011; Mukhopadhyay, 2012; Caracausi et al., 2016), comprise only 2% of the ^{40}Ar
6 outgassing budget today [$0.02 \text{ mol } ^{40}\text{Ar yr}^{-1}$; (Bender et al., 2008)], so a different degassing mode or
7 mechanism may be relevant. The emplacement of large igneous provinces and the evidence for mantle
8 superplumes during the breakup of Rodinia (Ernst et al., 2008; Li et al., 2008) suggests that direct
9 degassing of the primordial mantle reservoirs could have accelerated toward the end of the
10 Neoproterozoic.

11 The data therefore suggest a more complex structure to solid-Earth degassing than first-order
12 models would predict. After an initial “catastrophic” degassing period lasting <200 Myr (Ozima, 1975;
13 Pujol et al., 2013; Tucker and Mukhopadhyay, 2014) and 1 Gyr of outgassing that could resemble a first-
14 order loss process, the atmospheric Ar inventory may have stayed near 60% PAL for much of the
15 Proterozoic. The rapid accumulation between 815 Ma and 404 Ma was temporary and followed by
16 another period of relatively quiescent outgassing activity. If mantle outgassing fluxes are capable of such
17 punctuated rises and falls over geologic time, one may need to revisit the mechanisms through which
18 tectonic variability modulates greenhouse gases (e.g., CO_2) and climate on geologic timescales.

19 Another way to reconcile these measurements with the existing Ar record is to invoke enigmatic
20 preservation artifacts or contaminations within the silicate and halite archives. Arguably, the 800 ka ice-
21 core record of Ar degassing is the most reliable given our understanding of atmospheric bubble occlusion
22 and preservation (Bender et al., 1997) and the low K concentrations in Antarctic ice. However, in both the
23 Rhynie chert and Archaean quartz samples, the physics of atmospheric gas preservation are not known
24 well. Endmember mixing arguments are invoked to infer atmospheric compositions, but precise air
25 occlusion dates are difficult to determine. Thus the atmospheric Ar record derived from those archives
26 must be considered upper limits subject to revision. The processes through which atmospheric gas is
27 preserved in halite are also poorly studied (Freyer and Wagener, 1975), but primary air inclusions should
28 be syndepositional (Roedder, 1984) and non-fractionating, based on the relative accuracy of modern
29 halites and the observation that some halite crystals form inclusions at the air-water interface (Blamey et
30 al., 2016). Most post-depositional fractionation processes should yield overestimates in atmospheric Ar
31 inventory rather than underestimates using the Ar/N_2 ratio method. It is conceivable, however, that Ar
32 could be selectively excluded from halite fluid inclusions under certain conditions based on its size;
33 laboratory studies of the gas inclusion process would be informative.

Clearly, further investigation into the potential halite paleoatmospheric archive is warranted. Noble-gas studies would be especially useful, as they are not biogeochemically cycled. For example, simultaneous measurement of ^{40}Ar , ^{38}Ar , and ^{36}Ar in halite could yield a ^{40}Ar inventory insensitive to contamination by dissolved gases, mass-dependent fractionation, and size-dependent fractionation (Bender et al., 2008). In addition, noble-gas isotope signatures from primordial mantle sources (Mukhopadhyay, 2012; Caracausi et al., 2016) could be used to test whether outgassing from a primordial mantle reservoir led to an unprecedented rise in atmospheric Ar during the Neoproterozoic.

5. Concluding remarks

This reanalysis of gases extracted from Neoproterozoic halites highlights the need for a fuller understanding of how gases are trapped and preserved in these and other archives. Evidence for contamination by modern atmospheric and brine-dissolved air the initial conclusions of Blamey et al. (2016) in question. The covariation in O_2 and Ar relative to N_2 is difficult to explain otherwise. Instead of ~50% PAL O_2 , the data suggest that the Tonian atmosphere contained $\leq 6\%$ PAL O_2 (≤ 1 mol %). Moreover, the halite archive suggests that the atmospheric Ar inventory during the Tonian was unexpectedly low, i.e., $\leq 60\%$ PAL Ar. While the downward revision in Tonian O_2 content makes the halite record more consistent with existing models of atmospheric oxygenation in the late Neoproterozoic (Lyons et al., 2014), the downward revision in Tonian Ar content is more surprising, as it has no precedent and is not obviously incompatible with our understanding of the evolution of the solid Earth.

Can ancient atmospheric composition be inferred from gases trapped in halites? I would argue yes, in principle. However, additional laboratory and natural experiments should be undertaken before halite gas archives are further applied for paleo-atmospheric studies. Two key problems to address are (1) whether gas compositions drastically different from the modern atmosphere can be inferred without corrections for contamination and (2) whether the depositional environment and endolithic microbial communities influence the composition of gases locked within halite. With careful study, the systematics of these archives can be determined, and with them, a clearer picture of Earth's atmospheric history in deep time.

Acknowledgements

I would like to thank R. Dasgupta, C.-T. Lee, N. R. McKenzie, and H. M. Gonnermann for insightful discussions over the course of this work.

1

2 **Fig. 1. Variation in $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ with depth in the Empress 1A core.**

Fig. 2. Multicomponent analysis of Neoproterozoic halite gas archives. Measured $\delta\text{O}_2/\text{N}_2$ vs. $\delta\text{Ar}/\text{N}_2$ values are shown as (A) mean $\pm 1\sigma$ and (B) individual crushes for each sample. The origin represents the present-day atmospheric composition. Two-component mixing defines linear arrays between endmembers, such as that between the calculated $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values for air- and NaCl-saturated brines (stars) and the Empress 1A – 1478m sample (black triangle). Points along the mixing arrays represent increments of 25% in the mixing fractions. The samples here may display contamination by modern air, brine-dissolved air, and mass-dependent fractionation after initial deposition.

Fig 2. The history of atmospheric ^{40}Ar . With one exception, the Tonian halite data imply an Ar inventory below that predicted by the most recent first-order solid-Earth outgassing model of Stuart et al. (2016). Only one example output of that model is shown because the range of outputs compatible with both the Archaeon, Devonian, and modern inventories is similar to the thickness of the line at -815 Myr. On average, the halite data imply ~60% PAL Ar at -815 Myr (see main text) and potentially a step-like increase in atmospheric Ar at the end of the Neoproterozoic. Three possible values are shown for the Archaeon quartz because of an uncertainty in when the analyzed fluids were initially occluded (Pujol et al., 2013).

References

- Bender, M., Sowers, T. and Brook, E. (1997) Gases in ice cores. *Proc. Natl. Acad. Sci. U. S. A.* 94, 8343-8349.
- Bender, M., Sowers, T. and Labeyrie, L. (1994) The Dole effect and its variations during the last 130,000 years as measured in the Vostok ice core. *Global Biogeochem. Cycles* 8, 363-376.
- Bender, M.L., Barnett, B., Dreyfus, G., Jouzel, J. and Porcelli, D. (2008) The contemporary degassing rate of ^{40}Ar from the solid Earth. *Proc. Natl. Acad. Sci. U. S. A.* 105, 8232-8237.
- Bernau, J.A., Eichenlaub, L.A. and Benison, K.C. (2016) Preliminary fluid inclusion evidence of acid brines in halite of the Neoproterozoic Browne Formation, central Australia, Geological Society of America Abstracts with Programs. Geological Society of America Denver, CO.
- Berner, R.A. (1999) Atmospheric oxygen over Phanerozoic time. *Proc. Natl. Acad. Sci. U. S. A.* 96, 10955-10957.
- Berner, R.A. (2006) Geological nitrogen cycle and atmospheric N_2 over Phanerozoic time. *Geology* 34, 413-415.
- Berner, R.A. and Landis, G.P. (1987) Chemical analysis of gaseous bubble inclusions in amber: The composition of ancient air? *Am. J. Sci.* 287, 757-762.
- Blamey, N.J.F., Brand, U., Parnell, J., Spear, N., Lécuyer, C., Benison, K., Meng, F. and Ni, P. (2016) Paradigm shift in determining Neoproterozoic atmospheric oxygen. *Geology*.
- Cadogan, P.H. (1977) Palaeoatmospheric argon in Rhynie chert. *Nature* 268, 38-41.
- Canfield, D.E. (1998) A new model for Proterozoic ocean chemistry. *Nature* 396, 450-453.
- Caracausi, A., Avice, G., Burnard, P.G., Füri, E. and Marty, B. (2016) Chondritic xenon in Earth's mantle. *Nature* 533, 82-85.
- Cerling, T.E. (1989) Does the gas content of amber reveal the composition of palaeoatmospheres? *Nature* 339, 695-696.
- Cox, G.M., Halverson, G.P., Stevenson, R.K., Vokaty, M., Poirier, A., Kunzmann, M., Li, Z.-X., Denyszyn, S.W., Strauss, J.V. and Macdonald, F.A. (2016) Continental flood basalt weathering as a trigger for Neoproterozoic Snowball Earth. *Earth Planet. Sci. Lett.* 446, 89-99.
- Davila, A.F., Hawes, I., Araya, J.G., Gelsinger, D.R., DiRuggiero, J., Ascaso, C., Osano, A. and Wierzbos, J. (2015) In situ metabolism in halite endolithic microbial communities of the hyperarid Atacama Desert. *Front. Microbiol.* 6.
- Deschamps, F., Kaminski, E. and Tackley, P.J. (2011) A deep mantle origin for the primitive signature of ocean island basalt. *Nature Geosci.* 4, 879-882.
- Dhuime, B., Wuestefeld, A. and Hawkesworth, C.J. (2015) Emergence of modern continental crust about 3 billion years ago. *Nature Geosci.* 8, 552-555.
- Ernst, R.E., Wingate, M.T.D., Buchan, K.L. and Li, Z.X. (2008) Global record of 1600–700 Ma Large Igneous Provinces (LIPs): Implications for the reconstruction of the proposed Nuna (Columbia) and Rodinia supercontinents. *Precambrian Res.* 160, 159-178.
- Fennel, K., Follows, M. and Falkowski, P.G. (2005) The co-evolution of the nitrogen, carbon, and oxygen cycles in the Proterozoic ocean. *Am. J. Sci.* 305, 526-545.
- Freyer, H.D. (1978) Degradation products of organic matter in evaporites containing trapped atmospheric gases. *Chem. Geol.* 23, 293-307.
- Freyer, H.D. and Wagener, K. (1975) Review on present results on fossil atmospheric gases trapped in evaporites. *Pure Appl. Geophys.* 113, 403-418.
- Gilleaudeau, G.J., Frei, R., Kaufman, A.J., Kah, L.C., Azmy, K., Bartley, J.K., Chernyavskiy, P. and Knoll, A.H. (2016) Oxygenation of the mid-Proterozoic atmosphere: clues from chromium isotopes in carbonates. *Geochem. Persp. Lett.* 2, 178-187.
- Halverson, G.P., Dudás, F.Ö., Maloof, A.C. and Bowring, S.A. (2009) Evolution of the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of Neoproterozoic seawater. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 256, 109-129.

- 1 Hamano, Y. and Ozuima, M. (1978) Earth-atmosphere evolution model based on Ar isotopic data, in:
2 Alexander, J., E. C., Ozima, M. (Eds.), Terrestrial Rare Gases. Center for Academic Publications
3 Japan, Tokyo.
- 4 Hanes, J.A., York, D. and Hall, C.M. (1985) An $^{40}\text{Ar}/^{39}\text{Ar}$ geochronological and electron microprobe
5 investigation of an Archean pyroxenite and its bearing on ancient atmospheric compositions. *Can. J.*
6 *Earth Sci.* 22, 947-958.
- 7 Hawkesworth, C.J., Cawood, P.A. and Dhuime, B. (2016) Tectonics and crustal evolution. *GSA Today*
8 26, 4-11.
- 9 Kah, L.C., Lyons, T.W. and Frank, T.D. (2004) Low marine sulphate and protracted oxygenation of the
10 Proterozoic biosphere. *Nature* 431, 834-838.
- 11 Kirschvink, J.L. (1992) Late Proterozoic Low-Latitude Global Glaciation: The Snowball Earth, in:
12 Schopf, J.W., Klein, C., des Maris, D. (Eds.), The Proterozoic Biosphere: A Multidisciplinary Study.
13 Cambridge UP, Cambridge, pp. 51-52.
- 14 Laakso, T.A. and Schrag, D.P. (2014) Regulation of atmospheric oxygen during the Proterozoic. *Earth*
15 *Planet. Sci. Lett.* 388, 81-91.
- 16 Lee, J.K.W. (2009) Using argon as a temporal tracer of large-scale geologic processes. *Chem. Geol.* 266,
17 104-112.
- 18 Li, Z.X., Bogdanova, S.V., Collins, A.S., Davidson, A., De Waele, B., Ernst, R.E., Fitzsimons, I.C.W.,
19 Fuck, R.A., Gladkochub, D.P., Jacobs, J., Karlstrom, K.E., Lu, S., Natapov, L.M., Pease, V.,
20 Pisarevsky, S.A., Thrane, K. and Vernikovsky, V. (2008) Assembly, configuration, and break-up
21 history of Rodinia: A synthesis. *Precambrian Res.* 160, 179-210.
- 22 Lowenstein, T.K., Schubert, B.A. and Timofeeff, M.N. (2011) Microbial communities in fluid inclusions
23 and long-term survival in halite. *GSA Today* 21, 4-9.
- 24 Lyons, T.W., Reinhard, C.T. and Planavsky, N.J. (2014) The rise of oxygen in Earth's early ocean and
25 atmosphere. *Nature* 506, 307-315.
- 26 Macdonald, F.A., Schmitz, M.D., Crowley, J.L., Roots, C.F., Jones, D.S., Maloof, A.C., Strauss, J.V.,
27 Cohen, P.A., Johnston, D.T. and Schrag, D.P. (2010) Calibrating the Cryogenian. *Science* 327, 1241-
28 1243.
- 29 Martinez, M.L., York, D., Hall, C.M. and Hanes, J.A. (1984) Oldest reliable $^{40}\text{Ar}/^{39}\text{Ar}$ ages for
30 terrestrial rocks: Barberton Mountain komatiites. *Nature* 307, 352-354.
- 31 Marty, B., Zimmermann, L., Pujol, M., Burgess, R. and Philippot, P. (2013) Nitrogen Isotopic
32 Composition and Density of the Archean Atmosphere. *Science* 342, 101-104.
- 33 Matzke, H., Rickers, G. and Sørensen, G. (1969) Rare gas diffusion in NaCl. *Z. Naturforschung* 24, 820-
34 826.
- 35 Mory, A.J. and Haines, P.W. (2005) GSWA Lancer 1 well completion report (interpretive papers),
36 Officer and Gunbarrel basins, Western Australia. Australia Geological Survey, p. 81.
- 37 Mukhopadhyay, S. (2012) Early differentiation and volatile accretion recorded in deep-mantle neon and
38 xenon. *Nature* 486, 101-104.
- 39 Norgett, M.J. and Lidiard, A.B. (1968) The migration of inert gases in ionic crystals. *Philosophical*
40 *Magazine* 18, 1193-1210.
- 41 Norman, D.I. and Musgrave, J.A. (1994) N₂-Ar-He compositions in fluid inclusions: Indicators of fluid
42 source. *Geochim. Cosmochim. Acta* 58, 1119-1131.
- 43 Onda, K., Sada, E., Kobayashi, T., Kito, A. and Ito, K. (1970) Salting-out parameters of gas solubility in
44 aqueous salt solutions. *J. Chem. Eng. Jpn.* 3, 18-23.
- 45 Ozima, M. (1975) Ar isotopes and Earth-atmosphere evolution models. *Geochim. Cosmochim. Acta* 39,
46 1127-1134.
- 47 Planavsky, N.J., Reinhard, C.T., Wang, X., Thomson, D., McGoldrick, P., Rainbird, R.H., Johnson, T.,
48 Fischer, W.W. and Lyons, T.W. (2014) Low Mid-Proterozoic atmospheric oxygen levels and the
49 delayed rise of animals. *Science* 346, 635-638.
- 50 Porcelli, D. and Ballentine, C.J. (2002) Models for the distribution of terrestrial noble gases and evolution
51 of the atmosphere. *Reviews in Mineralogy and Geochemistry* 47, 411-480.

- Pujol, M., Marty, B., Burgess, R., Turner, G. and Philippot, P. (2013) Argon isotopic composition of Archaean atmosphere probes early Earth geodynamics. *Nature* 498, 87-90.
- Reinhard, C.T., Planavsky, N.J., Gill, B.C., Ozaki, K., Robbins, L.J., Lyons, T.W., Fischer, W.W., Wang, C., Cole, D.B. and Konhauser, K.O. (2017) Evolution of the global phosphorus cycle. *Nature* 541, 386-389.
- Rice, C.M., Ashcroft, W.A., Batten, D.J., Boyce, A.J., Caulfield, J.B.D., Fallick, A.E., Hole, M.J., Jones, E., Pearson, M.J., Rogers, G., Saxton, J.M., Stuart, F.M., Trewin, N.H. and Turner, G. (1995) A Devonian auriferous hot spring system, Rhynie, Scotland. *J. Geol. Soc.* 152, 229-250.
- Rice, C.M., Trewin, N.H. and Anderson, L.I. (2002) Geological setting of the Early Devonian Rhynie cherts, Aberdeenshire, Scotland: an early terrestrial hot spring system. *J. Geol. Soc.* 159, 203-214.
- Roedder, E. (1984) The fluids in salt. *Am. Mineral.* 69, 413-439.
- Rothschild, L.J., Giver, L.J., White, M.R. and Mancinelli, R.L. (1994) Metabolic activity of microorganisms in evaporites. *J. Phycol.* 30, 431-438.
- Schrag, D.P., Berner, R.A., Hoffman, P.F. and Halverson, G.P. (2002) On the initiation of a snowball Earth. *Geophysics, Geochemistry, Geosystems* 3.
- Schubert, B.A., Lowenstein, T.K., Timofeeff, M.N. and Parker, M.A. (2009) How do prokaryotes survive in fluid inclusions in halite for 30 k.y.? *Geology* 37, 1059-1062.
- Schubert, B.A., Lowenstein, T.K., Timofeeff, M.N. and Parker, M.A. (2010) Halophilic Archaea cultured from ancient halite, Death Valley, California. *Environ. Microbiol.* 12, 440-454.
- Severinghaus, J.P. and Battle, M.O. (2006) Fractionation of gases in polar ice during bubble close-off: New constraints from firm air Ne, Kr and Xe observations. *Earth Planet. Sci. Lett.* 244, 474-500.
- Siemann, M.G. and Ellendorff, B. (2001) The composition of gases in fluid inclusions of late Permian (Zechstein) marine evaporites in Northern Germany. *Chem. Geol.* 173, 31-44.
- Spear, N. (2013) A Multidisciplinary Analysis of Evaporite Rocks from the Mid-Neoproterozoic Browne Formation, Officer Basin, Western Australia, *Earth and Environmental Science*. University of Pennsylvania, Philadelphia, PA, p. 121.
- Spear, N., Holland, H.D., Garcia-Veigas, J., Lowenstein, T.K., Giegengack, R. and Peters, H. (2014) Analyses of fluid inclusions in Neoproterozoic marine halite provide oldest measurement of seawater chemistry. *Geology*.
- Sperling, E.A., Wolock, C.J., Morgan, A.S., Gill, B.C., Kunzmann, M., Halverson, G.P., Macdonald, F.A., Knoll, A.H. and Johnston, D.T. (2015) Statistical analysis of iron geochemical data suggests limited late Proterozoic oxygenation. *Nature* 523, 451-454.
- Stevens, M.K. and Apak, S.N.c. (1999) GSWA Empress 1 and 1A well completion report: Yowalga sub-basin, Officer Basin, Western Australia. *Western Australia Geological Survey*, p. 110.
- Stolper, D.A., Bender, M.L., Dreyfus, G.B., Yan, Y. and Higgins, J.A. (2016) A Pleistocene ice core record of atmospheric O₂ concentrations. *Science* 353, 1427-1430.
- Stuart, F.M., Mark, D.F., Gandanger, P. and McConville, P. (2016) Earth-atmosphere evolution based on new determination of Devonian atmosphere Ar isotopic composition. *Earth Planet. Sci. Lett.* 446, 21-26.
- Stüeken, E.E., Kipp, M.A., Koehler, M.C., Schwieterman, E.W., Johnson, B. and Buick, R. (2016) Modeling pN_2 through Geological Time: Implications for Planetary Climates and Atmospheric Biosignatures. *Astrobiology* 16, 949-963.
- Taylor, S.R. and McLennan, S.M. (1985) The continental crust: Its composition and evolution. Blackwell Scientific Publications, Palo Alto, CA.
- Tucker, J.M. and Mukhopadhyay, S. (2014) Evidence for multiple magma ocean outgassing and atmospheric loss episodes from mantle noble gases. *Earth Planet. Sci. Lett.* 393, 254-265.
- Turner, G. (1988) Hydrothermal fluids and argon isotopes in quartz veins and cherts. *Geochim. Cosmochim. Acta* 52, 1443-1448.
- Turner, G. (1989) The outgassing history of Earth's atmosphere. *J. Geol. Soc.* 146, 147-154.
- Vreeland, R.H., Rosenzweig, W.D. and Powers, D.W. (2000) Isolation of a 250 million-year-old halotolerant bacterium from a primary salt crystal. *Nature* 407, 897-900.

- 1 York, D., Evensen, N.M., Martínez, M.L. and De Basabe Delgado, J. (2004) Unified equations for the
2 slope, intercept, and standard errors of the best straight line. *American Journal of Physics* 72, 367-
3 375.
- 4 Zerkle, A.L. and Mikhail, S. (2017) The geobiological nitrogen cycle: From microbes to the mantle.
5 *Geobiology* 15, 343-352.
- 6 Zhang, Y. (2014) Degassing history of the Earth, in: Holland, H.D., Turekian, K. (Eds.), *Treatise on*
7 *Geochemistry*. Elsevier, Waltham, MA, pp. 37-69.