C. R. Geoscience xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Comptes Rendus Geoscience

www.sciencedirect.com

Petrology, Geochemistry

Salinity of the Archaean oceans from analysis of fluid inclusions in quartz

Bernard Marty [a,*], Guillaume Avice [b], David V. Bekaert [a], Michael W. Broadley [a]

[a] Centre de recherches pétrographiques et géochimiques, CNRS, Université de Lorraine, 15, rue Notre-Dame-des-Pauvres, 54500 Vandœuvre-lès-Nancy, France
[b] California Institute of Technology, Division of Geological and Planetary Sciences, 1200 E. California Blvd, Pasadena, CA 91125, USA

ARTICLE INFO

Article history:
Received 27 November 2017
Accepted after revision 12 December 2017
Available online xxx

Handled by Marc Chaussidon

Keywords:
Salinity
Archean oceans
Noble gases

ABSTRACT

Fluids trapped in inclusions in well-characterized Archaean hydrothermal quartz crystals were analyzed by the extended argon–argon method, which permits the simultaneous measurement of chlorine and potassium concentrations. Argon and nitrogen isotopic compositions of the trapped fluids were also determined by static mass spectrometry. Fluids were extracted by stepwise crushing of quartz samples from North Pole (NW Australia) and Barberton (South Africa) 3.5–3.0-Ga-old greenstone belts. The data indicate that fluids are a mixture of a low salinity end-member, regarded as the Archaean oceanic water, and several hydrothermal end-members rich in Cl, K, N, and radiogenic parentless ^{40}Ar. The low Cl–K end-member suggests that the salinity of the Archaean oceans was comparable to the modern one, and that the potassium content of the Archaean oceans was lower than at present by about 40%. A constant salinity of the oceans through time has important implications for the stabilization of the continental crust and for the habitability of the ancient Earth.

1. Introduction

Prokaryotic microbial life was already present during the Archaean aeon 3.8–2.5 Ga ago (Knauth, 2005, and refs. therein). These ancient forms of life developed in the Archaean oceans, whose properties – salinity, temperature, chemistry – are not well understood, and are subject to debated studies. Here we focus on the salinity of the Archaean oceans. The halogens would have been delivered early to the surface of the Earth by impacting bodies as well as by catastrophic degassing of the mantle. Holland (1984) estimated that the salinity of the ancient oceans could have been ~1.2 times the modern inventory by assuming that all evaporites found on the continents were once dissolved in the oceans. Unfortunately, the extent of Precambrian evaporites is unknown, due to their poor preservation. Knauth (2005) went a step further by also considering brines in stratified oceans and those presumably preserved in continents, and proposed an Archaean ocean salinity about 1.2–2 times the modern one. These authors considered that the only efficient process to decrease the salinity of the oceans is evaporite formation and isolation onto continental platforms. Consequently, most of halogens would have remained dissolved in the oceans before the major pulses of continental growth. However, another potential pathway for halogens to escape the surface reservoirs is subduction and recycling into the mantle, as suggested by recent budgets at arcs (Kendrick et al., 2012, 2017). The flux of halogens from the mantle to the oceans and from the oceans to the oceanic crust are

---

[*] Corresponding author.
E-mail address: bernard.marty@univ-lorraine.fr (B. Marty).

https://doi.org/10.1016/j.crte.2017.12.002
1631-0713/

Please cite this article in press as: Marty B, et al. Salinity of the Archaean oceans from analysis of fluid inclusions in quartz. C. R. Geoscience (2018), https://doi.org/10.1016/j.crte.2017.12.002

also poorly constrained (Berner and Berner, 2012), and it is difficult to evaluate the salinity of ancient oceans from geochemical mass balance considerations.

The composition of fluid inclusions in selected retentive mineral phases of Archaean age have already been used to provide an insight into the composition of the past hydrosphere (de Ronde et al., 1997; Weiershauser and Spooner, 2005). This approach is not without problems, since (i) fluid inclusions are not necessarily contemporaneous with their host mineral, many of them being secondary, and (ii) trapped fluids are generally a mixture of several components including hydrothermal end-members. de Ronde et al. (1997) estimated that the Archaean oceans' salinity was about twice the modern one, from correlations between relevant chemical species in fluid inclusions trapped in quartz-goethite deposits. These samples, initially interpreted as hydrothermal chimneys older than 3.2 Ga, were later on regarded as Cenozoic spring deposits (Lowe and Byerly, 2003). From statistical analysis of fluid inclusions trapped in hydrothermal quartz in Archaean terrains worldwide, Weiershauser and Spooner (2005) suggested that the Archaean oceans could have been more saline than the present-day oceans by up to one order of magnitude.

Given their chemical inertness, noble gases behave as physical tracers in the environment. In particular, the atmospheric partial pressures of non-radiogenic argon isotopes (^{36}Ar and ^{38}Ar) are unlikely to have drastically varied in the past since the Earth's building episodes, $\sim$4.5 Ga ago. The excellent match between the atmospheric ^{38}Ar/^{36}Ar ratio (two Ar isotopes of primordial origin) and that of Ar trapped in primitive meteorites attests that atmospheric Ar was not quantitatively lost to space. Independently, noble gas isotope systematics indicates that mantle degassing did not contribute quantitatively to the atmospheric inventory of these elements after the Earth's formation. The large difference in the ^{40}Ar/^{36}Ar values between the mantle ($\sim 10^4$) and the atmosphere (298.6) implies that less than 2% of mantle ^{36}Ar has been transferred to the atmosphere since the time of the Earth's formation (e.g., Ozima and Podosek, 2002). A similar conclusion is obtained from ^{36}Ar flux estimates. The modern flux of ^{36}Ar from the mantle is $\sim$2000 mol/year (e.g., Pujol et al., 2013 and refs. therein). Integrated over 3.5 Gy and assuming a constant flux through time, the amount of ^{36}Ar degassed from the mantle is only about 0.1% of its atmospheric inventory ($5.55 \cdot 10^{15}$ mol). The degassing rate of the mantle was probably higher in the past because of a higher thermal regime. Coltice et al. (2009) estimated that the melting rate of the mantle was by a factor of $\sim$20 higher 3.5 Gy ago as compared to the present-day rate. In this case, the contribution of mantle ^{36}Ar degassed to the atmosphere represents only 0.8% of the ^{36}Ar inventory, which is still negligible in the context of this study. Further constraints on the behaviour of atmospheric noble gases through time stem from the analysis of paleo-atmospheric gases trapped in Archaean fluid inclusions (FIs). The isotope compositions of neon, argon (^{38}Ar/^{36}Ar) and krypton of the Archaean atmosphere were found similar to those of modern air (Avice et al., 2017; Pujol et al., 2011), suggesting (i) no, or limited, escape to space for these elements since that aeon, and (ii) weak contribution from mantle noble gases (e.g., Ne). A closed system atmosphere for inert gases, including N_2, is consistent with models of atmospheric evolution through time since the Archaean aeon (Lichtenegger et al., 2010).

The concentration of noble gases in surface water is a function of their atmospheric partial pressure (assumed to be constant for, e.g., ^{36}Ar, see above) as well as water temperature and salinity. Thus, other dissolved species of interest can be scaled to noble gas concentrations to investigate their origin and behaviour through time. Our group previously analyzed N_2 together with Ar isotopes in a suite of Archaean FI-bearing quartz. In hydrothermal quartz FIs, argon is a mixture of dissolved atmospheric Ar and of one or several hydrothermal end-members rich in radiogenic ^{40}Ar (hereby ^{40}Ar*), thus permitting the identification of mixing trends and therefore the compositions of the different components. Such identification has otherwise been a major problem in previous FI studies. Based on ^{40}Ar/^{36}Ar versus N_2/^{36}Ar correlations, Marty et al. (2013) proposed that the Archaean partial pressure of atmospheric N_2 was comparable to, or lower than, the present-day one and that the ^{15}N/^{14}N ratio did not vary significantly since 3.5 Ga ago, in agreement with results from aeronomic modelling (Lichtenegger et al., 2010). In this work, we adopt the same approach for halogens (here Cl) and potassium, also quantified together with argon isotopes in neutron-irradiated quartz (e.g., Kendrick, 2012; Kendrick et al., 2001). Using samples for which fluids trapped in FIs have been demonstrated to be Archaean (Avice et al., 2017; Marty et al., 2013; Pujol et al., 2011, 2013), we define the surface water component, presumably seawater for the Cl/^{36}Ar and K/^{36}Ar ratios, and infer its salinity from solubility data for argon.

2. Samples

Several of the present samples have been previously analyzed to get insight into the composition of the Archaean atmosphere.

2.1. Dresser formation, North Pole, Pilbara Craton, NW Australia

Samples PI-02-39-# are from the 3.49-Ga-old Dresser formation, Warrawoona Group, Pilbara Craton at North Pole (Western Australia) (Foriel et al., 2004). These are quartz-carbonate aggregates forming pods in undeformed pillow basalts at the top of the Dresser formation. Quartz contains abundant, 1–25-μm, two-phase (liquid and $\sim$5% vapour) aqueous inclusions. They are randomly distributed throughout the host quartz, which supports a primary origin. The trapped fluids are interpreted as representing mixing between a "North Pole seawater" end-member and several hydrothermal components with variable Cl/K, Ba and metal contents. The salinity of trapped fluids is highly variable (average: $\sim$12%) with end-member values comparable to, or lower than, that of modern seawater (Foriel et al., 2004). The age of trapped fluids is likely >2.7 Ga, and probably contemporaneous with the Dresser formation (Pujol et al., 2013). Trapped fluids contain Archaean paleo-

Please cite this article in press as: Marty B, et al. Salinity of the Archaean oceans from analysis of fluid inclusions in quartz. C. R. Geoscience (2018), https://doi.org/10.1016/j.crte.2017.12.002