Concentrations and isotope ratios of He and other noble gases in the atmosphere during 1978–2011

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The concentration of He in the atmosphere (residence time ~10^6 years) is governed by the balance between its release from the solid earth and its loss into space. Due to the burning of fossil fuels, which is known to be rich in He, an increase of the atmospheric He concentration over the past decades has been predicted. However, the predicted increase is small, and the precision of currently available measurement techniques is insufficient to verify this potential increase.

An alternative approach to study this possible increase in the atmospheric He concentration is to analyse the $^3He/^4He$ ratio in historic air samples. The $^3He/^4He$ ratio in fossil fuels is commonly one to two orders of magnitude lower than in the atmosphere. An increase of the He concentration in the atmosphere due to burning of fossil fuel would therefore correspond to a decrease of the atmospheric $^3He/^4He$ ratio that might be detectable with currently available measurement techniques. However, while some studies claim to have found evidence for a decrease in the $^3He/^4He$ ratio in the atmosphere during the last few decades, other studies were not able to confirm this observation.

In an attempt to resolve this long-standing controversy, we conducted isotopic analyses of *all* the atmospheric noble gases (He, Ne, Ar, Kr and Xe) in air samples from a well-defined archive of marine boundary layer air in the southern hemisphere (Cape Grim Air Archive, Australian Bureau of Meteorology and CSIRO). In our presentation we will report the results of these analyses and discuss them in terms of a possible change in the atmospheric He concentration. The $^4He/^{20}Ne$ ratio in particular turned out to be a very sensitive proxy for this purpose. Because the $^4He/^{20}Ne$ ratio in fossil fuels is about 8 orders of magnitude lower than in the atmosphere, the addition of noble gases from fossil fuels to the atmosphere has a much stronger effect on the $^4He/^{20}Ne$ ratio than on the $^3He/^4He$ ratio. At the same time, if He and Ne are not separated from each other before analysis in the mass spectrometer, the $^4He/^{20}Ne$ ratio can be quantified with a better precision than the $^3He/^4He$ ratio. Broadening the atmospheric He analysis to include other noble gas isotopes therefore allows us to put much firmer constraints on possible changes in the atmospheric He concentration that may have resulted from the burning of fossil fuels during the last few decades.

Improving ^{182}Hf-^{182}W ages in altered CR chondrites

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Introduction

Despite their high content of segregated metal and their diverse degrees of alteration, CR chondrites are considered among the most primitive meteorites in the solar system. Applying the ^{182}Hf-^{182}W chronometer to these samples therefore seems interesting to better constrain the earliest stages of metal segregation. While NWA 721 and NWA 801 yield ^{182}Hf-^{182}W ages of ~5 Ma after CAIs, Renazzo is surprisingly ~50 Ma younger [1], which suggests that the ^{182}Hf-^{182}W chronometer may have been disturbed in this particular sample.

Hf and W behavior in natural processes

Although the ^{182}Hf-^{182}W chronometer may have been reset by thermal metamorphism [2], Renazzo seems free of thermal overprinting. However, this meteorite shows evidence of strong aqueous alteration [3] and Pourbaix (Eh-pH) diagrams indicate that tungsten is affected by this process [4]. $\varepsilon^{182}W$ values, which are corrected for mass dependent fractionation, will not be harmed, whereas the Hf/W (parent/daughter) ratios will. Hafnium is indeed far less mobile than W that, in neutral to high-pH fluids, are most likely lost as tungstate. The internal isochron is thus disturbed and the apparent age is younger.

A simple single-stage model suggests that aqueous alteration rotates the isochron around the y-intercept. Thus, the y-intercept seems suited to determine the timing of metal-silicate segregation, even in altered samples. This model reduces the time interval between NWA 701 / NWA 801 and Renazzo to 14 ± 14 Ma.

Tafassasset: an old unaltered CR chondrite

Tafassasset, an anomalous CR chondrite [5, 6] is metamorphosed but not aqueously altered. If alteration affects the Hf-W isochron, this meteorite is of particular interest to experimentally infer the timing of metal-silicate segregation in the CR parent body(ies). Seven different mineral phases (pure metal, several magnetic phases, silicate phases and two bulks) have been separated and analyzed. The W concentrations are 800 ppb and 15 ppb in metal and silicates, respectively. MC-ICPMS and N-TIMS measurements were performed, depending on the amount of W available in each fraction. Both techniques yield the same results within uncertainties. Data plot on a well defined line in an isochron diagram. Ages calculated from the slope or from the initial of this isochron relative to CAIs [7, 8] are consistent with each other: metal-silicate equilibration in Tafassasset occurred less than 2 Ma after Allende CAIs. This meteorite is thus older than the other CR2 chondrites analyzed so far, and among the oldest known chondrites.

[1] Quitté et al. (2010) *MAPS* **45**, A167. [2] Kleine et al. (2005) *EPSL* **231**, 41-52. [3] Schrader et al. (2008) *GCA* **72**, 6124-6140. [4] Lillard et al. (1998) *J. Electrochem. Soc.* **145**, 2718-2725. [5] Bourot-Denise et al. (2002) *LPSC 33rd* Abstr. #**1611** [6] Göpel et al. (2011) *Mineral. Mag.* **75**, 936. [7] Kleine et al. (2005) *GCA* **69**, 5805-5818. [8] Burkhardt et al. (2008) *GCA* **72**, 6177-6197.