Triple oxygen isotope compositions of late Cretaceous dinosaur eggshells and implications for atmospheric carbon dioxide

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It has recently been proposed that the triple oxygen isotope composition of minerals that incorporate oxygen from atmospheric O_2 is related to atmospheric carbon dioxide levels [1,2]. The mechanism is mass independent transfer of ^{17}O and ^{18}O from O_2 to O_3 and CO_2 during photochemical reactions in the stratosphere, leading to negative $\Delta^{17}O(O_2)$ values, and positive $\Delta^{17}O(O_3)$ and $\Delta^{17}O(CO_2)$. The effect is enhanced by the carbon cycle: the residence time of O in the CO_2 reservoir is far shorter than that of O in the O_2 reservoir, leading to preferential sequestration of positive $\Delta^{17}O(CO_2)$ anomaly to the biosphere + hydrosphere, and hence buildup of negative $\Delta^{17}O(O_2)$ anomaly in the atmosphere. This effect increases with increasing atmospheric CO_2 concentration.

Biominerals forming in equilibrium with body water sample the atmospheric $\Delta^{17}O(O_2)$ signal owing to metabolism ($CH_2O + O_2 \rightarrow CO_2 + H_2O$) [2]. We have developed a method that allows for high precision measurement ($\pm 0.02‰$ 1σ) of $\Delta^{17}O$ of CO_2 (and hence $CaCO_3$, including eggshell) using a scheme where O in CO_2 is converted to O in H_2O by reduction with H_2. The H_2O is then fluorinated to yield O_2 suitable for mass spectrometry. We apply the method to late Cretaceous (Campanian and early Maastrictian) dinosaur eggshell from Mongolia [3], as well as modern ostrich eggshell. The $\Delta^{17}O$ values of CO_2 extracted from dinosaur eggshell, $\sim$ -0.15 to -0.27‰ (relative to $\lambda = 0.528$), are similar to the observed range for modern ostrich ($\sim$ -0.21 to -0.25‰), suggesting that atmospheric CO_2 levels, or operation of the global carbon cycle and stratospheric photochemistry, or both, were not drastically different during the late Cretaceous compared to today. This generally agrees with results from the paleosol carbonate CO_2 barometer [4] and carbon cycle models [5].

[1] Bao *et al* (2008) *Nature* **453**, 504-506. [2] Pack *et al* (2013) *GCA* **102**, 306-317. [3] Montanari *et al* (2013) *Palaeo-3* **370**, 158-166. [4] Ekart *et al* (1999) *Am. J. Sci.* **299**, 805-827. [5] Royer *et al* (2007) *Nature* **446**, 530-532.

Determination of probabilistic Kd values for radionuclides in French rivers using a speciation code

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Environmental risk assessment of radionuclides (RN) depends to a great extent on modelling their fate and mobility based on solid-liquid partition coefficient (Kd). To take into account the variability of many environmental factors that influence the Kd value (pH, nature of particles…), Kd can be expressed as a probability density function (PDF). Several databases containing Kd values have been referenced and a weighted bootstrapping procedure was set up in order to built PDF for environmental conditions. However the relevance and robustness of PDF depends on the number of Kd values in the database. Also, different values of Kd can be used for a specific RN at a specific site (depending on the database used), which can indeed lead to major differences in the results.

The objective of this study is to define a new methodology to calculate site specific Kd values for French rivers. This is particularly interesting when a limited number of Kd value is available in the literature (chromium and nickel for instance). This method is based on a predictive chemical speciation calculation. So far, multi-linear regression models were favoured to predict Kd values. The observed field-based partition coefficient can be counter-intuitive because of the competing roles played by the solid and dissolved organic matter. Recently, new models have become available that can adequately describe metal ion binding to DOC, POC, clays and oxides: the NICA-isotherms [1], the CD-Music model. These new models have been shown to give good predictions of the behaviour of contaminants even in heterogeneous systems characteristics of the natural environment.

To validate this approach, *in-situ* experiments will be conducted as part of the COPA project (funded by NEEDS Environnement), focussing on the major RN released by the French nuclear power plants (NPP) (^{110m}Ag, ^{58}Co, ^{60}Co, ^{54}Mn, ^{63}Ni, ^{134}Cs, ^{137}Cs, ^{125}Sb). First, a steady-state approach will consist in studying the suspended particulate matter and the dissolved fractions collected at the SORA station on the Rhône River (France) since 2005 to extract annual averages or change in comportment during hydrological events (floods, low water periods, controlled released by NPP). Then, a specific and planned release from a NPP will be studied to better assess the non steady-state behaviour of a chosen RN through time and distance from the source.

The detailed methodology as well as preliminary results will be presented here.

[1] Kinniburgh, D.G., et al (1999). Colloids and Surfaces A: Physicochemical and Engineering Aspects, **151**(1-2): p. 147-166.