

⁴⁰Ca ISOTOPIC EVOLUTION OF THE OCEANS AND CRUST AND THE MAJOR ROLE OF HYDROTHERMAL CIRCULATION OVER GEOLOGIC TIME. ¹G. J. Wasserburg, ^{1,2}G. Caro, and ^{1,3}D. A. Papanastassiou. ¹LunaticAsylum, Caltech, Pasadena, CA 91125 (gju@gps.caltech.edu); ²Centre de Recherche Pétrographique et Géochimique - UPR2300 CNRS, Nancy Université, 15 rue Notre Dame des Pauvres, Vandoeuvre les Nancy, 54501 Cedex, FR; ³Science Div. 183-335, JPL, Caltech, Pasadena, CA 91109

Introduction: This study uses the decay of ⁴⁰K to ⁴⁰Ca to investigate the contributions of weathering silicate upper crust (SUC), with elevated K/Ca, to the oceans. This is in contrast to mantle contributions which have very low K/Ca. The expected isotopic effects are small (a few epsilon units) and require high precision measurements. It was found that there were no detectable enrichments in ⁴⁰Ca/⁴⁴Ca (<0.3 εu) for carbonates ranging in age from recent to ~3.6 Ga age. It follows that the Ca chemistry of the oceans has been governed by mantle contributions, through the ongoing activity of hydrothermal processes in the oceanic upper crust over geologic time. These hydrothermal exchange processes are a direct reflection of an ongoing mantle convection process over Earth history.

Results: We present high precision Ca isotopic data for Archean, Proterozoic carbonates, river waters and a series of terrestrial and extraterrestrial mafic rocks. The latter samples were analyzed to define the reference parameters for the ⁴⁰K-⁴⁰Ca system for the Earth and early solar system. The effects to be expected from average SUC contributions are:

$$\varepsilon^{40} = 10^4 x \beta (^{40}\text{K} / ^{40}\text{Ca})_0 x$$

$$[(e^{\lambda T} - e^{\lambda t}) / \lambda(T - t) - e^{\lambda t}]$$

Here, T is the age when crust is first preserved and t is the age of a sample; λ is the total decay constant for ⁴⁰K and β is the branching ratio. The subscript “0” refers to the present day value. Figure 1 shows the expected values of ε⁴⁰Ca/⁴⁴Ca for a model of uniform crustal growth. The requirement of high precision measurements of Ca isotopic ratios has been a technically formidable problem, because the dominant Ca isotope is ⁴⁰Ca (96.94%) while the isotopes used to correct for isotopic fractionation are of low abundance (⁴²Ca 0.647%; ⁴⁴Ca 2.086%). Making measurements with adequate precision required a very strict approach to data acquisition [1]. Figure 2 shows all the data on the samples. Sea water is indistinguishable from terrestrial basalts, ultrabasic rocks, lunar basic rocks and Angra dos Reis pyroxene. River water samples from the Mississippi and the Columbia are also indistinguishable from sea water. Samples from the Ganges and Brahmaputra are clearly enriched in ⁴⁰Ca from ⁴⁰K decay. Bulk samples of the meteorites Guareña and Murchison show enhancements that are correlated with K/Ca and are compatible with decay over ~4.5 Ga.

Since we are looking for minimum estimates for the Ca mantle flux, we consider a conservative value of ε⁴⁰Ca ~ 2.5 for silicate weathering during the Phanerozoic. This is relatively low compared with values measured in granitoids, shales and intermediate rocks [2].

If the concentration of Ca isotopes is in a quasi-steady state and if the sources of Ca are: 1) upper crustal silicates (S); 2) crustal carbonates and evaporates (C); and 3) hydrothermal exchange between marine basalts and sea water (H), then

$$\varepsilon^{40}_{\text{SW}} = \varepsilon^{40}_S f_S + \varepsilon^{40}_C f_C + \varepsilon^{40}_H f_H; \text{ and}$$

$$f_S + f_C + f_H = 1.$$

Here, the subscripts refer to the respective reservoirs; f_i is the fraction of the bulk Ca contributed by reservoir “i” to the oceans. From the data we conclude that ε⁴⁰_{SW} ≈ ε⁴⁰_H ≈ ε⁴⁰ ≈ 0, so that ε⁴⁰_Sf_S must be small. We consider that ε⁴⁰_{SW} < 0.2, relative to bulk Earth, so that f_S < ~0.08. It follows that hydrothermal and carbonate sources must contribute > 92% of the Ca budget in sea water. This appears to be true at the present time and over most of geologic time (see Fig. 1).

A comparison between the results for the ⁴⁰K-⁴⁰Ca and ⁸⁷Rb-⁸⁷Sr systems can be seen in Fig. 3. The evolution of the Ca isotopic evolution of shales (PAAS) is shown from 0 to 1 Ga age. The value of K/Ca=0.95 was assumed [3]. The cause of the major difference in the effects of ⁸⁷Rb decay into ⁸⁷Sr in sea water (a ~1% increase over the initial value) relative to ⁴⁰K decay into ⁴⁰Ca is the very low abundance of ⁴⁰K relative to ⁴⁰Ca.

The importance of hydrothermal exchange as the governing process for modern sea water chemistry is widely recognised. The present study shows that, for Ca and many other elements, hydrothermal exchange from ongoing volcanism, subduction and sea-floor spreading appears as the dominating agent in the chemical composition of sea water over almost all of geologic time.

References: [1] Caro, G., Papanastassiou, D. A. and Wasserburg, G. J. (2009) *EPSL* (submitted). [2] DePaolo, D. J. (2004) in Johnson, Beard & Albarède editors: *Geochemistry of non-traditional stable isotopes*, Min. Soc. of America. [3] Taylor, S. R. and McLennan, S. M. (1995) *Rev. of Geophys.* 33, 241. [4] Elderfield, H. and Schultz, A. (1996) *Ann. Rev. Earth Planet. Sci.* 24, 191.

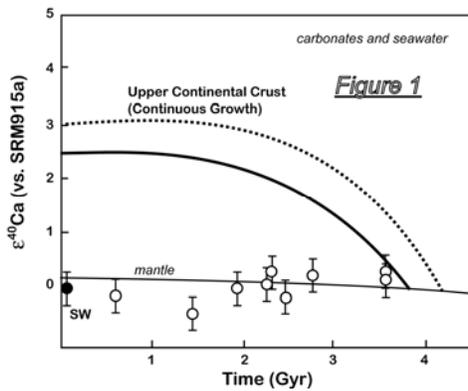


Figure 1. Evolution of the average value $^{40}\text{Ca}/^{44}\text{Ca}$ versus age for continuous growth of continental crust. Two curves are for different times when "first" continents are preserved. Data on sea water & carbonates are shown.

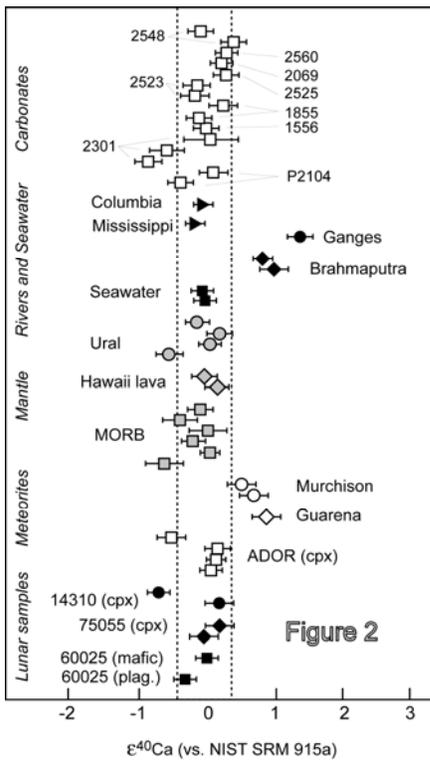


Figure 2. All data obtained under conditions of limited isotopic fractionation. Note enrichment effects for two river water samples and two meteorite. All other samples are virtually indistinguishable from $\epsilon^{40} \sim 0$.

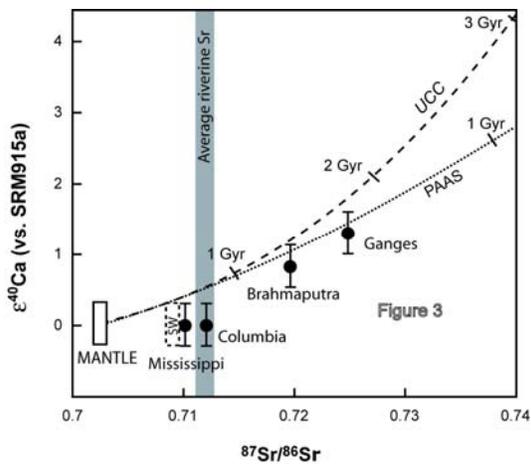


Figure 3. $^{40}\text{Ca}/^{44}\text{Ca}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ for upper crustal rocks with $\text{K}/\text{Ca}=0.95$ formed at different ages (dashed curve). The effects from erosion of Proterozoic shale (PAAS) at different ages is given by the dotted curve. Note the large shift in Sr relative to the mantle value. This is not the case for Ca.