

Variations of the $^{40}\text{Ca}/^{44}\text{Ca}$ ratio in seawater during the past 24 million years: evidence from $\delta^{40}\text{Ca}$ and $\delta^{18}\text{O}$ values of Miocene phosphorites

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To determine whether phosphates record the Ca isotopic composition of paleo-seawater or temperature dependant fractionation, the Ca, O, and Sr isotopic compositions have been measured on Miocene marine authigenic phosphates from California, North Carolina, and Malta. One Pleistocene sample from Peru was also studied in order to compare the Ca isotope fractionation between seawater and phosphorite to the present-day fractionation.

The Ca isotope variation is rather small compared to the corresponding changes in $\delta^{18}\text{O}$ values and the variations are not correlated over a temperature range of 7°C that characterizes the paleo-seawater temperatures for the Malta and North Carolina phosphorites. This suggests that the variations in $\delta^{40}\text{Ca}$ values primarily reflect changes in the Ca isotope composition of paleo-seawater and are less controlled by changes in temperature. The variations in Ca and Sr isotope composition are also decoupled, indicating that these systems record different sources and/or processes. The Ca isotopic composition of seawater not only depends on different fluxes of Ca but also on the rate of biological carbonate precipitation, leading to Ca isotope fractionation and ^{40}Ca depletion in seawater.

Phosphorites and carbonaceous ooze have low $^{40}\text{Ca}/^{44}\text{Ca}$ ratios for the Early Miocene, which points to a ^{40}Ca sink between 24 and 19 Ma. At that time the ocean was apparently not in a steady state. In contrast, between 19 and 9 Ma the Ca isotopic composition is relatively constant and similar to that of the Pleistocene sample. This suggests that the ratio between the weathering and sedimentation fluxes for Ca remained stable during this period.

Mid-Miocene and Pleistocene seawater thus had Ca isotope compositions similar to those of today, indicative of steady-state conditions. Hence the Ca isotope thermometer for foraminifera proposed by Nägler et al.¹ can be applied during this period.

Nägler T.F., Eisenhauer A., Müller A., Hemleben C and Kramers J. (2000), *G³*, 1(2000GC000091).

Decoupling of the Lu-Hf and Sm-Nd isotopic systems in granulitic lower crust beneath southern Africa

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Kimberlite-borne xenoliths provide a unique sampling of the lower crust of the Archean Kaapvaal craton and surrounding Proterozoic orogenic belts of southern Africa. A selection of granulite xenoliths from both on- and off-craton kimberlites have been examined for their whole rock and metamorphic accessory mineral Lu-Hf and Sm-Nd isotopic systematics, in order to deduce the geochemical and isotopic character of the lower crust beneath Precambrian cratonic regions. In these granulites, significant parent/daughter fractionations (during high grade metamorphism at 2.7 to 1.0 Ga) are reflected in their present day Hf and Nd isotopic compositions, and have resulted in decoupling of these generally well-correlated systems. Different senses of divergent evolution from the terrestrial Hf-Nd array are preserved in mafic metagneous versus metasedimentary granulites. The former exhibit a range of sub- to super-chondritic Lu/Hf and Hf isotopic compositions (IC) at consistently sub-chondritic Sm/Nd and Nd IC, while the latter have sub-chondritic Lu/Hf and Hf IC at a wide range of sub- to super-chondritic Sm/Nd and Nd IC. This decoupling is presently unique in magnitude among measured terrestrial reservoirs, and may be traced to as yet poorly understood fractionations induced by garnet as well as Hf- and REE-rich accessory minerals during crustal anatexis and melt extraction. Detailed analysis of these mineral modes and isotopic compositions will clarify controls on Sm/Nd and Lu/Hf fractionation during lower crustal differentiation.

