

Assessing the influence of glacial weathering on marine iron (Fe) inputs using Fe stable isotopes

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Marine concentrations of bioavailable and reactive Iron can modulate the Carbon cycle and Earth's climate [1,2] Previous studies of glacial weathering [3,4] suggest that biogeochemical processes at rock-glacier interfaces promote the formation of highly bioavailable and reactive nano-particulate iron oxy-hydroxides. Consequently, because glacial weathering is a climatically dependent process the marine export of glacially derived oxy-hydroxide should strengthen the feedback loop between Fe and the climate.

Iron stable isotopes ($\delta^{57}\text{Fe}$) have potential to trace weathering Fe exports as Fe oxy-hydroxide formation has been shown to fractionate Fe stable isotopes [5]. Preliminary data from Kangerlussuaq, Greenland indicates suspended particulate and dissolved material have heavy $\delta^{57}\text{Fe}$ values (-0.20 permil) compared to the surrounding bedrock and riverine bed loads (-0.10 to 0.00 permil). This study will incorporate further Fe isotope data from glacial and non-glacial catchments in Iceland and Greenland. Both Iceland and Greenland contain glacial and non-glacial systems that drain relatively uniform rock types allowing for the effects of the different weathering regimes to be compared. Comparisons between Greenland and Iceland then allow independent assessment of the role bedrock plays in controlling Fe exports from glacial and non-glacial weathering.

[1] Martin (1990) *Paleoceanography*, **5**(1), 1-13. [2] Lalonde *et al* (2012) *Nature*, **483**, 198-200 2012. [3] Raiswell *et al* (2006) *Geochem. Cosmo. Act.* **70**, 2765-2780. [4] Wimpenny *et al* (2011) *EPSL* **290**, 427-437 [6] Severmann *et al* (2008) *Geology* **36**, 487-490.

Exhalation and inhalation of Ceria lattice Oxygen: A triple Oxygen isotope perspective

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Ceria (CeO_2) is a fluorite type oxide that has been studied and used extensively as an oxygen storage media in three-way catalysts, as an oxygen partial pressure regulator, as a fuel additive for the reduction of soot, and for the production of syn-gas from water and CO_2 . It is known that exposing ceria powders to low $p\text{O}_2$ and/or high temperature conditions will cause ceria to partially reduce. This partial reduction drives off oxygen from crystal lattice (exhalation) and leads to the formation of oxygen vacancies. When partially reduced ceria is exposed to high $p\text{O}_2$ environments, such as open air, the ceria powders will readily reoxidize even at room temperature. The reoxidation effectively fills the oxygen vacancies with new oxygen (inhalation). We expect that oxygen isotope fractionation is associated with both the exhalation and the inhalation processes. Understanding the isotope effect will help us explore the molecular mechanism for the dissociation, association, migration of oxygen on the surface and within the lattice of ceria.

To determine this isotope effect, we have devised an experimental procedure utilizing triple oxygen isotope labelled initial ceria powders. These powders are heated (700°C) for one hour and cooled under vacuum prior to exposure to air. By combining the results from six independent experimental sets using different initial oxygen isotope labels we have determined the kinetic isotope fractionation factors for both exhalation and inhalation using a graphical method. Our results indicate that there is a $1.6\text{‰} \pm 0.6\text{‰}$ increase in the $\delta^{18}\text{O}$ value of the remaining ceria upon heating in vacuum. When the vacuum is broken at room temperature, the heated ceria will inhale 3% to 12% oxygen from air, with a $\delta^{18}\text{O}$ of 1.6‰ ($+4.6\text{‰}$; -5.6‰). These fractionation factors are consistent with the magnitudes of kinetic fractionation associated with the dissociation and association of atomic oxygen at the surface of ceria. The issue associated with room-temperature oxygen inhalation renders ceria a poor choice of exchange medium for triple oxygen isotope analysis of CO_2 or other oxygen-bearing gases. We have discovered a similar result for yttria stabilized zirconia as well, suggesting that this behaviour may be intrinsic to the fluorite type oxides.