

Evaluating the utility of K/Ca in marine carbonates as a recorder of seawater chemistry

ROMI NAMBIAR^{1,2}, HAGAR HAUZER³, JONATHAN EREZ³, JORIT F KNIEST^{1,2}, JACEK RADDATZ^{1,2}, WILLEM RENEMA⁴, WILLIAM R GRAY⁵, MICHAEL J HENEHAN⁶, LAURA COTTON⁷, WOLFGANG MÜLLER^{1,2} AND DAVID EVANS^{1,2}

¹Institute of Geosciences, Goethe University

²FIERCE, Frankfurt Isotope & Element Research Center, Goethe University

³The Fredy & Nadine Herrmann Institute of Earth Sciences, the Hebrew University of Jerusalem

⁴Naturalis Biodiversity Center

⁵Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL)

⁶GFZ German Research Centre for Geosciences

⁷School of the Environment Geography and Geosciences, University of Portsmouth

Presenting Author: Nambiar@geo.uni-frankfurt.de

Trace element ratios have been extensively applied to reconstruct parameters such as temperature and the carbonate system through geologic time. However, direct proxies for past changes in the elemental composition of seawater are scarce. Potassium is a major cation in seawater (K_{sw}) with a present-day concentration of ~ 10.3 mmol/kg, and is present in measureable concentrations in carbonates, despite the analytical challenges associated with this element when using Ar-plasma-based techniques. Given that the concentration of K was relatively constant throughout the Phanerozoic (9-11 mmol/kg) [1], we propose that the relation between $K/Ca_{calcite}$ and K/Ca_{sw} may be a potential tool to unravel the past history of changes in seawater-[Ca], overall similar to the basis of the Na/Ca-based [Ca]-proxy [2].

The key challenges of K-measurements by ICPMS is the presence of an interference on the ^{39}K peak by Ar-hydride, and an overall lack of well-characterised carbonate reference materials. We conducted K-measurements of the MPI-DING glass standards (GOR128-G, GOR130-G) and carbonate standards (MACS-3) using LA-SF-ICPMS, operated in both medium and high mass resolution. Our results demonstrate that medium mass resolution is sufficiently capable of minimising the ArH interference on the K peak, yielding accurate result with long-term precise of 6% at a concentration of 0.5 mmol/mol in carbonates using NIST SRM610 as the primary calibration standard.

In order to evaluate the effects of environmental parameters on the K/Ca of marine carbonates we examined a range of recent foraminiferal species, including both low-Mg calcite (*G. ruber*) and high-Mg calcite (*O. ammonoides*) producers from globally distributed sites characterized by a wide range in temperature and salinity. No significant correlation of foraminiferal K/Ca with temperature and salinity was observed, suggesting preliminarily that the distribution coefficient of K into marine calcite is not

dominantly controlled by temperature and salinity variation. Given this, we investigated the dependence of calcite K/Ca on seawater [Ca] based on *O. ammonoides* cultured at different Ca concentrations in the laboratory; these data will be presented.

1. Horita J, et al (2002) GCA 66:3733–3756
2. Hauzer H, Evans D, Müller W, et al (2018) EPSL 497:80–91