Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.33507

Deconvolving Foraminiferal Mn/Ca Ratios as a Palaeo Proxy into Palaeoceanography

MAURICIO SANTOS-ANDRADE[1,2], CHRISTIAN MÄRZ[3], ANDREA BURKE[2], SANDRA ARNDT[4], PATRICIA ROESER[5], ALAN FOREMAN[6], JIMIN YU[7] AND JAMES W. B. RAE[2]

[1]University of Bonn
[2]University of St Andrews
[3]Institute for Geosciences, University of Bonn
[4]The Arctic University of Norway
[5]University of Bonn, Institute for Geosciences, Environmental Geology Group, Bonn, Germany
[6]Max Planck Institute for Chemsitry
[7]ANU Research School of Earth Sciences

Foraminiferal calcite is a key archive for trace-element geochemistry in palaeoceanography. While several trace-element ratios are well-established proxies (e.g. Mg/Ca and B/Ca), the mechanisms controlling others, such as Mn/Ca, remain debated. Foraminiferal Mn/Ca ratios are commonly interpreted as indicators of contamination by different Mn-bearing host phases, including Mn oxides and Mn carbonates. In contrast, an alternative perspective proposes that Mn/Ca records bottom-water oxygenation. We adopt a novel approach to elucidate the role of Mn carbonates and oxides in Mg-cleaned foraminifera, aiming to clarify the Mn/Ca ratios as a paleo-proxy.

SEM-EDS and Raman analyses of benthic and planktic foraminifera, which yield Mn enrichments in their bulk chemistry, reveal no obvious localised Mn enrichments on either the inner or outer shells. This finding indicates that these Mn-bearing phases do not form discrete overgrowth structures. Instead, Mn host phases occur as a finely distributed phase or solid solution, below the detection limit of these in situ measurements, as indicated by mass-balance estimates.

From a thermodynamic perspective, Mn oxides are unlikely to persist across the oxic-anoxic boundary, whereas Mn carbonates are relatively much more stable in marine sediments. Comparison of the stoichiometric solubility product of the carbonate phases calcite, rhodochrosite, and kutnahorite reveals that kutnahorite is the most stable phase with solid-solution behaviour. Consequently, we hypothesise that partial dissolution of calcite at depth promotes Mn-Ca substitution into kutnahorite-type solid solution within foraminiferal calcite, providing a conceptual framework to explain observed Mn/Ca enrichments without invoking discrete Mn-enriched coatings.

Identifying Mn enrichments as Mn-carbonate kutnahorite has significant implications for using Mn as a contaminant tracer for other trace-element proxies. Mn enrichments are commonly attributed to Mn oxides, which, based on mass-balance calculations, can strongly affect trace-element ratios. However, we show that the presence of kutnahorite has minimal impact on Mg/Ca, B/Ca, Cd/Ca, Ba/Ca, Sr/Ca, and U/Ca. Overall, our results show that minor kutnahorite-type solid solutions are the most likely cause of Mn-enrichments in fossil foraminiferal calcite, posing minimal contamination risk to other trace element proxies. We further investigate controls on Mn-carbonate formation using reaction-transport modelling of benthic-redox dynamics, assessing the potential of Mn/Ca as a paleo-proxy.