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Impact of diagenetic alteration on sea urchin (Echinodermata) magnesium isotope signatures: Comparison of experimental and fossil data

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Due to their thermodynamically instable high-Mg calcite mineralogy, the skeletal elements of echinoderms are often regarded as unreliable archives of Phanerozoic marine climate dynamics. Nevertheless, traditional and non-traditional isotope and elemental proxy data from echinoderms have been used to reconstruct global changes in palaeoseawater composition (Sandberg-cycles). Recently, these data and the interpretation have been controversially discussed in context with ancient seawater properties. This paper tests the sensitivity of echinoderm skeletal hardparts, specifically sea urchin spines to diagenetic alteration based on magnesium isotope data. We apply a dual approach by: (i) performing hydrothermal alteration experiments using meteoric, marine, and burial reactive fluids; and (ii) comparing these data with fossil sea urchin hardparts. The degree of alteration of experimentally altered and fossil sea urchin hardparts is assessed by a combination of optical (fluorescence, cathodoluminescence (CL), scanning electron microscopy (SEM)) and geochemical tools (elemental distribution, carbon, oxygen and magnesium isotopes). Although initial fluid chemistry of the experiments did not allow the detection of diagenetic overprint by elemental distribution (Fe, Mn) and cathodoluminescence, other tools such as fluorescence, SEM, delta18O, Mg concentration and delta26Mg display alteration effects, which respond to differential fluid temperature, chemistry, and experiment duration time. At experiments run under meteoric conditions with no Mg in the initial fluid, the solid is enriched in the heavier Mg isotopomer due to preferential dissolution of the lighter isotope. In contrast, initial burial and marine fluids have medium to high Mg concentrations. There, the Mg concentration and the delta26Mg values of the altered sea urchin spines increase. Fossil sea urchin hardparts display partly very strong diagenetic overprint as observed by their elemental distribution, cathodoluminescence, delta18O, Mg elemental concentration and delta26Mg. The absence of luminescence might indicate both well-preserved sea urchin spines, but also the secondary enrichment of quenching elements such as iron along diagenetic pathways. The relation between Mg concentration and delta26Mg of the experimentally altered sea urchin spines is in agreement with observations from fossil spines, which also display a 26Mg-enrichment of the solid phase. There, it seems that with increasing degree of alteration, an increase in Mg concentration and delta26Mg occurs. Hence, the experiments performed in this study seem to reflect diagenetic processes under natural conditions. However, the patterns observed are complicated by the interplay of kinetic and thermodynamic processes and the presence of variable amounts of water soluble and water insoluble organic matter within these biominerals. Due to (i) a natural inter- and intra-species variability of the Mg concentration and Mg isotopic composition throughout the echinoderm skeleton and (ii) the fractionation of Mg isotopes during the transformation of ACC as a precursor phase to calcite, the use of delta26Mg values of sea urchin hardparts as a proxy for past seawater delta26Mg is deemed unsuitable. In general, the data shown here are considered significant for those aiming to reconstruct palaeoenvironmental parameters based on echinoderm archives.