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A pilot PGAA study on Miocene echinoid specimens from Hungarian public collections

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Ecological and marine-biological investigations of the past two decades on echinoids (sea urchins) prove the importance of these animals in understanding their environmental setting, as well as its changes during the Earth history. The shells of fossil sea urchins may provide insights to the geochemical conditions of contemporaneous environment, because they show specific geochemical compositional behaviour of growing their shells during their lifetime, but the postmortal sedimental filling of shells is controlled entirely by the actual environmental conditions. Complete shells therefore preserve both types of information.

Sea urchins have been systematically collected since the 19th century in Hungary; there are thousands of Miocene fossils in public collections, available for non-destructive studies. In this study, we focused on *Parascutella gibbercula*, a common Miocene echinoid of the Paratethyan area.

The prompt-gamma activation analysis (PGAA), a non-destructive method that can determine the chemical composition of the shell and the inner sediment of the specimen. We analysed 12 collection specimens from two localities (three from Mecsek Mts. and nine from Budapest). All specimens have been measured in two spots: near the shell perimeter ("posP") and the complete volume at central apical part including the internal cavity ("posC"). The cavity is presumably (partly) filled with post-mortally accumulated sediment.

"posP" measurements resulted in quite pure CaCO3 (>90%) indicating that animals extract high-purity shell material avoiding mostly other compounds. As "posC"s covered volumes of both shell and cavity, the total CaCO3 is much less (72-86%).

Si, Al, and Na contents at "posP"s are inversely proportional to the total CaCO3, whereas Fe, Cl, B, K show more complex behaviour. E.g., the inverse correlation of boron with the carbonate content shows locality-specific behaviour (Mecsek samples have lower B concentrations). In "posP"s, Gd and Sm show inverse correlation with CaCO3; unexpectedly, Nd does not follow this pattern.

At "posC"s (mixture of shell parts and cavity volume) correlations are less expected. The only clear inverse correlation is shown by Si; Sr show no correlation. The behaviour of B at "posC"s is interesting because it seems to be independent from carbonate content, but it may slightly depend on locality. Comparing "posP"s and "posC"s, we found an indication that B content of the environment could have differed in Miocene times at the two localities.

Plotting "posP" vs. "posC" concentrations on scatter plots, it is significant that different elements show higher or in other cases definitely lower concentrations. Al, Fe, Mg, K, B, Cl concentrations are always higher at "posC"s than at "posP"s, which is clearly the effect of the filling sediment material, characterizing the former marine conditions.

We conclude that the PGAA method is highly suitable for these non-destructive studies and the found indications contribute to palaeoenvironmental studies via in-depth characterization of echinoids.

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