

Isotopic composition and diagenetic alteration of Lower Carboniferous brachiopod shells: Constraints from proton microprobe (PIXE) trace element analysis

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Introduction

The chemical and isotopic evolution of ocean water mirrors the dynamics of the earth system. Information concerning seawater isotopic composition and its chemistry is derived from rock components that have precipitated in equilibrium with ambient seawater. For a correct interpretation of isotope data, samples that have suffered alteration by diagenetic processes must be avoided. Trace element analysis is frequently utilized as a diagnostic tool. Unfortunately, conventional techniques, such as AAS or ICP, frequently require more sample than is available or yield only a bulk mean composition (Veizer *et al.*, 1987). Furthermore, for most ancient calcitic materials, the concentrations for the elements of interest (e.g. Mn, Fe, Sr) are generally below the detection limit of standard electron microprobes (cf. Riciputti *et al.*, 1994). A microanalytical tool is therefore required that combines low detection limits with high lateral resolution. In this study, trace element compositions of Lower Carboniferous brachiopod shell fragments were analysed using the Bochum proton microprobe. The data are compared to the ICP 'bulk' analyses and the $\delta^{18}\text{O}$ data of a number of fragments prepared from the same shells.

Methods

For geological samples, the PIXE microprobe permits analysis of trace elements with atomic numbers ≥ 13 . Detection limits are generally less than 5 ppm, and lateral resolution is between 1 and 2 μm . For PIXE analysis, small chips of the secondary layer of articulate brachiopod shells were manually selected. The advantage of this approach is that the chips are aliquots from the same shells as the samples that were analysed for isotopes and by ICP. Furthermore, very small samples can be analysed, with some 10 ng sampled by a proton beam with a diameter of 10 μm . The

proton beam scanned an area of up to 500 x 500 μm^2 to insure comparison with the ICP 'bulk' trace element analyses. The evaluation of absolute concentrations is based on standards that are routinely utilized for XRF calibration (Meijer *et al.*, 1994). The internal precision is < 5 % and the external accuracy is 5–10%.

Discussion of results

Figures 1 to 3 display the comparison of PIXE measurements with the ICP data for the same brachiopod shells. The best correlation is that for Sr, while for Mn the circled samples deviate from the 1:1 trend, likely a consequence of inhomogeneous Mn distribution. Correlation between PIXE and ICP for iron is poor, probably because the phosphoric acid that was utilized to dissolve calcite for isotope (and ICP) analysis was, in some instances, contaminated by Fe, a fact evident from blank measurements. Consequently, we believe that PIXE yields more realistic Fe concentrations. Figures 4 to 6 show the relationship between PIXE trace element data and the $\delta^{18}\text{O}$ values. The field 'A' delineates the trace element contents in modern brachiopods (Morrison and Brand 1986), while the fields 'B' and 'C' outline our well preserved and altered samples, respectively. There is a general but not a complete agreement between isotope and trace element criteria (Bruckschen *et al.*, this volume) as to the degree of alteration overprint. In some cases, however, samples with reasonable $\delta^{18}\text{O}$ values contain 'bad' trace element signatures, particularly for Sr. Other samples, on the other hand, have an altered $\delta^{18}\text{O}$ signature (see '?') despite their low Mn and Fe concentrations.

Conclusions

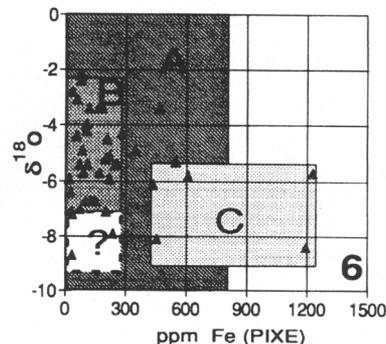
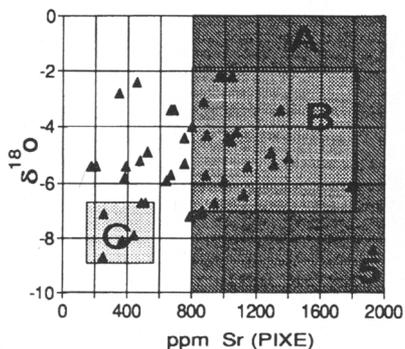
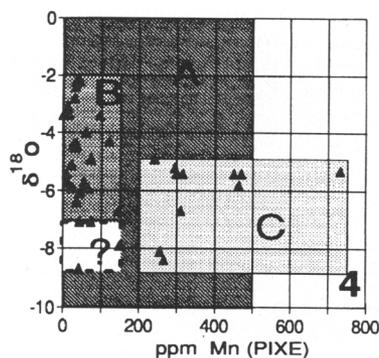
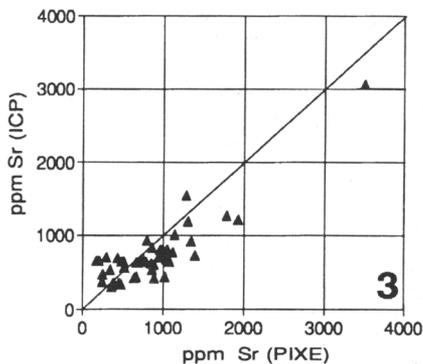
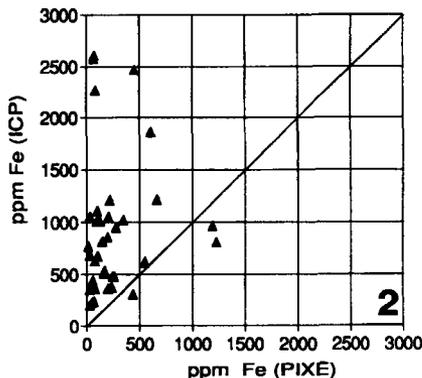
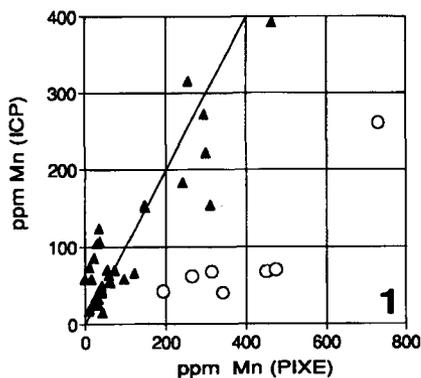
(1) PIXE is a valuable trace element tool that can be utilized to constrain diagenetic alteration of the shell material with even a very small sample size;

(2) In some cases, the trace element criteria may lead to misleading conclusions as to the state of preservation of the sample (cf. Wadleigh and Veizer 1992) and 'bad' trace element data should not automatically cause rejection of samples with a reasonable isotope signature.

References

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Figs. 1 to 6.