Multi-year, intra-annual climate signals from trace element records of Quahog shells (*Arctica islandica*) by LA-ICP-MS.

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For the first time a continuous high resolution marine climate record from the northern high latitudes, comparable to the coral records of the tropics might be in reach. The bivalve mollusc *Arctica islandica*, with a life span of over 100 yr, has potential for the construction of bio-chronicles of the boreal seas. The wide distribution of the shell in the North Atlantic and the North Sea will be of great value for its use in palaeoenvironmental studies.

We measured trace elements with high spatial resolution in relation to the growth banding of the *Arctica islandica* in order to establish its value as a recorder of chemical palaeoenvironmental signals.

We used an ICP-MS (PQ2+) with an in house constructed laser ablation system (193 nm, COMPEX) to measure trace elements of Quahog shells. Choosing spot sizes of 30 –60 micron, we measured profiles along the back of shells and along shell hinges. To quantify analyses masses were measured relative to ^{42}Ca and compared to standard reference materials (NIST610, NIST612, BCR2). Detection limits depend on spot size and ablation time, germane analytical parameters are provided in Table 1.

Currently, four profiles have been measured on three different shells. Trace element profiles are radially reproducible, implying that: (1) precision for the analytical method is high; (2) the shell's signal is of a true temporal nature. This is corroborated by a hinge transect, measured over <3 mm, correlating well with a shell back profile, measured over >4 cms.

Trace elements show cyclicity of Pb and Mn, corresponding primarily with the annual growth banding of the shell. On the other hand the Sr signal shows both annual and multi annual variability. The elements Ba and Cd are strongly correlated and show a distinct sharply defined maximum in each annual cycle. These signals are absent in shells from controlled growth experiments at the NIOZ experimental station.

We tentatively interpret these signals to reflect (1) sea water chemistry, (2) sea surface temperature; and (3) growth rate, possibly related to sea surface productivity.

Lead concentrations in the western North Atlantic have been shown to be largely water mass dependent. Changes in the Pb content might, therefore, indicate changes in the source of the water during the year.

Cadmium and barium levels in benthic foraminiferal tests are a function of seawater concentrations of these elements (Boyle, 1988). Since Cd and Ba concentrations are correlated ocean chemistry (e.g. phosphate contents, alkalinity), foraminiferal Cd and Ba records have been used for tracing ocean circulation during the geological past (Boyle and

TABLE 1.

	Detection limits	Range in *Arctica islandica*
Sr	8 ppb	700–1400 ppm
Ba	2 ppb	1–250 ppm
Pb	6 ppb	200–1000 ppb
Mn	0.15 ppm	0.5–2.0 ppm
Cd	40 ppb	80–4000 ppb

Keigwin, 1987). Analogous Cd and Ba measured with LA-ICP-MS in *Arctica Islandica* shells might provide multi annual proxy records of sea water phosphate concentration with a sub annual resolution.

The cycle of Mn in the ocean is largely controlled by oxygen concentrations in the water column. The oxidation of organic matter and the exchange of gas with the atmosphere, therefore, control Mn levels of the sea water. The annual changes of Mn in the shells might be related to yearly cycles of sea surface productivity and mixing of the water column.

The shells are built entirely of aragonite, in which the partition coefficient of Sr is 7–8 times higher than in calcite. Surprisingly the Sr contents of the shells are rather low. Growth rate possibly exerted a large influence on the incorporation of Sr in the carbonate. The well established relation between temperature and Sr in corals and the systematic changes in Sr in the Quahog shells, however, suggest that a temperature effect might still be present.

References

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