Geochemical Journal, Vol. 44, pp. 23 to 37, 2010

Effect of organic matrices on the determination of the trace element chemistry (Mg, Sr, Mg/Ca, Sr/Ca) of aragonitic bivalve shells (*Arctica islandica*) —Comparison of ICP-OES and LA-ICP-MS data

BERND R. SCHÖNE,[1]* ZENGJIE ZHANG,[1] DORRIT JACOB,[1] DAVID P. GILLIKIN,[2] THOMAS TÜTKEN,[3] DIETER GARBE-SCHÖNBERG,[4] TED MCCONNAUGHEY[5] and ANALÍA SOLDATI[1]

[1]Institute of Geosciences and Earth System Science Research Center, University of Mainz, Johann-Joachim-Becherweg 21, 55128 Mainz, Germany
[2]Department of Earth Science and Geography, Vassar College, Poughkeepsie, NY 12604, U.S.A.
[3]Steinmann Institute of Geology, Mineralogy and Palaeontology, University of Bonn, Poppelsdorf Castle, 53115 Bonn, Germany
[4]Institute of Geosciences, University of Kiel, Ludewig-Meyn-Straße 10, 24118 Kiel, Germany
[5]2906 Norman Dr., Boise, ID 83704, U.S.A.

(*Received September 1, 2008; Accepted May 31, 2009*)

The element chemistry of biogenic carbonates can provide important data on past environments. However, the Sr/Ca and Mg/Ca ratios as well as the Mg and Sr concentrations of biological carbonates, especially aragonitic bivalves often depart from apparent thermodynamic equilibrium. When measured *in situ* by means of LA-ICP-MS, the Mg concentration is often substantially enriched (two- to threefold) near the organic-rich, annual growth lines. To test the hypothesis that some organic components exert a major influence on the skeletal metal content, the element chemistry of different shell components (insoluble organic matrix, IOM; dissolved $CaCO_3$ and soluble organics, SOM) of *Arctica islandica* was measured by means of ICP-OES and LA-ICP-MS. The ICP-OES data indicate that the IOM is strongly enriched in Mg (130 ppm) and depleted in Sr and Ca (10 ppm and 0.22 wt%, respectively) when compared to the whole biomineral (Mg: 68 to 99 ppm, Sr: 860 to 1,060 ppm, Ca: ~35.72 wt%). Although the average relative abundance of the IOM barely exceeds 0.46 wt%, its chemical composition in combination with its heterogeneous distribution across the shell can significantly increase estimates of the Mg concentration if measured *in situ* by LA-ICP-MS. Depending on the distribution of the IOM, the Ca concentration may be significantly lower locally than the average Ca concentration of the whole shell (35.72 wt%). If this remains undetected, the Mg concentration of shell portions with higher than average IOM content is overestimated by LA-ICP-MS and, conversely, the Mg concentration is underestimated in shell portions with lower than average IOM content. Removal of the IOM prior to the chemical analysis by LA-ICP-MS or mathematical correction for the IOM-derived magnesium concentrations is therefore strongly advised. The different chemistry of the IOM may also exert a major control on the trace element to calcium ratios. Shell portions enriched in IOM will show up to 200 times higher Mg/Ca and up to two times higher Sr/Ca ratios than the average shell of *A. islandica*. Without removal of the IOM prior to the analysis, Mg/Ca and Sr/Ca ratios of shell portions with higher IOM content cannot be used as paleothermometers. Because it is currently impossible to remove the IOM prior to chemical analyses by LA-ICP-MS, we recommend the use of wet chemical techniques (= possibility to separate and measure individual shell components) such as ICP-OES at the expense of lower sampling resolution. The results of this study will significantly improve our understanding of shell-based climate and environmental proxies.

Keywords: trace elements, bivalve shell, organics, LA-ICP-MS, ICP-OES, sclerochronology

INTRODUCTION

Sr/Ca and Mg/Ca ratios of biogenic carbonates can provide quantifiable data on ambient water temperature during biomineralization. This has been empirically demonstrated for a variety of different organisms including echinoids (Pilkey and Hower, 1960), brachiopods (Lowenstam, 1961), bivalves (Dodd, 1965, 1967), corals (Smith, 1979; Beck *et al*., 1992; Mitsuguchi *et al*., 1996), foraminifera (Nürnberg *et al*., 1996) and ostracods (Corrége, 1993). These studies were also complemented by inorganic precipitation experiments (Kinsman and Holland, 1969; Mucci, 1987). As temperature increases, the Sr/Ca and Mg/Ca ratios of abiogenic aragonites de-

*Corresponding author (e-mail: schoeneb@uni-mainz.de)