Testing the effect of carbonate saturation on the Sr/Ca of biogenic aragonite: A case study from the River Ehen, Cumbria, UK

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[1] It has been suggested that the incorporation of strontium into biogenic aragonite may be influenced by the degree of carbonate saturation in aquatic environments. We measured the Sr/Ca ratios of river water and the aragonitic shells of freshwater bivalves (*Margaritifera margaritifera*) from two sites with different carbonate saturation states in the River Ehen, Cumbria, UK. Shell Sr/Ca and river water Sr/Ca are 0.1 mmol/mol and 0.42 mmol/mol lower, respectively, at the high carbonate saturation site. However, the distribution coefficients of strontium into aragonite (K_D) are the same ($\sim$0.28) at both sites. These analyses show that Sr uptake into aragonite bivalve shells is not affected by the degree of carbonate saturation of the water, perhaps reflecting a strong biological control on trace element incorporation.

1. Introduction

[2] The trace metal composition of biogenic carbonates is controlled at least in part by environmental factors, which makes them valuable in paleoclimate research and as monitors of pollution. Multiple environmental factors may control trace element incorporation, all of which need to be well constrained in order to achieve accurate and precise environmental reconstructions. For example, it has been suggested that the incorporation of Sr into coral aragonite may be controlled by both temperature [e.g., *Beck et al.*, 1992; *Guilderson et al.*, 1994; *McCulloch et al.*, 1999] and growth rate [*de Villiers et al.*, 1995], which in turn may be controlled by the saturation state of the precipitating fluid [*Cohen et al.*, 2001].

[3] Similar uncertainty exists in Sr incorporation into aragonitic marine bivalves where growth rate control is evident in some species but not others [*Gillikin et al.*, 2005]. These issues are at present unresolved, leading to uncertainties regarding reconstructed sea surface temperatures derived from biogenic aragonite Sr/Ca.

[4] This paper describes a simple case study to test whether carbonate saturation state exerts an influence on aragonite Sr/Ca in bivalves living in freshwaters. The advantages to conducting such a test in the nonmarine environment are (1) the
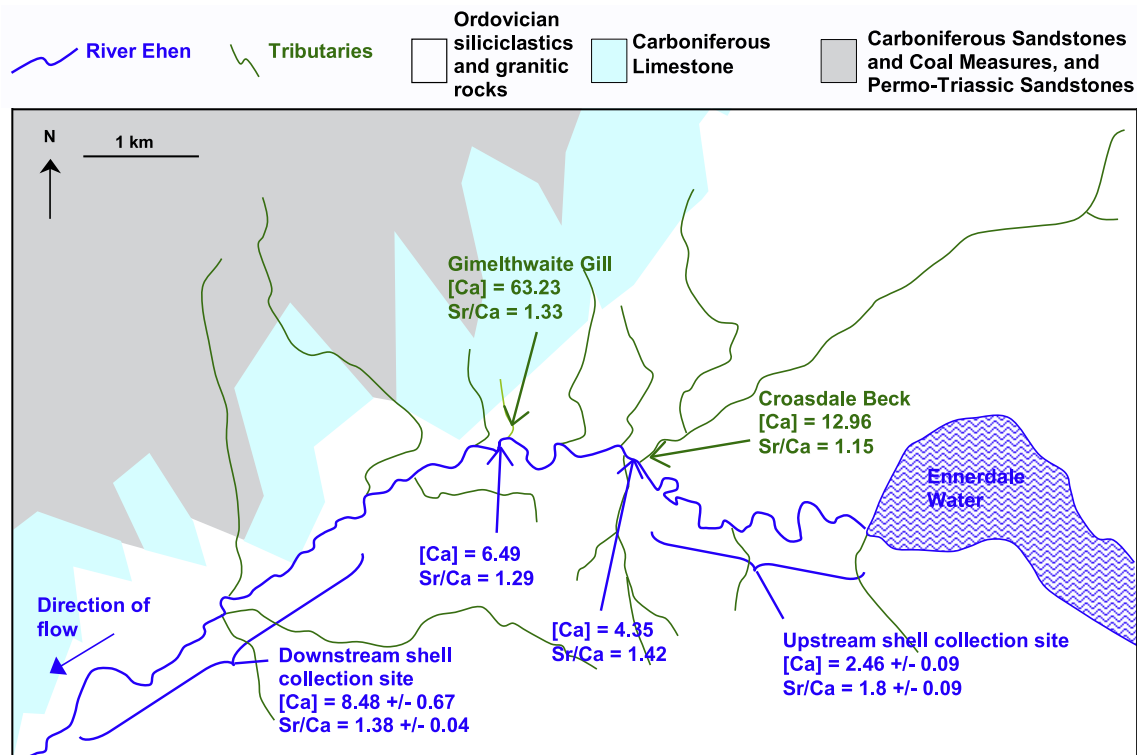
Figure 1. Sketch map of part of the River Ehen showing the underlying geology and points where water samples were taken. Water chemistry data are also shown: Calcium concentrations (Ca) are given in ppm; Sr/Ca is given in mmol/mol. (Geological map reproduced by permission of the British Geological Survey. © NERC. All rights reserved. IPR/67-11C.)

effects of temperature and carbonate saturation can be separated, unlike marine settings where these factors often covary, and (2) the Sr/Ca of the water is not affected by the mixing of fresh and marine waters which is an added complication in estuarine settings [*Dodd and Crisp*, 1982]. In addition, large changes in the carbonate saturation state of river water can be expected from rivers receiving drainage from areas of differing bedrock. The results of this study should also be of interest in the field of biomonitoring, where trace element data from freshwater bivalve shells have been used to track changes in riverine pollution [e.g., *Nyström et al.*, 1995; *Gundacker*, 2000; *Mutvei and Westermark*, 2001].

2. Methods

2.1. Sample Locality

[5] The River Ehen in Western Cumbria, UK drains two distinct types of bedrock; silicate-rich rock (granite and Ordovician siliciclastic sediment) at its source area and upper sections, and carbonate-rich rock (Carboniferous Limestone) a short

distance downstream (Figure 1). As river water chemistry is directly influenced by the bedrock geology through weathering, the carbonate saturation state of the river should be significantly higher downstream of tributaries draining the Carboniferous Limestone. A serendipitous relationship exists between the drainage, geology, and freshwater bivalve habitat such that water from limestone bedrock areas first enters the River Ehen at the confluence with Croasdale Beck, with bivalves found living both above and below this source of dissolved calcium carbonate (Figure 1).

[6] Shells of the freshwater pearl mussel *Margaritifera margaritifera* were obtained previously from two localities; upstream of the Croasdale Beck confluence, and downstream of tributaries draining the Carboniferous limestone (Figure 1). The localities are ~3.8 km apart and of ~35 m difference in elevation (exact locations are withheld to deter illegal fishing of this endangered species). *Margaritifera margaritifera* shells were loaned by Graham Oliver from collections held in the Department of Biodiversity and Systematic Biology, National Museums and Galleries of Wales.

Table 1. Chemistry of Water Samples and *Margaritifera* Shells From the Upstream and Downstream Shell Collection Sites and Comparison of K_D

Shell Collection Site	Calcium Concentration of Water, ppm	Strontium Concentration of Water, ppb	Water Sr/Ca, mmol/mol	Shell Sr/Ca, mmol/mol	K_D
Upstream	2.36	9.81	1.90	0.49	
	2.53	9.65	1.74	0.48	
	2.48	9.46	1.75	0.48	
				0.49	
				0.48	
				0.42	
				0.47	
				0.58	
			Mean ± s.d.	**Mean ± s.d.**	
			1.80 ±0.09	**0.49 ± 0.04**	**0.27**
Downstream	7.70	24.06	1.43	0.44	
	8.90	26.48	1.36	0.41	
	8.84	26.31	1.36	0.34	
				0.43	
				0.39	
				0.42	
				0.36	
				0.35	
			Mean ± s.d.	**Mean ± s.d.**	
			1.38 ± 0.04	**0.39 ± 0.04**	**0.28**

The bivalves were collected alive under license in 1996 as part of a population survey and conservation management plan [*Oliver and Killeen*, 1997].

2.2. Aragonite Analysis

[7] Eight different shells from the two localities were sectioned along the axis of minimum growth and perpendicular to the growth lines. A Merchantek Micromill was used to produce powdered carbonate from close to the umbo across the whole thickness of the shells to homogenize any internal variability in trace element content. Serial samples were taken across the cross-section of one shell from the downstream locality to constrain the magnitude of intrashell variability in trace element content.

[8] Powders were dissolved in 100 μl of 0.065N ultrapure nitric acid, and diluted with 320 μl of 0.5N ultrapure nitric acid. Samples were analyzed for Sr/Ca using a Thermo X-series quadrupole ICP-MS at the School of Earth, Ocean and Planetary Sciences, Cardiff University using a method modified from *Rosenthal et al.* [1999]. Transmission of Sr ions was dependent on the Ca concentration of the sample (the "matrix effect") and could not be corrected for using a simple equation as in *Rosenthal et al.* [1999]. Analyses were therefore run in sample-standard pairs; first a small aliquot of each sample (20 μl, diluted up to 300 μl with 0.5N ultrapure nitric acid)

was run to determine its Ca concentration, then our multielement standard was diluted with 0.5N ultrapure nitric acid to the same Ca concentration as the sample to ensure accurate matrix matching. Analytical precision of replicate analyses of a multielement standard was 2% (r.s.d.).

2.3. River Water Analysis

[9] Samples of river water were collected in triplicate from the same localities as the shells, additional points along the River Ehen, and two of its tributaries, on the evening of 28 and morning of 29 April 2005 (Figure 1). Water temperature was measured to ensure that samples were representative of the growing season of *Margaritifera* shells which do not calcify below 4°C [*Schone et al.*, 2004]; temperature varied between 10.5–11.5°C in the evening and 9–10.8°C the next morning. 50 ml water samples were passed through acid-cleaned 0.45 μm mixed cellulose esters syringe-driven filters and acidified with 50 μl concentrated ultrapure nitric acid to minimize postsampling modification of trace element ratios. Sr/Ca of water samples was calculated from Ca and Sr concentrations analyzed on the *JY Horiba Ultima-2 ICP-OES* at the School of Earth, Ocean and Planetary Sciences, Cardiff University using the standard additions method. Total experimental error on Sr/Ca determinations (which includes analytical precision and the natural
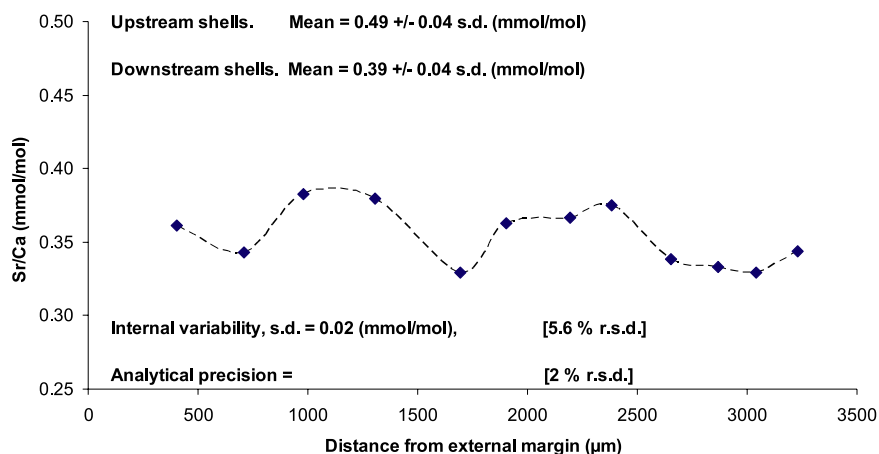
Figure 2. Serial sampling of a shell from the downstream locality showing intrashell variability in trace element content. Mean Sr/Ca values of the two shell populations are shown for comparison.

variability between triplicate samples) was smaller than the Sr/Ca difference between the two sampled sites (Table 1).

3. Results

3.1. River Water Composition

[10] Water chemistry analyses of the River Ehen and two of its northern tributaries draining the limestone area show that, as expected from the geological setting, the tributaries input water that is between 2 and 10 times higher in calcium concentration than the River Ehen (Figure 1). Water samples taken from different points along the River Ehen show increasing Ca concentration and concomitant decreasing Sr/Ca downstream, resulting in significant differences in these parameters between the upstream and downstream shell collection sites (Figure 1).

3.2. Aragonite Composition

[11] Serial samples collected from one shell at the downstream site display small intrashell variability in Sr/Ca (1 s.d. = 0.02 mmol/mol, n = 12) (Figure 2). Part of this variability possibly reflects a small ontogenetic effect of decreasing Sr/Ca with increasing age of the animal. However, this internal variability is five times smaller than the difference in measured Sr/Ca between the two populations of shells, showing that ontogeny is not a significant influence on the results of this study (Figure 2).

[12] The distribution coefficient (K_D) controls the extent to which Sr is incorporated into aragonite (equation (1)).

$$K_D = (Sr/Ca_{aragonite})/(Sr/Ca_{water}). \qquad (1)$$

Calculation of K_D from our data assumes that the ratio of Sr to Ca of the river has not changed significantly since the shells' growing period which ended in 1996. This is a reasonable assumption, as the water chemistry is controlled by bedrock geology. Despite the significant differences between the Sr/Ca of the shells and water at the two sites, the K_D at the upstream and downstream sites are identical within experimental error ($\sim$0.28) (Table 1). Our estimate of K_D is consistent with the range of 0.21–0.29 calculated from other species of aragonite freshwater mussels from waters ranging in Ca concentration from 9.9–28.7 ppm from the Great Lakes Basin [*Faure et al.*, 1967].

4. Discussion

4.1. Carbonate Saturation and Growth Rate Differences Between the Two Shell Populations

[13] Water temperatures at the two sites studied on the River Ehen are unlikely to be significantly different due to their close proximity, the small difference in elevation, and the lack of anthropogenic inputs to the river.

[14] However, as a result of the bedrock geology, the water at the downstream site has a calcium concentration $\sim$3 times greater than the upstream site (Figure 1). In addition, pH data show that the downstream site is more alkaline than the upstream site; over a period of annual sampling from 1980–1996, pH at the downstream site was consistently $\sim$0.4 units higher than the upstream site (Figure 3; from *Oliver and Killeen* [1997]).
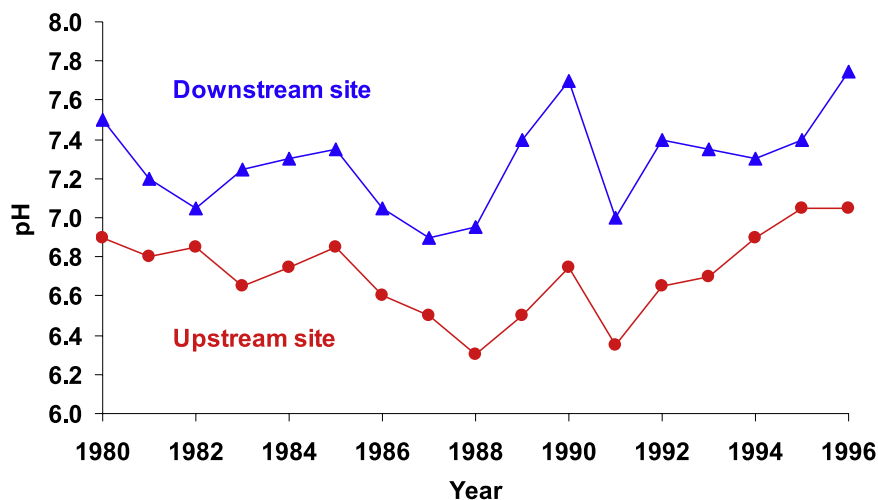
Figure 3.   pH variation at the shell collection sites on the River Ehen, 1980–1996 [*Oliver and Killeen*, 1997].

Therefore the river water at the downstream site must be more saturated with respect to carbonate than the upstream site. Though the downstream water has higher saturation state, shells from both sites have etching at the umbo showing that the river remains under-saturated with respect to aragonite.

[15] In the 1996 survey, the age structures of the two *Margaritifera margaritifera* populations were determined by counting annual growth lines on sectioned ligaments and measuring the size of the shells for ∼70 individuals covering the complete size range of each population [*Oliver and Killeen*, 1997]. The upstream population was found to have a greater maximum age (100 years) and reach a smaller maximum shell length (120 mm) than the downstream population of noticeably thicker shells (maximum age of 45 years and maximum shell length of 142 mm) [*Oliver and Killeen*, 1997]. The average linear shell growth rate at the downstream site is therefore about twice that at the upstream site. In marine bivalves the linear growth rate of aragonite shells can be affected by multiple variables such as temperature, food supply, and salinity [*Gillikin et al.*, 2005]. In the freshwater *Margaritifera* shells growth rates have been seen to increase dramatically in response to increased carbonate saturation caused by the liming of the River Slereboån, Sweden [*Mutvei and Westermark*, 2001]. In the River Ehen, the close proximity of the two sites means that carbonate saturation is the most likely variable to have caused the observed difference in linear growth rate [*Oliver and Killeen*, 1997], with faster rates downstream due to higher pH and greater availability of HCO_3^- ions. The similar value for K_D at both the upstream and downstream sites suggests that carbonate saturation state has not influenced the incorporation of Sr into these bivalve shells.

4.2. Comparison With Marine Bivalves and Biomineralization Mechanisms

[16] Typical Sr/Ca values of freshwater aragonite bivalves are on the order of 0.5 mmol/mol [*Faure et al.*, 1967; this study], compared to typical marine aragonite bivalve Sr/Ca of around 2 mmol/mol [*Stecher et al.*, 1996; *Gillikin et al.*, 2005]. However, the range of Sr/Ca K_D values seen in freshwater aragonitic bivalves, 0.22–0.28 [*Faure et al.*, 1967; this study] is equivalent to the K_D values of their marine equivalents, around 0.25 [*Gillikin et al.*, 2005].

[17] The two most likely steps in the biomineralization process which may affect the bivalves' Sr/Ca K_D are (1) preferential pumping of certain ions (e.g., Ca^{2+}) from the ambient water into the extrapallial fluid (EPF, the medium located between the mantle and the shell, from which precipitation occurs) and (2) during precipitation of aragonite from the EPF. The solute concentration of the EPF in marine bivalves is similar to the ambient water. Freshwater bivalves, which evolved from marine bivalves, have a solute concentration in their EPF which is significantly higher than the ambient water [*Weiner and Dove*, 2003]. The similarity in the freshwater and marine Sr/Ca K_Ds, calculated comparing shell and ambient water compositions argues against significant preferential transport to the EPF of Ca^{2+} relative to Sr^{2+} during the biomineralization process. Analyses of the Sr/Ca of EPF relative to ambient waters, similar to those

conducted on gastropods by [*Rosenthal and Katz*, 1989], are needed to verify this hypothesis.

5. Conclusions

[18] Carbonate saturation state influences the linear shell growth rate of the freshwater bivalve *Margaritifera margaritifera* without affecting the incorporation of strontium into its aragonite shell. If this holds true for other groups such as gastropods, this simplifies the interpretation of molluscan aragonite Sr/Ca in terms of environmental parameters [e.g., *Hendry et al.*, 2001]. However, the lack of correlation between linear growth rate and Sr/Ca in these bivalves could alternatively be interpreted as the result of a strong biological control over-riding environmental influences on Sr incorporation.

Acknowledgments

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