INTERPRETING THE TRACE ELEMENT RATIOS OF FRESWATER BIVALVE SHELLS AND THEIR APPLICATION TO UNDERSTAND ENVIRONMENTAL VARIABILITY

Sarah Tynan[1], Bradley Opdyke[1], David Ellis[1], Sara Beavis[1], Sue Welch[1], Dirk Kirste[1], Luke Wallace[1]

[1]CRC LEME, Department of Earth and Marine Sciences, The Australian National University, Canberra, 0200

Reconstruction of historical environmental regimes is a valuable tool in understanding a number of aspects of ecosystem dynamics. Without a clear understanding of how environments have changed over time, it is difficult to interpret any changes currently occurring, or make predictions regarding the future. Geochemical analysis of bivalve shells has been employed in several studies to try and understand past environmental conditions and has proved to be very useful for this purpose.

When using bivalve shells to interpret environmental parameters, it is useful to have a basic understanding of the process of shell secretion. Initially, the animal secretes the periostracum, an organic substance that forms an external protective coating on the shell. A layer of crystalline $CaCO_3$ is then deposited against this protein rich layer. As the animal grows, Ca and CO_3 ions are taken from the water and transported through the organism to the extrapallial fluid, between the mantle and the inner shell surface. Additional periostracum material is secreted into the extrapallial fluid, which forms the organic matrix for the nucleation of additional $CaCO_3$ crystals, in the form of either calcite or aragonite (Langston and Bebianno 1998; Westbroek and De Jong 1983). This $CaCO_3$ comprises the bulk of the shell. These growth cycles are seasonal, with $CaCO_3$ being deposited during periods of growth, and organic material secreted during dormant periods. These can be seen in shell cross sections as light and dark layers respectively.

As the $CaCO_3$ is deposited, other elements, such as Mg and Sr, can substitute in trace amounts (ppm) for Ca in the $CaCO_3$ crystal structure. The degree to which this occurs is a function of the salinity and/or temperature of the ambient water. Consequently, this trace element incorporation can provide valuable information about the environment in which the shell formed and, along with oxygen and carbon isotope analysis, forms the basis for most environmental investigations of carbonate skeletal material. Thus far, the vast majority of such work on freshwater shells has focussed on analysing oxygen isotope ratios, with little attention given to the potential of trace element ratios that also reflect changes in water temperature and salinity. This study will explore the viability of Mg/Ca and Sr/Ca in freshwater aragonitic bivalve shells as proxies for water temperature and salinity.

TRACE ELEMENT RATIOS - Mg/Ca and Sr/Ca

In inorganic carbonates, trace element incorporation is a function of both the carbonate mineralogy and the solution chemistry. However, in biogenic carbonates, where the carbonate shell is secreted from the extrapallial fluid produced by the organism, the relationships governing inorganic carbonate chemical compositions do not necessarily exert the greatest control over the trace element concentrations in the carbonate. While the chemical composition of the ambient water is still important, temperature and associated changes in growth rate can exert much stronger controls over trace element incorporation than the water chemistry. The degree that these factors affect the shell chemistry varies between different species (Lorens and Bender 1980), thus making careful examination and calibration of results from each individual species necessary.

It is generally accepted that in biogenic calcite, Mg/Ca and Sr/Ca vary as a function of temperature and salinity respectively. Despite the expectation that trace element ratios in biogenic aragonite would behave differently as a result of the minerals' different crystal structure, a number of studies have reported this same relationship for the trace element ratios in aragonite (Purton *et al.* 1999; Hendry *et al.* 2001; Takesue and Van Geen 2004). However, most studies also report that physiological effects such as growth rate, metabolic activity and ontogenetic age of the organism can also affect the trace element ratios found in the animals' shells (Rosenthal and Katz 1989; Purton et al 1999; Hendry et al 2001; Takesue and Van Geen 2004).

Furthermore, variations in salinity in freshwater systems can be highly variable in terms of dissolved ion concentrations as compared to the effectively constant ratio of dissolved ions found in seawater. Thus, a freshwater carbonate may be recording changes in solution chemistry, such as enrichment of particular elements, rather than simple increases or decreases in salinity (Lorens and Bender 1980).

The longer the animal lives, the more comprehensive the environmental history offered by the analysis of its shell. One sample of a marine species, *Arctica islandica* has been documented to be 374 years old (Schone *et al.* 2005). Other studies have used the freshwater mussel *Margaritifera margaritifera*, which has a life span of over 100 years (Carrel *et al.* 1987). This present study uses a mussel commonly found in the lakes and billabongs of the Murray River system, *Velesunio ambiguus*, which can live for up to 15 years (Walker 1992). The calcium carbonate of the *V. ambiguus* shells is in the form of aragonite.

Samples of *V. ambiguus* were collected from the northern end of the Loveday Basin, near the town of Berri, South Australia (Figure 1). The shells found in this location were quite large (ranging from 10 to 15 cm in length) and no living specimens were found. The area was once a floodplain of the Murray River, but has been cut off from the river, and was used as a discharge basin for highly saline irrigation runoff waters from the 1970s to the early 2000s. The wetlands became seriously degraded over this time and the area is now being extensively studied with a view to rehabilitate the site. Sulfur cycling and hydrogeological studies are currently being carried out in the basin, and an analysis of the biogenic carbonate record could well provide a useful insight into temperature and salinity variations over short term time-frames.

Figure 1. Aerial view of the Loveday Basin, Yatco Lagoon and Loch Luna

The shells were set into blocks of epoxy resin and then cut along the axis of maximum growth. One section was then made into a block for LA-ICP-MS (Laser Ablation – Inductively Coupled Plasma Mass Spectrometry) analysis. The mirroring section was made into thin sections for growth band identification.

Trace element analysis was conducted on two shells from the Loveday Basin, L1 and L2, which were 130 mm and 87 mm long respectively.

It is difficult to compare the patterns exhibited by each shell as it is impossible to determine exactly when each shell died, meaning that the record offered by each of their shells could well represent a different timeframe. However, some patterns and evidence of cyclicity can be seen in each of the shells' Mg/Ca and Sr/Ca (Figure 2).

In each of the shells, and particularly in L1, it can be seen that in the sections furthest from the umbo (shell hinge), which represent the most recent growth layers, cyclical patterns are much less distinct than in the preceding growth layers. This is consistent with findings from numerous other studies of bivalve shell chemistry and is largely attributed to a slowing of the growth rate in the later years of the animal's life, which affects the incorporation of trace elements into the shells (Purton *et al.* 1999, Hendry *et al.* 2001). An alternative explanation for these shells lies in the drastically altered environmental conditions of the Loveday Basin during the latter period of their life, when drying of the lagoon would have imposed marked and rapid changes in salinity and temperature upon the animals, most likely resulting in their death.

For illustrative purposes, the vertical axes of the charts have been scaled such that some extreme data points in the Mg/Ca (up to 25 times greater than the average Mg/Ca in shell L1 and 50 times greater in shell L2) are not visible. Sr/Ca in L1 is also up to 4 times greater than average Sr/Ca in this region. This dramatic increase in Mg/Ca in the most recent growth layers of the shells could also be indicative of rapid and extreme salinity fluctuations that may have occurred in the basin and may well represent conditions approaching and exceeding the tolerance levels of *V. ambiguus*.

A subtle inverse correlation between Mg/Ca and Sr/Ca can also be seen in each of the shells. In shell L1, and some sections of shell L2, peaks in Sr/Ca are generally mirrored by troughs in Mg/Ca. Similar patterns have been reported by Hendry *et al.* (2001) from their analysis of the estuarine aragonitic bivalve *Isognomon murchisoni*. They attributed higher Sr/Ca to physiological factors such as an increase in metabolic efficiency and a higher growth rate and Mg/Ca troughs as decreases in temperature. However, this explanation couples higher metabolic efficiency and higher growth rate with decreases in temperature, which would be contrary to the general tendency of molluscs to grow faster in warmer temperatures. To explain this, *Hendry et al.* (2001) proposed that faster growth rates despite the cooler temperatures could possibly be the result of marine inundation and associated increased nutrient availability. Whether or not this interpretation of nutrient supply can be applied to these *V. ambiguus* shells depends on the composition of the irrigation runoff water. These waters could well have been enriched in nutrients that would have promoted algal growth, which in turn could have led to an increased growth rate in the mussels.

The Mn/Ca of each shell also correlates quite strongly with the Sr/Ca. This is most likely representative of variations in salinity and metal concentrations that can be expected in the water of an irrigation runoff storage basin. Markich *et al.* (2002) found that Mn concentrations in shells of *Velesunio angasi*, a freshwater bivalve in the Finiss River, Queensland, strongly reflected the Mn concentrations of the ambient water.

There are definite patterns shown in the trace element ratios of the two shells discussed above and while there are a number of possible hypotheses for interpretation of these patterns, it would be premature to draw any firm conclusions without the establishment of a good calibration curve for the proxies. Analysis of samples collected alive, and comparison with the water in which they grew, will be essential to further investigate and understand these interpretations.

With this aim, additional samples of *V. ambiguus* were collected from two other locations near the town of Berri along the Murray River, South Australia (Figure 1). Finding live mussels proved to be difficult, and only five live mussels were found in total. Two samples were found in Yatco Lagoon, and three in Loch Luna. The shells were found in the upper 15-20 cm of sediment, approximately three-quarters of a foot's length (with toes outstretched and wriggling) beneath the sediment-water interface. The shells were all between 6 and 12 cm in length.

Water and sediment samples were taken from the two sites, along with *in situ* measurements of temperature, salinity (EC) and pH. As these are the only water samples currently available for the locations where the living shells were found, only the outermost growth band of each shell (the most recent growth layer, relating to the period immediately preceding collection) can be used to calibrate the relationship between the geochemistry of the shell and that of the water. This lack of a long-term record of water temperature and salinity makes the construction of a robust calibration curve for each of the various proxies difficult and highlights the need to obtain more data. However, these shells were collected with the aim of making a preliminary attempt to try and help understand the information found in shells L1 and L2, and to ascertain whether further work is warranted. It is anticipated that the results from these shells will at least provide a basis for comparison of the trace element ratios within *V. ambiguus* shells from two markedly different areas. The shells from the comparatively unaltered environments of Yatco Lagoon and Loch Luna will provide a picture of the "normal" patterns of trace element cyclicity within the shells as compared to those that grew in the significantly impacted Loveday Basin.

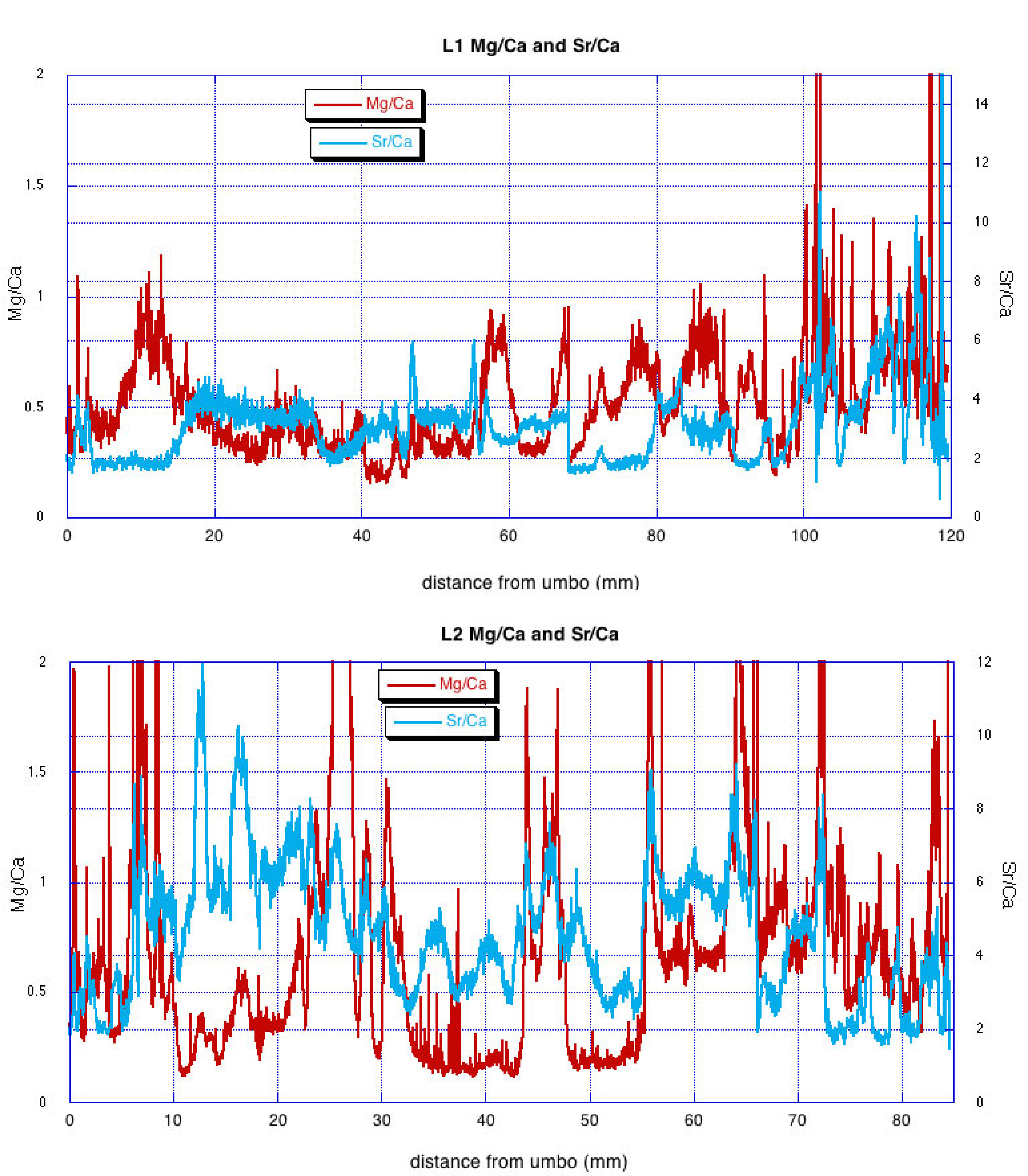

Figure 2. Mg/Ca and Sr/Ca ratios along transects of the growth axes of shells L1 and L2. Cyclic patterns in both Mg/Ca and Sr/Ca can be seen in each shell transect. Both Mg/Ca and Sr/Ca have been multiplied by 1000.

Further work is also necessary to try and determine the affects of growth rate on the trace element incorporation within the shells. This will aid in isolating changes in the element ratios resulting from the age of the animal from those induced by environmental parameters.

It is evident that the carbonate shells of *V. ambiguus* have the potential to provide us with information regarding environmental changes in their environment over time. Analysis of shells of various ages from other regions along the Murray River could help to interpret both small and large scale changes in temperature and salinity regimes.

REFERENCES

CARELL B., FORBERG S., GRUNDELIUS E., HENRIKSON L., JOHNELS A., LINDH, U., MUTVEL, H., OLSSON, M., SVARDSTROM, K. & WESTERMARK T. 1987. Can Mussel Shells Reveal Environmental History? *Ambio* **16(1)**, 2-10.

HENDRY, J. P., PERKINS, W. T. & BANE, T. 2001. Short-term environmental change in a Jurassic lagoon deduced from geochemical records in aragonite bivalve shells. *GSA Bulletin* **113(6)**, 790-798

LANGSTON W. J. & BEBIANNO M. J. 1998. *Metal Metabolism in Aquatic Environments*. London, Chapman & Hall

LORENS R.B. & BENDER M.L. 1980. The impact of solution chemistry on *Mytilus edulis* calcite and aragonite. *Geochimica et Cosmochimica* Acta **44**, 1265-1278

MARKICH S. J., JEFFREE R. A., & BURKE, P. T. 2002. Freshwater Bivalve Shells as Archival Indicators of Metal Pollution from a Copper-Uranium Mine in Tropical Northern Australia. *Environmental Science and Technology* **36(5)**, 821-832

PURTON L. M. A., SHIELDS G. A., BRAISIER, M. D. & GRIME G. W. 1999. Metabolism controls Sr/Ca in fossil aragonitic molluscs. *Geology* **27(12)**, 1083-1086

SCHONE B. R., FIEBIG, J., PFEIFFER, M., GLEB, R., HICKSON, J., JOHNSON, A. L. A., DREYER, W. & OSCHMANN, W. 2005. Climate records from a bivalve Methuselah (*Arctica islandica*, Mollusca; Iceland). *Palaeogeography, Palaeoclimatology, Palaeoecology* **228**, 130-148

TAKESUE, R. K. & VAN GEEN, A. 2004. Mg/Ca, Sr/Ca and stable isotopes in modern and Holocene *Protothace staminea* shells from a northern California coastal upwelling region. *Geochimica et Cosmochimica* Acta **68(19)**, 3845-3861

WALKER K. F. 1992. Ecology of the freshwater mussels in the River Murray. *Australian Water Resources Council Technical Paper* **63**

WESTEBROEK P. & DE JONG E. W. (eds) 1983. *Biomineralization and Biological Metal Accumulation*. Dordrecht, D. Reidel Publishing Company.