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Metals in the shell of *Bathymodiolus azoricus* from a hydrothermal vent site on the Mid-Atlantic Ridge

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Abstract

Specimens of the mussel *Bathymodiolus azoricus* were collected from Menez Gwen, a relatively shallow (850 m) hydrothermal vent field on the Mid-Atlantic Ridge. Each bivalve shell ($n=21$) was individually cleaned by selective chemical. The residual crystal matrix of each shell was individually analysed for the concentrations of the minor elements magnesium and strontium and the trace elements iron, manganese, copper and zinc. The chemical composition of the crystal matrix is unusual. *B. azoricus* is identified as a species having one of the most strontium impoverished shells amongst the marine molluscs. For a bimineral species the magnesium concentration is also extraordinary low. Despite originating from a trace metal rich environment; the metal concentrations in the shells were exceptionally low. Mean concentrations of iron, manganese, copper and zinc were 20.6, 3.7, 0.6 and 9.4 μg g^{-1} respectively. Minor and trace element concentrations exhibited a marked intra-population variability. Copper concentrations increased and iron and zinc concentrations decreased with increasing shell weight. Due to its insensitivity to the high environmental levels of trace elements and the variability in intra-population concentrations induced by shell weight the crystal matrix of the shell of *B. azoricus* has little potential for use in environmental trace metal monitoring in areas contiguous to deep-sea hydrothermal vents.

Keywords: Metals; Shells; *Bathymodiolus azoricus*; Hydrothermal vent field

1. Introduction

Hydrothermal vents, first observed at the Galapagos Ridge in the East Pacific Ocean in 1977 are very unusual environments (Little and Vrijenhoek, 2003; van Dover and Lutz, 2004). Areas contiguous to the vents are extreme environments with respect to both the prevailing physical and chemical conditions. The waters are characterised by high temperature and pressure, low dissolved concentrations of oxygen and elevated dissolved concentrations of hydrogen sulphide, methane and carbon dioxide. Moreover, concentrations of toxic trace metals in the solution, colloidal and particulate phases are generally extremely high (Desbruyères et al., 2001; Douville et al., 2002). Nevertheless, such areas are highly biologically productive (Rousse et al., 1997; Little and Vrijenhoek, 2003; van Dover and Lutz, 2004). Amongst the life forms associated with the chimneys of the hydrothermal sources the bivalve mussels (*Bathymodiolus* sp.) are normally found living in high densities (van Dover et al., 1996; von Cosel et al., 1999; Desbruyères et al., 2001; Hardivillier et al., 2004; Miyazaki et al., 2004).

A number of hydrothermal vent fields exist along the Mid-Atlantic Ridge in the vicinity of the Azores Triple Junction. Data on the physical and chemical properties of the water fluids in these areas are described by Fouquet et al. (1995, 1997), Charlou et al. (1997, 2000), Douville et al. (1997, 1999, 2002), Langmuir et al. (1997), von Damm et al. (1998), Sarradin et al. (1999). However significant spatial and temporal differences in both the physical and chemical conditions have been found at places where fauna live (Desbruyères et al., 2001). The fauna in

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the vicinity of these hydrothermal sources is dominated by the bivalve mussel *Bathymodiolus azoricus* (Colaço et al., 1998, 2002; Desbruyères et al., 2000, 2001; Company et al., 2004).

In view of the high and potentially toxic concentrations of metals present in hydrothermal vent areas attention has been given to metal concentrations accumulated in the soft tissues of a variety of associated fauna (Roesijadi and Crecelius, 1984; Roesijadi et al., 1985; Cosson-Mannevy et al., 1988; Smith and Flegal, 1989; Cosson and Vivier, 1997; Geret et al., 1998; Rousse et al., 1998; Company et al., 2004; Hardivillier et al., 2004). With respect to the molluscan fauna in the hydrothermal vent areas the high environmental trace metal concentrations will also influence the chemical assemblage associated with the shell. To date this aspect has received comparatively little attention (Roesijadi and Crecelius, 1984; Kádár and Costa, 2006).

The soft tissues of marine molluscs are generally more efficient accumulators of metals than shells (Brown and Depledge, 1998) and they have frequently been used to assess metal contamination of the aquatic environment. Similar studies using the shells are few although shells have several important practical advantages over the use of soft tissues (Cravo et al., 2002). When addressing the potential use of organisms as environmental indicators then, whether it be the soft tissues or the shells that are used, two preliminary considerations must be addressed. First, the specimens must be meticulously clean prior to analysis. If vestiges of surface contamination remain the specimens will *ipso facto* reflect the quality of the environment from which they were taken. Whilst obvious this consideration has not always been given the attention it deserves. Secondly, in order to draw meaningful conclusions from concentration data on specimens taken from different sites it is essential to first have an appreciation of both the magnitude and the causes of the intra-population heterogeneity in chemical concentration.

In view of the high concentrations of dissolved, colloidal and particulate trace metal concentrations in hydrothermal vent areas this paper addresses the cleaning problem and presents for the first time data on the chemical assemblage in the crystal matrix of the shell of a deep-sea hydrothermal mollusc, *B. azoricus*. These data are compared with the chemical assemblage of the crystal matrix in the shells of coastal analogues. The intra-population heterogeneity in the chemical composition of the crystal matrix of *B. azoricus* is presented and assessed with respect to evaluating the possible relevance of the shells of this species to environmental quality assessment in hydrothermal vent areas.

2. Materials and methods

2.1. Study area and sampling

Menez Gwen is one of the shallowest hydrothermal vents with a depth of 850 m (Company et al., 2004) occurring on the Mid-Atlantic Ridge, south west of the Azores Islands (Fig. 1). The precise location is given as 37°51′N, 31°31′ W. The chimneys here are small (Desbruyères et al., 2000) and water temperature range from 8 °C to 30 °C (von Cosel et al., 1999; VENTOX, 2003). At Menez Gwen *B. azoricus* is abundantly dispersed in the substratum occurring in densities ranging between 400 and 700 individuals m^{-2} (Colaço et al., 1998; Sarradin et al., 1999).

Specimens of the *B. azoricus* population at Menez Gwen were collected using the remote operated vehicle (ROV) "Victor6000" during the EU-funded ATOS cruise (June 22–July 21, 2001; Sarradin et al., 2001).

2.2. Sample cleaning

At the laboratory damaged or broken shells were rejected. The shells were washed in a jet of distilled water and scrubbed in distilled deionised water with a toothbrush to remove loosely attached biogenic and inorganic particles and dried at 80 °C to constant weight. Prior to metal analysis each individual shell pair was subject to a further cleaning process designed to remove material that was not an integral component of the crystalline shell matrix (Foster and Chacko, 1995). These authors provided a detailed discourse on the analytical problems arising with respect to analysis of trace metals in shell material. These problems are briefly stressed here as they are of particular relevance to the analysis of *B. azoricus* shells.

The trace elements associated with a shell are distributed among three distinct phases: (a) elements which constitute an integral part of the crystalline matrix (b) for those shells with a periostracum trace elements may be either adsorbed to or present as structural components of this tissue and (c) trace

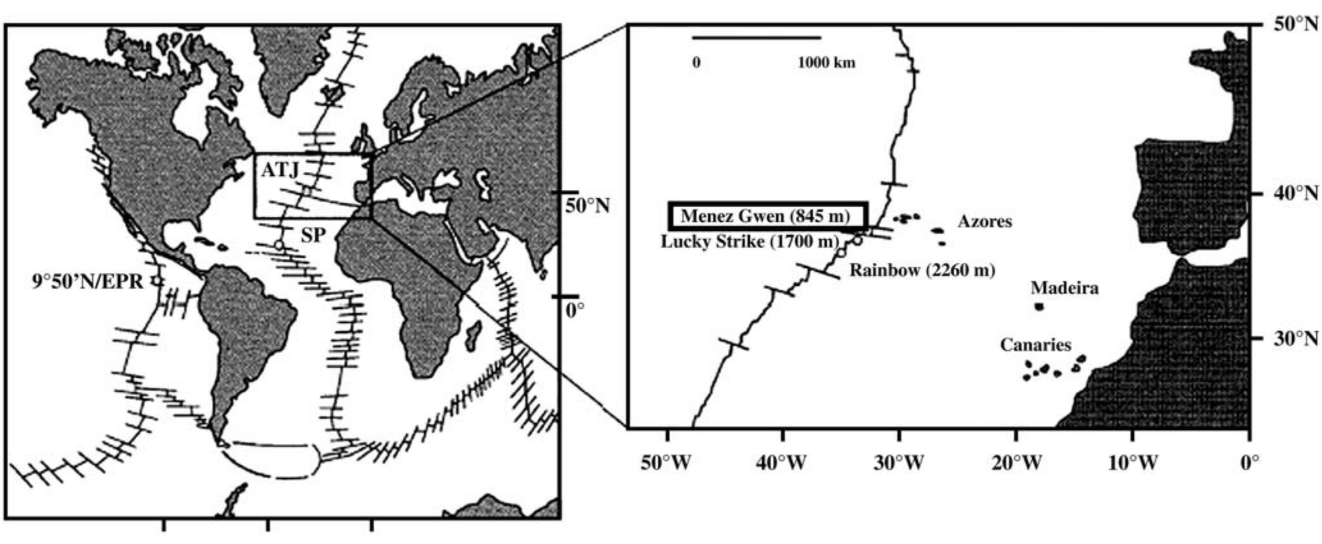

Fig. 1. Location of the Menez Gwen hydrothermal field in the Azores Triple Junction (adapted from Comtet et al., 2000).