Nickel and Cobalt Concentrations in the Tunicate *Halocynthia Pyriformis*: Evidence for Essentiality of the Two Metals

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It has been well established that marine organisms often contain trace elements at concentrations very much greater than those in the marine environment [1]. There has been a particular interest in tunicates, since they have been shown to concentrate a wide variety of metals including vanadium [2, 3], titanium and chromium [4], niobium [5, 6], tantalum [6, 7], iron [8, 9], selenium [10], manganese [11], copper and aluminum [12] and some lanthanons [13]. Up to now, no statistical studies of the analytical data have been performed, yet such studies can provide valuable information on the interaction of different elements in the organism. As part of the study on trace metals in tunicates [14], we report here on a significant correlation between nickel and cobalt concentrations in *Halocynthia pyriformis*. Our examination of previously published analytical data for two scallop species would suggest that such correlations may exist in other marine organisms.

Experimental

A total of 29 specimens were obtained from coastal waters at three sites: Cupids (8 specimens) and Bay Bulls (12 specimens), Newfoundland (obtained by Dr. J. F. Kingston, Memorial University, St. John's, Nfld.) and from Marine Research Associates, St. Andrews (9 specimens) New Brunswick. After freeze drying, samples were digested with nitric/sulfuric acid mixtures according to standard procedures. All analyses were performed by atomic absorption spectroscopy using a Jarrell Ash Dial Atom III.

Results and Discussion

Analytical data are given in Table I.

TABLE I. Geometric Mean Values for the Concentrations of Nickel and Cobalt (Dry Mass) and for Sample Mass.

Location	Nickel (ppm)	Cobalt (ppm)	Mass (g)
Cupids, Nfld.	114	15.8	3.48
Bay Bulls, Nfld.	224	29.8	1.43
St. Andrews, N.B.	157	23.6	3.17

Combining the values from the three locations gives the geometric mean concentration of nickel and cobalt as 172 ppm and 24.0 ppm respectively on a dry mass basis (complete analysis data can be obtained from the authors). These concentrations compare with North Atlantic seawater values of 0.3 ppm for nickel [15] and 0.13 ppm for cobalt [16], thus showing a considerable enrichment factor. Cobalt concentrations have been reported as 11 ppm in *Microcosmus sulcatus* and 3.6 ppm in *Phallusia mammilata* [13].

Of more significance, when the concentration of nickel and cobalt in each specimen were compared using Spearman's rank correlation coefficients, a value of 0.99 was obtained. This is a very significant correlation (a value of 1.00 would be an exact correlation). In fact, in each of the 29 specimens analysed, the nickel-cobalt ratio is almost exactly 7:1 (as cobalt and nickel have very similar atomic masses, this is both a mass ratio and an atom ratio). Also, the correlation coefficient of these elements with dry mass is −0.84 for nickel and −0.81 for cobalt. This negative correlation between mass and concentration would indicate that the tunicate contains a fixed mass of each of the two elements.

Both cobalt and nickel are known to be essential trace elements in humans [17] and the essentiality of nickel in higher plants has been indicated [18]. The very close correlation between concentrations of these two elements in samples from three different locations may indicate the essentiality of both nickel and cobalt in this tunicate. Of particular relevance, many plant species have fixed nickel-cobalt ratios [19, 20]. In the majority of plant species studied, the nickel-cobalt ratio was close to 2:1, though there were some significant exceptions.

Bryan [21] reported the trace metal content for two scallop species, *Pecten maximus* (L.) and *Chlamys opercularis* (L.). We have examined his reported values for cobalt and nickel concentrations in different tissues and we find there to be a consistent nickel-cobalt ratio throughout the tissues for a particular species. In the case of *P. maximus* the ratio is very close to 3:1 while it is 5:1 in *C. opercularis*.

We consider that the prevalence of fixed nickel-cobalt ratios is of significance. In particular, if these metals are essential trace elements, the fixed ratio

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may indicate that both elements are involved in the same biochemical processes.

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