

# The long-term environmental behaviour of strontium and barium released from former mine workings in the granites of the Sunart region of Scotland, UK

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Received 20 January 2004; received in revised form 30 August 2004; accepted 31 August 2004

## Abstract

The concentrations of strontium and barium have been measured in water, sediment and the shells of mussels (*Mytilus edulis*) from a river system in the Sunart region of Scotland, UK. The aim was to establish the fate and mobility of these elements, which are slowly being released from old mine workings on the Strontian granites. Enhanced strontium (1500–2000  $\mu\text{g l}^{-1}$  and 250–290  $\mu\text{g l}^{-1}$ ) and barium concentrations (316  $\mu\text{g l}^{-1}$  and 83  $\mu\text{g l}^{-1}$ ) were found in the waters originating from the two mine drains studied. Both element were also found at significant levels in the river sediments taken from the vicinity of each drainage site (Sr: 225  $\mu\text{g g}^{-1}$  and 120–125  $\mu\text{g g}^{-1}$ ; Ba: 1380  $\mu\text{g g}^{-1}$  and 126–170  $\mu\text{g g}^{-1}$ ). The data suggests that the sediments are acting as a reservoir for these group II cations from where they become distributed throughout the river system. Strontium is found to be incorporated into the shells (3.16–3.46  $\mu\text{g g}^{-1}$ ) and pearls (3.57  $\mu\text{g g}^{-1}$ ) of the blue mussel, located at the estuarine margin some 10 km downstream, at values close to the maximum expected (3.3% by weight of the calcium content). The study presents a view of the fate of barium and strontium in a river system over a prolonged period of time. As such it provides valuable information for studies that seek to model the impact of the accidental release of barium and strontium (including the important radionuclide <sup>90</sup>Sr) into the environment.

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**Keywords:** Water; Sediment; Mussel; Metal analysis; Sequential extraction

## 1. Introduction

The granitic intrusions found on the Ardnamurchan peninsula of Scotland have produced an area of the UK which is rich in minerals (Whittow, 1977). Some, such as galena (PbS), harmotome (BaAl<sub>2</sub>Si<sub>6</sub>O<sub>16</sub>), sphalerite (ZnS), calcite (CaCO<sub>3</sub>) and barite (BaSO<sub>4</sub>) are quite

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common in the UK. However, others are more unique to this region of the British Isles. In 1790 Crawford discovered a new mineral, strontianite ( $\text{SrCO}_3$ ) in this region, which he named after the nearby settlement on the banks of Loch Sunart. The prefix he gave to his mineral was transferred to the new element using established practice in 1808 when Davy (1808) successfully isolated a sample of the element.

This region of Scotland is subject to poor soil coverage and hence heavy erosion due to water action. As far back as Crawford's period the heavily mineralised granites have been exploited for their commercially viable deposits of species such as galena (lead) and more recently barite ( $\text{BaSO}_4$ ). As a result of these disturbances the more soluble cations i.e. the alkali metals (sodium, potassium) can be expected to be present at very low concentrations. However unlike the alkali metals, the salts of the alkali earth metals present in this region (strontium and barium) are much less soluble in water (Table 1, CRC Press, 1981). Consequently the deposits of strontium carbonate and barium sulphate in the exposed rock can be expected to be mobilised at a much slower rate. This action should ensure that there will be a steady input of low levels of strontium and barium salts into the adjoining rivers (Fig. 1). Strontium can be expected to remain in solution due to its relatively high ionic potential (Table 1, Mason, 1966) transferring to the sediments slowly over a prolonged period. In contrast, the tendency of barium to remain associated with sulphate will limit its solubility further. Thus it might be expected that barium will be preferentially associated with the sediments over the aqueous environment in this region.

The long term discharge of river water and sediments into the nearby sea loch may thus deposit significant amounts of strontium and barium bearing material into the margins of the marine environment (site D). This zone is inhabited by the common blue mussel (*Mytilus edulis*). As a sedentary filter feeder this species of marine bivalve has become popular for use in studies which seek to assess the impact of heavy metals in the marine environment (Segar et al., 1971; Haug et al., 1974; O'Connor, 1998). The shells of the blue mussel are made up of an outer layer of rhombohedral calcite and an inner layer of orthorhombic aragonite (Milliman, 1974). The nature of the packing of the cations and anions in

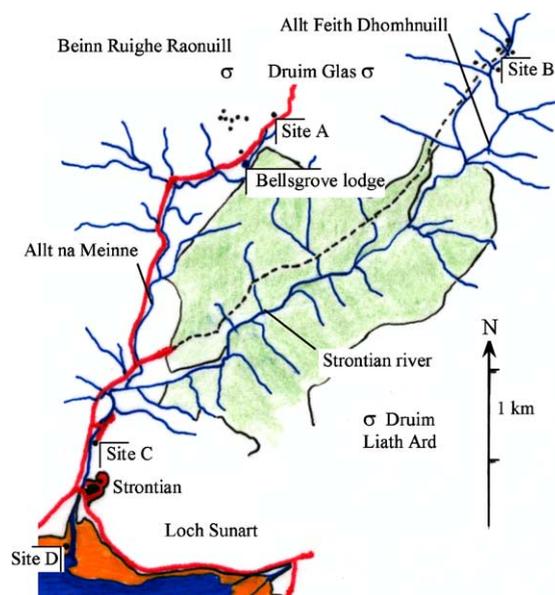


Fig. 1. The study area, showing the position of the sampling sites (A–D). Access to site B is by footpath (-----). Site A can be reached by road (—). Grid references: Site A, NM 832 655; Site B, NM 862 667; Site C, NM 816 624; Site D, NM 813 611. (■)—Forest, (■)—Foreshore. (For interpretation of the references in colour in this figure caption, the reader is referred to the web version of this article.)

these forms of calcium carbonate makes the orthorhombic form more pre-disposed to substitution of calcium by its group II partner strontium by a factor of 10 over the rhombohedral form (Milliman, 1974). Thus, where significant amounts of strontium are being discharged into the marine environment, the shells of the blue mussel might be expected to incorporate it into the inner layers.

The movement of elements such as strontium and barium in the environment can be difficult to model and monitor (Aberg, 1995; Spalding and Spalding, 2001). The need to do so usually follows an accidental discharge of these elements by industrial action. Thus although the immediate concentration and distribution of a species such as  $^{90}\text{Sr}$  can be established, good natural sites, which have achieved an environmental steady state with respect to strontium and to a lesser extent barium, are rare. The one discussed in outline above is unique

Table 1

The ionic radius, ionic potential (Mason, 1966), solubility (CRC Press, 1981) and typical river water concentration (Libes, 1992; Patrick, 1995) for the three group II cations calcium, strontium and barium

Element	Ionic radius (pm)	Ionic potential ( $\text{nm}^{-1}$ )	Solubility ( $\mu\text{g l}^{-1}$ )	Typical conc. river water ( $\mu\text{g l}^{-1}$ )
Calcium	99	20.0 (6 coord)	2120 as $\text{CO}_3^{2-}$	10000
	112	17.9 (8 coord)		
Strontium	118	16.9	2073 as $\text{CO}_3^{2-}$	60
Barium	135	14.8	1440 as $\text{SO}_4^{2-}$	43

and represents an industrially isolated but integrated study area which has remained undisturbed for some time. As such, it represents an opportunity to study the low-level discharge of strontium and barium and their fate and distribution within river water and marine environment.

## 2. Materials and methods

Samples were collected in June 2001 and August 2002. Additional water samples for barium analysis were collected in October 2003. Water samples were collected in pre-washed plastic bottles, acidified (1–2% HNO<sub>3</sub>) and refrigerated prior to analysis. Sediments were air dried and sieved (<1 mm). Mussels were cleaned, opened with a knife, and the flesh was separated from shell. The flesh was oven-dried (57°C).

A laboratory microwave oven (CEM MDS-2000 from CEM Corporation, CA, USA) was used to assist the digestion of sediment (1g sediment + 20ml aqua regia) and ground mussel flesh (1g tissue + 20ml nitric acid) samples. Shell samples were subjected to open, hot-plate dissolution (0.5 g shell + 5ml nitric acid). The analyte content of the sediment samples was fractionated by means of sequential extraction (Ure and Davidson, 2002) using the modified protocol developed under the auspices of the Commission of the European Communities, Community Bureau of Reference (BCR) (Ure et al., 1993; Sahuquillo et al., 1999; Rauret et al., 2000). The procedure is outlined briefly in Table 2.

Strontium in all samples types, and barium in sediment and biota, were determined by electrothermal atomic absorption spectrometry (ETAAS) using a Unicam SolAAr system (from ATi Unicam, Cambridge, UK). Furnace conditions were specifically optimised for use in the current study, and similar optima were obtained for both analytes in all matrices studied. The temperatures and durations of the steps in the optimised furnace program were: dry 120°C (30s); char 1700°C (20s); atomise 2800°C (3s); clean 2900°C (3s).

All ETAAS analysis was performed by the method of standard additions. Barium in water samples was determined by inductively-coupled plasma optical emission spectrometry (ICPOES) using a Jobin-Yvon JY-138

ULTRACE system. Checks for spectral interference were performed before analysis commenced (Standard Method 3120, 1989) and for instrument drift after every five analyses. Calcium was determined by flame AAS (Philips PU 9100 spectrometer, also from ATi Unicam). Calibration was with respect to commercial standard solutions (Spectrosol™, Merck, Dorset, UK). Relevant reagent and procedural blanks were included in each analysis. Laboratory-ware was soaked in 5% nitric acid and rinsed with distilled water before use. Reagents were of analytical grade or better.

## 3. Results and discussion

The study commenced with an analysis of water samples. Access to the upper reaches of the river system is limited by the topography of the region. However, it proved possible to collect water which emerges from the ground at positions which have been disturbed by anthropogenic activity, namely the mine drains at the head of the Allt na Meinne (site A) and on the Allt Feith Dhomhnuill (site B). A further water sample was collected at a point upstream of site B on the Allt Feith Dhomhnuill. This stream flows adjacent to the mine-shaft at site B but rises above the Strontian intrusions.

The water emerging from both shafts showed high levels of strontium compared to that found upstream on Allt Feith Dhomhnuill (Table 3). The levels of strontium in water at the sampling point above site B are commensurate with those reported for other lowland Scottish streams (Neal et al., 1997) devoid of industrialisation. This indicates that significant quantities of strontium are entering the river water from the Strontian granites (i.e. over a 20–50km<sup>2</sup> region). This is confirmed by the data obtained from the main river some three miles downstream just above the high water mark (site C). Here, a 1.5–2 fold increase in strontium compared to that observed above the Strontian intrusions was observed. The discharge of strontium into the river water at site A is six to seven times higher than that found at the site B. This difference probably arises from the fact that site B has remained undisturbed since the cessation of lead mining over 100 years ago whereas site A has been subject to more recent disturbance due to

Table 2  
The modified BCR sequential extraction scheme (Ure et al., 1993; Sahuquillo et al., 1999; Rauret et al., 2000; Ure and Davidson, 2002)

Step	Fraction	Nominal target phase(s)	Reagents
1	Exchangeable, water and acid soluble	Soluble species, carbonates, cation exchange sites	0.11 mol l <sup>-1</sup> acetic acid
2	Reducible	Iron and manganese oxyhydroxides	0.5 mol l <sup>-1</sup> hydroxylammonium chloride, pH 1.5
3	Oxidisable	Organic matter and sulfides	H <sub>2</sub> O <sub>2</sub> followed by 1.0 mol l <sup>-1</sup> ammonium acetate; pH 2
4	Residual		Aqua regia

Table 3

The concentration of strontium in the water samples obtained from the study area ( $\mu\text{g l}^{-1}$ )

Sites sampled	Strontium ( $\mu\text{g l}^{-1}$ )		Barium ( $\mu\text{g l}^{-1}$ )	pH
Allt na Meine: site A	2000 $\pm$ 120	1570 $\pm$ 29	316 $\pm$ 7	8.0
Allt Feith Dhomhnuill: site B	289 $\pm$ 15	251 $\pm$ 30	83 $\pm$ 9	7.5
Allt Feith Dhomhnuill: upstream of site B	60.0 $\pm$ 6.1	60.7 $\pm$ 4.8	nd	6.4
Strontian river: site C	106 $\pm$ 6	93.9 $\pm$ 10.7	77 $\pm$ 4	7.0
<i>Typical values</i> (Libes, 1992; Patrick, 1995)	60		43	
Tweed	41		nr	
Nidd	116		nr	
Teviot	72.3		nr	

Results are mean values  $\pm 1$  standard deviation for  $n = 3$  measurements; nd = not detected; nr = not reported. Values are also given for three other Scottish rivers (Neal et al., 1997) found in a lowland region south of the highland boundary fault. The discharge of significant amounts of alkaline earth carbonates significantly increases the pH of these waters.

the extraction of barite and hard core. The measurable quantities of barium in the river water (Table 3) are lower than those observed for strontium, and were below ICPOES detection limits in the river water taken upstream of site B. Thus, it would seem that the source of barium in this river system is also disturbance to the crustal rocks on the Strontian granites. Similar to strontium, the levels of barium in the water fall by a substantial amount (94%, Sr; 76%, Ba) on its movement from site A to site C due to the dilution effects of the river.

The analysis of the sediments (Table 4) indicates that substantial amounts of strontium and barium are associated with the solid matter in this river system. The values obtained for both barium and strontium at the mine drain on the Allt na Meine (site A) exceed the average values for other sites in the UK (Salomons and Forstner, 1984). Since the concentration of strontium in the discharge water is close to the solubility product of its carbonate (Table 1), the elevated sediment levels of strontium might be expected. However, this is not the case for barium, where elevated sediment content coincides with a water concentration considerably less than the solubility product. It is possible that this cation is

not migrating from the water to the sediments at this site but in the reverse direction i.e. from the sediments to the water. The results obtained for the second mine drain (site B) show a similar pattern. Although no barium was detected in the Allt Feith upstream of site B, presumably because the water at this point originates largely from outside the Strontian granites, a significant amount of the analyte was observed in the sediments. The concentrations of strontium and barium in sediments and water fall from site A to Site C. Strontium levels also decrease from site B to site C. These observations are generally consistent with a combination of dilution effects, and possible desorption of cations from the sediments, in a downstream direction.

Sequential extraction is now widely used in environmental studies to determine the partitioning of trace elements between operationally-defined sediment phases (Ure and Davidson, 2002). The partitioning of strontium at sites A, B and C, according to the revised, four-step BCR sequential extraction protocol is shown in Fig. 2. A large proportion of the total strontium present at sites A and B can be solubilised by treatment with acetic acid (BCR step 1). This supports the conclusion that the element is present predominantly in the form

Table 4

The concentration of strontium and barium in the river sediments obtained from the study area ( $\mu\text{g g}^{-1}$  dry weight)

Site	Strontium	Barium
Allt na Meine: site A	225 $\pm$ 14	1380 $\pm$ 166
Allt Feith Dhomhnuill: site B	125 $\pm$ 5	177 $\pm$ 10
	120 $\pm$ 9	126 $\pm$ 2
Allt Feith Dhomhnuill: upstream of site B	36.1 $\pm$ 2.6	201 $\pm$ 25
Strontian river: site C	38.7 $\pm$ 1.0	180 $\pm$ 27
Typical values (Salomons and Forstner, 1984)	160	460

Results are mean values  $\pm 1$  standard deviation for  $n = 3$  measurements.

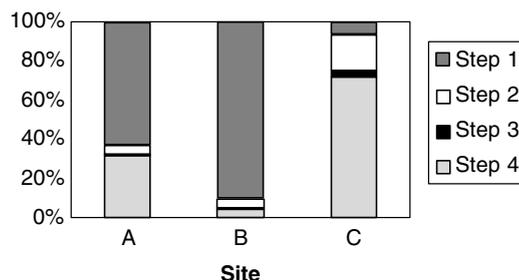


Fig. 2. Operationally-defined speciation of strontium in sediments from the study area by means of the revised BCR sequential extraction procedure (Table 2).

Table 5

The strontium, barium and calcium concentrations in biota samples from the study area, together with literature values (Segar et al., 1971)

		Strontium (mg g <sup>-1</sup> )		Barium (µg g <sup>-1</sup> )	Calcium (mg g <sup>-1</sup> )		Ca:Sr (mol:mol%)	
		Found	Typical values		Found	Typical values	Found	Typical values
Mussel	Shell	3.46 ± 0.47	0.014	10.6 ± 1.1	317 ± 3	390	0.500	0.0016
		3.18 ± 0.21						
	Flesh	0.18 ± 0.09	0.024		nr			
	Pearls	3.57 ± 0.18	nr	nr	nr	367		
Cockles	Shell	3.08 ± 0.25		14.9 ± 0.6	304 ± 2		0.463	
Whelks	Shell	2.82 ± 0.20		14.6 ± 4.6	316 ± 1		0.408	

of strontium carbonate. Extremely small amounts of strontium are associated with reducible (<5%), or oxidisable (<1%) fractions of the sediment at these sites. In contrast, at site C, less than 7% of the strontium is released in step 1, there are more significant contributions from reducible (18%) and oxidisable (4%) forms, and step 4 dominates (72%). Thus, although the total concentration of strontium decreases from sites A and B towards site C, the proportion found in association with more resistant mineral phases of the sediment increases. This confirms the view that, as the sediment moves down through the river system, more labile fractions are moving into solution.

Tables 3 and 4 indicate that substantial amounts of strontium and barium reach the marine horizon. Here they are available to the common filter feeders. Analysis of shell samples was carried out to assess incorporation of these elements into the biota at the tidal margin, some 10km downstream from the mine drains (Table 5). Interestingly, the mussel samples collected had a substantial number of pearls inside (Taburaix, 1985). These pearls and soft tissues of *Mytilus edulis* were thus also analysed to provide a global view of strontium within this organism.

Barium has an ionic radius too large for isomorphous substitution into the calcium sites in shells, but strontium is capable of substituting for calcium in aragonite, which is a major component of the shell. This is reflected in results of the present study. The incorporation of barium (~10–15 µg g<sup>-1</sup>) into the shells of mussels, cockles and whelks is poor (Table 5). In contrast, strontium reaches concentrations of ~3 mg g<sup>-1</sup>, which is commensurate with other study areas (Milliman, 1974) that have substantial amounts of strontium contamination. A cursory inspection of the shells from other species present at the tidal margin demonstrates similar levels of strontium incorporation.

Analysis of the pearls and flesh revealed that again a substantial amount of strontium appears in both of these materials (Table 5). As the pearls are predominantly (~97%) aragonite in nature (Taburaix, 1985) it is not surprising that they have a similar strontium con-

centration to that found in shell. The flesh however shows only a ~eight-fold enhancement in strontium compared to typical values from uncontaminated regions. Soft tissues, however, can be expected to have a lower alkali earth metal burden than the carbonate based structure and this lower concentration reflects its function as a processing area, rather than a repository, for divalent cations.

#### 4. Conclusions

This work provides an outline of a study area that would be expected to have come to equilibrium in terms of the distribution of both strontium and barium in environmental compartments. Strontium would seem to be moving within this region by virtue of its propensity to reside in the aqueous phase. In contrast, barium would seem to be transported preferentially in particulate form. The discharge of strontium over a prolonged period, by maintaining a significant concentration in the water system, leads to its incorporation into the shells of the inhabitants in the river estuary. The concentrations found would seem to agree with the maximal values reported elsewhere (Milliman, 1974).

#### Acknowledgments

ER acknowledges the Universidad del Pais Vasco, San Sebastian (Euskal Herriko Unibertsitatea, Donostia) for allowing her to spend a year as an exchange student at the University of Strathclyde. The authors are also grateful to Barbara Balfour and David Littlejohn, for assistance with the development of the ETAAS methodology.

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