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Association of ^{210}Po(^{210}Pb), $^{239+240}$Pu and ^{241}Am with different mineral fractions of a beach sand at Seascale, Cumbria, UK

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Abstract

The degree of association of ^{210}Po (in secular equilibrium with ^{210}Pb), $^{239+240}$Pu and ^{241}Am with iron oxide minerals in beach sand has been assessed using samples collected by panning and selective magnetic extraction techniques. The samples were obtained from Seascale beach (Cumbria), close to the BNF reprocessing plant at Sellafield (UK) and physically and chemically characterised in terms of their grain-size distribution, radionuclide content and magnetic properties. Low frequency (0.46 kHz) susceptibility (χ_{LF}) and saturation isothermal remanent magnetisation (SIRM) measurements were used to determine the magnetic properties of the bulk samples and the grain size fractions. Samples were also subjected to magnetic extraction, to concentrate the iron oxide minerals, and thence determine their degree of association with the radionuclides of interest. The efficiency of the magnetic extraction technique was estimated from rock magnetic measurements, before and after the extraction procedure. The placer deposits, enriched in iron oxide grains by environmental sorting processes, were both finer grained and more magnetic than the bulk sand. The mean particle diameter of the bulk sand was largely ($\sim 75\%$) greater than 200 μm, whereas for the placer material, $> 88\%$ of particles have mean diameters of < 200 μm. Whilst χ_{LF} and SIRM values of the 100–200 μm placer material were approximately 40–50-fold higher than those of the bulk sand of equivalent grain size, the radionuclide concentrations were approximately 4–13-fold higher. In terms of mass, the percentage of magnetic material extracted from samples of bulk sand (using a powerful, ~ 0.3 T, rare earth magnet), was small (approx. 1–3%). Nevertheless, $> 70\%$ of the magnetic signal was associated with these extracts. Concentrations of all three radionuclides in the magnetic extracts were enhanced relative to the weakly magnetic

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residue. The proportions of $^{210}Po(^{210}Pb)$, $^{239+240}Pu$ and ^{241}Am associated with the magnetic extracts were $\sim 18\%$, $\sim 12\%$ and $\sim 11\%$, respectively. Therefore, although the strongly magnetic iron oxide fraction contains measurably enhanced levels of these radionuclides, the majority of the α-radioactivity appears to be associated with the weakly magnetic residue. Crown Copyright © 2000 Published by Elsevier Science B.V.

1. Introduction

The predominant source of the α-particle radioactivity of sediments in the north-eastern Irish Sea arises from the legacy of large discharges of Pu radionuclides and ^{241}Am in the 1970s from the BNF reprocessing plant at Sellafield (Cumbria, UK). Although of less environmental impact than these artificial radionuclides, sediments in the region around Whitehaven (Fig. 1) also contain anthropogenically enhanced levels of uranium-series radionuclides as a result of discharges from the Albright & Wilson phosphate production plant, near Whitehaven (Kershaw, 1997). Particle reactive nuclides such as $^{239+240}Pu$ and ^{241}Am were rapidly removed from the water column to the seabed close to the Sellafield outfall as a result of sorption on suspended particulate material, and have been dispersed subsequently by nearshore sediment transport processes

Fig. 1. Map of Cumbrian coastline showing study area.

(Hetherington et al., 1975; MacKenzie et al., 1987). It has been estimated that approximately 85% of the total Irish Sea inventory of $^{239+240}Pu$ and ^{241}Am is contained in the sediments of a relatively narrow coastal strip approximately 30 km wide, from Kirkcudbright Bay in the north to the Ribble estuary in the south (Pentreath et al., 1984).

More recently it has been suggested that, in the Irish Sea sediment, the artificial α-radioactivity is largely associated with iron oxide minerals (Hamilton, 1996). Moreover, the mass of sediment associated with BNF-derived material is considered to be small, but highly radioactive, relative to the total mass of deposited sediment. The sources of these detrital iron oxide particles include natural geological sources and industrially derived debris, including blast furnace slag. The coastal sediments close to Sellafield consist of Permo-Triassic desertic sand, with iron oxides occurring both as coatings on quartz grains and as discrete particles of magnetite and haematite (Hamilton, 1999). Other possible sources include the glacial tills and volcanic rocks of the Cumbrian region. The nearshore distribution and redistribution of the iron oxides are controlled by water energy states. For example, because of their high specific gravity (relative to quartz, the major component of the nearshore sediment), iron minerals can be concentrated into placer deposits, under appropriate tidal conditions and in certain locations. To understand the dispersion pattern of radionuclide-contaminated sediment, it is important to quantify the distribution of the radionuclides between: (1) the different particle size fractions of the sediments; and (2) the two major mineral components, quartz and the iron oxides.

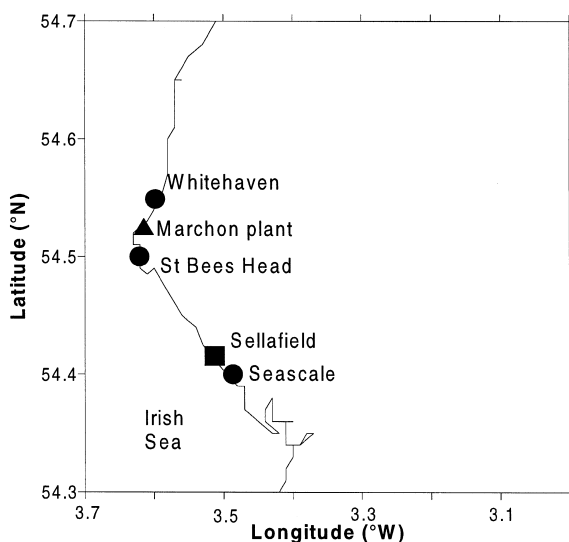A significant amount of data exists regarding the total α-particle radioactivity associated with

mineral surfaces of the nearshore Cumbrian sediment from studies using an autoradiographic (CR39 dielectric detector) technique (Hamilton, 1996, 1998). However, information concerning the behaviour of individual α-emitting radionuclides is more limited. The objective of the present study was to assess the extent of enrichment, and hence the degree of association, of the naturally occurring ^{210}Po (in secular equilibrium with the parent ^{210}Pb) and the artificial radionuclides $^{239+240}$Pu and ^{241}Am with iron oxide minerals, relative to the bulk quartz sand. Bulk sand and placer materials were obtained from the beach at Seascale (Cumbria, UK) close to the BNF reprocessing plant at Sellafield. The samples were characterised in terms of their grain-size distribution, radionuclide content and the magnetic properties, magnetic susceptibility (χ_{LF}) and saturation remanence (SIRM). A bulk sample, two grain-size fractions (200−500 and 100−200 μm) and a placer sample were also subjected to a magnetic extraction procedure to concentrate the magnetic iron oxides. The efficiency of the extraction technique was quantified using χ_{LF} and SIRM measurements before and after the extraction procedure.

2. Materials and methods

Placer material and bulk beach sand were collected, between high and low water, from the beach at Seascale (Fig. 1) in May 1997. Placer material was sampled by scraping black iron minerals from the surface of the pale yellow sand ripples and crudely purified in situ by panning. Separation by panning is possible because of the higher density of the heavy minerals relative to quartz grains. In the laboratory, samples of beach sand and placer material were subjected to optical microscopy. Grain-size separations were then carried out by wet sieving through 500 μm, 200 μm and 100 μm nylon mesh. Magnetic extracts from beach sand samples were obtained using a small rare-earth magnet (field $\sim$ 0.3 T) sealed in a polythene bag and swirled within a seawater/sand suspension. A weaker hand-held bar magnet was used to extract strongly magnetic particles

from the placer material. Extractions were repeated $\sim$ 30 times until removal of further material was minimal. Both fractions (magnetic extracts and residue) were dried and weighed prior to analysis.

Concentrations of ^{210}Po (supported by ^{210}Pb), $^{239+240}$Pu and ^{241}Am were determined using standard methods routinely carried out at CEFAS Lowestoft (Baker, 1984; Lovett et al., 1990). Samples were stored for 1 year to allow approximate secular equilibrium to be attained between the parent ^{210}Pb and daughter ^{210}Po radionuclides. These nuclides were assayed by conventional alpha spectrometry on silicon surface-barrier detectors, following chemical separation from all radiometric and gravimetric interference.

To characterise the mineralogy and concentration of magnetic minerals within the samples, the following magnetic measurements were undertaken: low field susceptibility (χ_{LF}) at 0.46 kHz using a Bartington meter; and isothermal remanent magnetisation (IRM) at 10, 20, 50, 100, 300 and 1000 mT using a Molspin fluxgate magnetometer, Molyneux pulse magnetiser and Newport electromagnet. These measurements were carried out at the Centre for Environmental Magnetism and Palaeomagnetism, School of Environmental Sciences, University of East Anglia, Norwich, UK. The susceptibility (χ_{LF}) data provide an indication of the concentration within the sample of strongly magnetic ferrimagnets, such as magnetite. The saturation isothermal remanent magnetisation (SIRM) is operationally defined as that imparted by the 1000 mT field. SIRM values reflect contributions from all remanence-carrying minerals, including the ferrimagnets and also weakly magnetic minerals such as haematite and goethite. The magnetically 'hard' remanence (HIRM), i.e. that acquired at high magnetic fields (between 300 and 1000 mT), reflects the concentration of these weaker magnetic minerals. Further information on the magnetic stability of selected samples was obtained by subjecting the SIRM to backfield (dc) demagnetisation (at 10, 20, 50, 100, 300 and 1000 mT) and alternating field (af) demagnetisation (at 5, 10, 20, 40 and 80 mT) to derive the coercivity parameters, coercivity of remanence [$(B_0)_{CR}$] and median destructive
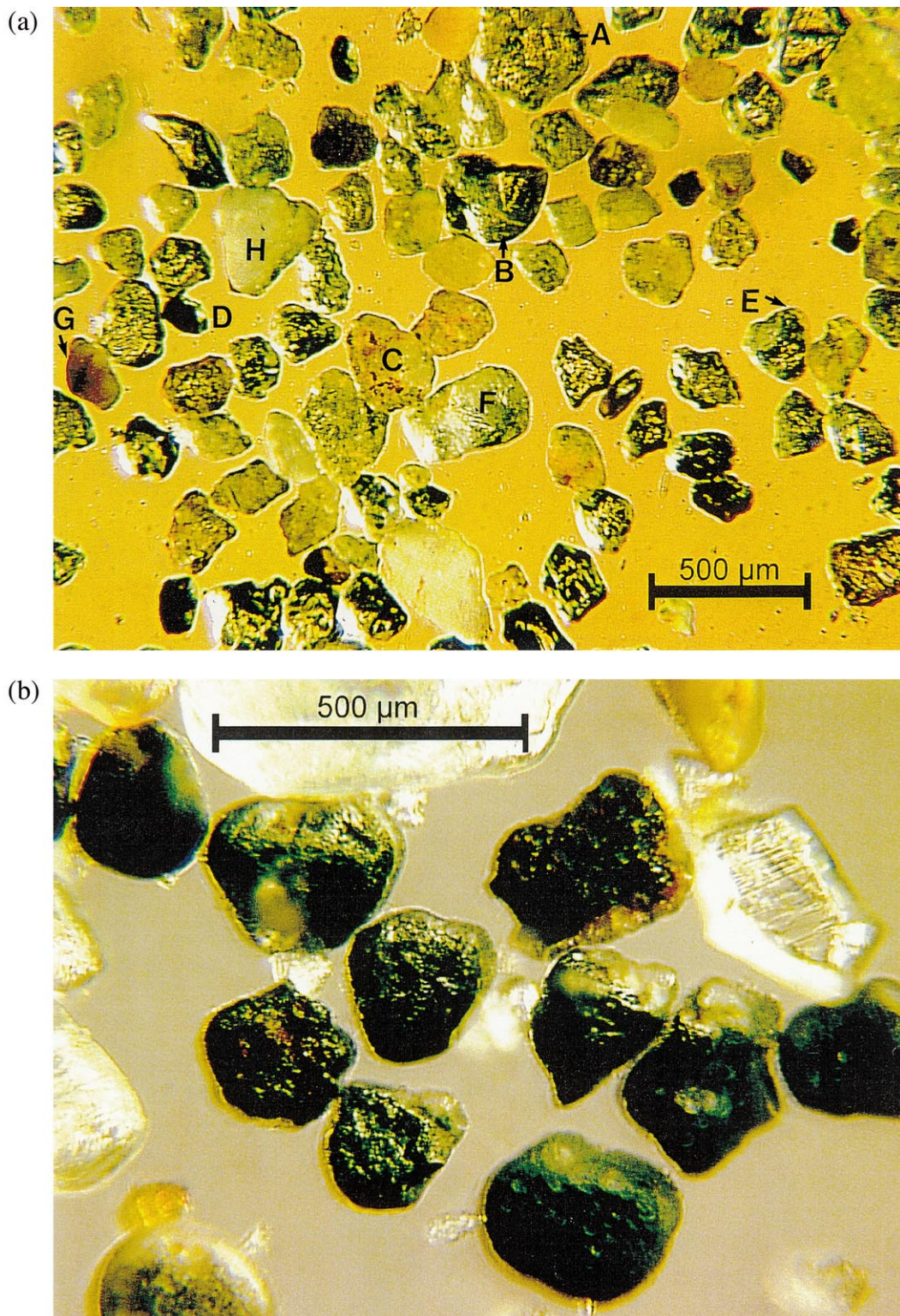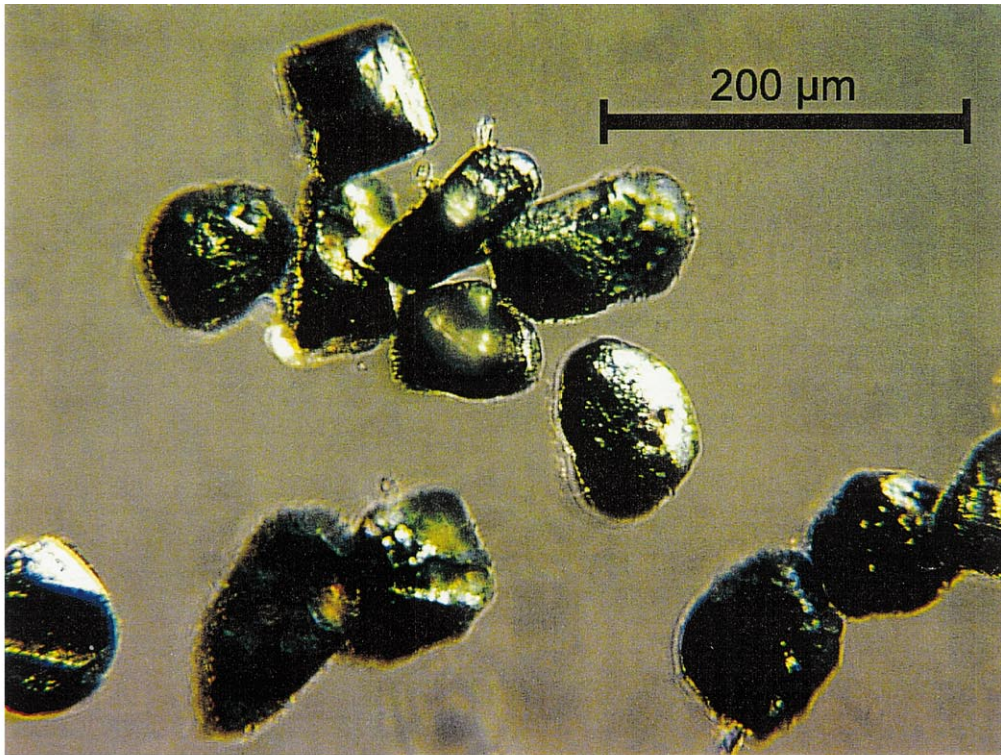
(a)

(b)

Fig. 2.

(c)

(d)

Fig. 2.

Table 1
Grain-size distribution for placer material/adjacent bulk sand and percentage of material extracted using 0.3 T magnet (samples obtained from Seascale beach, May 1997)

Sample	Mean particle diameter (%)			
	> 500 μm	$200−500$ μm	$100−200$ μm	< 100 μm
Seascale sand	4.3	72.4	23	0.3
Seascale placer	0.9	11.4	51.7	36
	Magnetic separation (% extracted)			
	Bulk	$200−500$ μm	$100−200$ μm	
Seascale sand	3.0	0.9	3.0	

field of IRM (MDF$_{IRM}$). (B$_0$)$_{CR}$ is the dc back-field which reduces the SIRM to zero and MDF$_{IRM}$ the af field that reduces the SIRM by 50%. Pure magnetite powders display remanent coercivity and MDF$_{IRM}$ values of approximately $10−25$ and $5−17$ mT, respectively (Maher, 1988). Haematite, in contrast, has a considerably higher remanent coercivity [(B$_0$)$_{CR}$ ∼ 400 mT (Thompson and Oldfield, 1986)], whilst (B$_0$)$_{CR}$ values for goethite can be even higher.

3. Results

Under the microscope (Fig. 2a), a mixture of particles were observed in the bulk sand, including clear quartz, red-stained quartz, quartz with black flecks of rutile (titanium dioxide), opaque iron minerals (magnetite and haematite) and green−grey slag. In the placer material, the abundance of opaque iron minerals was considerably greater (Fig. 2b), although quartz grains were also present. Data for the grain size distribution of placer material and the bulk sand are given in Table 1, together with the percentage of material extracted from aliquots of beach sand using the 0.3 T magnet.

The observed grain-size distributions illustrate the significant influence of environmental sorting/winnowing on the placer material and the disparity of the data with respect to that of the beach sand. The mean particle diameter of the beach sand was predominantly ($> 75\%$) greater than 200 μm whereas the placer material was significantly finer grained ($> 88\%$ of particles with mean diameter < 200 μm). The results of magnetic measurements on bulk sand, individual grain-size fractions of the sand and the placer material and on the magnetic extracts and the weakly magnetic residues are given in Table 2.

For the bulk sand sample χ_{LF} and SIRM values varied, by up to approximately two orders of magnitude, between the individual grain-size fractions. The finest grain sizes displayed the highest magnetic values. The χ_{LF} and SIRM values of the finest fraction (< 100 μm) were greater by approximately two orders of magnitude than those of the $200−500$ μm grain-size fraction. The relative importance of individual grain-size fractions is not only determined by magnetic property values but also by the percentage of the total mass of sediment each fraction represents. These parameters are combined in Fig. 3, which shows the contribution of the individual grain-size frac-

Fig. 2. Optical micrographs of different mineral fractions on beach at Seascale in May 1997: (a) bulk sand (A, composite fragment of slag; B, fractured rounded grain of haematite; C, hydrated iron oxide speckled quartz; D, magnetite; E, blast furnace calcic slag with enclosed blebs of iron; F, clear quartz; G, iron-stained quartz, Triassic sand grain; H, Feldspar) (b) 100−200 μm placer material; (c) magnetic extract from placer (note grains adhere because of magnetic properties; top grain exhibits cubic octahedral form); (d) quartz grain with haematite coating.

Table 2
Rock magnetic properties of individual sand fractions and placer material on beach at Seascale in May 1997[a]

Sample/ grain size	χ_{LF} $(10^{-8}\ m^3\ kg^{-1})$	SIRM $(10^{-5}\ Am^2\ kg^{-1})$	HIRM component: $(SIRM\text{-}IRM_{300mT})/$ $(SIRM)$	$(B_0)_{CR}$ (mT)	MDF_{IRM} (mT)
(1) Beach sand: grain-size splits upon bulk sand					
Unfractionated	18	217	0.24		
> 500 μm	15	63	0.15		
200−500 μm	6.2	80	0.21		
100−200 μm	26	300	0.19		
< 100 μm	820	7400	0.18		
(2) Placer material: grain-size splits and selective magnetic extraction					
100−200 μm	1400	11 000	0.21	27	15
< 100 μm	2200	14 000	0.21		
Magnetic extract	32 000	190 000	0.011	19	13
100−200 μm residue	150	2500	0.32		
< 100 μm residue	570	7200	0.46		
(3) Beach sand: magnetic extractions upon individual grain-size fractions					
Unfractionated extract	732	9400	0.13		
Unfractionated residue	2.0	20	0.47	242	> 80
200−500 μm extract	600	10 000	0.10		
200−500 μm residue	1.9	22	0.44		
100−200 μm extract	780	9200	0.27		
100−200 μm residue	2.5	26	0.50		

[a]*Note*. Residue refers to material remaining after extraction of magnetic material. Extract from placer obtained using weak hand held bar magnet and from beach sand using strong rare earth magnet.

tions for both magnetic properties and radionuclide activities. The percentage contribution was calculated using Eq. (1):

$$\text{Contribution} = \left[P_{gs} \times \text{grain-size}(\%) \right] / P_{bulk} \quad (1)$$

where P_{gs} and P_{bulk} are the magnetic property (i.e. χ_{LF} or SIRM) or radionuclide concentration of the individual grain-size fraction and unfractionated (bulk) sand, respectively. The sum of the percentage contribution from the individual grain-size fractions indicates the extent to which mass balance (i.e. recovery) was achieved during the separation procedure. These data are also given in Fig. 3.

Overall, more than half the magnetic signal was carried in the particle fractions finer than 200 μm. Assessment of mass balances of both magnetic properties (χ_{LF} and SIRM) indicate that losses of magnetic minerals were < 30% during the grain-size separation of the bulk sand. It is

most likely that incomplete recoveries were due to removal of iron oxide coatings from quartz grains, as a result of abrasion during sieving and shaking of sediment in seawater.

Subsequently, magnetic minerals were extracted from aliquots of bulk sand and selected grain-size fractions. Data given in Fig. 4 provide the sum of the contribution for the individual magnetic fractions and hence indicate the extent of recovery achieved during this separation procedure. The mass balance data in Fig. 4, for both χ_{LF} and SIRM properties, indicate the sum of the magnetic extract and residue fractions was greater (average of 20%) than the unfractionated material. The difference indicates the errors associated with carrying out measurements on small quantities of (magnetic extract) material. Nevertheless, it appears reasonable to conclude that losses of magnetic minerals were relatively small during the extraction process.

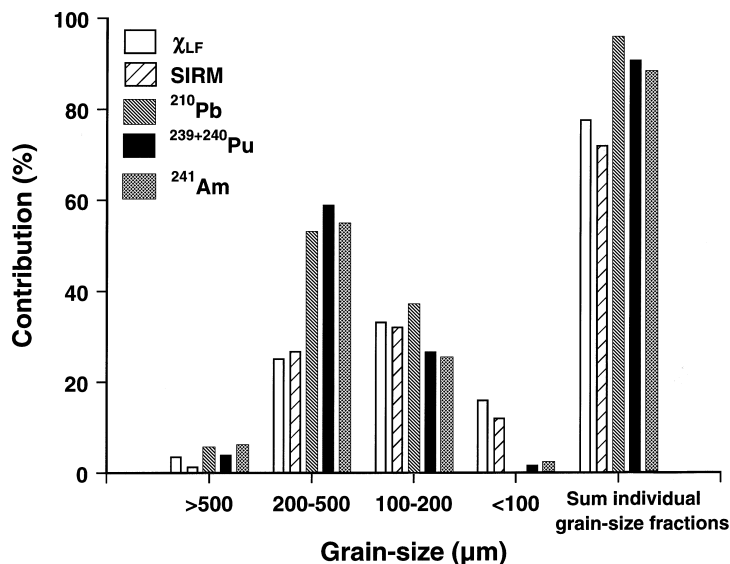For the placer material, the χ_{LF} and SIRM

Fig. 3. Contribution of individual grain-size fractions towards magnetic properties and radionuclide activity of Seascale beach sand. Contribution from individual fractions calculated using Eq. (1).

values of the 100–200 μm fraction were approximately 40–50-fold higher than those of the equivalent fraction of the beach sand (Table 2). Conversely, values for placer material of < 100 μm were only approximately two- to threefold higher than those of the corresponding sand fraction. These data indicate that the magnetic properties (hence the proportion of heavy mineral particles) of the finest sand fraction were of similar magnitude to the placer material.
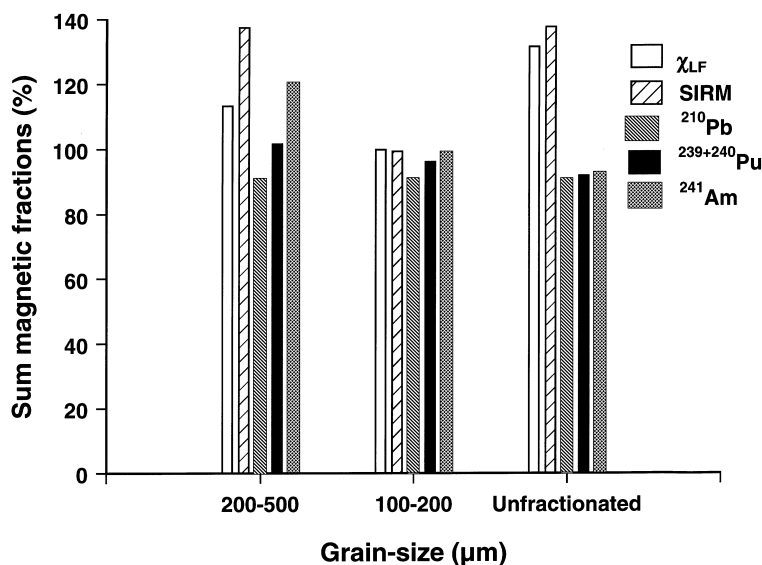

Fig. 4. Mass balance achieved during extraction of magnetic minerals from unfractionated, and selected grain-size fractions, Seascale sand for magnetic properties and radionuclide activity. The sum of the magnetic fractions is the total amount from extract and residue material.

For the unfractioned placer sample, a selective extraction of strongly magnetic material was achieved using a relatively weak hand-held bar magnet. The χ_{LF} and SIRM values of this magnetic extract were one–two orders of magnitude higher than those of the residues. The properties of strongly magnetic ferrimagnets like magnetite are dependent upon grain-size. Within the range 10–200 μm, reported χ_{LF} values for pure magnetite powders range from ~ 4.8 to 6.1×10^{-4} m^3 kg^{-1} and SIRM from ~ 1.1 to 5.1 Am^2 kg^{-1} (Maher, 1988). The susceptibility values reported for goethite and haematite are considerably lower [χ_{LF} approx. $60–70 \times 10^{-8}$ m^3 kg^{-1} (Thompson and Oldfield, 1986)]. Therefore, the susceptibility of the placer magnetic extract was $\sim 1/2$ that expected for pure magnetite of similar grain-size. From mass balance considerations, the proportion of the magnetic extract in its parent placer sample was $\sim 4\%$; the proportion of 'pure' magnetite present in the placer sample was, therefore, $\sim 2\%$.

The IRM component referred to as (SIRM-IRM$_{300mT}$)/SIRM in Table 2 is the fraction of the SIRM formed by the 'Hard' IRM (HIRM) component and reflects the concentration of imperfect antiferromagnets like haematite and/or goethite. HIRM values appear remarkably constant between the individual grain-size fractions of both the sand and the placer samples (average value = 0.2). Because of the much weaker magnetic properties of haematite, even small amounts ($\ll 1\%$) of magnetite will dominate the magnetic signal of the untreated samples of sand and placer material. For example, as shown in Table 2, the remanent coercivity of the untreated 100–200 μm placer material [$(B_0)_{CR} \sim 27$ mT] was only slightly higher than that of the magnetic extract. For the magnetic extract, low values of HIRM (~ 0.011), remanent coercivity [$(B_0)_{CR} \sim 19$ mT] and mean destructive field of IRM (MDF$_{IRM} \sim 13$ mT) are consistent with the behaviour expected for magnetite. Notably, however, HIRM values for the *residues* from the magnetic extractions were significantly higher, indicating preferential removal of the ferrimagnetic minerals from the residues and resultant concentration of their haematite/goethite phases. The presence of haematite/goethite is confirmed by the large remanent coercivity value [$(B_0)_{CR} = 242$ mT] obtained for the residue after magnetic extraction of the bulk beach sand sample.

The efficiency of the magnetic extraction procedure was crudely estimated by difference using Eq. (2):

Separation efficiency

$$= (Mp_{PLACER} - Mp_{RESIDUE})/Mp_{PLACER}$$
$$\times 100\% \qquad (2)$$

where Mp$_{PLACER}$ and Mp$_{RESIDUE}$ are the magnetic property (i.e. χ_{LF} or SIRM) of the placer material and 'non-magnetic' residue, respectively. The χ_{LF} data in Table 2 indicate that the extraction efficiency for removal of ferrimagnetic material from the 100–200 μm grain-size fraction was $\sim 89\%$. The extraction efficiency for the finest fraction (< 100 μm) was slightly less efficient ($\sim 74\%$). Under optical microscopy (Fig. 2c), the magnetic extract was dominated by black cubic particles (prisms) with truncated ends. The average grain-size was ~ 100 μm. The particles tended to cluster together because of the force of magnetic attraction. Some quartz grains and additional grey particles (possibly calcareous slag) were also present. The typical composition of magnetic placer material in this locality has been reported to be magnetite, blast furnace residue and other debris containing blebs of iron within other slag materials (Hamilton, 1998). A more efficient magnetic separation of different mineral fractions would probably be difficult to achieve because some black particles are composites of magnetic and non-magnetic material (Hamilton, 1996).

For the beach sand, a strong (0.3 T) rare-earth magnet was used to extract magnetic material from a bulk sample and from individual size fractions. The mass of material extracted was small, ranging from $\sim 1\%$ for the 200–500 μm grain-size fraction up to $\sim 3\%$ for the 100–200 μm material and the whole (unfractioned) beach sand (Table 1). The χ_{LF} and SIRM values of the magnetic extracts were considerably greater (by a factor of approx. 300–500) than those of the

residue material (Table 2). The χ_{LF} and SIRM values of the magnetic extracts from the bulk sand and from the two grain-size fractions were rather similar. They were also comparable to the χ_{LF} and SIRM values observed for the untreated < 100 μm sand fraction. Thus, the variations in χ_{LF} and SIRM apparent between the three grain-size fractions of the bulk sand were most likely due to differences in the percentage of magnetic minerals in each fraction. The HIRM values of the sand magnetic extracts (range 0.10–0.27) were higher than those observed for the placer magnetic extract (~ 0.01). This is probably due to the use of a more powerful magnet for the sand extracts, which had removed a mixture of ferrimagnets, quartz with magnetic inclusions and some of the haematite/goethite grains. The χ_{LF} and SIRM data indicate that the efficiency of the extraction procedure was $\sim 90\%$ for the bulk sand and the 100–200 μm fraction and $\sim 70\%$ for the 200–500 μm material.

Although the χ_{LF} of the residue materials was low, the values were nevertheless greater than those expected for quartz or feldspar which are diamagnetic [χ_{LF} approx. -0.5×10^{-8} m^3 kg^{-1} (Thompson and Oldfield, 1986)]. Also, as noted above, HIRM values for the residues (average value = 0.47) were enhanced relative to the original samples (average value = 0.22). Microscopic examination of the residues revealed the presence of secondary iron hydroxides associated with quartz grains (Fig. 2d), together with some discrete opaque particles. These observations, together with the high value of $(B_0)_{CR}$ (~ 240 mT), indicate that the weak magnetism of the extract residues were derived mainly from the presence of haematite coatings on quartz grains.

The results of radionuclide analyses for ^{210}Po(^{210}Pb), $^{239+240}$Pu, $^{239+240}$Pu:^{238}Pu ratio and ^{241}Am are given in Table 3. The use of mass balance calculations to monitor activity levels during the grain-size separation of bulk sand indicated that losses of all three radionuclides were relatively small ($< 12\%$; Fig. 3). Reasonable mass balance was also achieved for all three radionuclides during the magnetic extraction process

Table 3

Radionuclide concentrations in individual sand fractions and placer material on beach at Seascale in May 1997[a]

Sample/ grain size	^{210}Po(^{210}Pb) (Bq/kg)	$^{239+240}$Pu (Bq/kg)	$^{229+240}$Pu: ^{238}Pu	^{241}Am (Bq/kg)	^{241}Am: $^{239+240}$Pu
(1) Beach sand: grain-size splits upon bulk sand					
Unfractionated	7.0	103	5.44	139	1.35
> 500 μm	9.1	93	5.67	195	2.10
200–500 μm	5.1	84	5.08	105	1.26
100–200 μm	11	119	5.07	152	1.28
< 100 μm	–	455	5.54	881	1.93
(2) Placer material: grain-size splits and selective magnetic extraction					
100–200 μm	146	514	5.43	949	1.85
< 100 μm	262	496	5.34	828	1.67
Magnetic extract	68	766	5.40	1038	1.36
100–200 μm residue	104	422	5.16	787	1.87
< 100 μm residue	258	541	4.88	929	1.72
(3) Beach sand: magnetic extractions upon individual grain-size fractions					
Unfractionated extract	41	426	5.69	534	1.25
Unfractionated residue	5.3	85	5.35	116	1.37
200–500 μm extract	23	282	5.20	304	1.08
200–500 μm residue	4.5	84	5.35	125	1.50
100–200 μm extract	77	590	5.18	907	1.54
100–200 μm residue	8.0	100	4.97	127	1.27

[a]Note. 1σ counting errors associated with ^{210}Po(^{210}Pb), $^{239+240}$Pu and ^{241}Am data were $< 18\%$, $< 4\%$ and $< 6\%$, respectively.

(average difference between original material and sum of extract and residue was $-3 \pm 10\%$; Fig. 4).

Concentrations of all three radionuclides in the bulk sand varied significantly between the different grain size fractions. The lowest concentrations were observed in the 200–500 μm fraction (which comprises the greatest sample mass, Table 1). The largest grains (> 500 μm) contained levels of $^{210}Po(^{210}Pb)$ and ^{241}Am which were almost double those of the 200–500 μm fraction. Concentrations in the intermediate 100–200 μm fraction, compared with that observed in the coarse 200–500 μm grain-size fraction, were enhanced by a small but measurable amount (by $\sim 40\%$) whilst levels in the finest material (< 100 μm) were five- to eightfold higher. Mass balance considerations indicate that, in contrast to the magnetic signal (Fig. 3), most ($> 60\%$) of the $^{239+240}Pu$ and ^{241}Am activity was associated with material coarser than 200 μm.

Radionuclide concentrations in the 100–200 μm placer material were approximately 4–13-fold higher than those in the corresponding sand size fraction (Table 3). The finest grained placer material (< 100 μm) contained $^{239+240}Pu$ and ^{241}Am concentrations remarkably similar to those observed in the coarser 100–200 μm fraction, and in the < 100 μm sand fraction. In contrast, the $^{210}Po(^{210}Pb)$ placer concentration appeared to be dependent upon grain size (levels in the < 100 μm material were almost double those in the 100–200 μm fraction). Overall, these data indicate that differences in radionuclide concentration between individual samples probably result from differences in particle mineralogy rather than grain size (i.e. surface area).

Concentrations of $^{239+240}Pu$ and ^{241}Am in magnetic particles extracted from the placer material were less than two fold higher than in the residue material. Since the magnetic data indicate that the mass proportion of magnetic extract was small ($\sim 4\%$), variations in the magnetic mineralogy (i.e. ratio of haematite:magnetite) of the placer material do not seem to exert any significant influence on binding of Pu and ^{241}Am radionuclides. In contrast, levels of $^{210}Po(^{210}Pb)$ were four fold lower in the magnetic extract indicating significant dissociation between the ferrimagnetic minerals and Pb-derived radioactivity. Magnetic separation techniques have been applied to study the elemental distribution between different fractions of Lake Michigan sediment (Burger and Tisue, 1978). For this freshwater sediment, Pb was found to be concentrated in the least magnetically susceptible fraction (diatom fragments, fine-grained quartz, calcite and clay flocs), whereas Mn, Zn and Ti were concentrated in iron-rich spheres, magnetite and ilmenite that dominated the magnetically most susceptible fraction. The distribution of stable Pb in this particular freshwater sediment was, therefore, qualitatively similar to that observed in the present study.

Radionuclide data are also given in Table 3 for the magnetic extracts from the sand fractions. Concentrations of all three radionuclides in the magnetic extracts were significantly enhanced relative to the residue material. The extent of radionuclide enrichment was two- to threefold greater in the 100–200 μm fraction compared with the 200–500 μm fraction. Levels in the 100–200 μm magnetic extract were similar to those observed in placer material of the same grain size. Since the magnetic fraction constitutes $\sim 3\%$ by weight of the bulk (unfractionated) sand, then the proportion of $^{210}Po(^{210}Pb)$, $^{239+240}Pu$ and ^{241}Am associated with the strongly magnetic fraction was $\sim 18\%$, $\sim 12\%$ and $\sim 11\%$, respectively (Fig. 5). Therefore, although the ferrimagnetic minerals did indeed contain measurably enhanced levels of these radionuclides, the bulk of the radionuclides were associated with the weakly magnetic residue. For the weakly magnetic residues, the difference in concentrations of $^{239+240}Pu$ and ^{241}Am between the 200–500 μm and 100–200 μm grain-size fractions was small (Table 3). In contrast, the level of $^{210}Po(^{210}Pb)$ was two fold higher in the latter fraction.

The $^{239+240}Pu/^{238}Pu$ activity ratios observed in these samples (range approx. 4.9–5.7) were reasonably close to that estimated for the time-integrated Sellafield discharges (~ 5.6) but considerably greater than the ratio present in discharges since 1980 (< 3.4). This indicates that Pu bound to these samples was considerably aged. Variations in behaviour between the Pb, Pu and
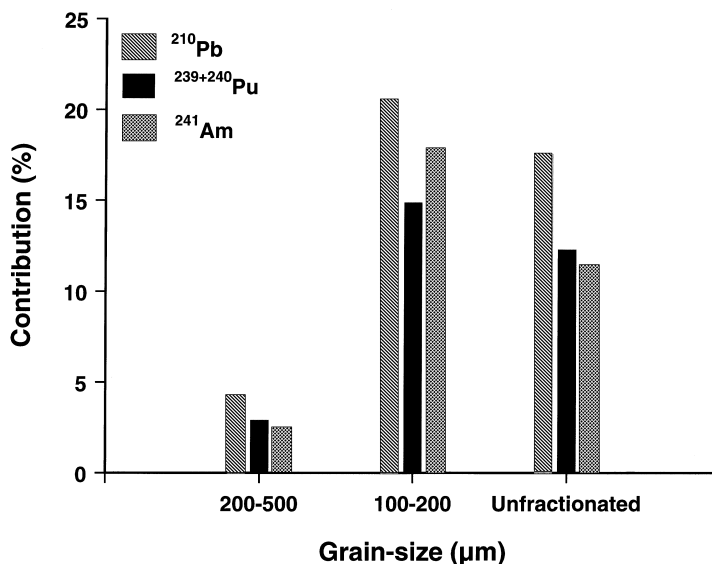
Fig. 5. Contribution of magnetic extracts towards radionuclide activity in unfractionated, and selected grain-size fractions, Seascale beach sand.

Am radionuclides are evident from the present data. For example, the ^{241}Am/$^{239+240}$Pu ratio ranged from 1.08 to 2.10, similar to that observed for surficial offshore Irish Sea sediment [1.02–1.90 (MacKenzie et al., 1999)]. The ratio for the time-integrated Sellafield discharge (allowing for grow-in from ^{241}Pu) was ∼ 1.55, i.e. in the middle of the range observed in the present shoreline samples and offshore sediment. The ^{241}Am/$^{239+240}$Pu ratios for the < 100 μm fraction (1.93) and for the placer material (approx. 1.7–1.9) were higher than those for the 100–200 μm and the 200–500 μm sand fractions (1.26–1.28). Thus, it appears that the extent of enrichment of ^{241}Am with strongly magnetic iron minerals was greater than that of $^{239+240}$Pu. However, given that remobilisation from contaminated sediment is now considered to be the predominant source term of Pu radionuclides and ^{241}Am in the Irish Sea (Leonard et al., 1999) the observed variation in enrichment may be due to selective re-dissolution of Pu, rather than preferential uptake of ^{241}Am.

The origin of ^{210}Po(^{210}Pb) is more complex than that of $^{239+240}$Pu and ^{241}Am. Discussion of the relative importance of ^{210}Pb sources for Cumbrian coastal sediments is given elsewhere (McCartney et al., 1992). The predominant source term, prior to 1992, was suggested to result from discharges of uranium-series radionuclides by the Albright & Wilson Marchon phosphate production plant. As a result of changes in plant operations, a large reduction in discharges has occurred since May 1992 (Poole et al., 1995). The ^{210}Po(^{210}Pb) bound to the samples analysed here may reflect the legacy of the earlier large discharges and, therefore, be aged. The influence of the Marchon source term upon levels of ^{210}Po(^{210}Pb), and the distribution between mineral fractions, remains uncertain. It is apparent, however, that the pattern of ^{210}Po(^{210}Pb) behaviour was more complex than $^{239+240}$Pu and ^{241}Am, and ^{210}Po(^{210}Pb) concentrations appear significantly more sensitive to grain size and iron mineralogy.

4. Discussion

The highest concentrations of most radionuclides in bulk Irish Sea sediments are associated with fine-grained material; this is usually interpreted as reflecting the greater surface area avail-

able (per unit mass) for sorption (Hetherington and Jefferies, 1974; Aston and Stanners, 1982; Assinder, 1983; McDonald et al., 1990; McCartney et al., 1994; MacKenzie et al., 1999). Indeed, magnetic measurements have been used previously as a tool to normalise for the effect of particle size upon radionuclide concentration (Oldfield et al., 1993). More recently, it has been suggested that the observed distribution may instead be a consequence of direct association of radionuclides with iron phases (Hamilton, 1996, 1998). The limited amount of data obtained in the present study indicate that Pu, Am and Pb radionuclides are significantly enriched in the strongly magnetic component of the beach sand at Seascale. However, this component constitutes a small proportion of the bulk sand ($\sim 3\%$ in this particular sample). Moreover, it is estimated that $< 20\%$ of these radionuclides are associated with this component in the bulk sand.

Similar levels of radionuclide enrichment with the magnetic fraction (of a finer-grained, estuarine sediment) were reported by Bulman et al. (1984) and Bulman and Johnson (1986). By mass, the sediment was predominantly composed ($\sim 90\%$) of silt (2–53 μm) and fine sand (53–250 μm). These authors used high-gradient magnetic separation to characterise the distribution of $^{239+240}$Pu and ^{241}Am within the clay fraction (< 2 μm). Although the clay fraction constituted $< 10\%$ by mass, it contained $\sim 40\%$ of the $^{239+240}$Pu, ^{241}Am and stable Fe. For clay particles with diameters in the range 0.2–2 μm, levels of $^{239+240}$Pu, ^{241}Am and stable Fe were enhanced in the magnetic fraction by a factor of ~ 7, 3 and 7, respectively, relative to the residue.

The present data support the hypothesis that both surface adsorption (and therefore available surface area) and iron mineralogy play an important role in controlling radionuclide distribution. In the Seascale beach sand samples, radionuclides bind both with the strongly magnetic discrete iron mineral grains, which are concentrated in the finer (< 100 μm) fraction, and with haematite occurring throughout the grain-size spectrum, both as discrete grains and as coatings on the surfaces of quartz grains.

A potential problem, with regard to assessing the association of radionuclides with the different magnetic components, is the difficulty of obtaining a representative sample. It has been suggested that only a small proportion of the individual grains are 'labelled' with α-radioactivity (Hamilton, 1996, 1998). Using an autoradiographic technique (CR-39 di-electric detector) to determine the distribution of total α-emitting radionuclides on the surface of individual grains, $\sim 30\%$ of the 'magnetic' particles extracted here from placer material were 'labelled'. The proportion of 'labelled' grains in the magnetic residue was even lower ($\sim 14\%$). In spite of the sampling problem, a similar level of enrichment of Pu radionuclides and ^{241}Am on placer material relative to bulk sand (comparable with that observed in the present study at Seascale) has been found at two other locations [St Bees and the Esk estuary some 10 km and 15 km to the north and south of Seascale, respectively (Hamilton, 1998)]. Concentrations in the placer material were approximately three- to sixfold greater than the bulk sand. However, caution needs to be exercised when comparing data between different sites. Account needs to be taken of the different potential sources of non-labelled grains of haematite and magnetite. Such a source is present in the form of red Permo-Triassic sandstone material which forms the bedrock on the beach at Seascale and also the cliffs at St Bees. Authigenic iron oxides in the St. Bees Sandstone have been reported to occur as discrete crystals of haematite and as fine-grained coatings of pigmentary haematite around detrital grains (Ixer et al., 1979).

As well as the natural sources, the Cumbrian coast has received large inputs of industrial waste solids arising from the production of iron and coal (Perkins, 1972; Perkins and Kendrick, 1978; Hamilton, 1996). Although the input of industrial iron has now largely ceased, the degree of cycling of radionuclides associated with industrial iron oxides is unknown. As stated earlier, the $^{239+240}$Pu/^{238}Pu ratios observed in our samples are reasonably close to that estimated for the time-integrated Sellafield discharges and indicate that the labelling on these particles arises from the legacy of large discharges of Pu radionuclides and ^{241}Am in the 1970s. Given that the source

term of the iron minerals in the Cumbrian sediments has changed with time, further work is required to assess what changes in radionuclide distribution between individual mineral fractions, if any, are likely to occur in the future.

There is potential to introduce artefacts in this type of study, resulting from the manipulation of samples during processing. In the natural context, some of the surficial iron-stained coating on the Permo-Triassic sediments is rapidly removed in seawater since, in contrast to the red colour of the cliffs, the beach sands are primarily yellow (Hamilton, 1996). The removal of the iron coatings may result from dissolution in seawater, or grinding resulting in the loss of fine-grained debris. In the present study, the application of mass-balance equations to the magnetic data indicated significant loss ($\sim 30\%$) of magnetic signal during grain-size separation (sieving). However, a similar mass-balance approach to monitoring radionuclide concentrations during sample processing indicated better agreement between unfractionated material and individual fractions (difference $< 20\%$). Thus, our assessment of the radionuclide/magnetic mineral association is not significantly affected by these sample treatment artefacts.

5. Conclusions

The radionuclides, ^{210}Po(^{210}Pb), ^{239,240}Pu and ^{241}Am are enriched, by a factor of ~ 7, in the strongly magnetic fraction concentrated in placer deposits and in magnetic material extracted from bulk beach sand samples from Seascale. In terms of mass, the percentage of magnetic material extracted from these samples of beach sand was small (approx. 1–3%). Nevertheless, $> 70\%$ of the magnetic signal was associated with these extracts. Conversely, they contained $< 20\%$ of the artificial α-radioactivity. The weak magnetism in the weakly magnetic residues is probably due to the presence of haematite coatings on quartz grains of quartz. Most of the ^{210}Po(^{210}Pb), ^{239,240}Pu and ^{241}Am present in the beach sand at Seascale is associated with these coatings or the surface of the quartz grains.

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