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THE GEOCHEMISTRY OF CAESIUM IN THE SECONDARY ENVIRONMENT AROUND THE ST AUSTELL GRANITE

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Interest in the geochemistry of caesium (Cs) in the secondary environment stems from the need to monitor the behaviour of ^{137}Cs resulting from nuclear accidents. Caesium abundance is generally low in crustal rocks (2.6 ppm) but is known to be strongly enriched in the south-west England granites. Granites from the St Austell pluton can contain in excess of 50 ppm Cs, while the Trelavour Down pegmatite contains 132 ppm. In soils over the St Austell granite, Cs levels generally range from 50 to 100 ppm, with the highest concentrations frequently being found in the deepest soil horizons where Cs contents often exceed those found in the parent material. As Cs is concentrated in the finest soil fractions it is probable that as the element is released during weathering so it is preferentially adsorbed by clays. Vegetation samples from the St Austell area show species variation for Cs uptake but the average content of the plants analysed is 2.3 ppm. While the Rb/Cs ratio for the granite is 27, similar to that found for literature data, the mean ratio for topsoils is 7.2 indicating a strong relative enrichment of Cs. The mean Rb/Cs ratio of plants (47) points to a preferential uptake of Rb.

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INTRODUCTION

Nuclear accidents such as that of Chernobyl cause the release of radioactive caesium (Cs). As a result, there is a great deal of interest in the behaviour of Cs in the secondary environment. The Cornubian granites are particularly enriched in the heavy alkalies (Floyd, 1972), while Exley (1959) and Hill and Manning (1987) have demonstrated that the St Austell pluton is extremely rich in Rb. Sediments and soils derived from these plutons would be expected to contain elevated levels of Cs.

During weathering Cs is released with relative ease but is strongly and rapidly trapped by solid material (Davis, 1963). Indeed, Jenne and Wahlberg (1968) suggested that of all the alkali metals Cs is preferentially adsorbed by most clays. While there is little data available on the geochemistry of Cs in soils it is apparent from the work of Merefield (1986) that it is concentrated in the fine-grained fraction. According to the estimated values of Vinogradov (1959), the Rb/Cs ratio of soils is similar to that of granitic rocks (~30).

In this study, based around the St Austell pluton, we have analysed granitic rocks, soils from fifteen profiles and vegetation growing over these soil sampling sites, to obtain data on the behaviour of Cs in the secondary environment and to compare its behaviour with that of Rb.

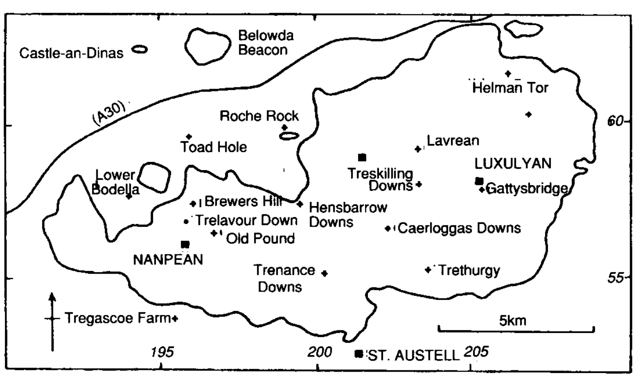

Fig 1: The St Austell pluton with soil and vegetation sampling sites indicated (+).

METHODOLOGY

Soil and vegetation samples were collected from the fifteen sites shown in Figure 1. These sites were chosen to be at fairly regular intervals, away from disturbed ground and, where possible, on moorland areas with abundant ling *(Calluna vulgaris),* bracken *(Pteridium aquilinum)* and gorse *(Ulex* sp.). Soil profile samples were collected at 10 cm intervals down to a maximum depth of 70 cm, but in cases where this was not possible the maximum attainable depth was sampled. Vegetation samples of the three species listed above were collected from the same sites, where several plants of each species were collected and bulked. In the case of ling, this was only available at eight sites.

The rock samples, which were collected where available and do not, in the main, relate to the soil sampling sites, were jaw crushed and milled in a swing mill with a tungsten-carbide pot. Following drying, the resultant powders were prepared for analysis by hydrofluoric and perchloric acid attack.

Vegetation samples were dried at 80°C and then comminuted in a stainless steel mill. Five gram samples of the crushed material were burned off at 450°C overnight and the resultant ash treated with 25% nitric acid. The solutions were then filtered into 100 ml graduated flasks.

Soil samples were dried at 80°C and then disaggregated and sieved, the samples being split into the following fractions: >1mm, 1mm to 500 µm, 500 to 250 µm, 250 to 106 µm, 106 to 53 µm and <53 µm. The finest fraction of soil was analysed, while for three sites, chosen at random, all fractions separated were milled in a tungsten-carbide ball mill and analysed.

For the analysis of soils the samples were treated with a 4:1 mixture of nitric and perchloric acid. This technique has been found to quantitatively release Rb and Cs from soil samples.

Analyses were performed by inductively coupled plasma-mass spectrometry using indium as an internal standard.

RESULTS AND DISCUSSION

Rocks

The data for several of the rocks encountered in the St Austell pluton are listed in Table 1. From this data it is apparent that Cs, like Rb, is extremely enriched in the St Austell granite (mean 58 ppm). The granite shows about a tenfold enrichment over average granites (3 to 7 ppm) (Taylor, 1964; Heier and Adams, 1964; Heier and Billings, 1970) and is even more enriched in the Li-pegmatite of Trelavour Dow

In this context it is of interest to note that Cs has been found to be preferentially enriched in Li—micas (Foster, 1960). The Rb/Cs ratio of the pegmatite and the granites (Table 1) is similar to those recorded in the literature for granitic rocks (25 to 38, Greenwood and Earnshaw, 1984; Taylor, 1964; Hedge, 1966; Heier and Adams, 1964).

TABLE 1: Cs and Rb in the granitic rocks of St. Austell

Rock type	Cs	Rb	Rb/Cs
	(ppm)	(ppm)	
Granite (8)	35-87	1124-1921	
Mean	58	1566	27
Li-mica pegmatite (Trelavour down)	132	3288	25
Quartz-tourmaline rock (Roche)	1.2	28	23
Luxullianite	0.9	13	14
Kaolinised granite	4.7	70	15
showing increasing	3.1	36	12
alteration	3.9	42	11

TABLE 2: Rb and Cs in various soil fractions.

	>1mm	500µm	250µm	106µm	53µm	<53µm
Gattysbridge, Luxulyan (Well drained brown earth)						
Surface soil (0-10 cm)						
Rb	105	120	105	140	134	549
Cs	16	18	18	20	21	82
Subsoil (40-50 cm)						
Rb	96	118	118	136	128	605
Cs	15	18	20	22	21	90
Heiman Tor (Well drained brown earth)						
Surface soil (0-10 cm)						
Rb	88	108	110	122	105	531
Cs	16	17	23	16	18	54
Subsoil (40-50 cm)						
Rb	102	116	114	112	98	405
Cs	9	10	10	10	10	37
Hensbarrow Downs (Organic rich surface soil, leached)						
Surface soil (0-10 cm)						
Rb	221	219	213	209	186	128
Cs	15	16	17	17	16	15
Subsoil (30- 40 cm)						
Rb	230	329	272	252	256	162
Cs	20	23	22	21	20	23

The low levels of Cs recorded for the quartz tourmaline rock and the luxullianite may reflect the absence of a suitable host mineral but could equally well reflect the mode of origin of these rock types. It is of interest to note that Power (1968) recorded relatively low levels of Cs and Rb in tourmalines from quartz-tourmaline rocks and tourmalines of hydrothermal origin, while those from pegmatites are generally richer in Cs.

The kaolinised granites analysed in this study are low in Cs and Rb and both elements show a general decrease with increasing alteration. While both these alkalies show low concentrations in the kaolinised granites, the Rb/Cs ratio (11 to 15) is much lower than in the unaltered rocks, presumably due to the incorporation of Cs in the kaolinite clay.

Soils

In two of the three profiles where all of the fractions listed above were separated and analysed, both in well drained brown earths, the Cs content of the finest fraction (<53µm) is between 3 to 4 times that occurring in all other fractions (Table 2). This behaviour is generally paralleled by Rb, which is enriched to a similar degree in the finest fractions. In the third profile where the surface soil is peaty, the Cs values are constant in all fractions, while Rb is depleted in the finest fraction and concentrated in the coarser fractions. There is no obvious reason for this variable behaviour of the two alkalies.

The low Rb/Cs ratio found in soils would seem to imply a loss of Rb relative to Cs during weathering, which is in marked contrast to the conclusions of Vinogradov (1959). In addition, while in two of the profiles the degree of enrichment of Cs in the finest fractions is similar to that of Rb (implying that both are retained through adsorption by the clay minerals) the Cs contents of the fine fractions are about the same or slightly higher than in the parent granitic material, Rb being much lower. From the observations of Merefield (1981a; 1981b; 1986) Cs is much enriched over Rb in the clay fraction of sediments and soils. It is somewhat surprising, therefore, that the Rb/Cs ratios of the differing soil fractions in these two samples are almost identical.

In the profile showing no relative enrichment of Cs and Rb in the fine fraction, the soil is gleyed and appears somewhat leached, which may explain the differing behaviour of the two alkalies.

For the rest of the profiles only the finest fraction of soil was analysed. In over half of these profile samples the Cs and Rb contents are highest at the base of the profile and in many cases Cs content is higher than that found in the granitic rocks. Some typical profiles are included in Table 3.

TABLE 3: Rb and Cs in some typical soil profiles

Depth (cm)	Rb (ppm)	Cs (ppm)	Rb/Cs	Depth (cm)	Rb (ppm)	Cs (ppm)	Rb/Cs
Gattysbridge, Luxulyan				**Heiman Tor**			
0-10	549	82	6.7	0-10	531	54	9.8
10-20	592	93	6.4	10-20	596	59	10.1
20-30	579	91	6.4	20-30	611	56	10.9
30-40	613	93	6.6	30-40	505	40	12.6
40-50	605	90	6.7	40-50	405	37	10.9
Treskilling Downs				**Hensbarrow Downs**			
0-10	757	121	6.3	0-10	128	15	8.5
10-20	795	130	6.1	10-20	136	17	8
20-30	1047	177	5.9	20-30	168	17	9.9
30-40	1492	212	7	30-40	162	23	7

The mean Cs content of all of the soil profiles sampled in this study are shown in Figure 2, while the corresponding Rb values are presented in Figure 3. From these figures it is apparent that both elements are very enriched in soils with Cs being relatively more enriched than Rb, as shown by the Rb/Cs ratios being between 4 and 12.

The work of Exley (1959) and Hill and Manning (1987) has shown that the St Austell pluton is composed of a range of chemically distinct granitic rock types, some of which Manning and Exley (1984) have suggested were formed by metasomatic alteration of magmatically differentiated granites.

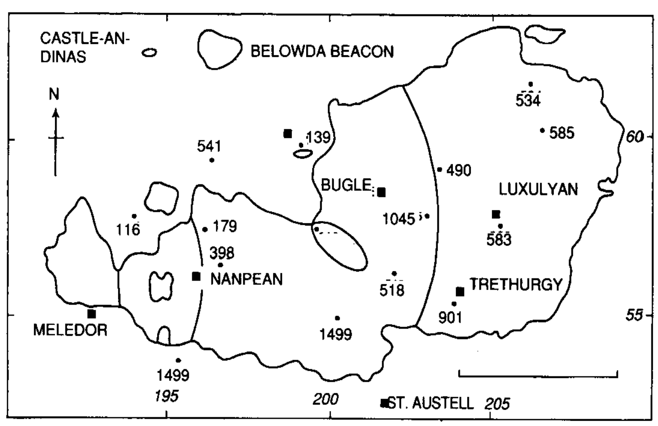

Figure 2: Mean Rb content of soil profiles (ppm in 53µm fraction).

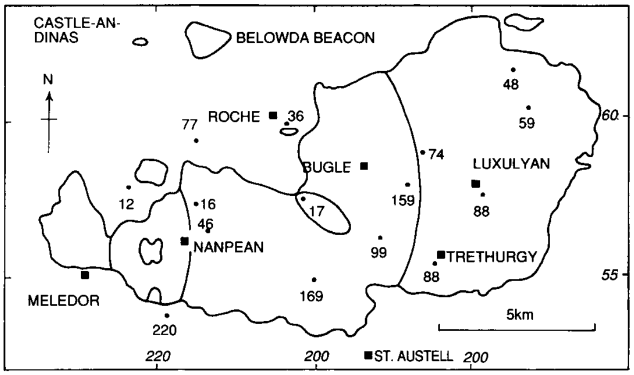

Figure 3: Mean Cs content of soil profiles (ppm in 53μm fraction).

Exley (1959) and Hill and Manning (1987) have shown that Rb concentration varies considerably in the different granite types and, therefore, it might be expected that the soil Rb and Cs contents should reflect any variation. Figures 2 and 3 suggest that the contents of the two alkalies in soils over the eastern end of the pluton, where biotite granite predominates, are fairly consistent. However, over the central part of the pluton, where Hill and Manning (1987) suggest a complex distribution of granitic types, soils show a wide range of both Rb and Cs contents.

The highest values recorded for both Cs and Rb in soils during the present study were for a profile collected over aureole rocks. According to Bowler (1958) and Stone and Awad (1988) Cs and Rb are extremely enriched in the contact rocks.

Vegetation

Table 4 summarises the data obtained for the three plant types analysed in this study. From this data it is apparent that there is a distinct species variation with the highest mean Rb value found in the bracken, and the highest mean Cs value occurring in ling, which also shows the lowest mean Rb values. The resultant Rb/Cs ratios vary greatly between species. The overall mean value for all vegetation samples analysed is 108 ppm Rb and 2.3 ppm Cs in the dry matter (mean Rb/Cs ratio of topsoils is 7.2); this points to a preferential incorporation of Rb in the plants. The degree of uptake of Cs and Rb from soils is illustrated in Table 5, which demonstrates that there is a preferential incorporation of Rb relative to Cs in all three plant species analysed, with the greatest relative enrichment being in bracken.

TABLE 4: Rb and Cs in vegetation (ppm in dry matter)

Species	Rb	Cs	Rb/Cs
Ling (8)	31.5-89	1.2-10.7	
Callum vulgaris	X = 57	X = 4.7	12
Bracken (15)	64-434	0.2-7.8	
Pteridium aquilinum	X = 150	X = 2.4	63
Gorse (15)	44-158	0.4-1.5	
Ulex sp.	X = 94	X = 0.8	112

The ease with which Rb is incorporated into the plants probably reflects its similarity to K. However, the relatively large ionic radius of Cs (167 pm) would tend to limit its ability to substitute for K (138 pm). This may account for the generally low concentration of Cs in the plants. Another reason for the low degree of Cs uptake by the plants may be the way in which it is bound in soils. It seems likely from the low Rb/Cs ratios of soils that while both elements are adsorbed on clay fractions, Cs is more firmly bound. Thus Cs may not be as freely available to plant root systems as is Rb.

Rubidium uptake in plants has been assumed to mimic that of K but this has, in part, been disputed by Tyler (1983), who demonstrates that high soil acidity promotes Rb absorption by plants while not affecting the uptake of K. This effect of increased acidity on Rb uptake is probably related to its greater release from clays in the acid conditions. The soils of the St Austell moorland area are generally acidic and this may promote a higher than normal uptake of Rb while Cs is retained in the soils.

TABLE 5: Plant uptake of Cs and Rb

Species	Cs in soil X 100 / Cs in dried plant	Rb in soil X 100 / Rb in dried plant
Ling	1.4-53.0	6.7-64.4
	X = 15.3	X = 24.4
Bracken	0.3-39.8	8.8-221
	X = 8.2	X = 63.6
Gorse	0.3-10.1	5.7-124
	X = 2.2	X = 33.8

CONCLUSIONS

i) Caesium like Rb shows about a ten-fold enrichment in the St Austell granite compared to average granite.

ii) Soils formed over the granites are preferentially enriched in Cs which is concentrated in the finest fractions.

iii) The Rb/Cs ratio in plants (mean 47) compared to topsoils (mean 7.2) indicates a preference for Rb uptake because of its smaller ionic radius (152pm) and stronger retention of Cs by the finer soil fractions.

iv) Plant samples show species variation with highest values of Cs in ling *(Calluna vulgaris).*

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