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A classification of British Caledonian granites based on uranium and thorium contents

JOHN HENNESSY

Department of Physics, University of Sheffield, Sheffield, S3 7RH

ABSTRACT. A method of epithermal neutron activation analysis for uranium and thorium is discussed in relation to other rapid analytical methods for these elements. Caledonian granites are divided into four main groups on the basis of U and Th contents: (*a*) a group of evolved late granites with high U and Th contents and high Th/U ratios, (*b*) a group of uranium-enriched mineralized granites, (c) granites containing approximately average levels of U and Th, and (*d*) a group of granites with low thorium content.

THE data presented here were obtained in a reconnaissance survey of the Caledonian granites (*sensu lato*) of the British Isles, aimed at identifying variations in U and Th content between intrusions. The data set comprises 260 analyses of granite from northern England, Scotland, and Ireland; sample coverage is incomplete particularly in northeast Scotland and southern Ireland and many intrusions are represented by only a small number of sample values. Where possible fresh samples were collected away from surface weathering, hydrothermal alteration and mineralization but no attempt was made to distinguish between tonalites, granodiorites, and more evolved adamellites and granites. Nevertheless, the data enable a preliminary classification of Caledonian granites to be made, although this may be refined by further studies. A method of epithermal neutron activation analysis is briefly discussed in relation to other rapid analytical methods for uranium and thorium.

Analysis for uranium and thorium. In this study instrumental neutron activation with a beam of epithermal neutrons (energies about 1 ev) is used to induce the following reactions:

$$^{238}U(n,\gamma)^{239}U \xrightarrow{\beta^-} {}^{239}Np \xrightarrow{\beta^-} {}^{239}Pu$$

$$^{232}Th(n,\gamma)^{233}Th \xrightarrow{\beta^-} {}^{233}Pa \xrightarrow{\beta^-} {}^{233}U$$

The first nuclides produced have half-lives of a few minutes and, if the samples are counted some days after irradiation, it may be assumed that complete conversion to neptunium and protoactinium has occurred. Detection and counting of gamma photons from the decay of the second nuclides, which have half-lives of 2.35 and 27 days respectively, is relatively simple. Furthermore, other activated species may be detected, allowing simultaneous determination of such elements as the rare earths. A limitation of the method is that a high epithermal/thermal neutron flux ratio is needed to minimize the amount of uranium fission products which would complicate the gamma spectrum. This is normally achieved by irradiating samples in cans lined with Cd foil, and by utilizing an irradiation position with a high energy flux. The method has advantages over indirect methods of analysis such as gamma, beta, and alpha spectrometry which can be used in the field and to obtain precise results in the laboratory. These methods depend on the determination of intermediate nuclides rather than the parents or stable daughters of the radioelement decay chain, and assumptions about the state of secular equilibrium of the decay series are required. This may be particularly difficult if data are obtained by field gamma spectrometry because surface weathering processes may have destroyed the equilibrium, resulting in the over or under estimation of the uranium and thorium contents.

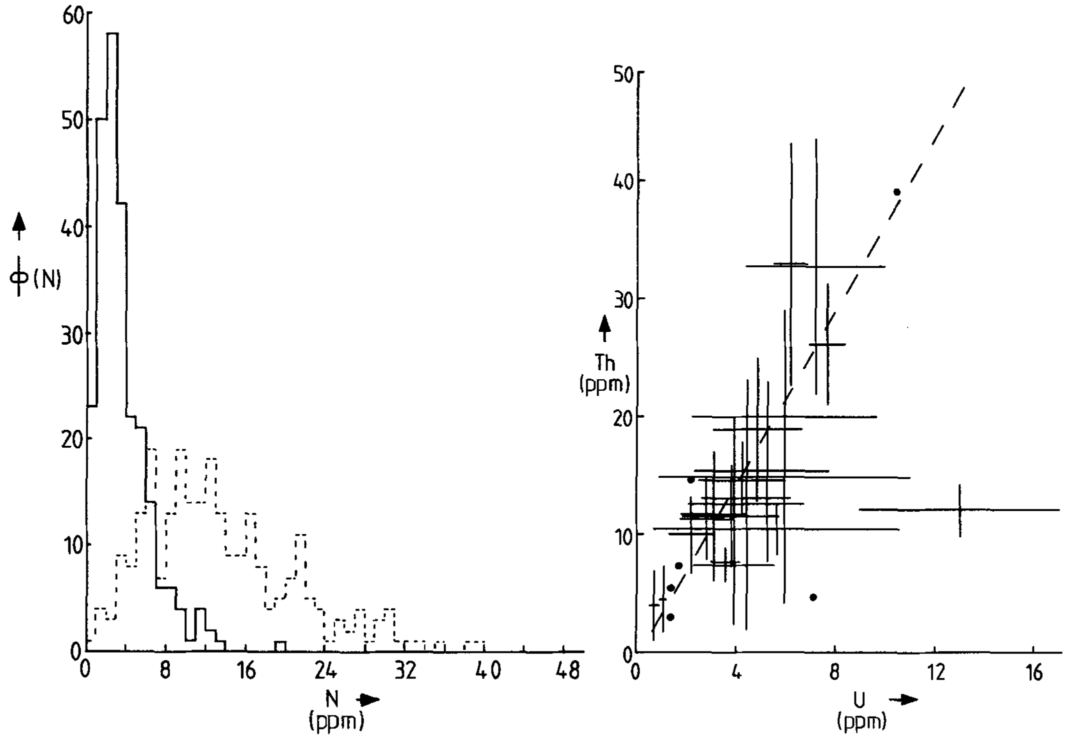
Field gamma spectrometry has the advantage however of detecting or resolving small scale features in the distribution of radioelements which would easily be missed using laboratory-based analysis of rock samples. Epithermal neutron activation analysis also has advantages over the delayed neutron method (Amiel, 1962) in which a separate irradiation is required for thorium and which depends for its accuracy on careful control of the neutron flux and travel times of the sample to the counting devices.

Experimental method. Finely ground samples each weighing 0.5 g are packed in high purity silica tubes and enclosed in cans lined with Cd foil; these are irradiated for approximately eight hours in the 300 kw reactor at the Liverpool and Manchester

Universities Research Reactor centre, Risley. In order to obtain a high energy neutron flux, the graphite moderator stringer near each can is removed during irradiation. Irradiated samples are counted for about 600 seconds using a GeLi detector and 4096 channel multichannel analyser some eight days after irradiation. Each can also contains standards prepared from uranium and thorium oxides and mixed thoroughly in a matrix prepared from 'Spec-Pure' elements and approximating to granodioritic composition. The procedure for reduction of the data to concentrations of uranium and thorium has been described elsewhere (Hennessy, 1979). The over-all accuracy of the method is $\pm 10\%$, based on replicate analysis, the error probably being due to slight changes in counting geometry between samples. The lower limit of detection of the method, which is a function of the counting room background and the ability of the spectrum analysis programme to detect small peaks reliably is 0.5 ppm for uranium and thorium.

Results for uranium and thorium. The data obtained for the British Caledonian granites are shown in fig. 1: the mean uranium content is 4.70 ± 4.61 ppm, and the mean thorium content is 14.63 ± 9.36 ppm. Elimination of data for a radioelement-enriched pegmatite from the Carrigmore diorite reduces the means to 4.47 ± 2.74 ppm uranium and 14.34 ± 8.1 ppm thorium. The uranium data are unimodal (mode, 4 ppm) while the thorium data are multimodal suggesting that the intrusions may be classified on the basis of their thorium content. The means obtained for individual intrusions are listed in Table I and are plotted as a scatter diagram in fig. 2. A line fitted to points for intrusions with more than one analysis has a slope of 3.79 ± 0.71, which is within one standard deviation of the average value of 4 for the Th/U ratio of granites (Clarke, 1966).

Initially the classification of Caledonian granites developed by Brown and Locke (1979), based on the geophysical expression of the intrusions, and extended to include separate groups for Irish and English granites was used to identify systematic differences between intrusions (Table I and fig. 3). Group 1 of the classification includes Scottish granites described by Read (1961) as 'older' and 'newer forceful', whereas group 2 includes Read's



FIGS. 1 and 2. 1 (*left*). Histogram of U and Th data for 260 analyses of Caledonian granites. The solid line represents U, the dashed line, Th. 2 (*right*). Mean U and Th values for the intrusions listed in Table I. The error bars are ± 1 standard deviation. Dots represent intrusions for which only one sample was analysed.

TABLE I. *Uranium and thorium data for Caledonian granite intrusions*

No.	Intrusion name	No. of samples	U	Th	Th/U	Class
1	Ardara	9	4.4±1.8	13.2± 6.0	3.2±1.1	Irish
2	Rosses	4	5.6±4.9	10.6± 2.3	3.4±2.3	Irish
3	Leinster	19	3.9±1.6	7.5± 5.0	2.3±1.7	Irish
4	Carrigmore	9	3.6±0.6	7.6± 1.5	2.1±0.9	Irish
5	Strontian	25	3.8±2.0	11.7± 4.4	3.6±1.6	2N
6	Ballachulish	8	4.4±2.3	12.7±10.9	2.1±2.1	1
7	Rannoch	24	3.1±1.3	11.8± 5.6	3.8±1.2	2N
8	Cairngorm	5	5.9±5.0	15.0±10.9	3.2±1.5	2N
9	Geal Charn Mor	2	7.6±0.7	26.6± 5.3	3.5±0.4	—
10	Lochnagar	8	5.9±3.7	20.3± 9.2	3.9±1.9	2N
11	Mt. Battock	7	7.1±2.8	33.3±11.0	5.2±2.2	2N
12	Aberdeen	8	2.8±1.1	11.5± 3.5	4.1±2.4	1
13	Peterhead	10	4.2±1.8	14.9± 3.2	4.2±2.0	1
14	Foyers	2	1.1±0.1	4.6± 2.9	4.1±2.8	1
15	Laggan	2	0.7±0.2	4.0± 3.0	5.5±3.0	—
16	Ben Nevis	3	2.2±0.9	10.1± 3.3	4.9±0.9	2N
17	Loch Doon	32	5.2±2.5	15.6± 7.9	3.2±1.3	2S
18	Fleet	37	4.8±1.8	19.2± 6.3	4.7±2.3	2S
19	Criffel	12	3.9±1.3	15.6± 4.8	4.2±1.3	2S
20	Portencorkrie	4	3.1±0.8	15.6± 1.4	5.3±1.5	2S
21	Weardale	6	12.9±4.0	12.3± 2.3	1.0±0.3	English
22	Cheviot	2	6.1±0.7	33.4±10.4	5.5±1.1	English
23	Dufftown	1	1.7	7.4	4.4	
24	Moy	1	1.4	5.5	4.0	
25	Coignafearn	1	1.4	3.0	2.1	
26	Carsluith	1	2.2	14.8	6.6	
27	Shap	1	10.0	40.0	3.8	
28	Ardlethan	1	7.1	4.7	0.7	

Classification has been modified after Brown and Locke (1979). Some intrusions remain unclassified, and Irish and English intrusions are distinguished. 1—Older granites, 2—Newer granites, N—North of the Midland Valley of Scotland, S—South of the Midland Valley.

'newer permitted' Scottish granites—the 'late discordant' suite of Dewey and Pankhurst (1970). It is apparent from fig. 3 that the Irish granites (I) are similar to Group 1 Scottish granites in containing low levels of thorium, the Leinster and Carrigmore intrusions in particular contain exceptionally low levels of thorium, while the English intrusions (E), Shap, Cheviot, and Weardale are enriched in uranium.

Cluster analysis. Problems associated with classification based on subjective evaluation of data (fig. 3) may be overcome by using cluster analysis (Davis, 1973; Wishart, 1978). The uranium and thorium data and the intrusion means were processed using the University of Bradford CLUSTAN 1C programme which allows a range of clustering methods to be tested.

The results presented here were obtained from hierarchical clustering of standardized variables whereby two clusters to be merged are selected on the basis that the resulting cluster will be that having the smallest scatter (Ward, 1963); furthest neighbour and group average fusion methods give similar results. Analysis of the uranium and thorium data was carried out to see whether large-scale processes which had caused systematic variations in uranium and thorium contents could be identified and analysis of intrusion means to identify groups with distinct uranium and thorium contents.

Uranium and thorium data (R mode analysis). The results of cluster analysis of the data are shown in Table II (see also fig. 4). The following groups are distinguished:

1. A 'background' group, A and B, with uranium contents of approximately 4.5 ppm and thorium contents of approximately 14.5 ppm.

2. A group, E and F, with low contents of uranium and thorium of about 2.5 ppm and 7.5 ppm respectively.

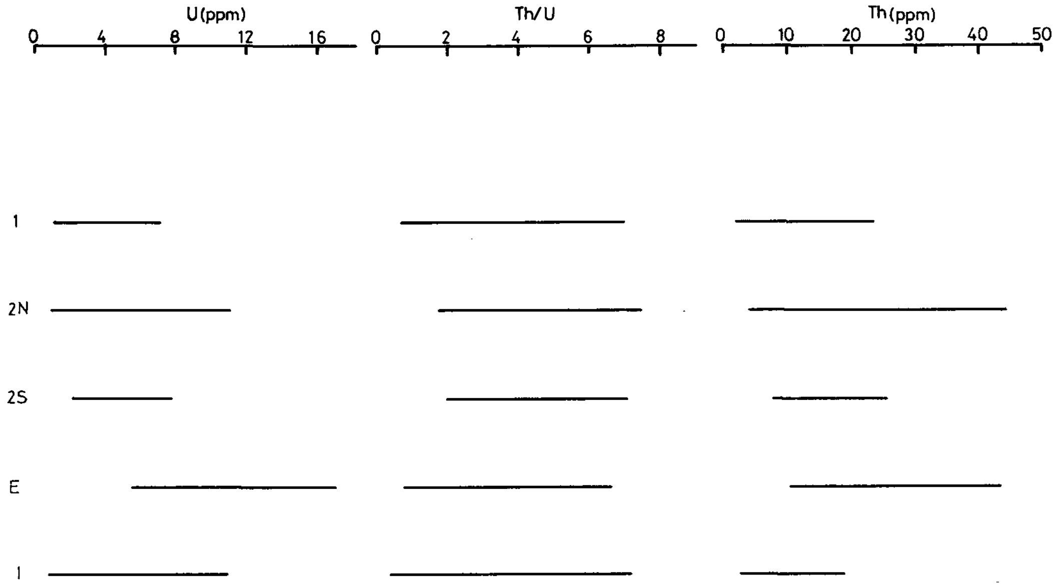


FIG. 3. Th, U, and Th/U for classes of intrusions listed in Table I.

3. A group, G and H, with high content of uranium and thorium of about 7 ppm and 30 ppm respectively.

4. A group, C and D, with unusually low Th/U ratios with (*a*) approximately equal amounts of each element of around 14 ppm (cluster C) and (*b*) with Th contents slightly higher than those of uranium (cluster D).

The levels of U and Th in the first two groups are attributed to variation due to fractional crystallization. Group 3 consists of samples which are mostly from the Geal Charn Mor, the Mount Battock intrusion and the centre of the Loch Doon granite with high values of U and Th and high Th/U ratios. Brown *et al.* (1979*a*) found an antipathetic variation of Zr and uranium towards the centre of the Loch Doon intrusion where, despite a decrease in total zirconium content, there is enrichment of uranium in an alkali feldspar granite. The uranium occurs in zircons, however, which must have an average Zr/U atomic ratio of about 18. The models of Brown *et al.* (1979*a*) for Loch Doon, and of Simpson *et al.* (1979) for such uraniferous granites as Cairngorm in Scotland and the Hercynian Granite batholith of SW England attribute the chemistry of such intrusions to evolution of predominantly juvenile magmas produced in a crustal or subcrustal environment associated with active subduction. A similar provenance for the other group 3 samples is postulated here.

The final group consists mainly of samples from the Rookhope borehole in the uranium-enriched Weardale granite (Holland, 1967). The uranium and thorium values follow bulk chemistry and reflect the division of the body into two phases of intrusion. It has been suggested (Brown *et al.*, 1979*b*) that there was a long-lived geothermal system associated with the emplacement of this body and circulation of meteoric water and other volatiles could have remobilized uranium from county rock or from warmer regions of the intrusion (cf. Plant *et al.*, 1980), producing secondary uranium enrichment.

Granite means (*Q mode*). The results of clustering of the means for individual intrusions are presented as a dendrogram in fig. 5*a* and as a plot of the clusters at the fifth cluster level in fig. 5*b*. The Rookhope borehole data plot as a single high uranium cluster (cluster C in Table II). A cluster representing low contents of radioelements consists mainly of data for the Foyers and Laggan intrusions although it should be noted that there is only a small number of sample values, particularly for Foyers. The data for Geal Charn Mor, Mount Battock, and Cheviot form a high radioelement, high Th/U ratio cluster comprising most of the samples in group 3 of the raw data. The remaining granites form two 'background' clusters, which reflect the bulk chemistry and, perhaps, level of exposure of these intrusions. The lower of these two clusters contains the Leinster granite and Carrigmore diorite, which contain relatively low levels of thorium, and the less evolved tonalite-granodiorite intrusions of Scotland and Ireland.

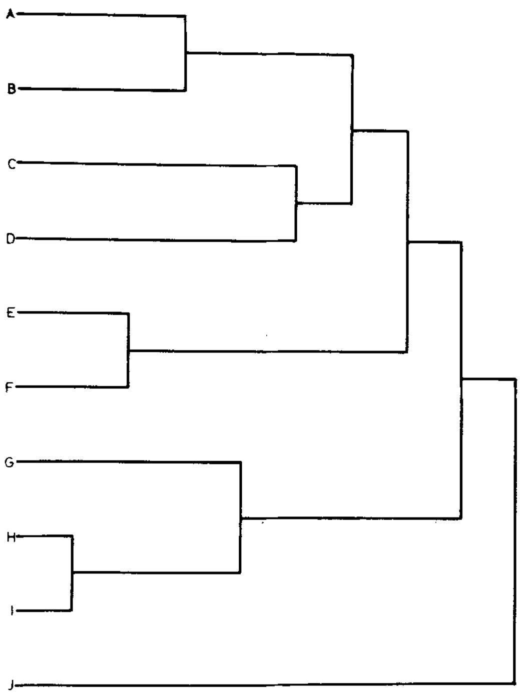


TABLE II. *Cluster groupings derived from 260 uranium and thorium determinations of Caledonian granites*

Cluster	Points	U	Th
A	57	4.43 ± 1.42	19.18 ± 2.51
B	43	3.36 ± 0.79	13.64 ± 1.14
C	6	13.88 ± 3.11	13.88 ± 4.93
D	34	6.63 ± 1.57	9.21 ± 4.11
E	53	2.92 ± 0.72	9.07 ± 1.66
F	32	1.61 ± 0.60	4.93 ± 2.06
G	23	5.90 ± 1.81	26.88 ± 3.49
H	10	9.80 ± 2.32	32.68 ± 5.17
I	1	10.80	55.4
J	1	64.4	89.3

The means and standard deviations of clusters refer to a region in 'U–Th space' where samples are likely to be found.

FIG. 4. Dendrogram of raw data clusters (Ward, 1963).

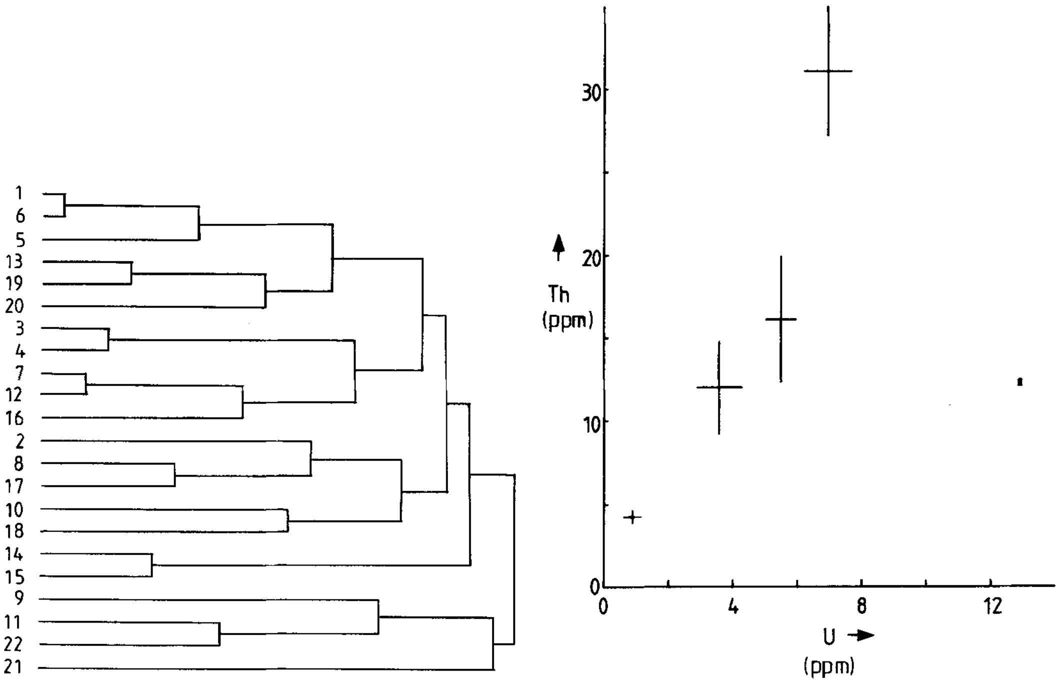


FIG. 5 (*a*, left). Dendrogram of intrusion mean clusters (Ward, 1963). Intrusions with a single sample were not included in this analysis. (Numbers correspond to intrusions listed in Table I). (*b*, right). Mean U and Th values (± 1 standard deviation) for the five cluster level clusters from fig. 5*a*.

In summary, taking into account the regional geological criteria discussed earlier (cf. fig. 3) and the clusters in fig. 5*b*, the main groupings of the data are:

(*a*) The radioelement enriched, high Th/U ratio late Caledonian granites such as Geal Charn Mor, Mount Battock and the central parts of Loch Doon in Scotland, and the Shap and Cheviot intrusions in England. All these intrusions are of the late discordant group of Dewey and Pankhurst (1970), Group 2 of Brown and Locke (1979) and the metallogenic granites of Plant *et al.* (1980).

(*b*) The uranium-enriched Weardale granite, which is probably mineralized.

(*c*) The background granites, which form two closely associated clusters in fig. 5*b*. The intrusions near to the Great Glen Fault in Scotland appear to be most radioelement depleted in this group; for example, the Strontian complex has a uranium content of 3.8 ppm and a thorium content of 11.7 ppm.

(*d*) The low thorium northern unit of the Leinster batholith, and the Carrigmore diorite. Hypotheses to account for the low thorium are that: the parent magmas were derived from a Th depleted zone; the parent magma was low in Th and later hydrothermal activity added uranium to give contents closer to the mean value for Caledonian granites or fractionation removed Th from the magma reservoir from which the granites evolved. The last hypothesis is unlikely because of the similar geochemistry of uranium and thorium. The first hypothesis is also unlikely as it would require a reservoir with a different Th/U ratio from that of other Caledonian granites. The second hypothesis is favoured because the Leinster batholith has undergone hydrothermal alteration, (Bruck and O'Connor 1977), which may have deposited uranium in secondary sites.

Conclusions. Uranium and thorium are readily determined by several rapid methods of analysis. Many reported analyses are for uranium alone, however, although the thorium content and Th/U ratio are important, and may be measured simultaneously by INAA methods. Systematic study of the mineralogical distribution of uranium and thorium in primary or mineralized sites is essential to understanding the genesis and, in particular, the late stages of consolidation of granites.

The Caledonian granites show systematic variation of radioelement contents which enable several groups to be identified including:

(*a*) An evolved group with high U contents of 6–7 ppm and high Th contents of 27–35 ppm and high Th/U ratios of *c.*5.

(*b*) A uranium-enriched group with exceptionally high U contents of 13 ppm and background Th contents of 14 ppm and low Th/U ratios of *c.*1.

(*c*) A large group of 'background' granites with U contents of 3–6 ppm and Th contents of 10–20 ppm and Th/U ratios of 3–4.

(*d*) A low Th group with U contents of 3–5 ppm, Th contents of 3–12 ppm and Th/U ratios of *c.*2.

Any model for the genesis of the granites should account for the different groups of intrusions and their distribution in relation to the main structural features of the Caledonian orogen.

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REFERENCES

Amiel, S. (1962). *Analyt. Chem.* **34,** 1683–92.

Brown, G. C. and Locke, C. A. (1979). *Earth Planet. Sci. Lett.* **45,** 69–79.

—— Cassidy, J., Tindle, A. G., and Hughes, D. J. (1979*a*). *J. geol. Soc. London,* **136,** 745–53.

—— Plant, J. A., and Lee, M. K. (1979*b*). *Nature,* **280,** 129–31.

Bruck, P. M. and O'Connor, P. J. (1977). *Geol. Surv. Ireland Bull.* **2,** 107–41.

Clark, S. P. (1966). *Handbook of Physical Constants.* Geol. Soc. Am. Memoir, 97, 587 pp.

Davis, J. C. (1973). *Statistics and Data Analysis in Geology.* New York: John Wiley Sons Inc.

Dewey, J. F. and Pankhurst, R. J. (1970). *Trans. R. Soc. Edinburgh,* **68,** 361–89.

Hennessy, J. (1979). *Computers and Geosciences,* **5,** 281–7.

Holland, J. G. (1967). *Proc. Yorks. geol. Soc.* **36,** 91–113.

Plant, J. A., Brown, G. C., Simpson, P. R., and Smith, R. T. (1980). *Trans. Inst. Mining Metall.* **89,** B198–B210.

Read, H. H. (1961). *Liverpool and Manchester Geol. J.* **2,** 653–83.

Simpson, P. R., Brown, G. C., Plant, J. A., and Ostle, D. (1979). *Phil. Trans. R. Soc. Lond.* **291**A, 385–412.

Ward, J. H. (1963). *J. Am. Stat. Ass.,* **58,** 236–44.

Wishart, D. (1978). *CLUSTAN User Manual.* Program Library Unit, University of Edinburgh.

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