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COLLECTION, PREPARATION AND ANALYSIS OF NH4-1: A STANDARD REFERENCE MATERIAL FOR AMMONIUM DETERMINATION

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Collection, Preparation and Analysis of NH4-1: A standard reference material for Ammonium determination

A D Bradley

1. INTRODUCTION

Bradley et al. (1990) discussed the need for a standard reference material for ammonium determinations. Subsequently, it was decided to collect a bulk sample and prepare this first as a BGS in-house standard; later, if resources permitted, full international certification would be obtained. The material chosen needed to have a fairly high ammonium content; to be available in quantity within a reasonable distance of Keyworth; to have a similar matrix to the majority of samples currently analysed for ammonium at BGS and, ideally, to be fairly fine-grained to enable easy homogenisation with the available sample preparation equipment. These factors, coupled with the author's knowledge of possible suitable areas of the Lake District, led to the decision to collect a sample of the Skiddaw Slate Group.

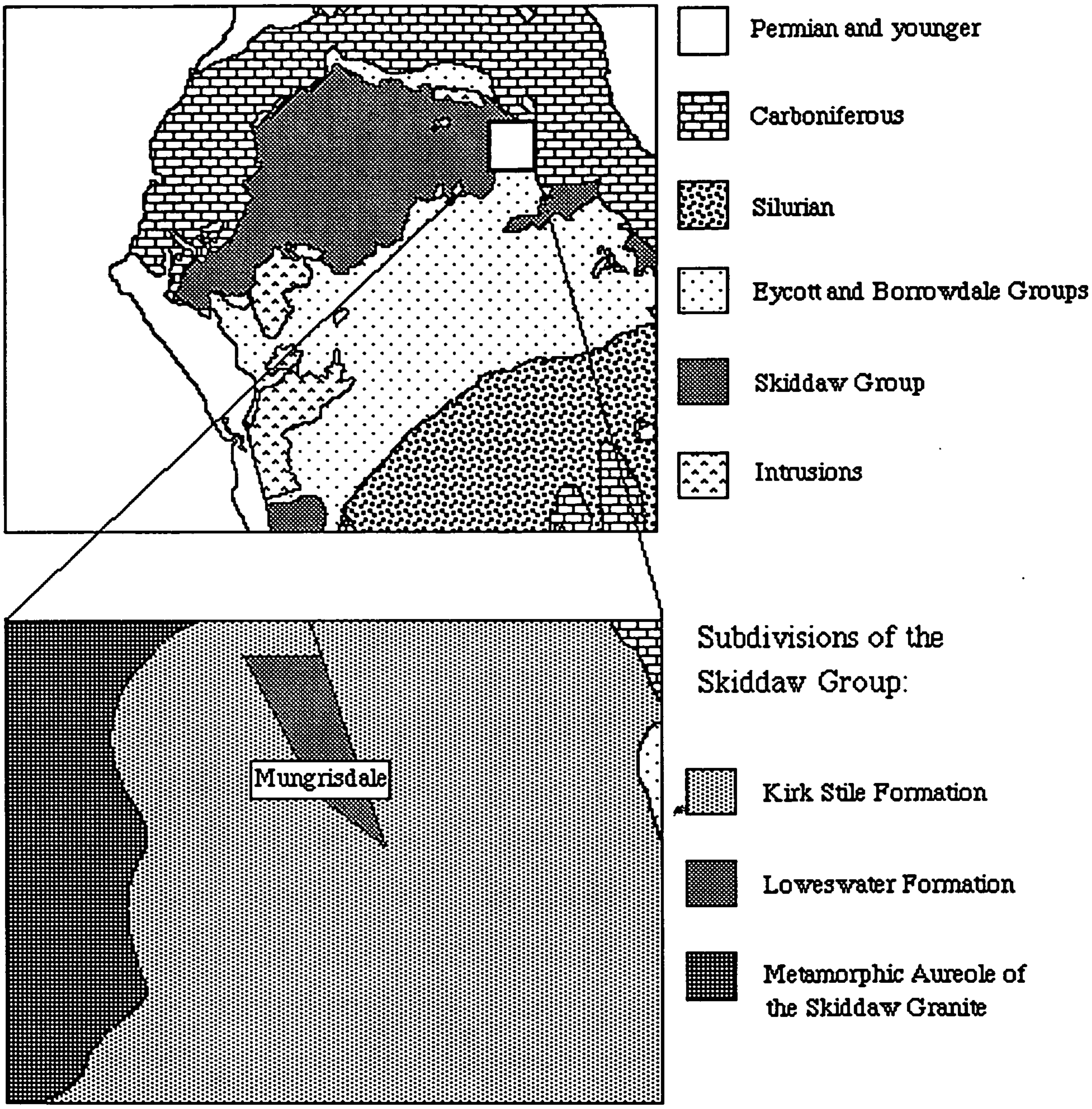
2. SAMPLE COLLECTION

The chosen sampling site was in a disused quarry at the village of Mungrisdale (NY 3632 3058) about 16kms WNW of Penrith, (Figure 1). The quarry has been excavated in a fault-bounded block of the Loweswater Formation of the Skiddaw Slate Group, which is surrounded by the Kirk Stile Formation. Many different sub-divisions of the Skiddaw Slates have been proposed over the years; the ones used here follow the nomenclature used by Jackson in Moseley (ed.) (1978). The sampling site lies near the outer edge of the metamorphic aureole of the Skiddaw Granite. Descriptions and analyses of a series of samples comprising a traverse across the slates, plus several samples of the Skiddaw granite, were published by Cooper and Bradley (1990).

Where the cleavage planes were readily accessible, blocks of material were broken off with a hammer and chisel. However, this could be done only in a small area because of a combination of overgrown vegetation and lack of suitable surfaces to work on. Thus a large proportion of the sample was derived from fallen blocks; only the least weathered of these were collected. Any piece which split too readily along bedding or cleavage planes, or which showed iron-staining, was discarded. Altogether about 50kg of material was collected.

Figure 1

Central Lake District - Simplified Geology



At Keyworth, the material was further sorted; pieces showing obviously weathered surfaces, areas of lichen or minor iron staining were discarded. The remainder, consisting of rock fragments up to approximately 20cms in diameter and weighing 30–35kg in total, was then ground.

3. SAMPLE PREPARATION

3.1 Size reduction

The sample was reduced to pieces measuring 2–3mm in diameter by using two passes through a chrome steel jaw crusher. The crushed sample was then reduced to approximately 150μm (-100mesh British standard sieve) in a vibrating cup mill. Agate milling vessels with a maximum load capacity of 250g were then repeatedly filled by repeatedly coning and quartering several kilos of the sample, which was held on a clean piece of paper on a bench top. When the coned and quartered subsample was reduced to less than one kilo it was replenished from the bulk sample (30kg) and the process repeated.

3.2 Homogenisation

The milled material was transferred from its container directly into two riffle splitters using a scoop. These two portions were then mixed by passage through a third riffle splitter before being transferred to a second container. This whole process was then repeated once more.

4. ANALYSIS

4.1 Tests for Homogenisation

Before bottling, the sample was tested for homogeneity by extracting ten sub-samples of 12g each from the bulk sample and mixing with 3g of Elvacite™ binder to make ten pellets for analysis by X-ray fluorescence (XRF) spectrometry. These were analysed for a range of major and trace elements using Phillips PW1480 (for major elements and As) and PW1404 (other elements) XRF spectrometers. The results for the trace elements are shown in Table 1.

TABLE 1 **Trace element content of 10 pressed powder samples analysed by XRF spectrometry**

Element	Mean Concentration (ppm)	Range (ppm)	RSD (%)
V	135.1	132–137	1.326
Cr	124.4	122–126	0.864
Co	17.7	17–18	2.729
Ni	30.5	30–31	1.728
Cu	15.2	14–16	4.155
Zn	84.2	83–85	0.751
Rb	168.5	167–169	0.420
Sr	145.6	145–147	0.480
Y	30.4	29–32	2.733
Zr	167.0	166–168	0.489
Nb	19.8	19–21	3.192
Ba	635.6	624–642	0.897
La	57.0	55–59	2.188
Ce	89.5	84.97	5.679
Pb	18.3	16–21	10.32
Th	15.1	14–17	7.288
As	46.3	44–49	3.678

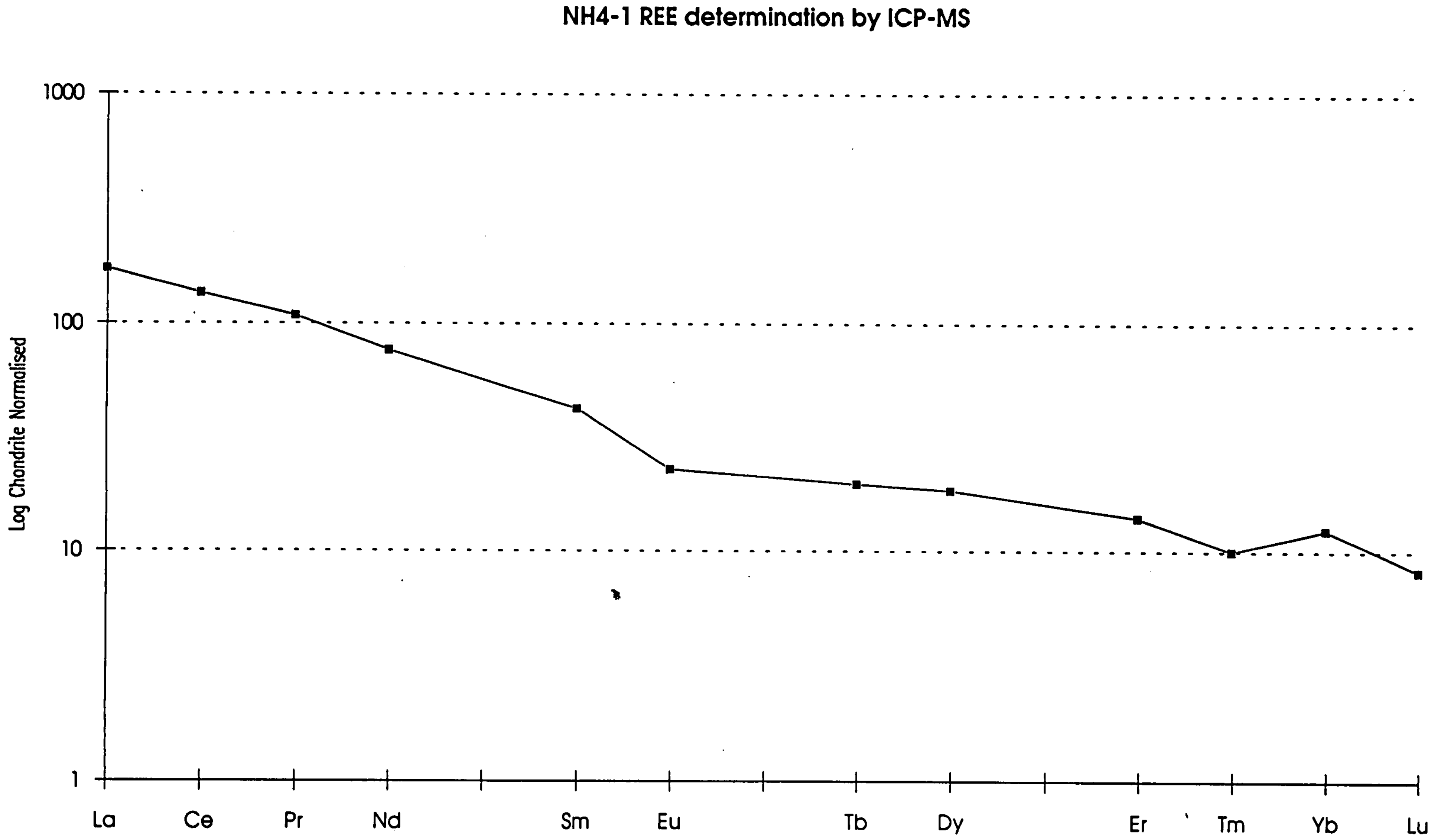
The results show precision within the limits of the analytical method, i.e. the relative standard deviations (RSD) are comparable to those expected from a single sample with the same concentrations of each of the elements (M N Ingham pers.comm.) The relatively poor precision for some elements is due to the concentrations approaching the detection limits. To obtain a more accurate measurement of the major element content, three fused beads were prepared using lithium tetraborate flux and analysed by the Phillips PW1480 XRF spectrometer. The results are shown in Table 2.

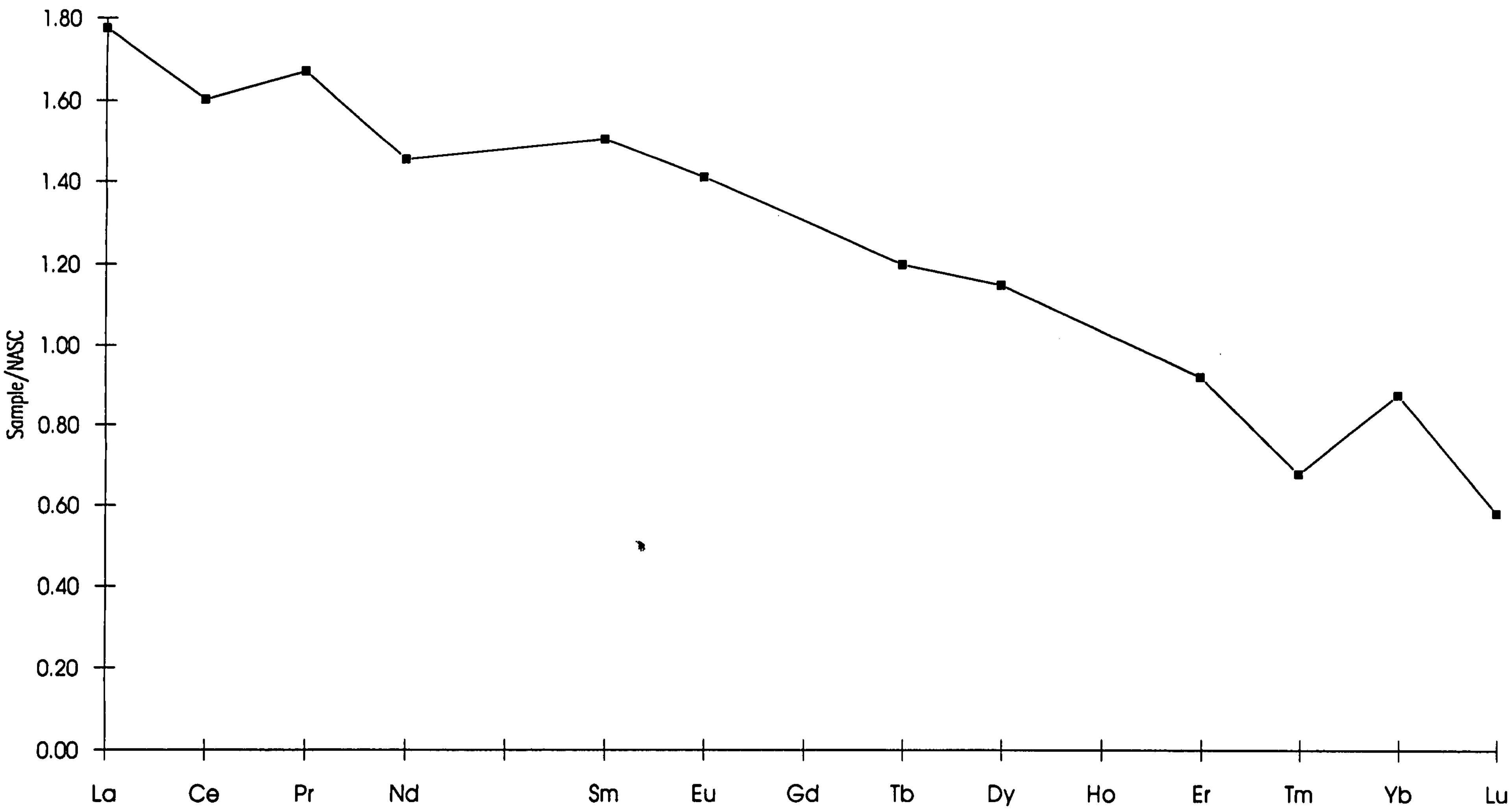
TABLE 2 **Major element concentration of three fused beads analysed by XRF spectrometry**

Element	**Mean concentration %**
SiO_2	54.39
Al_2O_3	24.52
Fe_2O_3	8.54
MgO	1.76
CaO	0.37
Na_2O	1.11
K_2O	3.91
TiO_2	1.17
P_2O_5	0.21
MnO	0.302
LOI	4.29
TOTAL	**100.52%**

The sample was also analysed for Rare Earth Elements (REE) by ICP-MS. The results are shown in Table 3, and as a chondrite-normalised plot in Figure 2 and against 'average shale' in Figure 3.

Figure 2


NH4-1 REE determination by ICP-MS
Log Chondrite Normalised
1000
100
10
1
La
Ce
Pr
Nd
Sm
Eu
Tb
Dy
Er
Tm
Yb
Lu



Shale normalised (North American Shale Composite) REE abundance in NH4-1

Figure 3

TABLE 3 **Rare earth elements determined by ICP-MS (three determinations)**

Element	Mean concentration ppm
La	56.83
Ce	117.43
Pr	13.24
Nd	48.0
Sm	8.58
Eu	1.75
Tb	1.02
Dy	6.33
Er	3.14
Tm	0.34
Yb	2.72
Lu	0.28

The bulk sample was then bottled and labelled ready for distribution to other laboratories.

4.2 Ammonium Determinations

Ammonium determinations were carried out by the following method:

4.2.1 Reagents

HF, 40% MERCK™ ultra-pure; heated to boiling point, prior to use, to expel dissolved atmospheric gases.

H_2SO_4 high purity; diluted 50:50 with distilled water.

NaOH 10M; dissolve 400g NaOH pellets in 600ml distilled water, allow to cool, dilute to 1 litre and store in a polythene bottle.

HCl concentrated reagent grade.

HCl 2M reagent grade; add 18ml of concentrated acid to 70ml distilled water and dilute to 100ml.

4.2.2 Apparatus

50ml PTFE high sided dishes
Hotplate
Markham still (steam distillation apparatus)
25ml volumetric flasks
Gas sensing, ammonia specific ion electrode with suitable meter
Fume cupboard

4.2.3 Method

Weigh 1.00g of sample into a 50ml PTFE high sided dish.

Add 10ml of HF, followed by 2ml of 50% H_2SO_4; cover the dish and leave to stand overnight in a fume cupboard.

Next day, uncover the dishes, and heat at 130°C on a hotplate until the HF has boiled off.

Add 10ml of distilled water, and warm to dissolve the caked salts.

Meanwhile, prepare the Markham still and run a blank (distilled water) sample through it, to remove adsorbed atmospheric ammonia.

Transfer the first sample to the still using the minimum amount of distilled water possible.

Add 2 drops of 2M HCl to the collection flask and sufficient distilled water to cover the bottom of the distillation tube.

Slowly add 15ml of 10M NaOH to the sample, making sure that the sample remains at boiling point, and collect 20ml of distillate.

Transfer the distillate to a 25ml volumetric flask and dilute to the mark.

Clean the Markham still between samples by boiling HCl through it, and rinse by boiling distilled water through the still.

Determine the NH_4^+ by specific ion electrode (SIE), calibrated using $NH_4Cl(aq)$ standards in the appropriate range.

4.2.4 Results

The proposed reference material has been analysed 14 times. The results (to the nearest 10ppm) are summarised below:

Mean concentration	**Range**	**RSD**
1740 ppm	1500–1910 ppm	6.67 %

The results show that the method is inherently rather imprecise; the sample attack stage possibly contributing the greatest variability to the data.

Exchangeable ammonium (determined after shaking in 2M KCl for two hours) is at or near the detection limit, i.e. <10ppm, so the value quoted is equivalent to the fixed ammonium concentration.

4.3 Nitrogen Isotope Analysis

Because of the comparatively high total nitrogen content of the standard, the NERC Isotope Geoscience Laboratory (NIGL) expressed interest in using the standard for $\delta^{15}N$ determinations. Initial results were disappointing as the nitrogen yield during sample attack was not sufficient to enable precise results to be obtained with the current sensitivity of the mass spectrometer. However, the value is probably in the region of +0.6‰ $\delta^{15}N$ with respect to air.

5. DISCUSSION

Cooper and Bradley (1990) analysed a large number of silty mudstones (SiO_2 52–59%) from a traverse across the Skiddaw granite aureole. This standard sample, with 54.39% SiO_2, falls near the middle of this range but is from a different lithological unit. The organic carbon content of any of the Skiddaw samples has not been quantified, therefore the possible influence of differing original organic carbon content cannot be ascertained. However, any variations in organic carbon content might account for the higher ammonium content in the standard sample compared with the mean value of the traverse samples (approximately 1050 ppm).

The standard described above should prove useful to all who analyse geological materials for ammonium. It has been shown to be homogeneous within the limits of analytical precision.

The ammonium concentration is fairly high compared with published average shale values e.g. 400 to 1500 ppm in a range of Recent to Palaeozoic sediments (various authors quoted in Itihara and Honma 1979).

6. ACKNOWLEDGEMENTS

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7. REFERENCES

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