A NOVEL METHOD FOR BORON DETERMINATION IN ROCK THIN SECTIONS: FIRST RESULTS FROM NGAWHA

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SUMMARY - Previous studies of boron in New Zealand rocks have relied on whole rock analyses, In order to gain more detailed knowledge of the sources of boron in rocks, we have developed a nuclear probe technique based on the $^{11}B(p,\alpha)$ nuclear reaction. The technique performs well on powdered USGS standards down to below 10 wt. ppm, and we have applied it with a proton beam focused down to 25 x 25μm on a hydrothermally unaltered greywacke from Puketona, near Ngawha, Northland. There appears to be little variation in the boron concentrations in the sedimentary groundmass, but in the veins the boron appears to be more concentrated in the prehnite than in the quartz.

1. INTRODUCTION

Elevated levels of boron in geothermal waters place severe constraints on the disposal options available to developers, and hence on the technical and economic viability of exploitation of geothermal resources. For instance discharge of geothermal waters fiom the Wairakei and Kawerau systems to the Waikato and Tarawera Rivers respectively significantly elevates boron concentrations in the river waters, which is of concern primarily because this may limit the usefulness of the waters for irrigation purposes (Ellis and Mahon, 1977; Sheppard, 1979; Darby, 1980). The carryover of boron in steam discharges can also be a problem for the surrounding vegetation (Crittenden, 1989; Darby, 1980).

High boron levels occur in some geothermal waters and steams. For instance at Ngawha in Northland, New Zealand, up to 1000 mg/kg of boron occurs in discharge waters. Common characteristics in the systems which have high levels of boron are the presence of limestones and/or metasedimentary rocks (i.e. greywackes), high temperatures, and dry systems, but the first of these seems to be the universal common feature. The question then asked is "where does the boron come from?", and along with this, "what does it take to mobilise the boron?".

Experiments and measurements have been performed to determine which rocks contain boron and if it can be mobilised (Ellis and Sewell, 1963; Ellis and Mahon, 1963, 1964, 1967; Mahon, 1967). The boron contents of various rock types as determined by Ellis and Sewell (1963) are given in table 1. Mahon (1967) also showed that siltstones and shales release more boron into solutions than greywackes.

These studies of boron in rocks employed whole-rock measurements using classical chemical and spectroscopic techniques, shedding little direct light on the question of where the boron comes from. Electron microprobe (EMP) analysis is the tool of choice when the composition of individual mineral grains is sought, but boron, especially when present in minor or trace amounts, is inaccessible to the electron probe since the low energy characteristic X-rays are so strongly absorbed in the sample and the Si(Li) detector window.

Table 1. Whole rock boron levels fiom Ellis and Sewell (1963)

Rock type	average boron concentration (mg/kg)	range
Rhyolites	23	12-30
Ignimbrites	29	15-50
Pumices	23	16-34
Obsidians	24	19-30
Greywackes	28	19-75
Greywacke[1]	140	
Shales	70	60-90
Limestone[2]	130	

[1] single sample (Ellis and Mahon, 1964)
[2] single sample

For such light elements nuclear reactions induced by high energy ion beams are a useful alternative, since the cross sections for nuclear reactions between beams of light ions such as protons, and the lighter elements are generally very favorable for analytical application. A good local example of such an approach is the pioneering work of Coote et al (1982) using the Lower Hutt nuclear microprobe for determining fluorine distributions in petrological thin sections.

In the present work we have developed and demonstrated such a method with a macro-beam of a few mm diameter, and then applied the method to selected areas of a geological thin section with a microbeam focused down to 25 x 25 μm.

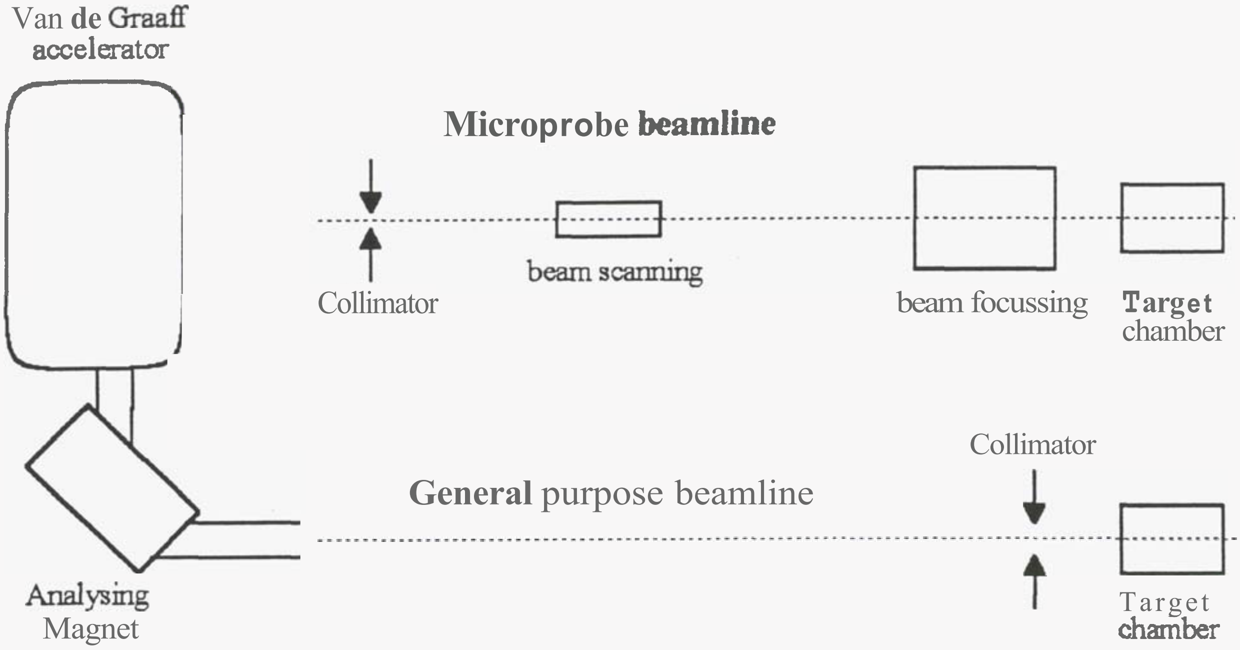

Figure 1. Schematic overview of the principal components of the Geological and Nuclear Sciences Ion Beam Analysis facility. The detectors and control and data acquisition components are omitted for clarity

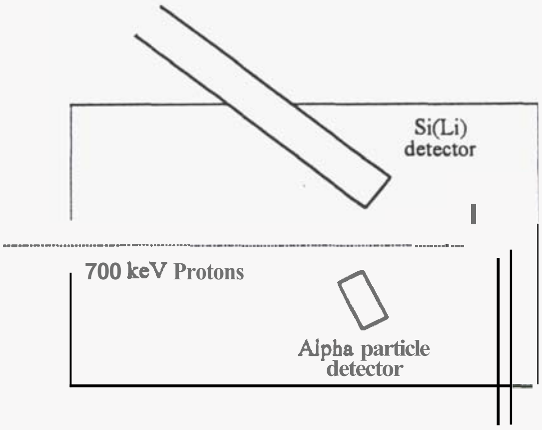

Figure 2. Experimental geometry employed for determination of boron. The sample is viewed with a binocular microscope via a removable mirror (not shown).

2. METHOD

The 3MV KN Van de Graaff accelerator at GNS provided the beams of charged particles used in this work (fig. 1). Two beamlines are dedicated to Ion Beam Analysis (IBA) work. The first employs a collimated beam and is furnished with a general purpose automated target chamber for use with beams down to 0.5mm diameter. The second is the microprobe beamline, the main components of which are described in Coote and Sparks (1981), Vickridge (1984), and Coote and Vickridge (1988). Since these reports, an improved target chamber has been designed, built and installed, with special attention being paid to possible geological applications. The main improvements are the incorporation of a modem Si(Li) detector (donated by Industrial Research Ltd) with improved geometry and energy resolution; improved provision for charged particle detection; improved gamma ray detection geometry; and improved sample illumination (including transmission illumination) and observation.

As with EMP determinations, the concentration of the element of interest in the sample is inferred from the amplitude of a characteristic *spectral* feature and a sound knowledge of the physical processes involved, usually augmented by the use of quantitative standard materials.

The proton microprobe measurements reported in this work were made with the beam focused to a spot of approximately 25 x 25μm, and with an incident beam current of 3 to 5 nA, yielding measurement times of 15 to 30 minutes per point. Optimisation of beam parameters and experimental design could reduce these times significantly, although as with the EMP, attention will always have to be paid to the possibility that the probing beam is altering the boron content. As smaller beam spots are applied, or higher currents used to reduce measurement times, the possibility of radiation-induced movement of the boron or other components of the rock will increase.

2.1 Choice of reaction and detection conditions.

For determination of boron the $^{11}B(p,\alpha)^{8}Be$ nuclear reaction between protons and ^{11}B is exploited, the concentration of boron being inferred from the number of characteristic alpha particles detected. Lappalainen et al. (1985) described the determination of boron in biological materials using this reaction, and boron in coal has been studied via this reaction with the Lower Hutt nuclear microprobe (Coote and Sparks (1980), Vickridge et al (1990)). Experimental details are given in figure 2. A beam energy of 700 keV is chosen because of the high cross section here (Ligeon and Bontemps (1972)), and the reaction angle of 150 degrees, as used by other authors, was convenient for use in both the general purpose and the microprobe chambers. A 300 mm^2 silicon Surface barrier detector is used to detect the alpha particles, and a thin mylar foil in front of the detector prevents the high flux of backscattered primary beam from entering the detector.

The concentration of boron may be calculated with the following formula:

$$[B_{\text{unknown}}] = [B_{\text{standard}}] \frac{N_{\text{unknown}} R_{\text{standard}}}{N_{\text{standard}} R_{\text{unknown}}} \qquad (1)$$

where N_{unknown} and N_{standard} are the numbers of alpha particles detected from the irradiation of the unknown and the standard sample respectively, and R_{unknown} and R_{standard} are the ranges of the protons in the unknown and the standard respectively. The proton ranges depend on the overall composition of the material, and in a first approximation we have assumed that the protons have the same range in all rocks. That this is reasonable for a range of powdered whole rock samples is demonstrated below, however for analysis of individual grains, which may have substantially different compositions, this simplification is questionable.

Charged particle beams used for determining light elements via nuclear reactions also stimulate the emission of characteristic X-rays from the sample. These X-rays may be detected during the boron measurement and used to provide major and trace element distributions via the PIXE (Particle Induced X-ray Emission) method. PIXE provides an order of magnitude or more improvement in detection limits compared with the electron probe. (See Mitchell and Barfoot (1981) for a general introduction to PIXE). In this work we simply used the characteristic X-rays induced by the ion beam to assist in identifying which minerals the beam was hitting.

2.2 Sample preparation

Standard 30μm petrological thin sections (without cover slip) need no further treatment for nuclear microprobe measurements. If PIXE spectra are to be exploited, the sections should be carbon coated to prevent charge buildup and bremstrahlung interfering with the X-ray detection We have also found that in some minerals subsurface charging and discharging can interfere with charged particle detection.

USGS standard rock powders were prepared by pressing them into pellets, with no other preparation performed. Usually, for PIXE work, a similar technique is used except that a small amount of graphite is added to the powdered rock. Our first measurements showed that there was a considerable boron impurity in the graphite that we used and so we simply omit the graphite from the sample, accepting that these samples will not be good conductors. This had no observable effect on the charged particle measurements. The pellets were glued onto standard half-inch SEM mounts for use in either chamber. Spectra from the pressed standard rocks were accumulated for 20μC of incident charge in a 1mm diameter beam spot, each such measurement taking 10 to 12 minutes to accumulate.

3. RESULTS

3.1 USGS Standards

Figure 3 shows the alpha particle spectra obtained from bombardment of USGS AGV1(6.8 ppm) and USGS SDO1 (130 ppm). One feature not observed in our previous studies, which were not aimed at materials containing considerable quantities of oxygen, is the substantial contribution to the spectrum from the $^{18}O(p,\alpha)$ reaction. For reference, the particle spectrum from a thin target of Ta_2O_5 artificially enriched in ^{18}O is also shown. We avoided this interference by only counting those alpha particles with energies greater than the maximum energy of the alpha particle from ^{18}O. In figure 4 we present the results of our measurements on a series of USGS standard rocks including granite, basalt, and shale, and spanning boron concentrations in the range 0.33 to 130 ppm. These results demonstrate that our simplified approach to data

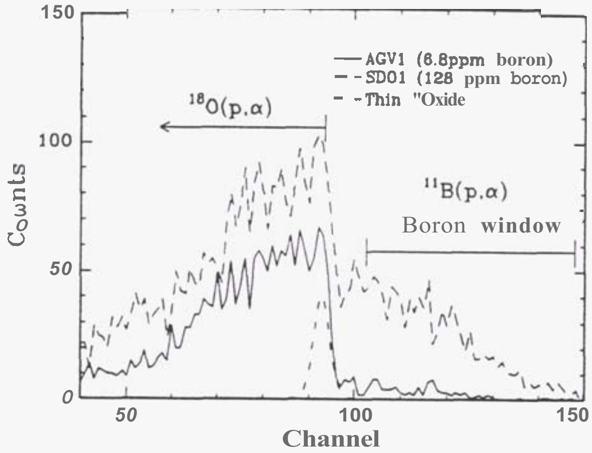

Figure 3. Alpha particle spectra recorded from USGS standard samples containing high and low quantities of boron.

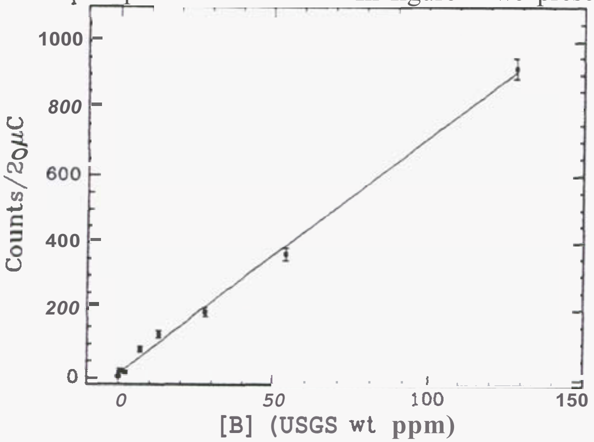

Figure 4. Alpha particle counts versus USGS boron concentration. The error bars are ± la due to the counting statistics

reduction is justified and that we may readily determine boron below **10** ppm.

3.2 Unaltered Greywacke (HWPUK P 55311)

A sample of Waipapa Group greywacke from the Puketona quarry (about **15** km east of Ngawha Springs in Northland) **was** prepared **as** a standard petrological polished thin section. The section is composed of a fine-grained matrix rich in clay minerals (including illite and chlorite), cut by numerous veins up to 1mm thick. Some veins are mostly prehnite, others are mostly **quartz,** and some are composite. The matrix contains some **amorphous dark** ***streaks,*** and bedding defined by layers of different grain sizes. Sites for analysis were selected to cover representative areas of the section. **A** sketch of the thin section is shown in figure ***5*** with the target points indicated and the measured boron contents and raw PIXE **data** are given in Table 2. At present **our** PIXE set up is not fully quantitative, and we simply list raw peak areas for Si, K, Ca, and Fe. These areas are not proportional to the concentration of the element, and are **used** only to provide a qualitative indication of the mineral or minerals that are in the probing beam.

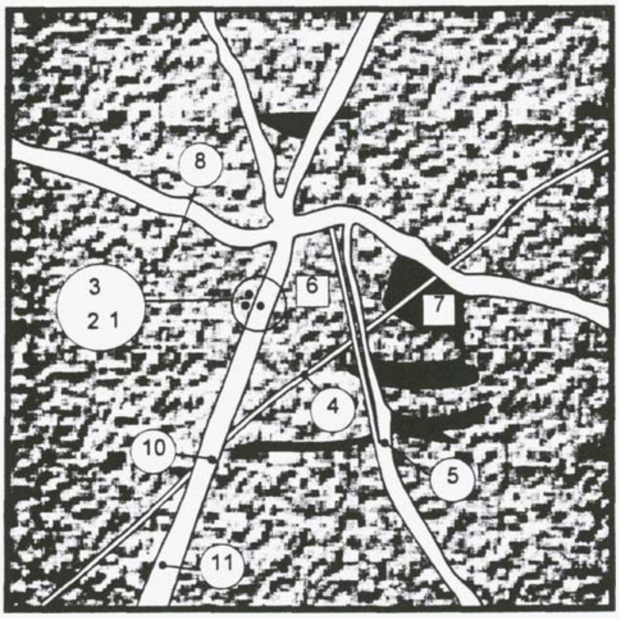

Figure 5. ***A sketch showing the analysed regions of HWPUK. The drawing covers an area of 8mm x 8mm. The squares labeled '6' and '7' correspond to the areas analysed, and the black dots are the points analysed with a 25 x 25µm beamspot. The numbers correspond to the entries in table 2 (below).***

Table **2**. Measured boron concentrations in various **parts** of an unaltered greywacke from the Puketona quarry, near Ngawha hot **springs.** The numbers in brackets after the boron concentrations correspond to **the** 1σ errors due solely to counting statistics, and do not include any estimate of systematic errors

Description	**Boron (wt ppm)**	**Si**	**K**	**Ca**	**Fe**
1. Prehnite in vein	27 (4)	1110	210	3599	149
2. dark material	53 (6)	1040	904	756	517
3. fine grain material	27 (4)	1420	848	571	578
4. narrow quartz vein	13 (3)	1840	813	598	852
5. less fluorescent grain	41 (5)	1100	555	728	337
6. light coloured fine grain **material**[1]	35 (3)	1540	1192	677	804
7. semi-opaque fine grain material[1]	53 (3)	1420	1521	811	1112
8. dark material	26 (2)	1510	1110	*709*	955
10. **Prehnite** in vein	44 (3)	1150	412	4658	456
11. **Quartz** in vein	15 (3)	1700	253	2256	244

[1] The **proton** beam was **defocused** to 0.5x0.5 **mm for** these **measurements**

4. DISCUSSION

The primary purpose of **this** paper is to present the development of **a** novel analytical technique which could be of use in addressing problems of interest to the geothermal community. The methodology **has** been established, and some measurements made on greywacke from the Ngawha Springs region. In themselves the measurements go only a small way to addressing the questions posed earlier in the paper.

The Waipapa greywacke from Puketona is assumed to represent the basement rock in which the fluids in the Ngawha system largely circulate. The Puketona rock is not hydrothermally altered, and should indicate the mineral grain-scale distribution of boron prior to such alteration. The results for the single thin section **must** be used with caution but some observations may **be** instructive.

Boron concentrations range from 13 to 53 ppm which is within the range observed by Ellis and Sewell **(1963)** for greywackes **from** all over New **Zealand,** although well below the single value **of** **140** ppm found by Ellis and Mahon **(1964)** for a greywacke from west of Lake Taupo. The lowest values from points **4** and **11** correspond to the highest rates of silicon X-ray generation, and low levels of Ca X-rays. We noted that in the veins, ***grains*** assumed to be prehnite fluoresced strongly orange under the proton **beam,** whereas **grains** assumed **to be quartz** fluoresced more weakly blue. Points **4** and 11 were weakly fluorescent in the blue. This **to** be compared with **points** 1 and 10 (orange fluorescence), which show relatively higher boron levels, reduced Si X-ray count rates, and high Ca X-ray count rates. We conclude from these results that in the veins, the boron is to be found preferentially in the prehnite.

In the fine grained matrix, our beam size is still too large to allow convincing analyses of single mineral grains. ***Our*** analyses of the **0.5** x 0.5mm areas 6 and 7 indicate a slightly higher level of boron in the semi-opaque **dark** bands, **compared** to the more abundant lighter material. **A** more extensive series of measurements is now planned to ***see*** if these initial observations stand up to detailed scrutiny.

In addition to this further work on the unaltered Puketona greywacke, we plan further work along three main axes.

Firstly, we intend to examine geothermally altered greywacke from the Ngawha Springs system with the proton probe, and to extend the *study* to greywackes and other rocks from other geothermal systems, in particular in the Taupo Volcanic Zone. We will apply the Ion Beam Analysis method to obtain whole rock values by crushing the rocks, and preparing samples in the same way that the USGS samples were prepared. We expect to be able to determine the boron in 25 samples with one day of accelerator time.

Secondly, the boron from these rocks will be extracted and isotopically analysed in order to obtain further information on source. This work will be done in collaboration with Melita Keyworth at ANU, who is also determining the isotopic composition of a range of geothermal waters from New Zealand.

Thirdly, we intend to improve the proton probe equipment and methodology. We will implement improved sample viewing, with crossed polarisers built into the chamber to assist identifying minerals for analysis. We will attempt to determine boron at levels below 5 ppm, and we intend to implement a quantitative PIXE analysis capability.

5. CONCLUSIONS

A proton probe method has been developed for determining boron concentrations down to below 10 weight ppm in spots down to 25 x 25µm in area in polished rock thin sections.

First results from an investigation of a hydrothermally unaltered greywacke from Puketona - assumed to represent the source rock for the hydrothermally altered greywackes underlying the Ngawha Springs geothermal system - indicate higher levels of boron (up to 44 ppm) in the prehnite than in the quartz (~15 ppm) in the veins. In the fine-grained groundmass, semi-opaque dark regions contain slightly higher boron (53 ppm) than the more abundant light coloured regions (35 ppm).

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