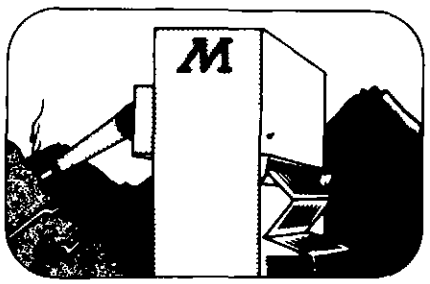

Machinations

Why Boron? Prompt-Gamma Neutron Activation Analysis at McMaster Nuclear Reactor

Michael Denis Higgins
Department of Geology
McMaster University
Hamilton, Ontario L8S 4M1

I am frequently asked why I study boron, to which the facetious answer is "Because it's there". Boron is an uncommon constituent of most rocks and has some unusual and even paradoxical properties. It is usually considered to be a volatile element, but appears to be remarkably stable once incorporated into tourmaline, its most common host mineral. Although generally present at low concentrations, boron is unusually abundant in quartz veins, which may be associated with gold, and in certain granites and pegmatites. Boron is relatively abundant in seawater and, hence, has been used as a paleosalinity indicator in sedimentary rocks, with shales and cherts having the highest boron abundances. Boron is also of interest at low levels in rocks and minerals, as I will describe later.

Boron geochemistry has received little attention until recently, except in sediments, because of the lack of a suitably sensitive analytical method. The classical method, emission spectroscopy, is little used now because of poor detection limits (~ 20 ppm) and low accuracy. Inductively coupled plasma (ICP) emission spectroscopy can give more accurate results, but the detection limits are similar to that of conventional emission spectroscopy. The analytical method used at McMaster is Prompt-Gamma Neutron Activation Analysis (PGNAA). It is a nuclear technique which is quick, accurate and requires no matrix corrections in most samples. The possibility of contamination is reduced because sample preparation is limited to crushing and packaging and the method looks at the whole sample, not just its surface. The effects of sample heterogeneity are reduced because of the large sample analysed (~ 2 g). The main disadvantage of the method is that it requires a large sample and a highly specialized facility: a medium or high-flux nuclear reactor with provision for extraction of thermal neutron beams. For this reason, the McMaster facility is the only one in Canada and the only one in North America largely devoted to Earth Science research. A detailed description of the facility is given in Higgins *et al.* (1984).

Conventional Instrumental Neutron Activation Analysis (INAA) uses neutrons from a reactor to convert stable nuclei into radioactive species within the reactor. At some later time, when the sample has been removed from the reactor, the gamma-rays emitted during the decay of the radioactive nuclei are sorted by energy (each element produces gamma rays of characteristic energy) and counted to determine the elemental abundances. However, some elements produce stable (non-radioactive) species during irradiation and cannot be analysed by this method. Boron is such an element. It has a large cross-section for neutrons (i.e., it can readily absorb neutrons) but produces stable lithium-6 by the reaction ^{10}B + neutron $\longrightarrow$ ^{6}Li + alpha particle + 478 KeV gamma-ray. However, if the gamma-rays produced during the irradiation are examined, the 478 KeV gamma-ray can be readily detected and the boron abundance measured. Most elements produce gamma-rays during irradiation, but only H, B, Cl, Cd, Gd and Sm can be detected at trace levels. The method has also been used to measure S in coal.

A detector cannot be placed within the reactor itself, where the intense radiation would quickly destroy it, so it is necessary to extract a beam of neutrons through the reactor shielding by using a hollow tube called a beam-port (Fig. 1). Neutrons cannot be focused readily, so the neutron beam is shaped using collimators and filtered using Al_2O_3 and Si crystals to remove the fast neutrons that might damage the detector. The sample is packed in 1 cm teflon tubing and suspended in the beam some four metres from the core. The gamma-rays produced by the sample impinge on an intrinsic Ge detector similar to that used in conventional INAA, and the data from the detector are processed in the same manner. The complexities of the facility arise from the copious quantities of shielding needed to protect the detector from gamma-rays and neutrons and to provide a safe working environment. One tonne of lead, two tonnes of wax, three tonnes of concrete together with small quantities of lithium and, paradoxically, boron are currently used in the shielding (Fig. 2). Most of the developmental work has been concerned with this shielding.

The detection limit, 0.1 ppm in a 2 gram sample, is largely controlled by the boron blank of the system. This blank is caused by boron-bearing components in the detector and sample holder and is therefore very stable. A typical rock with 5 ppm boron can be analysed with an accuracy of ± 10 per cent in less than half an hour.

I will briefly describe three projects from the large number currently active in our laboratory:

There is interest in the cosmochemistry of boron because it is one of the few elements not formed in the interior of stars. This is the major reason why it is not abundant in the solar system. The other factor that controlled terrestrial boron abundance was the temperature at which boron condensed from the solar nebula that was parental to the planets. Higgins and Shaw (1984) have measured the boron content of mantle-derived material and compared it with the abundances of other volatile elements. They concluded that boron condensed at much higher temperatures than originally estimated, by forming a solid-solution in feldspar.

The behaviour of boron in basalts during alteration by seawater has important implications for the geochemical cycle of boron in the oceanic crust. Bergeron (1984) ex-

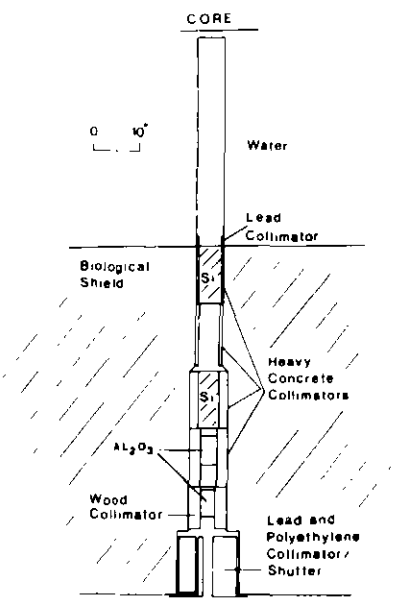

Figure 1 *Cross section of the beam-port used to extract neutrons from the reactor core. Neutrons move from top to bottom in the diagram. They are filtered and thermalized by crystals of silicon (Si) and alumina (Al_2O_3) and collimated by concrete, wood, lead and polyethylene. The final collimator may be rotated to shut off the neutron beam*

amined altered basalt from dredged and drilled sea-floor and ophiolites and concluded that boron was readily adsorbed at low temperatures on the sea-floor, but was progressively lost as the temperature of metamorphism increased. Greenschist facies basalts from drill holes and ophiolites have low boron contents as compared to similar rocks altered on the sea-floor.

Cherts are known to be a sink for boron in the oceans, due to the ability of silica-secreting organisms to concentrate boron in their skeletons. Truscott and Shaw (1984) have found high boron abundances in Phanerozoic nodular cherts and slightly less in bedded cherts. Boron appears to be readily remobilized and lost as the biogenic opal recrystallizes to quartz. Boron in Precambrian banded iron formations (BIF) is very low, although analysis of marine shales indicates that Precambrian seawater was little different from later seawater. Therefore, these data indicate that BIF are not of biogenic origin.

Other projects involve the association of boron with gold, boron in granites, serpentines, kimberlites, spilites, basalts and various minerals. Future plans include a study of boron in metamorphic rocks, particularly high-grade ones, to interpret the "fate" of boron incorporated into sediments when exposed to deep crustal processes. Although we have to endure endless jokes on the theme of boredom, we can see many details of earth processes in the study of this little known element.

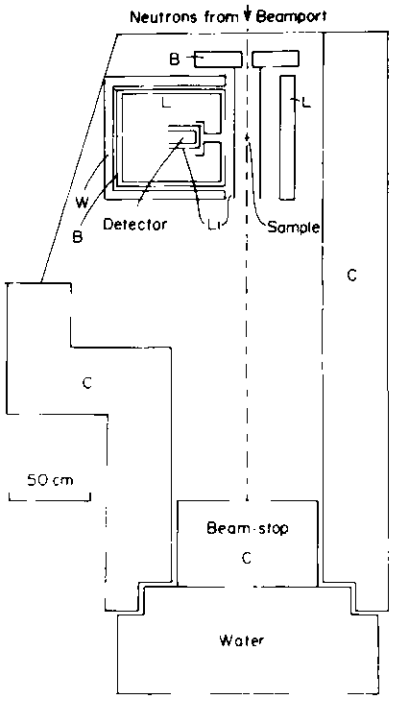

Figure 2 *A "cave" of neutron shielding concrete (C) with a wax (W) roof completely encloses the experiment. Neutrons enter the cave at the top of the diagram and finally end up at the bottom in the beam-stop. Detector shielding consists of lead (L), wax (W), $^6Li_2CO_3$ in wax (Li), and boron carbide loaded rubber (B)*

Acknowledgements

The PGNAA team is Michael D. Higgins, Marylyn G. Truscott, Mario Bergeron, Denis M. Shaw and Sheldon Landsberger. The facility was created using NSERC grants to DMS and McMaster Nuclear Reactor, and a BILD (Ontario) grant to Nuclear Activation Services Ltd. We would like to thank the reactor staff for all their help.

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MS received, as revised, July 19, 1984