

THE GEOCHEMISTRY AND ORIGIN OF AMPHIBOLITES FROM BAMBLE, SOUTH NORWAY

I. The determination of zinc in amphibolites by atomic absorption spectroscopy.

By

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Abstract. A simple, but rapid and accurate, atomic absorption spectroscopic technique for determining the trace zinc contents of basic silicates is described. The potentially interfering effects of certain co-existing ions necessitates the use of separate working curves for the various types of silicate material. The method is applicable to all basic rocks and certain mineral groups including amphiboles, micas and garnets. The zinc contents of nine amphibolite samples from the Precambrian Bamble-area, South Norway, are given together with repeated determinations of the standard diabase W 1.

Introduction

Prior to the advent of atomic absorption spectroscopic techniques, work on the geochemistry of zinc had been greatly hampered by the lack of a rapid and accurate analysis method for zinc when present only in trace quantities. As part of a program designed to determine the geochemistry of a suite of Precambrian amphibolites from the Kongsberg-Bamble series west of the Levang peninsular, South Norway, the author has initiated an atomic absorption procedure for zinc which is applicable to basic rock and mineral groups. The advantages and limitations of this technique are given below in some detail together with the results obtained for nine amphibolite samples. Complete analyses of these rocks will be given and discussed in a later publication. Zinc is theoretically very suitable for analysis by atomic absorption spectroscopy since, in a normal temperature flame, it

may be considered that all introduced vapour is in the atomic ground state. The procedure has the additional advantage that no involved sample preparation is necessary.

Limitations of other analysis methods

The detection limit using normal emission spectrographic methods is about 100 ppm. The average abundance in igneous rocks has been given by WEDEPOHL (1953) as 40 ppm and hence zinc may be determined only in silicates that are likely to have concentrations considerably in excess of this. Several specialized spectrographic methods have successfully lowered the detection limit (the double arc procedure of WEDEPOHL should be noted in particular) but a further difficulty lies in the fact that the most sensitive zinc line is at 2138 Å, necessitating the use of special sensitized plates. Also, since zinc tends to substitute for ferrous iron, there is a very real danger of interference from the strong 2138.589 Å iron line.

The majority of data relating to the geochemistry of trace quantities of zinc has been provided by spectrophotometric analysis, but the silicate samples invariably contain varying quantities of potentially interfering ions which must be initially separated before forming the coloured complex. The dithizone extraction procedure devised by SANDELL (1937) has not been entirely successful and has more recently been superseded by various techniques based on ion exchange separation (e.g. HUNTER and MILLER 1956). The analysis scheme of HUFFMAN *et al.* (1962) combines the better features of several earlier publications. Separation of the zinc is here effected by an ion exchange resin and zincon is used as the colourimetric reagent as proposed by RUSH and YOE (1954). RONA *et al.* (1962) have used Zn⁶⁵ as a tracer to control the extraction conditions but, in spite of such recent improvements it is considered that spectrophotometric procedures are both complicated and time consuming.

Apparatus

A Hilger S.P. 900 spectrophotometer with attached burner and vapourizing unit was used for this work. For the resonance line source, a Hilger hollow cathode lamp was operated at the recommended cur-

rent of 44 ma. The most suitable spectral line at 2138 Å is somewhat weak and the spectrophotometer is least sensitive over this region of the spectrum so that a 1 mm slit width was found to be necessary and the burner height was set on the 5 mark. These settings gave very adequate sensitivity but flame flicker occasionally introduced momentary needle fluctuation.

An air-propane flame was used with the air pressure set at 15 psi. The initial calibration curve data were obtained with the propane pressure as low as was consistent with a steady flame and, for subsequent runs, this pressure was initially adjusted to reproduce the calibration curve conditions.

These investigations entailed the use of very concentrated solutions which tended to block the inlet nozzle at the base of the burner. Also, while testing for acid interferences, wildly fluctuating results were obtained which were attributed to the acids re-dissolving salts deposited before reaching the burner during previous tests. The burner was slightly modified to prevent solids from blocking this jet and the complete burner unit was frequently dismantled and thoroughly cleaned. These precautions — coupled with a lengthy flushing sequence — solved this experimental problem.

Tests for interferences

The large number of co-existing atoms encountered during silicate analysis greatly increases the possibility of interference phenomena affecting the test element, though DAVID (1958) and WALLACE (1962), working on plant and metallurgical material, have noted only minor effects. Such phenomena are, to some extent, a function of the combustion mixture employed, i.e. to the flame temperature.

The effects of ferrous iron, calcium and magnesium were tested in the range 0 to 2000 ppm at the 5 and 10 ppm zinc concentration levels and aluminium over the same range at the 10 ppm zinc level only. The 2000 ppm concentration is equivalent to 20 per cent of the particular oxide in a solution prepared as below. The results are shown in Figs. 1-4. Calcium appears to have no notable effect on the zinc absorption, whereas ferrous iron produces a small but constant enhancement in concentrations greater than 100 ppm. Aluminium enhances below 100 ppm but depresses above this value. Magnesium

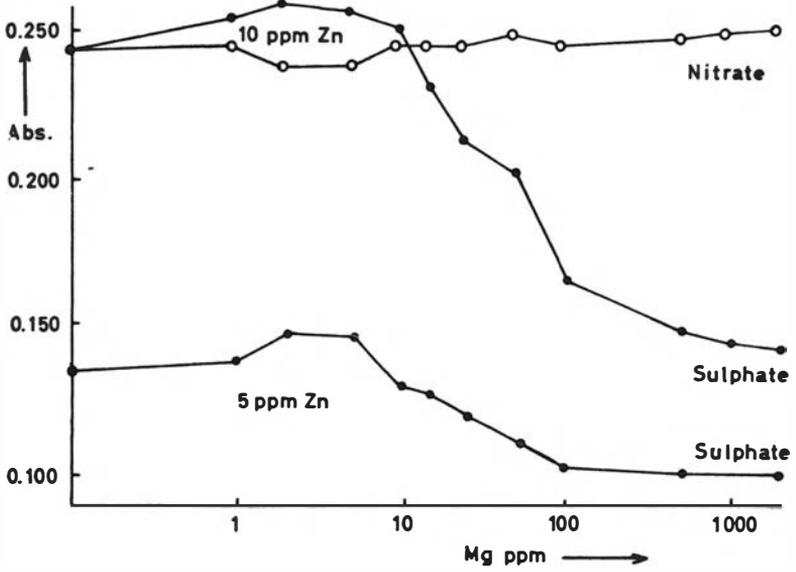


Fig. 1. The effect of magnesium on zinc absorption.

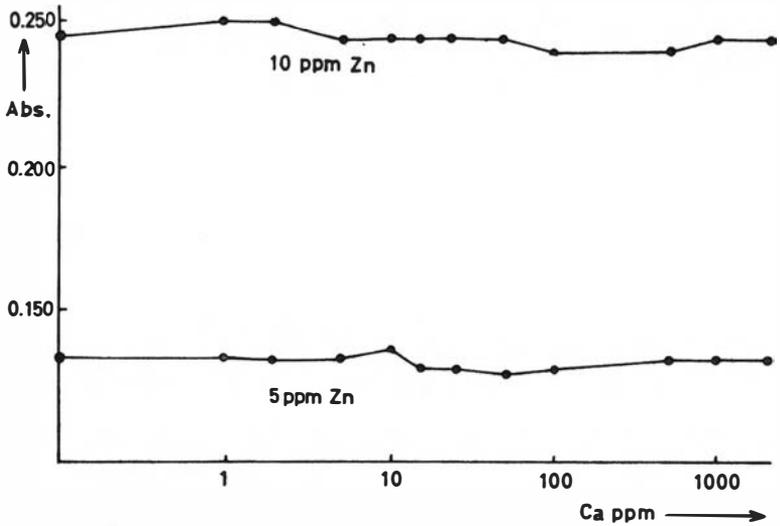


Fig. 2. The effect of ferrous iron on zinc absorption.

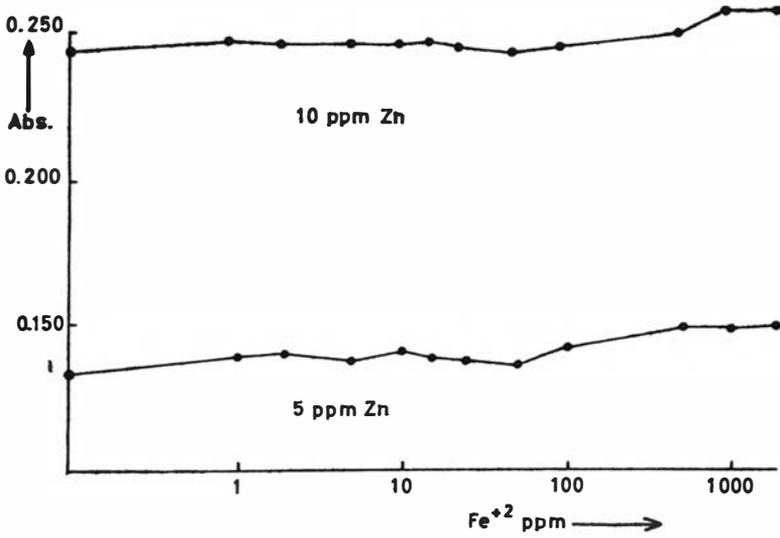


Fig. 3. The effect of calcium on zinc absorption.

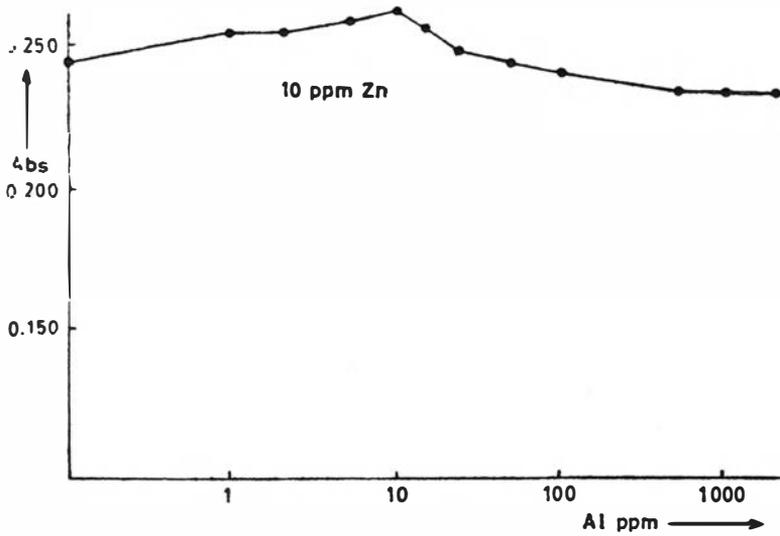


Fig. 4. The effect of aluminium on zinc absorption.

sulphate gives the marked depression indicated in Fig. 1, while the nitrate has little effect. The obvious conclusion that this depression may be attributed to the sulphate radical is borne out by the effect of sulphuric acid, but this depression is not seen in Fig. 2 where the iron is present as ferrous ammonium sulphate.

The possibility of fusing unknown silicate samples with sodium or potassium salts was considered and, to this end, 25,000 ppm of each alkali in turn were added to standard zinc solutions to prepare working curves for the range 0 to 20 ppm. The results showed that neither sodium nor potassium has interfering effect on zinc absorption. Slight deviations in the slopes of these compared with the standard could be safely attributed to the greatly increased viscosity of the alkali-bearing solutions.

Difficulties — noted above — were initially encountered with tests for acid and anion interference. Phosphoric, nitric and hydrochloric acids had no effect on the 5 ppm zinc absorption up to 25 per cent v/v, but sulphuric acid, above 7.5 per cent v/v, showed a marked depression. No interference from fluorine was noted up to a concentration of 1000 ppm on the 10 ppm zinc concentration level.

Working curves

Three working curves covering the range 0 to 20 ppm zinc are shown in Fig. 5. Instrument settings were identical for these curves and for all subsequent determinations. Curve A is for zinc in aqueous solution and B for 50 per cent iso-propyl alcohol. Use of alcohol as a solvent increases the sensitivity up to 5 ppm zinc two-fold but it is difficult to maintain a steady flame. With or without alcohol, the detection limit is below 0.5 ppm zinc.

Curve C is the working curve employed for analysis of basic silicate material. This was determined from a synthetic oxide mix prepared from analytical grade reagents such that the final mix was equivalent to 51 per cent SiO_2 , 1 per cent TiO_2 , 15 per cent Al_2O_3 , 10 per cent FeO , 10 per cent MgO , 10 per cent CaO , 2 per cent Na_2O and 1 per cent K_2O . 1 g samples from this mixture were treated as described below with the relevant quantity of zinc added. This procedure was designed to allow for multiple interference effects likely to be encountered and also corrected for possible reagent impurities.

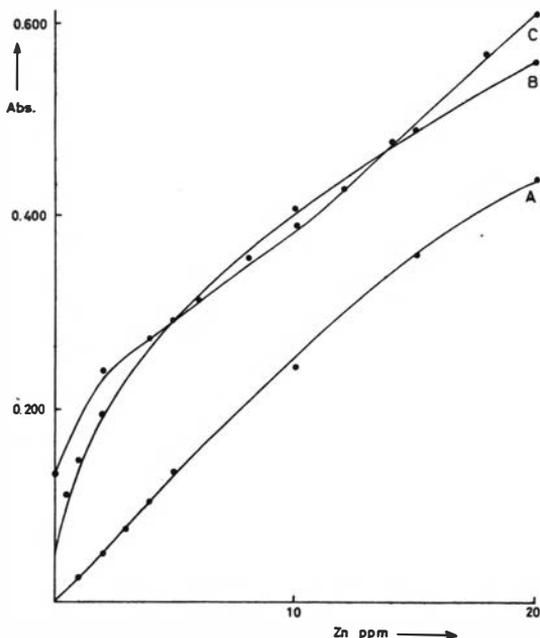


Fig. 5. Zinc working curves. A = Aqueous; B = 50% Iso-propyl alcohol; C = Synthetic silicate mix.

The spectrophotometer was 'checked' prior to each determination on a fog of distilled water, and the burner was flushed for a minimum of ten minutes using, in order, alcohol, dilute nitric acid and distilled water. Every reading was triplicated.

Silicate analysis

Approximately 1 g of silicate powder was weighed into a platinum crucible. 20 ml of 40 per cent hydrofluoric acid and exactly 5 ml of concentrated sulphuric acid were added and the crucible was covered and left to stand on a water-bath over night. (Longer periods were necessary for the more resistant minerals.) The cover was removed and the water allowed to evaporate. 10 ml of concentrated nitric acid were then added and the crucible was heated on a water-bath for a further period of between four and six hours before evaporating to dryness on a hot-plate. The crucible was filled with 50 per cent v/v nitric acid, warmed on the water-bath and allowed to cool to room

temperature. This procedure usually resulted in the final solution being over-saturated. The contents were washed into a 50 ml flask, made up to the mark, thoroughly mixed and allowed to stand for one hour, before being filtered into a second, dry 50 ml flask.

Perchloric acid could be used in place of sulphuric acid but this reagent was decided against in view of the reported action of halogen acids on brass burners (ELWELL and GIDLEY 1961) though, as noted above, the author found hydrochloric acid had no effect up to 25 per cent v/v.

Reproducibility

To assess the reproducibility of the method, one standard W 1 solution was measured fifteen times over a period of three days. The measured absorption was 37.7 per cent with a standard deviation of 0.98 per cent.

Table 1. Zinc content of the standard diabase W1

Reference	Separation	Method	Zn ppm
Greenland (1963)	Dithizone	Dithizone	72
	—	Atomic absorption	66
	Ion exchange	Dithizone	65
Author	—	Atomic absorption	71
	—		66
	—		69

Table 2. Zinc contents of Bamble amphibolites

Specimen number	Mineralogical assemblage	Zn ppm
61/152	Quartz—Plagioclase—Hornblende—Sphene	18
61/175	Plagioclase—Hornblende—Biotite—Ilmenite	121
61/251	Quartz—Plagioclase—Hornblende	49
61/252	Quartz—Plagioclase—Hornblende—Ilmenite	96
61/264	Plagioclase—Hornblende	77
61/479	Plagioclase—Hornblende—Ilmenite	120
61/537	Quartz—Plagioclase—Hornblende	142
61/643	Quartz—Plagioclase—Hornblende	73
61/720	Plagioclase—Hornblende—Biotite	106

Results

The results for repeated determinations of the standard diabase W 1 are given in Table 1, compared with the values given by GREENLAND (1963) using various techniques. The zinc contents of the nine Bamble amphibolites are shown in Table 2. These data will be fully discussed in a later publication. The calculated accuracy of each individual determination is ± 5 p.p.m.

Discussion

The results show a good order of reproducibility. Where zinc contents are lower than 100 ppm, solution concentration limits impose an accuracy not greater than ± 5 ppm. This is better than the accuracies given by polarographic and spectrographic procedures but still less than that of colourimetric methods. For silicate material containing zinc in concentrations greater than 100 ppm, the author considers atomic absorption spectroscopy to be superior to all commonly employed analytical techniques. Apart from the greatly increased rapidity, freedom from complex initial extraction procedures inherent in colourimetric methods must tend to increase accuracy. The largest single source of errors lies in possible zinc impurities present in reagents used to prepare the synthetic oxide mix.

Atomic absorption spectroscopy is not a commonly employed technique at present, though the basic equipment required is relatively simple and inexpensive. Thus the apparatus used for this work consisted only of a simple atomiser, burner attachment and lamp in addition to a spectrophotometer of a type common to the majority of silicate analytical laboratories. Many refinements of this basic equipment are possible but are not, as yet, readily available commercially.

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