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Trace Boron Concentrations in Geologic Standard Materials Determined by Fluoride-Volatilization Arc Spectrography

by

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Abstract

Trace boron concentrations recently measured in laboratories of the U.S. Geological Survey are reported for diverse geologic standards, including U.S. Geological Survey rock standards and National Bureau of Standards standard reference materials. Determination of boron in the concentration range from 0.2 to 600 micrograms per gram is accomplished by emission spectrography that is based on the volatilization of fluorides into a direct-current arc.

Introduction

Boron is a lithophilic element that is widely dispersed in geologic materials as borates and borosilicates. Unaltered rocks generally exhibit a small range of boron concentrations, whereas high secondary accumulations of. boron, which is a very mobile element, can occur in postmagmatic processes (Wedepohl, 1974). Typically, boron occurs at trace concentrations that range from 3 µg/g in ultramafic rocks to more than 300 µg/g in clays from deep-sea sediments (Wedepohl, 1974). Correlations of trace boron concentrations in sedimentary rocks with the salinity of contact waters have been reported (Turekian, 1963). Boron may be used as an indicator of the genesis of phosphorites because it is always present in marine phosphorites and frequently is absent from continental phosphorites, especially non-argillaceous varieties

(Wedepohl, 1974). Implications for the boron cycle in oceans are suggested by studies of the serpentinization of peridotite rocks in the oceanic crust that may be made possible by trace concentrations of boron in juvenile boron-containing solutions (Thompson and Melson, 1970). Increasing interest in the roles of boron in geochemical and biogeochemical processes requires that appropriate standards, now scarce, be readily available to the analyst to assure the accuracy of analyses by chemical or instrumental methods. Concentrations of boron in 37 reference materials have been determined by a modified emission spectrographic method. The method provides a lower determination limit that is better by approximately a factor of 50 over conventional direct-current arc methods (Bastron and others, 1960; Meyers and others, 1961).

Detectability and sensitivity in determinations of boron by conventional direct-current (d.c.) arc spectrographic methods are adversely affected by the formation of highly refractory boron carbide (melting point = 2623 K) in the walls of graphite electrodes. Limits of determination seldom are below 10 to 20 µg/g (Bastron and others, 1960), and thus, these methods are inadequate for determinations of boron in many basalts, granites, and carbonate rocks. The formation of boron carbide can be inhibited through use of a volatilization buffer, such as copper hydroxyfluoride (CuOHF, supplied by Spex Industries*). This compound, which possibly is an intimate mixture of two or more copper compounds, is thoroughly mixed with a pulverized sample to provide reactive fluorine in the molten sample that exists in the

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* The use of trade names is for identification only and does not imply endorsement by the U.S. Geological Survey.

anode during operation of the arc. The resulting boron trifluoride (boiling point = 173 K) readily volatilizes into the high-temperature arc column, thus transporting a larger portion of the boron into the arc column and consequently improving the determination limit for boron.

Equipment and Materials

Instrumentation

The spectrograph, excitation source, arcing conditions, and microphotometer used in this investigation are described in Table 1.

Materials

1) Copper hydroxyfluoride, 99.999% pure (Spex Industries*);
2) Graphite electrodes, U-2, ultra "F" purity (Ultra Carbon Corporation*);
3) "Specpure" ferric oxide, Johnson-Matthey Company*;
4) Natural quartz and microcline from Shelby, North Carolina; and
5) Standards from the U.S. Geological Survey, the Geological Survey of Japan, and the National Bureau of Standards.

Experimental

Preparation of Samples

Thoroughly mix and grind 10 mg of each sample with 40 mg of copper hydroxyfluoride (CuOHF) in an agate mortar. The CuOHF should be handled only in a well-ventilated area of the laboratory, and contact of the compound with the skin should be avoided.

Preparation of Calibration Standards

First, combine the following finely pulverized materials in the weight proportions indicated: 60 parts quartz, 40 parts microcline, and one part ferric oxide. Mix and grind together these components to provide a homogeneous matrix similar to that of the sample. Dilute the NBS standard reference material No. 92, which is a low-boron glass (B_2O_3 concentration = 0.70 percent), to 1000 µg/g with the above mixture. Then, using the reciprocal of the cube root of 10 (0.4642) as the dilution factor (Bastron, and others, 1960), make nine sequential dilutions of the mixture containing 1000 µg B /g to provide homogeneous mixtures with boron concentrations that range down to 1 µg/g . One part of each of these calibration standards then is mixed with four parts of copper hydroxyfluoride in an agate mortar.

Exposure of Photoplates

Duplicate 75-s exposures of arc spectra in the region 240 to 310 nm are recorded on a III-0 photographic emulsion for both standards and samples.

Processing of Emulsion

Each exposed photographic emulsion is first developed for 3 minutes in Kodak* D-19 developer solution at 20° C. Then, the emulsion is immersed in indicator stop bath for 30 seconds, and subsequently placed in Kodak* fixer solution for 10 minutes. Afterwards, the emulsion is washed in circulating water for 15 minutes, and finally, dried for 4 minutes on a plate dryer by a gentle flow of warm air.

Microphotometry

The transmissions of 20 iron lines in 2 exposures made through a two-step neutral density filter (100 and 50 percent transmission) are determined by microphotometry for calibration of the photographic emulsion in the 250-nm region. The iron spectra were produced by a 5-A arc between a graphite cathode and a small quantity of iron in a cup-shaped graphite anode.

The transmissions of the boron line at 249.68 nm and the adjacent background are measured for spectrograms of both the standards and the samples.

All calculations for quantitative spectrographic analysis and plots of the emulsion calibration and analytical curves are accomplished on a Hewlett-Packard* 9830A table-top computer equipped with a model 9862A xy-plotter (Golightly, 1978).

Discussion

An evaluation of the accuracy of the method necessarily includes the possible heterogeneity of the various materials analyzed. Sample homogeneity on the 2- to 10-mg scale is required for the method. Tests of the homogeneity of boron, based on the analysis of two 10-mg samples from each of three bottles of standard (Flanagan, 1976), indicate that no significant heterogeneity exists for any of the standards included in the study. None of the NBS standard reference materials (SRMs) was part of this study because a certificate of analysis issued for each SRM provides a statement describing the homogeneity of the SRM. Both accuracy and precision of measurements follow characteristic dependencies on concentration (Table 2). For boron concentrations above 20 µg/g, the accuracy of measurements generally appears to be within ± 10 percent of the accepted value; whereas, for concentrations below 20 µg/g, typical accuracy is within ± 20 percent of the accepted value (Flanagan, 1976; Gladney, 1976; Gordon, and others, 1979; Hall and others, 1986). Conspicuous exceptions to this generalization are provided by the boron concentrations determined for G-2, AGV-1, SGR-1, and NBS-1633. The NBS-1633 coal ash is certified to be homogeneous only on a 100-mg scale; but, currently, there are no obvious reasons for the disparities between measured and accepted boron concentrations for the other three materials. Trends in the precision of measurements also generally follow the concentration level. Thus, for boron concentrations greater than 100 µg/g, the relative standard deviation (RSD) is 7 to 8 percent. The precision of the method deteriorates to 10 to 15 percent RSD for boron concentrations that range from 10 to 100 µg/g, and further degrades to 25 to 50 percent RSD for concentrations that fall between 0.2 and 10 µg/g. The lower determination limit for the method is approximately 0.2 microgram of boron per gram of sample, which corresponds to an absolute determination limit of 2 ng of boron.

The new data presented in Table 2 on boron concentrations in diverse, readily-available geologic standards are expected to contribute to future geochemical investigations that focus on trace concentrations of boron. Also, the copper hydroxyfluoride vaporization buffer provides a practical approach to the sensitive determination of boron that should be useful in such studies.

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Table 1. Instrumentation and Operating Conditions.

Instrument or Function	Operating Conditions
Spectrograph	Eagle-mount, 3-m focal length. Grating has 590 grooves per mm, and is blazed for the 2nd order ultraviolet region. A 1.3-mm high central portion of the arc is focused on the grating by a cylindrical quartz lens that has a focal length of 35 cm. Both this lens and the two-step neutral density filters used for emulsion calibration are located at the Sirks secondary focus of the spectrograph. The height of a mask at the grating is 11 mm.
Slit	0.025 mm wide; 2.5 mm high.
Dispersion	0.28 nm/mm reciprocal linear dispersion, 2nd order.
Wavelength region	237.5 to 375.0 nm, 2nd order.
Excitation source	25-A direct-current arc in Ar.
Arcing of material	10 mg (2 mg of sample or standard plus 8 mg of copper hydroxyfluoride) arced for 75 s.
Analytical gap	4 mm, maintained constant throughout arcing process.
Upper electrode	Cathode, Ultra Carbon* No. 5001, 3.2-mm diameter x 3.8-cm long graphite rod.
Lower electrode	Anode, Ultra Carbon* No. 101-L-6, 6.15-mm diameter x 44.5-mm long graphite, undercut crater electrode.
Atmosphere	Argon flow of 6.6 L/min directed by a ceramic jet concentric to the anode (Helz, 1964).
Photoplates	Kodak* III-O emulsion, 102 x 254 mm.
Emulsion calibration	A 60-s exposure through a 2-step neutral density filter (50 - 100 percent transmission) is made for a 5-A iron arc. The slit height is adjusted to 5 mm, and further attenuation of radiation entering the slit is produced by a neutral density filter having 30 percent transmission.
Microphotometer	Jarrell-Ash*, model 2100. Slit: 0.007 mm width, 0.7 mm height.

Table 2. Concentrations of Boron in Thirty-seven Geochemical Standards Determined by D.C. Arc Spectrography with a Copper Hydroxyfluoride Volatilizer.

Standard[a]	Material	Boron Concentration, µg/g			
		D.C. Arc[b]	PGAA[c]	ICP[d]	Other[e,f,g]
DTS-1	dunite	0.29 ± 0.14 (6)			<10[g]
BIR-1	Icelandic basalt	0.36 ± 0.12 (6)	0.24 ± 0.08 (1)		
GSP-1	granodiorite	0.58 ± 0.21 (6)	0.7 ± 0.2 (1)		< 3[g], 0.08±0.06[f]
NBS-70A[h]	potassium feldspar	0.77 (1)			<10[g]
G-2	granite	0.93 ± 0.23 (6)	2.6 ± 0.1 (1)		2[e], 3.9 ± 0.7[f]
G-1	granite	1.2 (1)			1.7[e]
DNC-1	N. Carolina diabase	1.2 ± 0.6 (6)	1.0 ± 0.2 (1)		
NBS-70[h]	feldspar	1.3 (1)			<10[g]
PCC-1	peridotite	1.5 ± 0.7 (6)	1.4 ± 0.1 (2)		6[e]
ARHCO-1[j]	basalt	1.7 (1)			<10[g]
NBS-99A[h]	feldspar	1.8 (1)			<10[g]
BHVO-1	Hawaiian basalt	2.0 ± 0.2 (6)	2.3 ± 0.2 (2)	<1 (4)	
BCR-1	basalt	2.8 ± 1.2 (6)		2.2 ± 0.4 (4)	5[e]
STM-1	nepheline syenite	3.9 ± 1 (6)		4.0 ± 0.4 (4)	<10[g]
AGV-1	andesite	4.3 ± 0.6 (6)	5.9 ± 0.1 (1)	6.1 ± 0.4 (4)	5, 13[e], 3.9±0.7[f]
JG-1[i]	granodiorite	4.6 (1)			
NBS-99[h]	soda feldspar	4.8 (1)			<10[g]
SDC-1	mica schist	10 ± 3 (6)	11.2 ± 0.2 (1)	10.1 ± 0.7 (4)	
JHK-2[i]	aphyric basalt	11 ± 1 (6)			<10[g]
W-1	diabase	12 ± 1 (6)			15[e]
W-2	diabase	13 ± 1 (6)	11.3 ± 0.2 (2)		
RJM-1	rhyolitic pumice	23 ± 0.6 (6)			
RGM-1	rhyolite	30 ± 4 (6)	26.5 ± 0.4 (2)	23.8 ± 0.9 (4)	33[f]
SGR-1	Green River shale	33 ± 7 (12)	50.4 ± 0.4 (2)	50.3 ± 1.4 (4)	29.8[g]
QLO-1	quartz latite	34 ± 5 (6)	33.3 ± 0.5 (2)	32.2 ± 0.8 (4)	37[g]
NBS-25C[h]	manganese ore	34 (1)			
NBS-1A[h]	limestone	45 (1)			
NBS-97A[h]	flint clay	69 (1)			69[e]
NBS-98[h]	plastic clay	71 (1)			78[e]
NBS-97[h]	flint clay	74 (1)			71[e]
SCo-1	Cody shale	77 ± 10 (12)	72.1 ± 0.5 (1)	71.5 ± 1.9 (4)	64.4[e]
SDO-1	Devonian Ohio shale	120 ± 7 (6)			170[g]
MAG-1	marine mud	130 ± 10 (12)	128 ± 2 (1)	132 ± 3 (4)	130[f]
NBS-98A[h]	plastic clay	130 (1)			120[g]
NBS-25B[h]	manganese ore	140 (1)			135[g]
NBS-28A[h]	iron ore	190 (1)			200[g]
NBS-1633[h]	coal fly ash	580 (1)	433 ± 4 (5)		480 ± 40[f]

a. U.S. Geological Survey analyzed sample, unless noted otherwise (Flanagan, 1976).
b. Uncertainty in the mean value is one standard deviation for the number of determinations shown in parentheses.
c. PGAA: Neutron capture prompt gamma-ray neutron activation analysis (Gordon and others, 1979).
d. ICP: inductively coupled plasma spectrometry (Hall and Pelchat, 1986).
e. Average value (Flanagan, 1976).
f. Average value (Gladney, 1976).
g. Semiquantitative value from d.c. arc spectrography (Flanagan, 1976).
h. National Bureau of Standards, standard reference material.
i. Geological Survey of Japan, reference standard.
j. Atlantic Richfield Company, geochemical standard.