

Determination of Boron in Chondrodite by Ion Microprobe Mass Analysis

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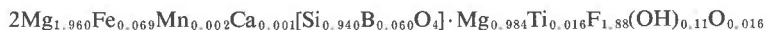
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Abstract

Boron concentrations up to 0.71 atomic percent (the equivalent of 1.20 wt percent B_2O_3) have been recorded by ion microprobe mass analysis in chondrodites previously found to be silicon-deficient by Jones, Ribbe, and Gibbs (1969). The formulas [normalized to $2(Si + B)$] for the two most boron-rich chondrodites are:



The charge-balancing substitutions are thought to occur in the hexagonal closest-packed anion array, probably as hydroxyl for oxygen. Only trace levels of monovalent cations (Li, Na, K) were found in the mass spectra of these orthosilicates, and these are effectively charge-compensated by trace levels of trivalent octahedrally-coordinated cations (Al, Cr).

Introduction

The humite minerals are hexagonal closest-packed orthosilicates with the general formula $nM_2SiO_4 \cdot M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$, where $n = 1$ for norbergite, $n = 2$ for chondrodite, $n = 3$ for humite, and $n = 4$ for clinohumite, and where $x < 1$ and the octahedrally-coordinated M atoms are Mg, Fe, Mn, Ca, and Zn in decreasing order of abundance. The crystal chemistry of the humites was studied in detail by Ribbe, Gibbs, and Jones (1968), Jones (1968), and Jones *et al* (1969). Of 55 specimens analyzed by conventional electron microprobe techniques, several of the chondrodites were found to be significantly deficient in silicon.

For stoichiometric humites, the ratio $S_t = 2Si/[2n/(2n + 1)]M_{Ti}$ should be 1.000 (Si and M_{Ti} are, respectively, the atomic proportions of tetrahedrally coordinated Si and octahedrally coordinated cations, $M_{Ti} = Mg + Fe + Mn + Ca + Zn + Ti$). Jones (1968) found that two of his chondrodites (#9 from Franklin, New Jersey—U.S. National Museum #R14660; and #10 from Amity, New York—U.S.

National Museum #36081) had values of S_t as low as 0.928 and 0.953, respectively. Single crystal and X-ray powder patterns confirmed that both of these were indeed chondrodites, and the cell volume of #9 was observed to be significantly smaller (by 1.8 \AA^3) than Jones' chondrodite #2 which contains only one-third as many larger-cation substituents for magnesium (see Fig. 1; *cf* Tables 1 and 3 in Jones *et al*, 1969). From these observations Jones *et al* (1969, p. 396) implied ". . . the presence of another tetrahedrally coordinated cation which is smaller than Si." Careful microprobe analysis indicated that phosphorus is not present in detectable amounts in humite minerals; thus the only alternative was boron, since beryllium is as large as silicon and aluminum is considerably larger and is, in any case, present in only trace amounts.

This ion microprobe study determined that boron can indeed substitute for at least 6 percent of the silicon atoms in chondrodites, although in the other humite minerals it has not yet been found in excess of 0.7 percent.

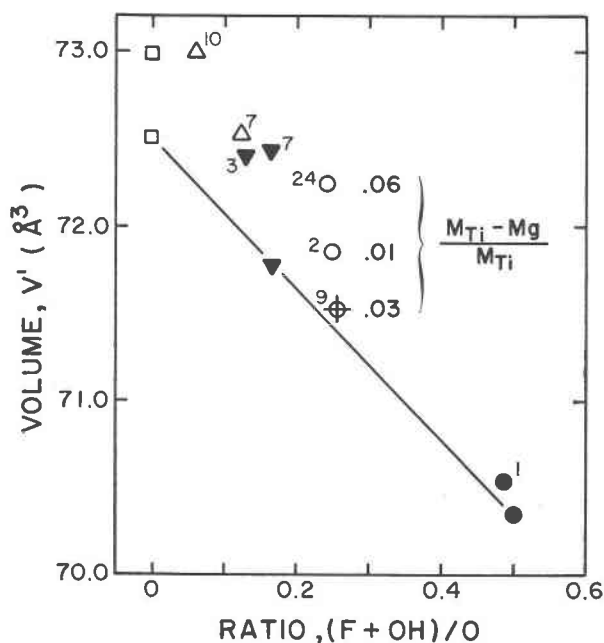


FIG. 1. The relation between the normalized cell volume $a \times b \times (d_{001}/n)$ and $(F + OH)/O$ in norbergite (solid circles), chondrodite (open circles), humite (solid triangles), clinohumite (open triangles), and forsterite (squares). Numbers next to humite mineral data points correspond to those in Table 1 of Jones *et al* (1969). The solid line connects synthetic Mg_3SiO_4 (data from Yoder and Sahama, 1957), $3Mg_2SiO_4 \cdot MgF_2$, and $Mg_2SiO_4 \cdot MgF_2$ (data from Van Valkenburg, 1961). FO_{00} data from Birle *et al* (1968). Ratios indicate percent substitution of octahedral cations for Mg.

Experimental Techniques

The boron values reported in Table 1 were obtained using the Ion Microprobe Mass Analyzer, IMMA, at Applied Research Laboratories, Hasler Research Center, Goleta, California (see Andersen and Hinthorne, 1972). A primary beam of $^{16}O^-$ ions accelerated to 17 keV was used to sputter the samples. The negatively charged beam effectively eliminated any electrostatic charge build-up on the sample surface (Andersen, Roden, and Robinson, 1969). The beam diameter was approximately 20 μm and the beam current 6.0 nanoamps.

The samples analyzed in this study were grains from the same electron microprobe mounts previously prepared and analyzed by Jones (1968). The grain mounts were carbon-coated to facilitate secondary ion collection. Using the light microscope of the IMMA, it was possible to avoid mineral and fluid inclusions and microfractures during the analyses.

Because of favorable detection limits and the rela-

tively high abundance of boron (>100 parts per million atomic [ppma]) in these chondrodites, an integration time of only two seconds was adequate to measure the $^{11}B^+$ isotope peak. The peak-to-background ratio for chondrodite #6, the sample with the lowest boron concentration, was greater than 100, and using counting statistics the estimated error 2σ is 7.5 percent of the amount present, or 5 ppma. For the most boron-rich specimens, 2σ is 2 percent of the amount present, or <150 ppma. The boron data were quantitatively reduced using sensitivity factors derived from a theoretical ionization model (Andersen and Hinthorne, 1973), thus eliminating the need for boron calibration standards.

Analyses were also performed for other cations which may occur in tetrahedral coordination. Aluminum was the most abundant of these elements, averaging about 100 ppma with a range in the 15 samples from 75 to 200 ppma. Phosphorus constituted less than 100 ppma and beryllium less than 20 ppma in all samples. Quantitative analyses were also made for the following elements: lithium (average value, 13 ppma; range, 1.9–31), sodium (120; 16–530), potassium (100; 5–880), titanium (1150; 12–3700), vanadium (16; 9–26), manganese (720; 67–3400), strontium (1.8; <0.1–7), yttrium (0.8; <0.1–2.7), zirconium (2.7; 0.4–8.7) and chromium (<130). In addition, chlorine was detected in two of the samples, at the 40 ppma level in #24 and 80 ppma in #25 (detection limit ~ 20 ppma).

Discussion

Table 1 and Figure 2 summarize the data for the 15 chondrodites analyzed for boron. The number of atoms per formula unit, normalized to 2(Si + B), was calculated for each sample using the IMMA results for boron and the electron microprobe analyses of Jones *et al* (1969, Table 1). The +4 charge on titanium is assumed to be compensated by oxygen substituting for fluorine and hydroxyl according to the formula:



Hydroxyl contents were calculated in the manner suggested by Jones *et al* (1969, p. 394), assuming that the tetrahedral sites are filled with silicon and that each specimen is charge-balanced:

$$OH = 0.4M_{Ti} - 2Ti - F.$$

However, since B^{3+} replaces Si^{4+} , there must be either monovalent cations substituting for divalent

TABLE 1. Boron Content and Revised Cell Contents for 15 Chondrodites^a

Specimen number	S_t	Boron (ppma)	Number of atoms per formula unit, normalized to 2(Si + B)										Stoic. ^c
			Mg	Fe	Mn	Ca	Zn	Si	B	Ti	F	OH ^b	
1	1.002	1865	4.89	.026	.002	.000	.000	1.969	.031	.000	1.03	0.93	1.018
2	1.009	425	4.89	.033	.008	.001	.002	1.993	.007	.001	1.25	0.72	1.013
5	0.975	1530	4.98	.064	.003	.002	.004	1.974	.026	.009	1.51	0.49	0.988
6	1.012	80	4.85	.063	.008	.002	.003	1.999	.001	.010	1.23	0.73	1.012
9	0.928	7110	4.90	.138	.005	.002	.001	1.880	.120	.016	1.88	0.11	0.987
10	0.953	6275	4.81	.137	.006	.002	.000	1.894	.106	.014	1.69	0.26	1.007
11	0.996	310	4.84	.141	.012	.001	.000	1.995	.005	.010	1.44	0.54	0.998
14	0.985	1380	4.79	.153	.007	.001	.001	1.977	.023	.071	1.27	0.59	0.996
15	0.986	1180	4.81	.156	.010	.001	.000	1.980	.020	.044	1.45	0.47	0.996
16	0.994	990	4.76	.159	.006	.002	.003	1.983	.017	.058	1.48	0.40	1.002
22	0.995	640	4.72	.237	.015	.000	.001	1.989	.011	.023	0.98	0.98	1.001
23	0.991	100	4.69	.251	.081	.004	.008	1.998	.002	.009	1.31	0.68	0.992
24	0.998	830	4.66	.275	.015	.000	.001	1.986	.014	.020	1.06	0.89	1.005
25	0.966	1790	4.73	.317	.014	.003	.003	1.969	.031	.027	1.47	0.51	0.981
30	0.986	135	4.61	.353	.089	.005	.010	1.998	.002	.001	1.38	0.65	0.989

^a Specimen numbers and data for $S_t = 2.5 \text{ Si}/M_{\text{Ti}}$ and for Mg, Fe, Mn, Ca, Zn, Si, Ti and F from Jones et al (1969, Table 1 -- NAPS Document #00345). The number of oxygens per formula unit is $(8 + 2x)$ where x is the number of Ti atoms.

^b Hydroxyl content calculated using the method of Jones et al (1969, p. 394): $\text{OH} = 0.4M_{\text{Ti}} - 2\text{Ti} - \text{F}$.

^c Stoichiometric ratio = $2.5(\text{Si} + \text{B})/M_{\text{Ti}}$.

metals in the M sites or further hydroxyl substitution for oxygen in the hexagonal closest-packed anion array. The anion substitution is presumedly the correct one, because the analyses of these chondrodites referred to above showed only trace concentrations of monovalent cations (Li, Na, K). In any case the effect of these would be offset by the trace amounts of trivalent cations (Al, Cr) also recorded in the spectra.

To our knowledge this is the only reported occurrence of boron substitution for silicon in orthosilicates. The levels of boron observed in one norbergite (Jones' #4) and five humites (#3, 4, 5, 7, 9) were less than 400 ppma, although two (#3, 4) of the five clinohumites we analyzed contained 800 and 950 ppma, respectively.

This study also serves to indicate the absolute analytical accuracy achievable with the electron microprobe using the proper standards and analytical techniques. Assuming that the tetrahedral sites in these minerals are completely filled with silicon plus

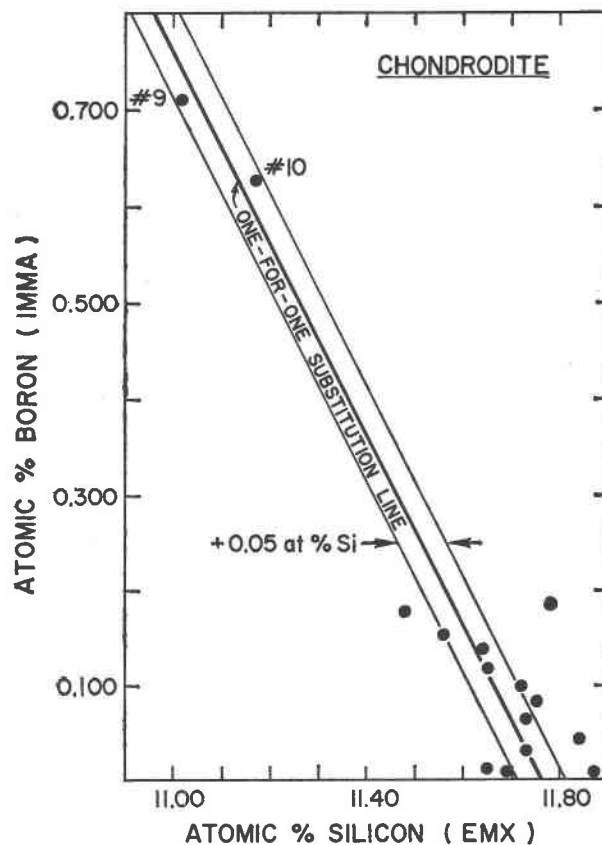


FIG. 2. Atomic percent boron determined by IMMA plotted against atomic percent silicon determined by electron microprobe (Jones et al, 1969) for 15 chondrodites. The theoretical one-for-one substitution line is shown with parallel lines marking ± 0.05 atomic percent silicon.

boron (*i.e.*, $\text{Si} + \text{B} = 2.000$), the errors in the silicon determinations average approximately 0.5 percent of the silicon abundance.

Acknowledgments

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