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A Note on the Chemical Composition of the Silicoborate Garrelsite

By *Horstpeter H. Ulbrich* (Basel) *) and *Subrata Ghose* (Seattle) **)

With 1 figure and 1 table in the text

Abstract

The silicoborate garrelsite is a rare barium mineral found as authigenic crystals in dolomitic shales in the Green River Formation of Utah and elsewhere. The composition reported originally was given as $(\text{Ba}_{0.65}\text{Ca}_{0.29}\text{Mg}_{0.06})_4\text{H}_6\text{Si}_2\text{B}_6\text{O}_{20}$ and is based on bulk chemical analysis. Work performed during the structure determination of garrelsite indicated lack of Ca and Mg and the presence of Na and suggested $\text{NaBa}_3\text{Si}_2\text{B}_7\text{O}_{16}(\text{OH})_4$ as the true formula, later confirmed by electron probe spot analysis.

Introduction

The silicoborate garrelsite was first described by MILTON et al. (1955) as colorless to brown monoclinic bipyramids occurring as authigenic minerals in dolomitic shales – as well as a fissure filling phase (MILTON and EUGSTER, 1959) – from the Green River Formation of Utah, USA. It has also been reported from the Kramer Borate District in California (MORGAN and ERD, 1969). For details on paragenesis and morphology see MILTON and PABST (1973). The formula of garrelsite is based on bulk chemical analysis (table 1) and is given (MILTON et al., 1955) as: $(\text{Ba}_{0.65}\text{Ca}_{0.29}\text{Mg}_{0.06})_4\text{H}_6\text{Si}_2\text{B}_6\text{O}_{20}$. It has been rewritten as $(\text{Ba}, \text{Ca}, \text{Mg})_4\text{B}_4(\text{SiO}_4)_2(\text{BO}_3\text{OH})_2(\text{OH})_4$ (CHRIST, 1959) to compare it with the structural formulae of datolite and bakerite. During the course of a crystal structure analysis of garrelsite, it was suspected that garrelsite does not contain Ca or Mg, but Na instead. A reexamination of the chemical composition of garrelsite was therefore undertaken.

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Table 1. *Chemical composition of garrelsite*

	a)	b)	c)	d)
BaO	46.1		51.64	51.52 ± 0.30
CaO	7.7			
MgO	1.2			
Na ₂ O		3.5	3.48	3.33 ± 0.20
B ₂ O ₃	24.0		27.36	
SiO ₂	14.6		13.48	13.81 ± 0.30
H ₂ O	5.9		4.04	

- a) Bulk analysis (B. Ingram, 1955, U.S. Geol. Survey). Formula:
 $(Ba_{0.65} Ca_{0.298} Mg_{0.065})_4 B_{5.96} Si_{2.1} H_{5.6} O_{20}$.
- b) New Na-analysis on clear garrelsite crystals (B. Ingram, 1972).
- c) Weight percentages based on $Na Ba_3 Si_2 B_7 O_{16} (OH)_4$.
- d) Partial analysis, electron microprobe. Errors are estimated from different analytical values obtained from several crystals, uncertainties in corrections and the spread of points in the working curve.

Analytical Results and Discussion

Several brown semi-transparent grains of the Green River garrelsite were mounted as a polished section and analyzed with the ARL probe at Berkeley's Department of Geology. Excitation voltage was 15 kv, sample currents around 0.02–0.05 microamps (the lower values for Na analysis), spot size between 2–4 microns. Previous chemical and structural information indicated that the following elements had to be analyzed: Si, Ba, Na, K, Mg, Ca, Sr, Fe. All grains are crowded with inclusions. The inclusion-free parts of the crystals were very stable under beam influence, and counts derived from these areas showed only background response to Ca, Mg, K, Fe and Sr. On the other hand, parts with inclusions proved to be highly inhomogeneous and in some cases up to a few percent of CaO and MgO were detected. This explains the high Ca- and Mg-content in the bulk chemical analysis of garrelsite. Quartz, andalusite, synthetic Mg-Al spinel, NiO, wüstite and metallic Co were used as background standards, while the standards for the different elements included the following: Tiburon albite (100% albite, mean atomic number Z = 10.7), celsian ($BaAl_2Si_2O_8$, Z = 27.2), sanbornite ($Ba_2Si_4O_{10}$, Z = 33.3), gillespite ($FeBaSi_4O_{10}$, Z = 25.8), cymrite ($BaAl_2Si_2O_8 \cdot H_2O$, Z = 24.8), benitoite ($BaTiSi_3O_9$, Z = 26.7), and several garnets, olivines, K-feldspars and a synthetic Sr-anorthite. Instrumental setting was chosen to minimize dead time effects.

For analytical purposes, Ba and Si counts in standards were corrected for background, and then divided by the beam current. The factor so computed is represented for the different standards as a function of oxide weight percentage in fig. 1. The working curves thus obtained are satisfactory and can be used as such for BaO and SiO₂ determinations in garrelsite, without further

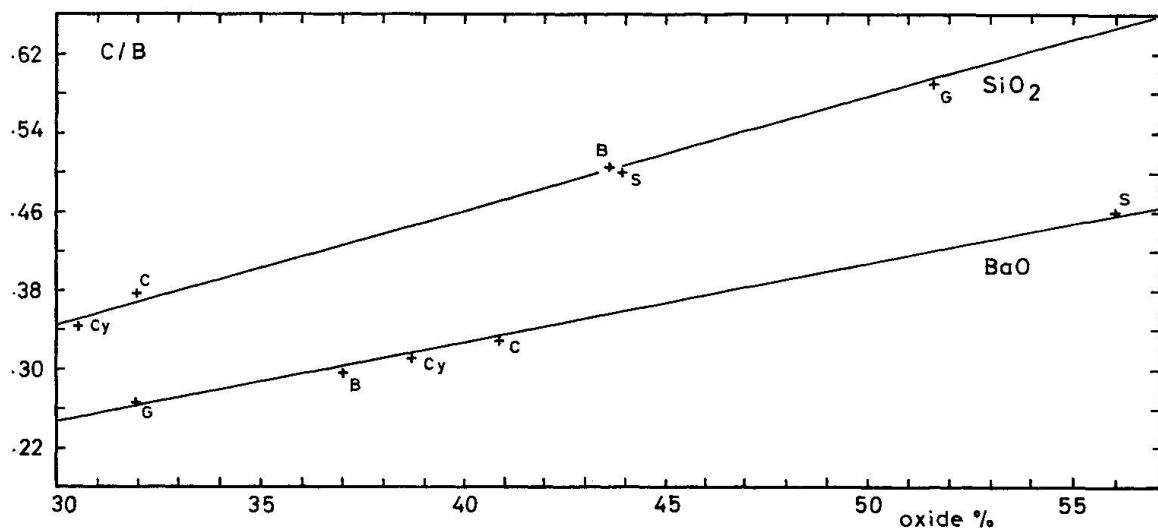


Fig. 1. Working curves for BaO and SiO₂. Plot of counts/beam current (C/B) vs. oxide weight percent of standards. C: celsian, Cy: cymrite, B: benitoite, G: gillespite, S: sanbornite.

corrections¹). Values obtained for garrelsite were: 51.52% BaO and 13.81% SiO₂.

The average, drift-corrected Na₂O content for garrelsite obtained from several runs is 2.42%, with Tiburon albite as standard. Corrections were calculated using the Bence-Albee scheme (BENCE and ALBEE, 1968), with values taken from ALBEE and RAY (1970). The β -coefficients for Na in garrelsite and albite are, respectively, 1.6966 and 1.2313, so that the correction factor is 1.38 (Evans, pers. comm., 1973). From here, the corrected value for garrelsite is Na₂O: 3.33%, close to a new wet analysis performed by B. Ingram (1972) (table 1).

Structural considerations (GHOSE and ULBRICH, 1973) suggested for garrelsite the formula NaBa₃Si₂B₇O₁₆(OH)₄, and it is seen that the corresponding weight percentages for Si, Ba and Na agree rather closely with the ones derived from probe analysis (table 1).

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¹) An average conversion factor, representing the slope of the line in fig. 1, can be computed as $A = ((C_i/B_i))/n$, where B_i = counts/beam current, C_i = oxide weight % of standard i, and n = number of standards used in the working curve.

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