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Gamagarite: a re-examination and comparison with brackebuschite-like minerals

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Abstract

Gamagarite from Postmasburg district, Cape Province, Republic of South Africa, is re-examined using analytical chemical, infrared spectra, and X-ray diffraction techniques. The data indicate that gamagarite is isostructural with brackebuschite; space group is $P2_1/m$ (assumed center of symmetry) with unit cell constants a = 9.15(1), b = 6.17(1), c = 7.88(1)Å, β = 112.7(2)°. Infrared spectra indicate that strongly hydrogen-bonded OH^- is the dominant hydrogen-bearing species in both gamagarite and brackebuschite. Consequently, with a reevaluation of previously published structure data, our interpretation prefers the brackebuschite-type structure as a partially acid vanadate (arsenate and phosphate) containing HVO_4^{2-}-type units rather than as a hydrated vanadate containing structural water, as previously described. However, there are uncertainties with the assignment of Mn oxidation state.

Introduction

Gamagarite was originally described by de Villiers (1943) from the Postmasburg district, Cape Province, Republic of South Africa, which remains the only known locality. Its crystallography was described in morphological terms by de Villiers, who noted that study by X-ray techniques would be necessary to establish the true composition of gamagarite and validate a suggested analogy to brackebuschite. The present study was undertaken to obtain such data and examine the relationship to brackebuschite.

Experimental technique

Crystals of type gamagarite (NMNH 105142) were analyzed using an ARL-SEMQ electron microprobe operating at 15 kV and 0.025 μA sample current (on brass). The compound standards used were synthetic V_2O_3 (V), barite (Ba), manganite (Mn), and hornblende (Fe,Al,Ca,Mg). The data were corrected using a modified version of MAGIC-4 (ZAF correction) from the Geophysical Laboratory of Washington. No measurement of water or hydroxyl was made, though infrared measurements were (see below). The resulting analysis is given in Table 1, together with that of de Villiers (1943) which has been recalculated.

Iron has been calculated as Fe^{3+} based on a number of considerations. Microchemical tests of the analyzed material gave a strong positive reaction for Fe^{3+} but only a weak one for Fe^{2+}. The presence of hematite and bixbyite in intimate association with and as inclusions in the gamagarite suggests a high oxidation state for the assemblage. The assignment of the oxidation state of Mn is less certain. de Villiers (1943) found adequate oxygen for approximately half of the Mn and Fe to be in the 3+ state, but this is not conclusive. Coexisting phases support the Mn^{3+} state, but many examples exist of minerals containing Fe^{3+} and Mn^{2+} (e.g., strunzite, laueite, sicklerite, and landesite). The red-brown to salmon-buff pleochroism is similar to that of piemontite in which Mn^{3+} predominates, but optical spectra have been unable to either support or discredit this interpretation.

Crystal fragments less than 200 μm on an edge were attached to glass fibers (c* ‖ to fiber axis) and examined by X-ray diffraction with Zr-filtered Mo$K\alpha$ X-radiation on a Huber

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Table 1. Chemical analyses of gamagarite

	1 Original Analysis	2 Original Recalculated[a]	3 Present Study		4 Ideal[c]	
BaO	52.4	52.4	53.5	53.5	53.35	53.38
Fe_2O_3	7.6	8.4	8.1	8.1	7.36	7.37
Al_2O_3	nil.		0.8	0.8	0.80	0.80
MnO	5.5	5.5	5.1	--	4.69	--
Mn_2O_3	--	--	--	5.7	--	5.22
V_2O_4	29.1					
V_2O_5		31.9	31.9	31.9	31.64	31.66
O	3.55					
H_2O	1.06	1.06	1.90[b]	1.91[b]	2.16	1.57
Total	99.2	99.3	101.3	101.9	100.00	100.00

a - Analysis #1 recalculated so that V and Fe are given as V_2O_5 and Fe_2O_3.

b - To obtain electroneutrality and/or no site vacancies.

c - Theoretical composition for $Ba_2(Fe^{+3}_{0.53}Mn^{+2}_{0.38}Al_{0.09})_{\Sigma 1.00}(VO_4)_2(OH_{0.68}H_2O_{0.32})$ and $Ba_2(Fe^{+3}_{0.53}Mn^{+3}_{0.38}Al_{0.09})_{\Sigma 1.00}(VO_4)_2(OH)$.

Accuracy of data for analysis of present study: ±4% of the amount present.

precession camera. The *a*- and *b*-axis nets for levels 0 to 2 were examined and measured. For comparison, crystals of brackebuschite from Sierra de Cordoba, Argentina (AMNH C78071) were examined in the same manner. Diffraction intensities for gamagarite were sharp and consistent with space group $P2_1/m$ (inferred center of symmetry). Crystal fragments were also X-rayed using Ni-filtered Cu$K\alpha$ X-radiation in a Gandolfi camera (both with and without Si as an internal standard). Gandolfi diffraction patterns were measured and indexed using the precession camera results; these data are presented in Table 2. Cell parameters were refined with a modified version of Burnham's (1962) LCLSQ and are: a = 9.15(1), b = 6.17(1), c = 7.88(1)Å, β = 112.7(2)°, V = 410.0(1.1)Å^3 (standard deviations in parenthesis refer to the last digits).

Infrared spectra were obtained with a Perkin Elmer model 180 spectrophotometer. Samples were weighed, preground under toluene, and mixed with 40 mg KBr. We used 200 μg brackebuschite and 242 μg gamagarite contained in the 5 mm diameter pressed pellets. Computer generated figures of spectra have been scaled to different effective sample concentrations for clarity of presentation. The optical spectrum, obtained on a 32 μm thick, doubly polished crystal of Gamagarite, consisted only of a broad, weak band centered at approximately 990 nm which was positioned upon the tail of an intense, high energy feature which began to rise steeply at about 650 nm. Attempts to thin the crystal to observe additional features were unsuccessful, and there was too little material available to proceed any further.

Table 2. Powder diffraction data for gamagarite

d_{obs}(Å)	d_{calc}(Å)	I/Io	hkl
4.969	4.979	10	110
4.627	4.628	10	111
3.898	3.933	5	102
3.711	3.730	10	111
3.469	3.502	10	202
3.309	3.316	100	112
3.051	3.051	80	301,(212)
2.897	2.896	10	120
2.805	2.811	80	211
2.653	2.660	10	112
2.547	2.539	10	221,(312)
2.416	2.421	10	003?
2.349	2.350	50	022
2.238	2.239	5	402
2.167	2.169	10	321
2.135	2.135	5	411
2.114	2.110	5	400
1.995	1.9787	5	031?
1.966	1.967	10	204
1.821	1.816	10	004

Infrared spectra

Infrared spectra of gamagarite and brackebuschite, compared in Figure 1, help to establish the speciation of the hydrogen. The spectrum of brackebuschite is broadly similar to that of descloizite, $PbZn(VO_4(OH)$, (Von Rahden and Dicks, 1967), especially in the region of the spectrum corresponding to motions of the VO_4 group. The peaks in our brackebuschite spectrum essentially coincide with those measured by Moenke (1966) and assigned by Farmer (1974, p. 392) to individual motions of the VO_4 unit.

The gamagarite spectrum has general similarities in the number of peaks to that of brackebuschite but is somewhat shifted in frequency and in relative intensity (Fig. 1). The most intense absorptions are at 841, 837, 770, 698, 552, 486, 433, and 379 cm^{-1}. The proposed isostructural relationship is not clear from these spectroscopic data.

The infrared spectra of both minerals contain broad, low-energy absorptions in the OH stretching region. The band centered at 3000 cm^{-1} in the gamagarite spectrum is proportionally more intense than that in the brackebuschite spectrum centered at about 2750 cm^{-1}. Broad bands in this region are found in systems containing OH groups which are strongly hydrogen bonded (short H · · · · · O bond distance), as in acid complexes.

Whereas support for an acid vanadate interpretation should be recorded in the VO_4 (or HVO_4) motions, there are few data for making comparisons. The increased number of peaks and greater overall band width, particularly towards lower frequency is similar to spectra for acid phosphates (e.g., monetite, see Farmer, 1974, p. 393).

The IR spectra provide evidence against the occurrence of molecular water in either mineral. In the 1600 cm^{-1} region, where the H_2O bending modes are active, absorption comparable in intensity to the higher energy OH stretching absorption is not observed. Instead, there is only weak, structured absorption compatible with overtone absorption of the 800 cm^{-1} region in addition to variable, weak absorption correlated in intensity with the extent to which the sample and/or pellet have been dried, and accordingly is assigned to minor amounts of absorbed water. Furthermore, no absorption features occur in the 1900–2000 nm region of the single-crystal optical spectrum where the combination bend plus stretch mode of

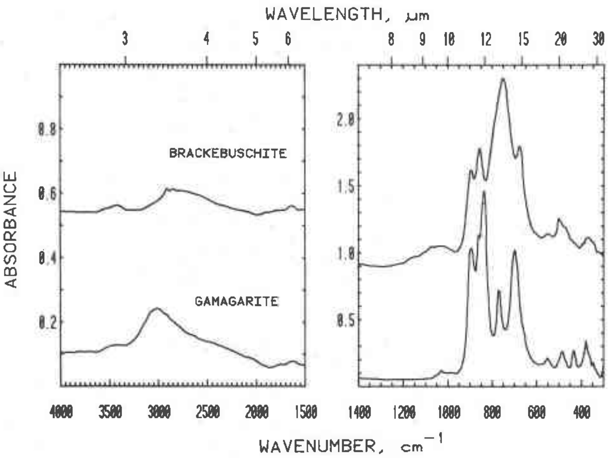

Fig. 1. Comparison of the infrared spectra of brackebuschite (top: 300 μg/40 mg KBr) and gamagarite (bottom: 220 μg/40 mg KBr). The brackebuschite spectrum has been translated vertically for clarity, and both spectra have been corrected for a sloping baseline due to mismatch of index of refraction between the sample and KBr. The OH region on the left has been vertically expanded.

molecular water occurs. In summary, the infrared data indicate that strongly hydrogen bonded OH is the dominant species in both minerals.

Crystal chemical interpretation

The similarity in chemical formulae of gamagarite and brackebuschite was noted by de Villiers (1943). Considering the similarity in cell dimensions (see Table 3) and the relative distribution of diffraction intensities between gamagarite and brackebuschite, our interpretation of isostructural crystallography is reasonable. The minerals that are presumed to have the same structure as brackebuschite are listed in Table 3 and we designate these as the brackebuschite group. The assignment of oxidation state for Mn in gamagarite is not constrained by the available chemical data. Both a large bivalent cation (Zn^{2+}) for arsenbrackebuschite (Hofmeister and Tillmanns, 1978) and small trivalent cation (Al^{3+}) for goedkenite (Moore et al., 1975) are found in the metal (M) site where Mn should reside in the gamagarite structure. Consequently, there is no apparent preference on the basis of oxidation state alone. The available structure data for arsenbrackebuschite (Hofmeister and Tillmanns, 1978) show that the octahedral coordination of this M-site is not distorted as might be expected for Zn in arsenbrackebuschite, if Jahn–Teller distortions were important, so distortional factors should not need to be considered for assigning Mn^{3+} in gamagarite.

Perhaps a more significant aspect of this analysis is the apparent structure of the brackebuschite group and the constraints it places on bonding and coordination of OH. In the refinement of the arsenbrackebuschite structure of Hofmeister and Tillmanns (1978), and by comparison, the structure of brackebuschite of Donaldson and Barnes (1955), O(w7), the oxygen site assigned for hydroxyl or water, is coordinated with a Pb cation in 11-fold coordination and two (Fe^{3+},Zn) in 6-fold coordination. We have shown that H_2O is not present in gamagarite or brackebuschite, so a reinterpretation of the existing structure is required. Carrying out a simple electrostatic bond strength summation (Pauling, 1960), for theoretical M^{2+} and M^{3+} analogs, we see the following for O(w7):

$$1 \times 0.18(\mathrm{Pb}) + 2 \times 0.33(\mathrm{M}^{2+}) = 0.84$$
$$1 \times 0.18(\mathrm{Pb}) + 2 \times 0.5(\mathrm{M}^{3+}) = 1.18$$

A value of 1.0 would satisfy hydroxyl, so this site is a good choice. However, a trivalent cation requires a whole additional hydroxyl site somewhere else in the structure. For arsenbrackebuschite (M occupancy is $Fe^{3+}_{0.65}$,$Zn_{0.35}$) the average bond sum is 1.06, but another oxygen site must be reduced by 0.35 in its bond sum. The bond

Table 3. Brackebuschite group mineral data

	a(Å)	b(Å)	c(Å)		Idealized formula	Reference
GAMAGARITE	9.15	6.17	7.88	112.7	$Ba_2(Fe^{3+},Mn)(VO_4)_2(OH,H_2O)^{\dagger}$	Present study
ARSENBRACKEBUSCHITE*	9.022	6.045	7.764	112.5	$Pb_2(Fe^{3+},Zn)(AsO_4)_2(OH,H_2O)$	Abraham et al. (1978)
BRACKEBUSCHITE*	8.88	6.15	7.68	111.8	$Pb_2(Mn,Fe)(VO_4)_2\ H_2O$	Donaldson and Barnes (1955)
GOEDKENITE	8.45	5.74	7.26	113.7	$Sr_2Al(PO_4)_2(OH)$	Moore et al. (1975)
TSUMEBITE*	8.70	5.80	7.85	111.5	$Pb_2Cu(SO_4)(PO_4)(OH)$	Nichols (1966)
AS-TSUMEBITE*+	8.85	5.92	7.84	112.6	$Pb_2Cu(SO_4)(AsO_4)(OH)$	Bideaux et al.(1966)

* - a and c interchanged here to show group similarity.

\+ - referred to as Tsumebite (As-analogue) by Bideaux et al. (1966)

† - as previously interpreted, with structural H_2O, now interpreted as OH and acid complex.

strength for the O(5) oxygen, which is coordinated only to Pb(1) and As(1) (see Hofmeister and Tillmanns, 1978) is only 1.58 for a Pauling sum which suggests that O(5) is a likely additional site for hydroxyl. Consequently, on the basis of this reasoning and our infrared spectra, an alternate interpretation to that of Hofmeister and Tillmanns (1978) of arsenbrackebuschite being a hydrated/hydroxyl arsenate is that it has only hydroxyl and partial acid arsenate character, that is having some $HAsO_4$ oxyanions and no molecular water in the structure.

Structural formula

Calculation of chemical formulae using the newly determined unit cell parameters and de Villiers' density of 4.62 g/cm^3 and the new interpretation of an acid vanadate structure bearing no molecular water yields the following:

$Ba_{1.95}(Fe^{3+}_{0.60}Mn^{2+}_{0.44})_{\Sigma 1.04}(VO_4)_{1.95}(HVO_4)_{0.05}\ (OH)_{0.63}$ for analysis 2 and
$Ba_{1.99}(Fe^{3+}_{0.58}Mn^{2+}_{0.41}Al_{0.09})_{\Sigma 1.08}(VO_4)_{1.80}(HVO_4)_{0.20}(OH)_{1.0}$ or
$Ba_{1.99}(Fe^{3+}_{0.58}Mn^{3+}_{0.41}Al_{0.09})_{\Sigma 1.08}(VO_4)_{2.0}(OH)_{1.22}$ for analysis 3.

As can be seen above, the Mn^{2+} assignment yields the better formula for analysis 3.

Conclusion

Gamagarite is now shown to be a member of the brackebuschite group. Structural water does not play a measureable role in these apparently isostructural minerals and the preferred interpretation of the group is as a vanadate (arsenate, phosphate) with partial acid character containing hydroxyl. This interpretation presents a new kind of "phosphate" compound, because other acid compounds are either anhydrous or hydrated. The general formula that would apply to this group is

$$^{viii}A^{2+}\ {}^{xi}A^{2+}[{}^{vi}M^{2+}_{X},{}^{vi}M^{3+}_{1-X}]H_{X+Y}(TO_4)_2[O_Y,(OH)_{1-Y}].$$

A detailed examination of the structures of the brackebuschite group would be useful.

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