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	Particle	
	Given Name	M.
	Suffix	
	Division	Dept. Cristallografia, Mineralogia i Dip. Minerals, Fac. Geologia
	Organization	Universitat de Barcelona
	Address	c/ Martí i Franquès, s/n, Barcelona, 08028, Spain
	Email	maitegarciavalles@ub.edu
Author	Family Name	Alfonso
	Particle	
	Given Name	P.
	Suffix	
	Division	Dept. de Enginyeria Minera i Recursos Naturals
	Organization	Universitat Politècnica de Catalunya
	Address	Avd. de les Bases de Manresa. 61-73, Manresa, 08242, Spain
	Email	
Author	Family Name	Arancibia
	Particle	
	Given Name	J. R. H.
	Suffix	
	Division	Dept. de Ingeniería Química
	Organization	Universidad Técnica de Oruro
	Address	C/ 6 de Octubre-Cochabamba, Oruro, Bolivia
	Email	
Author	Family Name	Martínez
	Particle	
	Given Name	S.
	Suffix	
	Division	Dept. Cristallografia, Mineralogia i Dip. Minerals, Fac. Geologia
	Organization	Universitat de Barcelona
	Address	c/ Martí i Franquès, s/n, Barcelona, 08028, Spain
	Email	
Author	Family Name	Parcerisa
	Particle	
	Given Name	D.

Suffix
Division Dept. de Enginyeria Minera i Recursos Naturals
Organization Universitat Politècnica de Catalunya
Address Avd. de les Bases de Manresa. 61-73, Manresa, 08242, Spain
Email

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Abstract Large volumes of borate resources exist in Bolivia, with the most important being the Rio Grande deposit, located close to the Salar of Uyuni. Here, borates occur in beds and lenses of variable thickness. A mineralogical and thermal characterization of borates from the Rio Grande was made using XRD, FTIR, SEM and DTA–TG. The deposit is mainly composed of B_2O_3 , CaO and Na_2O , with minor contents of MgO and K_2O . Some outcrops are constituted by pure ulexite aggregates ($NaCaB_5O_6(OH)_6 \cdot 5H_2O$) of fibrous morphology; in other cases, gypsum, calcite and halite also are present. The thermal decomposition of ulexite begins at 70 °C and proceeds up to ~550 °C; this decomposition is attributed to dehydration and dehydroxylation processes in three steps: at 115, 150–300 and 300–550 °C. The last weight loss of 1–5 % at 800 °C is due to the removal of Cl_2 from the decomposition of halite. DTA shows two endothermic events related to the removal of water; in the first, $NaCaB_5O_6(OH)_6 \cdot 5H_2O$ evolved from $NaCaB_5O_6(OH)_6 \cdot 3H_2O$, at 108–116 °C; in the second, $NaCaB_5O_6(OH)_6$ is formed at 180–185 °C and $NaCaB_5O_9$ (amorphous) is formed at 300–550 °C. The exothermic peak (658–720 °C) is related to the crystallization of $NaCaB_5O_9$. A small endothermic peak appears due to the halite melting. Later, another endothermic event (821–877 °C) appears, which is related to the decomposition of $NaCaB_5O_9$ into a crystalline phase of CaB_2O_4 and amorphous NaB_3O_5 . The XRD pattern evidences that, at 1050 °C, CaB_2O_4 still remains in the crystalline state.

Keywords (separated by '-') Borate minerals - Ulexite - Thermal evolution - DTA–TG - XRD - FTIR

Footnote Information

7

3 Mineralogical and thermal characterization of borate minerals 4 from Rio Grande deposit, Uyuni (Bolivia)

5 M. Garcia-Valles¹ · P. Alfonso² · J. R. H. Arancibia³ · S. Martínez¹ ·
6 D. Parcerisa²

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10 Bolivia, with the most important being the Rio Grande
11 deposit, located close to the Salar of Uyuni. Here, borates
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14 Rio Grande was made using XRD, FTIR, SEM and DTA–
15 TG. The deposit is mainly composed of B₂O₃, CaO and
16 Na₂O, with minor contents of MgO and K₂O. Some out-
17 crops are constituted by pure ulexite aggregates (NaCaB₅-
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19 gypsum, calcite and halite also are present. The thermal
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21 to ~550 °C; this decomposition is attributed to dehydra-
22 tion and dehydroxylation processes in three steps: at 115,
23 150–300 and 300–550 °C. The last weight loss of 1–5 % at
24 800 °C is due to the removal of Cl₂ from the decomposi-
25 tion of halite. DTA shows two endothermic events related
26 to the removal of water; in the first, NaCaB₅O₆(OH)₆·5H₂O
27 evolved from NaCaB₅O₆(OH)₆·3H₂O, at 108–116 °C; in
28 the second, NaCaB₅O₆(OH)₆ is formed at 180–185 °C and
29 NaCaB₅O₉ (amorphous) is formed at 300–550 °C. The
30 exothermic peak (658–720 °C) is related to the crystal-
31 lization of NaCaB₅O₉. A small endothermic peak appears

due to the halite melting. Later, another endothermic event 32
(821–877 °C) appears, which is related to the decomposi- 33
tion of NaCaB₅O₉ into a crystalline phase of CaB₂O₄ and 34
amorphous NaB₃O₅. The XRD pattern evidences that, at 35
1050 °C, CaB₂O₄ still remains in the crystalline state. 36

Keywords Borate minerals · Ulexite · Thermal 38
evolution · DTA–TG · XRD · FTIR 39

40 Introduction 40

Bolivia has large volumes of borate resources, the most 41
important being the playa -lake type deposit of the Rio 42
Grande, which has total reserves estimated at approxi- 43
mately 1.6 Mt of boron [1, 2]. This deposit comprises an 44
area of approximately 50 km² located close to the southern 45
part of the Salar of Uyuni in the contact between fluvio- 46
deltaic and lacustrine sediments in the Río Grande de Lipez 47
delta. The deposit is being exploited, and borates are 48
commercialized after a natural dehydration process, calci- 49
nation and grinding. 50

Borates are classified as critical materials by the Euro- 51
pean Union [3]. Borate minerals are the main source of 52
boron and have a multitude of industrial applications [4]. In 53
addition to classical applications of boron in glass, 54
ceramics, fertilizers, special alloys, aeronautics, nuclear, 55
military vehicles, fuels, electronics and communications, 56
new uses appear daily, such as for polymeric materials [5] 57
and for imparting halogen-free flame-retardant properties 58
to cellulose-based materials [6]. Ca-, Na-borate minerals 59
are mainly applied for making fiberglass, but are also used 60
for ceramics and ceramic glazes [7, 8]. Other applications 61
reported for Ca-rich borates include nuclear technology [9] 62
and the refractory industry. 63

A1 ✉ M. Garcia-Valles
A2 maitegarciavalles@ub.edu

A3 ¹ Dept. Cristallografia, Mineralogia i Dip. Minerals, Fac.
A4 Geologia, Universitat de Barcelona, c/ Martí i Franquès,
A5 s/n, 08028 Barcelona, Spain

A6 ² Dept. de Enginyeria Minera i Recursos Naturals, Universitat
A7 Politècnica de Catalunya, Avd. de les Bases de Manresa.
A8 61-73, 08242 Manresa, Spain

A9 ³ Dept. de Ingeniería Química, Universidad Técnica de Oruro,
A10 C/ 6 de Octubre-Cochabamba, Oruro, Bolivia

64 The industrial uses of borate minerals greatly depend
65 upon its thermal properties. Therefore, to recommend the
66 optimal application of borate minerals, knowing the ther-
67 mal properties is important.

68 Numerous studies on the thermal properties of borate
69 minerals have been reported; some of them use mixtures of
70 different borate minerals [10, 11] or a specific mineral,
71 such as ulexite [12–14].

72 In this paper, we present a mineralogical and thermal
73 characterization of borates from the Rio Grande deposit in
74 Bolivia with special emphasis on the mineralogy of the
75 different events during thermal treatment.

76 Geological setting

77 The Bolivian Altiplano is a major basin filled with thick
78 sequences of continental sediments of Cretaceous to Ter-
79 tiary age [15]. In the quaternary, endorheic basins of the
80 Altiplano were occupied by large lakes, which progres-
81 sively reduced its size due to intense evaporation and low
82 precipitation that occurred in the region during the last
83 10,000 years, giving rise to the salt lakes and salars, such
84 as Poopó, Uyuni and Coipasa, in the Central Altiplano.

85 The western and southern areas of the Altiplano were
86 strongly affected by an intense volcanic activity from the
87 Oligocene to the Quaternary. Volcanic rocks range from
88 andesites to rhyodacites with abundant ignimbrites [2],
89 which are considered to be the source of lithium and boron
90 of the salars and nearby evaporitic deposits [16].

91 More than 40 borate deposits occur in the Andean belt
92 related to salars [17]. The Rio Grande borate deposit occurs
93 in the southern region of the salar of Uyuni, the largest on

94 Earth, and is composed of deltaic-lacustrine sediments in
95 contact with the salt crust (Fig. 1) [18]. Borates precipi-
96 tated by capillary rise and subsequent evaporation of the
97 groundwater. Silty sediments occur in contact with the
98 water of the salar; groundwater rises due to porosity and
99 drops evaporate when they reach the surface and the dis-
100 solved components precipitate when they come into con-
101 tact with the water layer. The borate deposit is not in the
102 area of higher concentrations of Li, K and B, but rather
103 further to the south. Ulexite precipitation is controlled by
104 the concentrations of Ca, Na and B in the brine [2].

105 In this deposit, borates occur in beds and lenses of
106 variable thickness, from 0.5 to 5 m. In the western region
107 of the deposit, the lenses outcrop in small reliefs of several
108 cm. In the eastern area of the deposit, the bed of borates is
109 present at a depth up to 2 m below the clay level. Borate
110 minerals form brittle nodules with a cotton-ball texture
111 near the surface interbedded within the fluvial-deltaic
112 sediment layers constituted by gypsum, clays and sands.
113 The clays are mainly montmorillonite, illite and kaolinite
114 [2].

115 Materials and methods

116 Seven samples of borate minerals were obtained from
117 different outcrops in the Rio Grande deposit along 4.5 km,
118 and all the samples were collected from the natural
119 occurrence in the deposit (Fig. 1).

120 The chemical composition was determined by induc-
121 tively coupled plasma mass spectrometry (ICP-MS) using
122 an Agilent 7500ce OPTIMA 3200RL ICP-MS spectrome-
123 ter with a reaction cell.

124 The mineralogy of the natural and thermally treated
125 samples was determined by X-ray diffraction (XRD). The
126 spectra were obtained from powdered samples (particles
127 under 45 μm) in a Bragg–Brentano PANalytical X'Pert
128 Diffractometer system (graphite monochromator, automatic
129 gap, $K\alpha$ radiation of Cu at $\lambda = 1.54061 \text{ \AA}$, powered at
130 45 kV, 40 mA, scanning range 4–100° with a 0.017° 2θ step
131 scan and a 50-s measuring time). The identification and
132 semiquantitative evaluation of phases were conducted using
133 a PANalytical X'Pert HighScore software. Chemical
134 bonds in the borate structure were also characterized by
135 Fourier transform infrared spectroscopy (FTIR). Vibra-
136 tional spectra were obtained in the 400–4000 cm^{-1} range
137 using a Perkin Elmer Frontier FTIR spectrophotometer.
138 Original borates textures were observed by scanning elec-
139 tron microscopy (SEM) using a Quanta 200 FEI, XTE
140 325/D8395 environmental scanning electron microscope.

141 Thermal evolution of each mineral phase and the nature
142 and mechanisms of thermal decomposition were obtained
143 by differential thermal analysis and thermogravimetry



Fig. 1 Location of the Rio Grande borate deposit

(DTA–TG) using a Netzsch equipment (STA 409C model). Analyses were conducted under N₂ inert atmosphere at 80 ml min⁻¹ constant flow ratio, using Pt crucible, temperature range 25–1200 °C with a linear rate of temperature gradient set to 10 °C min⁻¹. According to DTA–TG results, to determine the mineral evolution with temperature, the heat treatment temperatures were established with a setting time of half an hour, and subsequent analysis by XRD was performed. The heat treatment ranged from 550 to 1050 °C.

154 Results and discussion

155 Chemical composition

The chemical composition of the Rio Grande borate deposit is presented in Table 1. The main components are B₂O₃, between 36.21 and 42.60 wt%, CaO, between 12.70 and 13.74 wt%, and Na₂O, from 7.61 to 13.04 wt%, which suggests that borate minerals constitute the main mineral. In some outcrops, the chemical composition is close to that of pure ulexite (NaCaB₅·5H₂O) with 42.95 % B₂O₃. In other cases, Na is relatively high. Other elements occur in minor amounts; for example, MgO is up to 1.5 wt%, and K₂O up to 0.67 wt%. Fe, Al, Sr and other elements occur in trace amounts.

167 Mineralogy

In accordance with the data obtained by the chemical analyses, the XRD patterns show that ulexite (NaCaB₅O₆(OH)₆·5H₂O) is the main mineral phase in the borate deposit. Among the wide range of over 160 species of borate minerals, ulexite is one of the most economically

important [19]. In some cases, it is the only mineral present. However, in most outcrops, other evaporite minerals, mainly halite (NaCl) and gypsum (CaSO₄·2H₂O), also occur. Figure 2 shows a representative XRD pattern from the Rio Grande deposit.

Ulexite occurs as crystalline aggregates with morphology of elongated fibers oriented parallel to each other along [001], greater than 100 microns in length (Fig. 3a). Equant sodium chloride crystals giving rise to dissolution phantoms are located among ulexite fibers (Fig. 3b). Gypsum also forms euhedral crystals up to several cm in size (Fig. 3c).

Infrared spectroscopy, FTIR (Fig. 4), was used to confirm the mineral phases determined by XRD. Ulexite from Rio Grande shows peaks in different spectral ranges. In general, the first bands correspond to water stretching vibrations and the other bands are simply defined as rhombohedral and tetrahedral borate bending modes. A broad band with several overlapping peaks is displayed between the 3600 and 3150 cm⁻¹ region assigned to the stretching vibration mode of the O–H group. The bands at 1667 and 1632 cm⁻¹ are assigned to the bending mode of H–O–H and free water, respectively. The asymmetric stretching of three-coordinate boron (BO₃) was observed in the range of 1479–1240 cm⁻¹. The bands between 1240 and 1155 cm⁻¹ correspond to B–O–H in plane bending modes. An asymmetric stretching mode of B–O in BO₄ was observed between 1027 and 959 cm⁻¹. The bands at 887–839 and 756 cm⁻¹ are assigned to the asymmetric and symmetric stretching of B–O in BO₄, respectively. The band at 663 cm⁻¹ is the bending to the symmetric stretching mode of three-coordinate boron. The final peaks, located at 561–546 cm⁻¹, are assigned to the bending modes of BO₄ groups [14].

207 Thermal evolution

Thermal decomposition of borates is a complex mechanism which involves dehydration, polymorphic transition and

Table 1 Chemical composition of the borates from the Rio Grande deposit

wt%	RG-1a	RG-1b	RG-2	RG-3	RG-4	RG-5	RG-7
CaO	13.38	13.74	11.82	13.83	12.90	13.59	12.70
MgO	0.67	0.42	1.46	0.13	0.69	0.94	1.08
Na ₂ O	9.71	8.36	13.04	7.61	9.95	9.33	10.90
K ₂ O	0.22	0.16	0.67	0.02	0.25	0.28	0.41
B ₂ O ₃	41.13	40.99	36.21	42.60	39.34	41.65	38.91
Traces/ppm							
Sr	151	786	230	247	441	140	149
Mn	1.51	16.6	2.23	5.90	8.74	3.17	2.40
Al	16.6	676	10.6	200	87.6	12.1	17.0
Fe	9.39	376	6.75	105	72.7	18.7	18.3
Ti	–	28.1	–	9.52	–	–	–
As	1.90	8.20	2.00	4.30	9.30	3.40	1.60

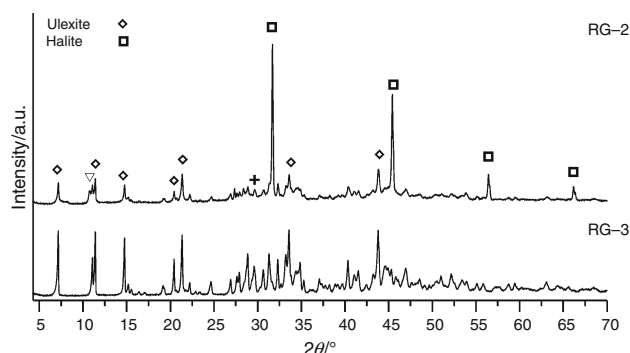


Fig. 2 XRD patterns of two representative samples. RG-2 is the halite rich sample, and RG-3 is nearly pure ulexite

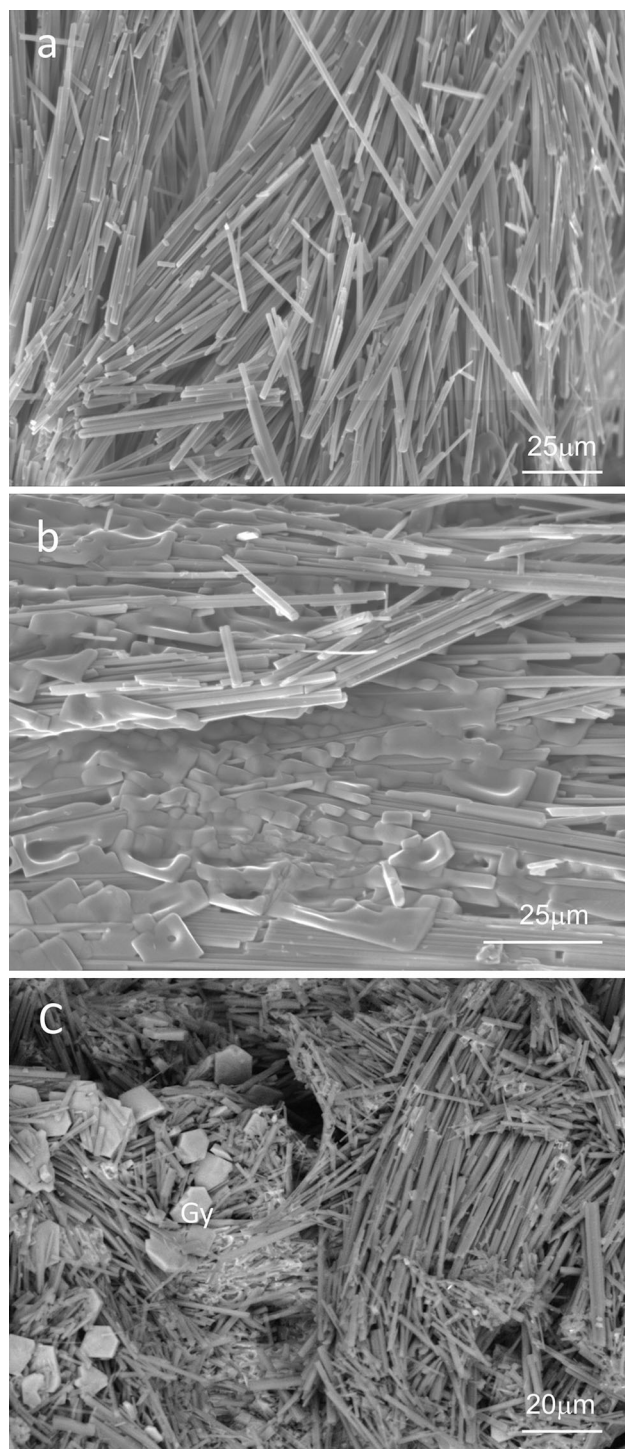


Fig. 3 SEM images of borates from Rio Grande, **a** fibrous ulexite, **b** ulexite with deliquescent halite, **c** ulexite accompanied with euhedral gypsum crystals

210 solid phase transformation [20]. In the case of ulexite, the
 211 decomposition process develops in the different stages
 212 shown in the DTA–TG curves (Figs. 5, 6). Decomposition

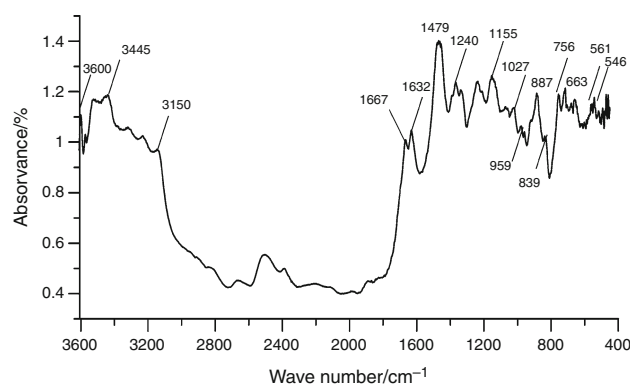


Fig. 4 FTIR spectrum of ulexite from Rio Grande salar

begins at approximately 70 °C and proceeds up to ~550 °C; these temperatures can be attributed to dehydration and dehydroxylation processes [21–23].

The TG curves indicate that these processes present a weight loss in three steps (Table 2); 3.4–5.7 wt% of mass loss is attributed to the release of two molecules of crystal water at approximately 115 °C (1). This loss is lower than the expected for the loss of two molecules of water, which is likely due to sample manipulation. The second loss, 11–14.9 wt%, between 150 and 300 °C, is attributed to the removal of the three molecules of crystal water (2), and the last, 11–16.2 wt% of mass loss is due the release of another three molecules of crystal water, between 300 and 550 °C, that corresponds to dehydroxylation of ulexite (3). Sener et al. [20] indicate that in the first stage of dehydration 1.5 of water molecules is released at approximately 118 °C. During the second stage, between 118 and 260 °C, 0.5 in 2.5 water molecules is lost in two endothermic events. Later, the OH groups are liberated as three water molecules. However, Seyhun et al. [22] attributed the loss of three water molecules to the first event and two molecules to the second event.

Figure 5 shows the TG curve of the pure ulexite sample; in this case, the global weight loss of 33.5 % corresponds to eight water molecules, similar to the results obtained in other studies of ulexite [14, 22].

All samples, with the exception of RG-3, exhibit a final weight loss of 1–5 % at 800 °C due to the removal of chlorine from the decomposition of the sodium chloride present in the samples.

The transformations were controlled by XRD analysis at temperature intervals (Fig. 5). In the DTA analysis, four endothermic and one exothermic events are observed. The first two are related to the removal of the crystal water shown in the TG measurements at the interval of 108–116 °C (1) and 180–185 °C (2) according to the following reactions:

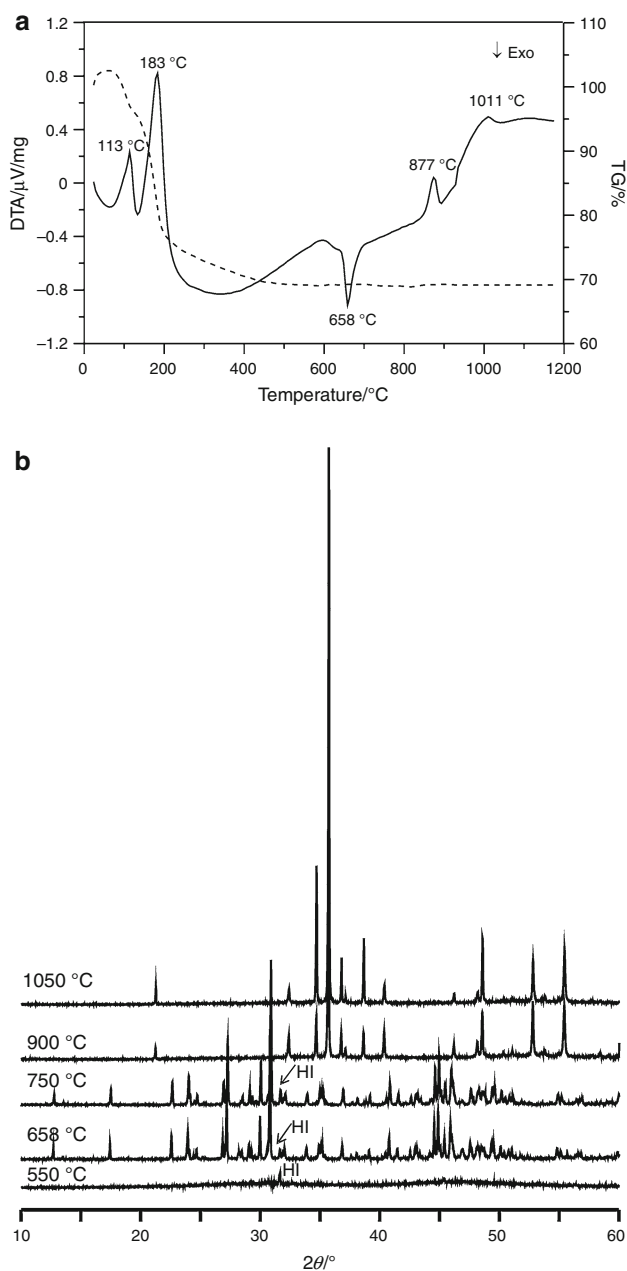
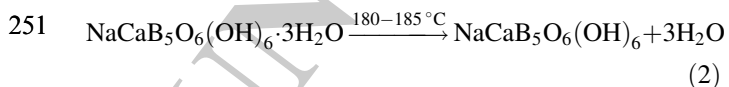
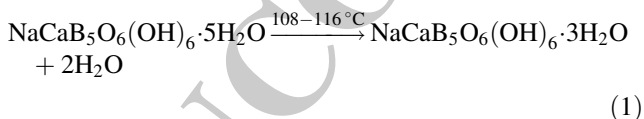


Fig. 5 Pure ulexite (RG-3) **a** DTA–TG curves and **b** sequential XRD patterns showing the new phases formed at each treatment temperature



The next reaction, corresponding to the loss of OH groups, did not explicitly show an endothermic phenomenon due to the slow process (3):

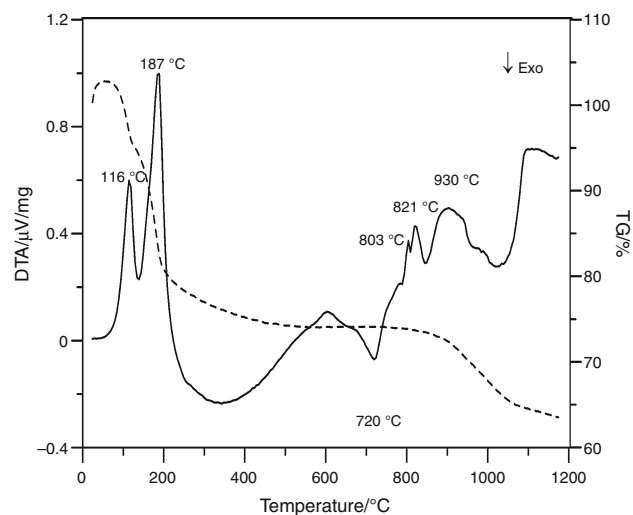
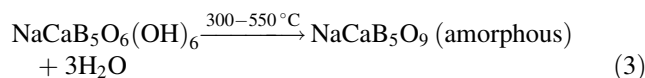


Fig. 6 DTA–TG curves corresponding to a borate sample rich in halite (RG-7)

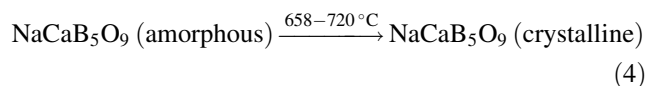
Table 2 Mass loss (wt%) for different ranges of temperature of the Rio Grande borate deposit

Sample	Range of temperature/°C		
	70–115	150–300	300–550
RG-1a	3.4	12.7	13.6
RG-1b	3.4	14.1	13.4
RG-2	3.4	11.0	11.0
RG-3	4.0	14.4	14.8
RG-4	3.7	12.1	12.8
RG-5	3.6	14.1	14.7
RG-7	5.7	14.9	16.1



Ulexite releases eight mol of water in the range of 70–550 °C, and it changes to the CaNaB_5O_9 form (amorphous borate phase). The XRD patterns (Fig. 2) show the amorphous structure of the borates at 550 °C. At this temperature, the only crystalline phase present is halite.

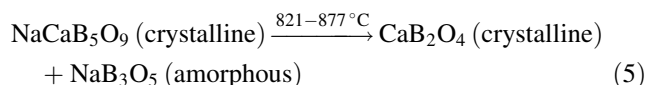
The exothermic peak at the interval of 658–720 °C is related to the crystallization process of the amorphous NaCaB_5O_9 given as follows (4):



When the sample is rich in halite, a new endothermic peak appears near 803 °C due to halite melting (Fig. 6). This temperature increases with the halite content.

The endothermic peak at the interval of 821–877 °C (Fig. 5) is related to the decomposition of NaCaB_5O_9 (5).

271 Similar values have been reported for pure ulexite samples
272 [14, 20]. The temperature of this endothermic peak
273 decreases when the halite content increases in the borate
274 sample, up to 821 °C in a sample with 23 wt% of halite
275 (Fig. 6).



277 The thermal evolution of the Rio Grande borates pro-
278 ceeds as mentioned for other ulexite occurrences [20]. On
279 the contrary, other authors, for example Stoch and
280 Waclawska [21], attributed an endothermic peak at 854 °C
281 to the melting temperature of CaB_2O_4 . The crystallization
282 of amorphous NaCaB_5O_9 directly to CaB_2O_4 and amorphous
283 NaB_3O_5 was also previously suggested.

284 The melting of the previous phases was reported at
285 862 °C [14]; Gazualla [24] determined that NaB_3O_5 melted
286 at 873 °C and CaB_2O_4 melted at 1014 °C. Nevertheless, in
287 the present work the experimental temperature reached
288 1050 °C, and the XRD patterns indicated the presence of
289 crystalline CaB_2O_4 at least up to 1050 °C (Fig. 5). In
290 addition, in the DTA diagram, obtained up to 1200 °C, any
291 endothermic peak characteristic of melting is observed.

292 The endothermic temperature related to the formation of
293 CaB_2O_4 depends on the alkalis and boron contents. The
294 temperature of NaCaB_5O_9 decomposition increases with an
295 increase in the boron ratio in tetrahedral coordination to
296 achieve a maximum value, and then, it decreases again
297 (Fig. 7). This point coincides with the boric anomaly,

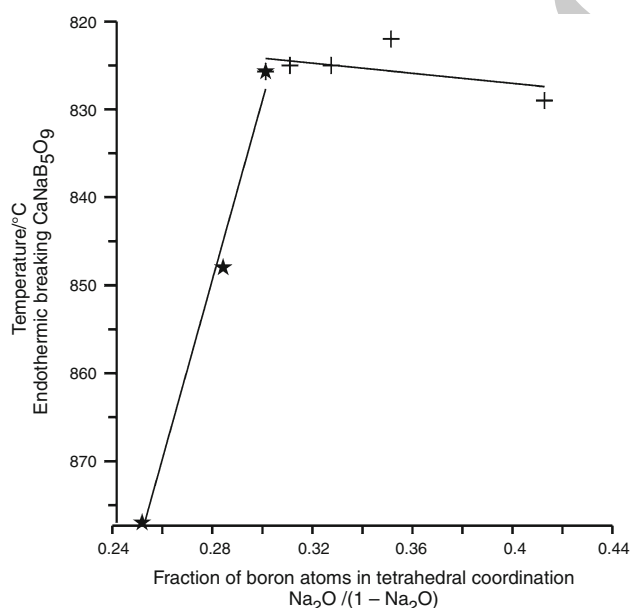


Fig. 7 Representation of the temperature of NaCaB_5O_9 decomposition as a function of the fraction of boron atoms in tetrahedral coordination

298 which occurs at approximately 30 % molar in Na_2O . This
299 reaction is produced without mass loss (Fig. 5).

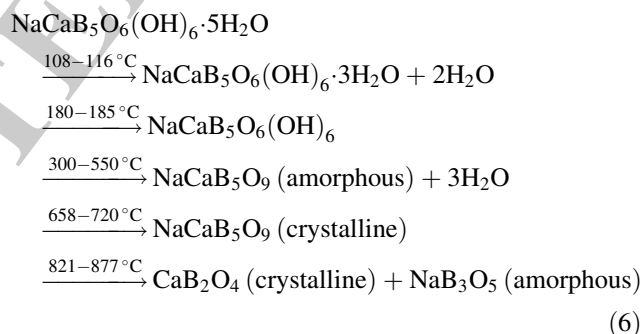
300 The crystal structure of $\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ has
301 three borate tetrahedra and two borate triangles [25]. When
302 the structure is heated, water is released and NaCaB_5O_9 is
303 formed, and the new structure is composed of two borate
304 tetrahedra and three borate triangles [26]. Finally, when the
305 structure decomposes into $\text{CaB}_2\text{O}_4 + \text{NaB}_3\text{O}_5$, in the Ca-
306 borate, crystalline, all the boron groups are in a plane tri-
307 angular coordination [27].

308 The borate crystal structure was destroyed by dehydra-
309 tion, and an amorphous structure was formed; however,
310 under heat, the crystalline structure is formed again [28].
311 Then, with the temperature increase, ulexite dehydration
312 causes changes in the stable phases and, thus, in the ratio of
313 tetrahedral and triangular boron coordination.

314 Conclusions

315 The Rio Grande borate deposit is mainly comprised of
316 ulexite, as well as occasional other evaporite minerals, such
317 as halite and minor gypsum.

318 The thermal evolution of ulexite from the studied
319 deposit is shown in the next sequence (6):



321 Regarding the heat treatment of borates, this study has
322 shown that, at 1050 °C, the CaB_2O_4 crystalline phase is
323 still present; therefore, the melting temperature will be
324 above this temperature.

325 The decomposition temperature of NaCaB_5O_9 is influ-
326 enced by the halite content. This temperature decreases
327 when the halite content increases in the sample; however,
328 the halite melting temperature rises with the halite content.

329 Halite should be removed from borates of the Rio
330 Grande deposit to improve the industrial treatment of
331 borates.

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