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2	Thermal behavior of borax Na ₂ B ₄ O ₅ (OH) ₄ ·8H ₂ O
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ABSTRACT

18	Globally, borax is one of the most important borate minerals both
19	industrially and from a technological viewpoint. However, despite its great
20	importance, few reports on the crystal structure changes of borax during the
21	heating process have been reported to date. Thus, in this study, to bridge the gap
22	in the literature, the thermal behaviors and structural features of borax were
23	investigated using thermal analysis, in-situ high-temperature synchrotron X-ray
24	diffraction, in-situ variable-temperature single-crystal X-ray diffraction, and
25	quantum chemical calculation. The DSC curve showed a large endothermic peak
26	at 349 K corresponding to the dehydration reaction of borax. The X-ray
27	diffraction peak remained almost unchanged up to 353 K. Above 363 K, the borax
28	peaks gradually became less intense until they disappeared at 403 K. The unit cell
29	volume continuously increased with increasing temperature and became constant
30	just before phase transition to tincalconite. The volumetric thermal expansion
31	coefficient between 113 K and 323 K was 7.84×10^{-5} K ⁻¹ . The <i>a</i> and <i>c</i> lattice
32	parameters exhibited a slight increase trend with increasing temperature, whereas

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33	the b lattice parameter was significantly increased. Therefore, the thermal
34	expansibilities followed the order $b/b_0 >> c/c_0 > a/a_0$. The increasing b lattice
35	parameter was closely related to the elongation of the O4…H7B hydrogen-bond
36	interaction along the <i>b</i> -axis. Na–O bond lengths were isotropically expanded with
37	increasing temperature, whereas the B-O bond lengths and angles remained
38	unchanged even after the phase transition to tincalconite. Molecular orbital
39	calculation revealed that an electron cloud shared on the two borate tetrahedra led
40	to the formation of a large electron cloud distribution over the $B_4O_5(OH)_4$ cluster.
41	The intramolecular interactions with substantial covalent character made the
42	cluster quite rigid. The existence of borate minerals containing the $B_4O_5(OH)_4$
43	clusters in their structure evidenced the presence of moderately acidic or alkaline
44	water, wherein the borate minerals were grown via the incorporation of
45	$B_4O_5(OH)_4$ clusters. Our results indicate that the connection geometry of
46	fundamental building block consisting of $B\phi_3$ triangles and $B\phi_4$ tetrahedra (ϕ : O ²⁻ ,
47	OH ⁻) can potentially be used as a palaeoenvironmental indicators.

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49 Keywords: Borax; sodium tetraborate decahydrate; dehydration; single-crystal
50 X-ray diffraction; quantum chemical calculation.

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INTRODUCTION

53 The cosmic scarcity of boron has resulted in a low boron concentration in the solar system. The boron concentration can be approximated from type CI 54 55 carbonaceous chondrite, coming out at 0.78 ppm (Shearer and Simon 2017). 56 Earth's primitive mantle was accordingly depleted in boron. The boron concentration in fresh MORB is lower than 1 ppm (Wunder et al. 2005); however, 57 58 its extrusion is accompanied by the release of boron into seawater. Thus, boron is 59 gradually concentrated in seawater, resulting in a boron concentration of 4.5 ppm (Wunder et al. 2005). Subsequently, the sediment pore water and hydrous 60 61 minerals including the seawater are carried to the continental crust, which is 62 presently a typical reservoir of boron. The current estimated average boron concentration reaches 17 ppm (Rudnick and Gao 2014). Since boron is 63 64 incompatible with many silicate minerals (Bindeman et al. 1998), it is further

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65	concentrated into residual melts during rock formation. Consequently, the boron
66	concentration in granitic pegmatites, which is the largest reservoir of boron, falls
67	within the range of 213–287 ppm (Stilling et al. 2006; Simmons et al. 2016).
68	Thereafter, weathering causes boron to dissolve into the surface water, which
69	flows out and is gathered in basins to form large non-marine evaporite boron
70	deposits (Helvaci and Palmer 2017). Currently major commercial resources of
71	borates are colemanite $CaB_3O_4(OH)_3 \cdot H_2O$, ulexite $NaCaB_5O_6(OH)_6 \cdot 5H_2O$, borax
72	$Na_2B_4O_5(OH)_4 \cdot 8H_2O$, tincalconite $Na_2B_4O_5(OH)_4 \cdot 3H_2O$, and kernite
73	$Na_2B_4O_6(OH)_2{\cdot}3H_2O.$ These are dominant in Turkey, the United States, and
74	Russia which together supply more than 80% of the world's borate (Helvaci and
75	Palmer 2017).

Borax is one of the most important borate minerals worldwide. From an
industrial and technological point of view, borax is a valuable research material,
owing to its broad application including borosilicate glasses, glass wool, ceramics,
cement enamels, and detergents (Garrett 1998). Borax is closely related to its
dehydration product tincalconite, Na₂B₄O₅(OH)₄·3H₂O. Indeed, the two minerals

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- 81 interconvert rapidly and reversibly at a relative humidity of 60% and temperatures
- 82 of 20–25 °C (Christ and Garrels 1959). In addition, the dehydration–hydration
- 83 reaction between borax and tincalconite can store and release a large amount of
- 84 latent heat as follows:

85 Na₂B₄O₅(OH)₄·8H₂O \leftrightarrow Na₂B₄O₅(OH)₄·3H₂O + 5H₂O (g), Δ H = 271 kJ/mol.

- Notably, this value is almost six times larger than the latent heat of the phase
 transition between liquid water and vapor (Rossini et al. 1952). Therefore, borax
 is also an important phase change material (PCM) that is attracting significant
 attention, owing to its high energy storage capacity (Raoux and Wuttig 2009;
 Sharma et al. 2009; Zhou et al. 2012).
- Despite its great importance, to date, there are few reports on the crystal structure changes of borax during the heating process (Waclawska 1995; Ekmekyapar et al. 1997; Dumanli et al. 2022; Nishiyasu and Kyono, 2023). Therefore, in this study, we investigated the thermal behaviors and structural features of borax using thermal analysis, *in-situ* high-temperature synchrotron

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- 96 X-ray diffraction, *in-situ* variable-temperature single-crystal X-ray diffraction,
- 97 and quantum chemical calculation.
- 98
- 99 EXPERIMENTAL METHODS

100 Commercially available borax, sodium tetraborate decahydrate 101 (guaranteed reagent grade, Fujifilm Wako Pure Chemical, Osaka, Japan), was 102 used as the starting material. First, single crystals of borax were recrystallized 103 from a saturated aqueous solution of borax at 293 K. Thermal analysis was 104 performed by differential scanning calorimetry (DSC) using a thermal analyzer 105 (X-DSC7000, Seiko Instruments, Chiba, Japan). Approximately 10 mg each of 106 borax and α -alumina reference were placed into flat-bottomed aluminum pans. 107 Each sample was first cooled to 143 K at a cooling rate of 10 K/min and 108 subsequently heated across the temperature range from 143 K to 323 K with a 109 heating rate of 10 K/min. Measurement was performed under argon gas flow at a rate of 50 mL/min. 110

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The in-situ high-temperature synchrotron powder XRD measurements

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112	were performed at BL-8B of the Photon Factory (PF), High Energy Accelerator
113	Research Organization (KEK), Japan. The incident beam was monochromatized
114	using a Si(111) double-crystal monochromator. The X-ray wavelength was
115	determined to be 0.6841(1) Å using CeO2 (NIST Standard Reference Material
116	674a), while the X-ray beam was collimated to a diameter of 0.5 mm. Data were
117	recorded on a large Debye-Scherrer camera with radius of 191.3 mm equipped
118	with a curved imaging plate (IP) detector (R-AXIS RAPID, Rigaku Corporation,
119	Tokyo, Japan). The borax powder was inserted into a Lindemann glass capillary
120	($\phi = 0.7$ mm), which end was fully opened. The capillary was then mounted and
121	aligned with a goniometer, introduced into a heating furnace, and subsequently
122	heated under an ambient atmosphere at a fixed temperature step of 10 K from 303
123	K to 473 K. After reaching the target temperature, the sample was maintained at
124	this temperature for 5 min before the measurements were collected. The actual
125	temperature was estimated in advance by direct measurement at the sample
126	position using a chromel-alumel type K thermocouple. The oscillation method
127	was used with an oscillation angle $\Delta \omega = 10^{\circ}$ and the X-ray exposure time was 3

128	min for one measurement. IP data was integrated into a two-dimensional pattern
129	using the Rigaku software (Rapid-Auto, Rigaku Corporation, Tokyo, Japan).
130	A single crystal, approximately $0.1 \times 0.1 \times 0.05$ mm in size, was selected
131	under a stereoscopic microscope (SMZ1270, Nikon Corporation, Tokyo, Japan)
132	and fixed in a 0.7 mm Lindemann glass capillary with nitrocellulose adhesive
133	dissolved in acetone to prevent dryness and degradation of the single crystal
134	during measurement. Determination of the lattice parameters and intensity data
135	collection were performed using a single-crystal diffractometer (Smart Apex II
136	Ultra Bruker AXS, Karlsruhe, Germany) equipped with a CCD detector,
137	multilayer optics, and graphite monochromated MoKa radiation ($\lambda = 0.71073$ Å)
138	generated by a rotating anode. The <i>in-situ</i> variable-temperature single-crystal
139	X-ray diffraction measurements were performed using a N2-gas-flow cryostat
140	(DX-CS190LD, Japan Thermal Engineering, Sagamihara, Japan) with a
141	temperature accuracy of \pm 1 K. The actual sample temperature was estimated in
142	advance at the sample position with a chromel-alumel thermocouple. The single
143	crystal in the capillary was mounted on the diffractometer and then cooled down

144	to 113 K in the cryostat. The measurements were performed during the heating
145	procedure from 113 K to 323 K with a 30 K step. The heating experiment of
146	borax was terminated at 323 K because of the loss of crystallinity at 333 K. The
147	initial lattice parameters and orientation matrix were determined from 36 frames
148	collected with an exposure time of 5 s. A total of 720 frames were collected with
149	an exposure time per frame of 5 s using the $\omega\text{-scan}$ mode with $\Delta\omega=0.5^{\circ}$ at three
150	different $\boldsymbol{\phi}$ positions. Intensity data were integrated and corrected for Lorentz
151	polarization effects using APEX3 software (Bruker 2018). The collected data
152	were reduced using the SAINT software package (Bruker 2017). Empirical
153	absorption correction was also applied using SADABS software (Sheldrick 2012).
154	The structure was solved by a combination of the direct method and the difference
155	Fourier methods provided by the program package SHELXS-2013/1 (Sheldrick
156	2008). The atomic coordinates and atomic displacement parameters were refined
157	by full matrix least squares methods on F^2 using the program SHELXL-2014/7
158	(Sheldrick 2008). The atomic labels were taken from the reported structure (Levy
159	and Lisensky 1978). Hydrogen positions were refined using the constraint that the

160	OH bond length is 0.95 Å, while for the $\mathrm{H}_2\mathrm{O}$ molecules, the atomic distance
161	between the H atoms was constrained to 1.50 Å. All atoms, except for the
162	hydrogen atoms, were refined on the basis of the anisotropic displacement model.
163	The data collection and crystal structure refinement details are listed in Table 1.
164	Ab initio quantum chemical calculations of the electronic structure were
165	performed with the density functional theory method (RB3LYP) with the
166	6-311+G basis set, using the quantum chemical calculation software package
167	Gaussian-16 (Frisch et al. 2016). The structural model was built based on the
168	atomic coordinates experimentally determined by the single-crystal X-ray
169	diffraction measurement at 113 K. The cell dimension of the simulation region
170	was approximately $-0.1 \le x \le 1.1$, $-0.7 \le y \le 0.7$, $0.5 \le z \le 1.1$, which includes one
171	$B_4O_5(OH)_4$ cluster constituting two BO_4 tetrahedra and two BO_3 triangles
172	surrounded by 12 Na(H ₂ O) ₆ polyhedra. The molecular orbital (MO) surfaces were
173	rendered with the GaussView molecular visualization package (Dennington et al.
174	2016) and the MOs were drawn at an interface value of 0.02 au.
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176 RESULTS AND DISCUSSION

177 Phase transition from borax to tincalconite

178	Fig. 1 shows the DSC curve of borax. The first large endothermic peak
179	started at 331 K and reached a maximum at 349 K. A previous study showed the
180	first endothermic peak as being centered at 347 K (Waclawska 1995). This peak
181	corresponds to the dehydration reaction of borax, which suggests that the phase
182	transition from borax to tincalconite occurred. The second endothermic peak,
183	which corresponds to the dehydration reaction of tincalconite, starts at 383 K and
184	reached a maximum at 408 K. We previously confirmed by TG-DTA
185	measurement that after the dehydration of tincalconite the TG curve shows a
186	continuous mass loss up to approximately 1073 K (Nishiyasu and Kyono 2023).
187	Fig. 2 illustrates the continuous variation in the XRD pattern of borax as
188	a function of temperature. The XRD pattern observed at 303 K was in excellent
189	agreement with that of borax. The peak intensities of borax remained almost
190	unchanged until 353 K. Above 363 K, the borax peaks gradually became less
191	intense until they were no longer observed at 403 K. In contrast, the peaks of

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192	tincalconite started to appear above 353 K. The tincalconite peaks remained at
193	low intensity and continued to appear up to 473 K. The difference in the
194	dehydration temperature between the XRD and DSC measurements was attributed
195	to the measurement conditions of an open versus a semi-open system.
196	

197 Thermal structural changes in borax

198 The crystal structures of borate minerals contain clusters of corner-sharing $B\phi_3$ triangles and $B\phi_4$ tetrahedra (ϕ : O^{2-} , OH^{-}) that polymerize to 199 200 form large clusters, chains, sheets, or frameworks. The borate structures are 201 therefore classified based on the connection geometry of this fundamental 202 building block (FBB) consisting of borate polyhedra. Fig. 3 shows the crystal 203 structure of borax. The FBB in the borax crystal structure is an isolated 204 $B_4O_5(OH)_4$ cluster consisting of two $BO_2(OH)$ triangles and two $BO_3(OH)$ 205 tetrahedra linked by common oxygen atoms to form a double ring with two common tetrahedra (Fig. 3a). According to the structural representation proposed 206 207 by Burns et al. (1995), the FBB is expressed as $2\triangle 2\Box:\langle \triangle 2\Box \rangle = \langle \triangle 2\Box \rangle$, where \triangle

208	and \square represent the B ϕ_3 triangle and B ϕ_4 tetrahedron, respectively. The FBBs are
209	linked by hydrogen bonding with adjacent zigzag chains of edge-sharing
210	Na(H ₂ O) ₆ octahedra running along the <i>c</i> -axis. The zigzag chains are further
211	stacked together along the a- and b-axes. Fig. 4 displays the variations in the
212	lattice parameters determined by the single-crystal X-ray measurements. The a
213	and c lattice parameters exhibited a slight increase trend with temperature,
214	whereas comparatively, the b lattice parameter was significantly increased.
215	Because sin β increases with the decrease in β from 106.870° to 106.537° (Table
216	1), the decrease in β results in an increase in the unit cell volume ($V = abc \sin \beta$).
217	Consequently, the unit cell volume continuously increased with increasing
218	temperature but became constant just before the phase transition to tincalconite.
219	Because water oxygen or hydroxyl oxygen atoms might be partially released from
220	borax at 323 K, we tried to refine the site occupancy factors of the water oxygen
221	and hydroxyl oxygen atoms in borax. As a result, however, they remained at
222	approximately ± 1.0 within the experimental error. This therefore revealed that
223	neither the water molecules nor the hydroxyl oxygen atoms were yet lost from

224	borax at this temperature. This indicates that borax loses its single crystallinity
225	immediately after dehydration. The volumetric thermal expansion coefficient
226	between 113 K and 323 K calculated by the equation $\alpha_V = \frac{1}{V_0} \cdot \frac{V_1 - V_0}{T_1 - T_0}$ was 7.84
227	$\times 10^{-5}$ K ⁻¹ . For lattice parameters <i>a</i> , <i>b</i> , and <i>c</i> , the thermal expansion coefficients
228	obtained between 113 K and 323 K were $\alpha_a = 8.04 \times 10^{-6} \text{ K}^{-1}$, $\alpha_b = 5.33 \times 10^{-5}$
229	K ⁻¹ , and $\alpha_c = 8.61 \times 10^{-6}$ K ⁻¹ , respectively. The thermal expansibilities therefore
230	followed the order $b/b_0 >> c/c_0 > a/a_0$ and the thermal expansion was the most
231	sensitive to temperature along the <i>b</i> -axis.
232	The fractional atomic coordinates and displacement parameters are listed
232	in Table S1. The variations in the selected bond lengths are given in Table S2 and
232 233 234	in Table S1. The variations in the selected bond lengths are given in Table S2 and plotted in Fig. 5. The Na–O bond lengths were isotropically expanded with
232 233 234 235	in Table S1. The variations in the selected bond lengths are given in Table S2 and plotted in Fig. 5. The Na–O bond lengths were isotropically expanded with temperature; however, the Na2–O6 and Na1–O7 bond lengths slightly decreased
232 233 234 235 236	in Table S1. The variations in the selected bond lengths are given in Table S2 and plotted in Fig. 5. The Na–O bond lengths were isotropically expanded with temperature; however, the Na2–O6 and Na1–O7 bond lengths slightly decreased at 323 K. Consequently, since the Na2–O6 and Na1–O7 bonds lie in the <i>ac</i> plane,
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232 233 234 235 236 237 238	The fractional atomic coordinates and displacement parameters are listed in Table S1. The variations in the selected bond lengths are given in Table S2 and plotted in Fig. 5. The Na–O bond lengths were isotropically expanded with temperature; however, the Na2–O6 and Na1–O7 bond lengths slightly decreased at 323 K. Consequently, since the Na2–O6 and Na1–O7 bonds lie in the <i>ac</i> plane, the <i>a</i> and <i>c</i> lattice parameters also slightly decreased at 323 K. The variation in the hydrogen bonds between the FBB and zigzag chain is shown in Fig. 5d. The

240	toward the a -, b -, and c -axis, respectively. It is apparent that the increasing b
241	lattice parameter is closely related to the elongation of the O4…H7B hydrogen
242	bond interaction along the b -axis (Fig. 5d). The most characteristic point in this
243	study is that the B-O bond lengths remained almost unchanged or even slightly
244	decreased with increasing temperature (Figs. 5b and 5c). The crystal structure of
245	lithium tetraborate (Li ₂ B ₄ O ₇) possesses the same FBB connection geometry as
246	that of borax (Krogh-Moe 1962), which is expressed as $\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$ (Fig. 3a).
247	Senyshyn et al. (2010) previously investigated the crystal structural changes of
248	$\mathrm{Li}_2\mathrm{B}_4\mathrm{O}_7$ at low temperature from 3.4 K to 268 K using the neutron powder
249	diffraction method. They reported that the variations in the B-O bond lengths in
250	the triangular and tetrahedral coordination were within 0.01 Å and 0.015 Å,
251	respectively (Senyshyn et al. 2010). Sennova et al. (2007), on the other hand,
252	investigated the crystal structural changes of $\mathrm{Li}_2\mathrm{B}_4\mathrm{O}_7$ at high temperature, in the
253	range from 293 K to 773 K, using an <i>in-situ</i> high-temperature X-ray powder
254	diffraction technique. Their results revealed that even in the temperature range of
255	480 K from 293 K to 773 K, the individual B-O bond length changes were

256	insignificantly small (≤ 0.005 Å). The study by Sennova et al. (2007) suggested
257	that the $\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$ cluster was extremely stable as an FBB even under
258	high-temperature conditions. It can be therefore concluded that the B-O bond
259	lengths in the borax FBB are essentially unaffected by temperature. In addition,
260	tincal conite possesses the exact $B_4O_5(OH)_4$ cluster as that of borax in its structure
261	(Fig. 3a) (Giacovazzo et al. 1973; Luck and Wang 2002). These B ₄ O ₅ (OH) ₄
262	clusters in tincalconite are directly linked with the surrounding NaO ₆ octahedra,
263	wherein the connection geometry of the NaO ₆ octahedra in tincalconite has a
264	three-dimensional framework with large cavities filled by the $B_4O_5(OH)_4$ clusters.
265	Notably, the B-O bond lengths and angles in the B ₄ O ₅ (OH) ₄ cluster are
266	essentially invariant before and after the phase transition of borax. The nature of a
267	rigid FBB might be effective for the rapid and reversible phase transition between
268	borax and tincal conite. After the dehydration of tincal conite, the $\mathrm{B_4O_5(OH)_4}$
269	cluster itself should remain stable until the crystallization of the anhydrous borax
270	phases: α -Na ₂ B ₄ O ₇ and γ -Na ₂ B ₄ O ₇ (Nishiyasu and Kyono 2023).
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272 Molecular orbital surface of the isolated B₄O₅(OH)₄ cluster

273	Burns (1995) evaluated cluster geometries consisting of four borate
274	polyhedra by the Hartree-Fock method using the 3-21G* basis-set. His results
275	indicated that the most stable cluster comprises double three-membered rings
276	consisting of one $B\phi_3$ triangle and two $B\phi_4$ tetrahedra expressed as $\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$.
277	The FBB of the isolated $B_4O_5(OH)_4$ cluster and its MO are shown in Fig. 6. The
278	MO is largely localized in the cluster as positive (purple) and negative (light blue)
279	electron clouds. An observed characteristic feature is that a positive electron cloud
280	is shared on the two borate tetrahedra, leading to the formation of a large electron
281	cloud distribution over O4-B1-O1-B1-O4. The shared electron cloud possesses
282	a covalent bonding nature. A negative electron cloud is also shared between two
283	O3 atoms, and thus, the electron cloud yields another covalent bond in the cluster.
284	It is important to emphasize that the intramolecular interactions with substantial
285	covalent character make the cluster quite rigid. In contrast, after the phase
286	transition, the arrangement of the NaO ₆ octahedra readily changes from the zigzag
287	chain to a three-dimensional framework with large cavities. Notably, the rigidity

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288	of the isolated B ₄ O ₅ (OH) ₄ cluster and the flexibility of the NaO ₆ octahedral
289	connection geometry can lead to a large structural modification between borax
290	and tincalconite without any significant energy requirements.

291

292 IMPLICATIONS

293 Borate minerals display extensive structural complexity resulting from 294 the great diversity of FBBs. The structural chemistry of borate is quite similar to that of silicate. In particular, the $B\phi_3$, $B\phi_4$, and $Si\phi_4$ groups (ϕ : O^{2-} , OH^{-}) have a 295 296 marked tendency to polymerize in the solid, which gives rise to the structural 297 complexity of both groups. Burns et al. (1995) examined topologically possible 298 clusters of borates and indicated that there are nine types of clusters consisting 299 solely of $B\phi_3$ triangles, 39 types of clusters consisting solely of $B\phi_4$ tetrahedra, and 108 clusters consisting of both $B\phi_3$ triangles and $B\phi_4$ tetrahedra. Most of 300 301 these clusters are not observed in borate minerals, while several types are very 302 common. Furthermore, Burns et al. (1995) described that the connection geometry 303 that includes a three-membered ring consisting of one $B\phi_3$ triangle and two $B\phi_4$

304	tetrahedra expressed as $\left< \bigtriangleup 2 \square \right>$ seems to be favored relative to the other possible
305	combinations. The $\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$ cluster is a common FBB in borate minerals,
306	e.g., in borax $Na_2B_4O_5(OH)_4 \cdot 8H_2O$ (Levy and Lisensky 1978), tincalconite
307	Na ₂ B ₄ O ₅ (OH) ₄ ·3H ₂ O (Luck and Wang 2002), hungchaoite MgB ₄ O ₅ (OH) ₄ ·7H ₂ O
308	(Wan and Ghose 1977), fedorovskite Ca ₂ Mg ₂ B ₄ O ₇ (OH) ₆ (Kobayashi et al. 2020),
309	and roweite Ca ₂ Mn ²⁺ ₂ B ₄ O ₇ (OH) ₆ (Moore and Araki 1974). Our study revealed
310	that a large electron cloud shared on the two borate tetrahedra leads to an
311	extremely rigid $\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$ cluster. Borax is quite soluble in water (4.81 g/100
312	mL 20 °C; Garrett 1998) but is readily recrystallized from saturated water. It is
313	therefore highly possible that the $\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$ cluster exists in water as it is. In
314	addition, consideration of the stability at high temperatures indicates that the
315	$\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$ cluster will be stable under hydrothermal conditions. On the other
316	hand, borax is unstable in strong acid solutions and its dissociation leads to the
317	formation of sassolite, as follows:

318 Na₂B₄O₅(OH)₄·8H₂O (borax) + 2HCl
$$\rightarrow$$
 4H₃BO₃ (sassolite) + 2NaCl + 5H₂O

319	The FBBs in sassolite comprise isolated $B\phi_3$ triangles expressed as $1\triangle$ (Gajhede
320	et al. 1986). Thus, once the $\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$ cluster is formed, it is very stable as
321	long as it is not exposed to strong acidic environments. In conclusion, the
322	existence of borate minerals containing the $\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$ cluster should evidence
323	the existence of moderately acidic or alkaline water where the borate minerals
324	were grown via the incorporation of $\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$ clusters. These types of
325	clusters consisting of $B\phi_3$ triangles and $B\phi_4$ tetrahedra in borate minerals can
326	potentially be used as a palaeoenvironmental indicator.
327	
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449		Figure captions				
450	Figure 1.	DSC curve of borax obtained using a heating rate of 10 K/min.				
451	Figure 2.	Variation in the <i>in-situ</i> high-temperature synchrotron powder X-ray				
452		diffraction pattern in the temperature range of 303–473 K.				
453	Figure 3.	(a) Fundamental building block (FBB) of an isolated $B_4O_5(OH)_4$				
454		cluster consisting of two triangular and two tetrahedral coordination				
455		units linked by common oxygen atoms to form a double ring. This				
456		FBB is expressed as $\langle \triangle 2 \Box \rangle = \langle \triangle 2 \Box \rangle$ (Burns et al., 1995). Crystal				
457		structure of borax viewed in the direction of the (b) b-axis and (c)				
458		a-axis. Sodium, boron, oxygen, and hydrogen atoms are shown as				
459		yellow, green, red, and pink spheres, respectively. Sodium atoms are				
460		coordinated by six oxygen atoms, whereas boron atoms are				
461		coordinated by four or three oxygen atoms.				
462	Figure 4.	Variations in the lattice parameters of (a) a , (b), b , (c) c , (d) β , (e) unit				
463		cell volume, and (f) expansibility of the lattice as a function of				
464		temperature.				

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465	Figure 5.	Variations in the (a) Na–O, (b) B1–O, (c) B2–O, and (d) $O \cdots H$ bond
466		lengths as a function of temperature.
467	Figure 6.	(a) Local environment around the isolated $B_4O_5(OH)_4$ cluster and (b)
468		the molecular orbitals. Sodium, boron, oxygen, and hydrogen atoms
469		are shown as yellow, green, red, and pink spheres, respectively. The
470		purple and light blue orbitals represent positive and negative
471		wavefunctions, respectively. In (b), the hydrogen atoms are not shown
472		for clarity. The orbitals are drawn at an isosurface value of 0.02 au.
473		Contours of the electron density isosurface are plotted on the <i>ac</i> plane.
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Table caption

477 Table 1. Crystal data and summary of the parameters describing the data

478 collection and refinement for borax.

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481 Figure 1. DSC curve of borax obtained using a heating rate of 10 K/min.

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484 Figure 2. Variation in the *in-situ* high-temperature synchrotron powder X-ray

diffraction pattern in the temperature range of 303–473 K.

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486

Figure 3. (a) Fundamental building block (FBB) of an isolated $B_4O_5(OH)_4$ 488 cluster consisting of two triangular and two tetrahedral coordination 489 units linked by common oxygen atoms to form a double ring. This 490 FBB is expressed as $\langle \Delta 2 \Box \rangle = \langle \Delta 2 \Box \rangle$ (Burns et al., 1995). Crystal 491 structure of borax viewed in the direction of the (b) b-axis and (c) 492 a-axis. Sodium, boron, oxygen, and hydrogen atoms are shown as 493 yellow, green, red, and pink spheres, respectively. Sodium atoms are 494 coordinated by six oxygen atoms, whereas boron atoms are 495 coordinated by four or three oxygen atoms.

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498 cell volume, and (f) expansibility of the lattice as a function of499 temperature.

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lengths as a function of temperature.

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Figure 6. (a) Local environment around the isolated B₄O₅(OH)₄ cluster and (b)
the molecular orbitals. Sodium, boron, oxygen, and hydrogen atoms
are shown as yellow, green, red, and pink spheres, respectively. The
purple and light blue orbitals represent positive and negative
wavefunctions, respectively. In (b), the hydrogen atoms are not shown
for clarity. The orbitals are drawn at an isosurface value of 0.02 au.
Contours of the electron density isosurface are plotted on the *ac* plane.

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Temperature (K)	113	143	173	203	233
			Crystal data		
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	C2/c
<i>a</i> (Å)	11.843(5)	11.853(5)	11.854(5)	11.851(5)	11.861(5)
<i>b</i> (Å)	10.535(5)	10.556(5)	10.569(5)	10.582(5)	10.605(4)
<i>c</i> (Å)	12.165(5)	12.175(5)	12.177(5)	12.176(5)	12.182(5)
β (°)	106.870(5)	106.846(5)	106.772(5)	106.735(5)	106.724(5)
$V(\text{\AA}^3)$	1452.5(11)	1458.0(11)	1460.7(11)	1462.2(11)	1467.4(11)
Z	4	4	4	4	4
Maximum observed 20 (°)	57.98	57.93	57.89	57.85	58.08
Measured reflections	4353	4374	4386	4418	4439
Unique reflections	1756	1769	1783	1783	1786
Reflections $F_{o} > 4\sigma(F_{o}), R_{int}$	1586, 0.0322	1618, 0.0340	1621, 0.0257	1608, 0.0265	1574, 0.0298
Range of h, k, l	$-15 \le h \le 13$				
	$-13 \le k \le 14$				
	$-16 \le l \le 8$				
$R1 [Fo > 4\sigma(Fo)]$	0.0334	0.0317	0.0303	0.0294	0.0339
wR2	0.1010	0.0906	0.0884	0.0891	0.0967
Goodness of fit	1.098	1.041	1.066	1.065	1.053
Number of l.s. parameters	147	147	147	147	147
Residual highest and deepest peaks $(e/Å^3)$	0.30, -0.27	0.30, -0.30	0.34, -0.25	0.32, -0.23	0.31, -0.24

512 **Table 1.** Crystal data and summary of the parameters describing the data collection and refinement for borax

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Revision 1

515 Table 1. Continued

Temperature (K)	263	293	323		
	Crystal data				
Crystal system	monoclinic	monoclinic	monoclinic		
Space group	C2/c	C2/c	C2/c		
<i>a</i> (Å)	11.868(5)	11.868(5)	11.863(6)		
<i>b</i> (Å)	10.624(4)	10.642(4)	10.653(5)		
<i>c</i> (Å)	12.195(5)	12.198(5)	12.187(6)		
β (°)	106.628(5)	106.579(5)	106.537(6)		
$V(\text{\AA}^3)$	1473.2(10)	1476.6(10)	1476.4(12)		
Z	4	4	4		
	Data collection and refinement				
Maximum observed 2θ (°)	57.97	57.91	57.95		
Measured reflections	4454	4464	4446		
Unique reflections	1793	1799	1808		
Reflections $F_{o} > 4\sigma(F_{o}), R_{int}$	1604, 0.0257	1588, 0.0284	1505, 0.0220		
Range of h, k, l	$-15 \le h \le 13$	$-15 \le h \le 13$	$-15 \le h \le 13$		
	$-13 \le k \le 14$	$-13 \le k \le 14$	$-13 \le k \le 14$		
	$-16 \le l \le 8$	$-16 \le l \le 8$	$-16 \le l \le 8$		
$R1 [Fo > 4\sigma(Fo)]$	0.0315	0.0339	0.0336		
wR2	0.0899	0.0982	0.0945		
Goodness of fit	1.065	1.071	1.062		
Number of l.s. parameters	147	147	147		
Residual highest and deepest peaks $(e/Å^3)$	0.30, -0.21	0.30, -0.23	0.28, -0.24		

