

1 **Revision 1**

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3 **Crocobelonite,  $\text{CaFe}^{3+}_2(\text{PO}_4)_2\text{O}$ , a new oxyphosphate mineral, the product of pyrolytic**  
4 **oxidation of natural phosphides**

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## Abstract

22 Crocobelonite,  $\text{CaFe}_2^{3+}(\text{PO}_4)_2\text{O}$ , is a new natural oxyphosphate discovered in the pyrometamorphic  
23 complexes of the Hatrurim Formation in Israel and Jordan. Crocobelonite-bearing assemblages  
24 contain a series of anhydrous Fe-Ni phosphates, hematite, diopside, anorthite, and phosphides –  
25 barringerite  $\text{Fe}_2\text{P}$ , transjordanite  $\text{Ni}_2\text{P}$ , murashkoite  $\text{FeP}$ , hlamishite  $\text{Ni}_5\text{P}_4$ , and negevite  $\text{NiP}_2$ .  
26 Crocobelonite forms submillimeter-sized aggregates of prismatic to acicular crystals of saffron-red  
27 to pinkish-red colour. There are two polymorphic modifications of the mineral whose structures are  
28 interrelated by the unit-cell twinning. Crocobelonite-2O is orthorhombic, *Pnma*, *a* 14.2757(1), *b*  
29 6.3832(1), *c* 7.3169(1) Å, *V* 666.76(1) Å<sup>3</sup>, *Z* = 4. This polymorphic modification is isotypic with  
30 synthetic oxyphosphates  $A\text{V}^{3+}_2(\text{PO}_4)_2\text{O}$  where *A* = Ca, Sr, Cd. The crystal structure has been refined  
31 to *R*<sub>B</sub> = 0.71% based on the powder XRD data, using the Rietveld method and the input structural  
32 model obtained from the single-crystal study. Chemical composition (electron microprobe, wt.%) is:  
33 CaO 16.03, MgO 0.56, Fe<sub>2</sub>O<sub>3</sub> 43.37, Al<sub>2</sub>O<sub>3</sub> 0.33, SiO<sub>2</sub> 0.32, P<sub>2</sub>O<sub>5</sub> 39.45, Total 100.06. The empirical  
34 formula based on O = 9 *apfu* is  $\text{Ca}_{1.02}(\text{Fe}^{3+}_{1.94}\text{Mg}_{0.05}\text{Al}_{0.02})_{2.01}(\text{P}_{1.98}\text{Si}_{0.02})_{2.00}\text{O}_{9.00}$  with *D*<sub>calc.</sub> = 3.555 g  
35 cm<sup>-3</sup>. The strongest lines of powder XRD pattern [*d*(Å)(*I*)(*hkl*)] are: 6.54(16)(200), 5.12(26)(201),  
36 3.549(100)(102), 3.200(50)(401), 2.912(19)(220), 2.869(40)(411), 2.662(21)(501). Crocobelonite-  
37 1M is monoclinic, *P2*<sub>1</sub>/*m*, *a* 7.2447(2), *b* 6.3832(1), *c* 7.3993(2) Å, β 106.401(2)°, *V* 328.252(14) Å<sup>3</sup>,  
38 *Z* = 2. This polymorphic modification does not have direct structural analogues. Its crystal structure  
39 has been solved and refined based on the single-crystal data to *R*<sub>1</sub> = 1.81%. Chemical composition  
40 is: CaO 15.56, MgO 0.16, NiO 0.78, Fe<sub>2</sub>O<sub>3</sub> 41.28, Al<sub>2</sub>O<sub>3</sub> 0.45, V<sub>2</sub>O<sub>3</sub> 0.42, Cr<sub>2</sub>O<sub>3</sub> 0.23, TiO<sub>2</sub> 0.79,  
41 P<sub>2</sub>O<sub>5</sub> 39.94, Total 99.61, corresponding to the empirical formula (O = 9 *apfu*)  
42  $\text{Ca}_{0.99}(\text{Fe}^{3+}_{1.85}\text{Ni}_{0.04}\text{Ti}_{0.04}\text{Al}_{0.03}\text{V}^{3+}_{0.02}\text{Cr}_{0.01}\text{Mg}_{0.01})_{2.00}\text{P}_{2.01}\text{O}_{9.00}$  with *D*<sub>calc.</sub> = 3.604 g cm<sup>-3</sup>. The  
43 strongest lines of powder XRD pattern [*d*(Å)(*I*)(*hkl*)] are: 6.98(17)(100), 4.40(22)(101),  
44 3.547(100)(-201), 3.485(21)(200), 3.195(50)(020), 2.855(38)(102), 2.389(33)(-122). Crocobelonite

45 represents a specific novel type of phosphate mineralization formed by oxidation of phosphide  
46 minerals at temperatures higher than 1000 °C and near-atmospheric pressure (pyrolytic oxidation).

47

48 **Keywords:** phosphate, oxyphosphate, oxophosphate, phosphide, pyrolytic oxidation, crystal  
49 structure, new mineral, pyrometamorphism, Dead Sea, Middle East, Hatrurim Formation

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## Introduction

53 Since the discovery of combusted sedimentary beds in the Judean Desert (Picard 1931) and the  
54 recognition of similar rocks elsewhere in Israel, Palestinian Authority and Jordan (Bentor et al. 1963;  
55 Gross 1977; Khoury and Nassir 1982a,b; Burg et al. 1992), pyrometamorphic complex known as the  
56 Hatrurim Formation or the Mottled Zone (Fig. 1) attracts substantial mineralogical interest. A  
57 combination of high-temperature combustion processes, intense hydrothermal activity and  
58 weathering in a desert climate have lead to the emergence of dozens of exotic mineral species (e.g.,  
59 Sokol et al. 2014, 2019; Britvin et al. 2015, 2022a; Khoury 2020). As an example, the anomalous  
60 chromium mineralization is represented by a suite of Cr<sup>3+</sup> species, such as bentorite  
61 Ca<sub>6</sub>Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O (Gross 1980) and ellinaite CaCr<sub>2</sub>O<sub>4</sub> (Sharygin et al. 2021; Galuskina et  
62 al. 2021a), along with chromates – chromatite CaCrO<sub>4</sub> (Eckhardt and Heimbach 1963), hashemite  
63 BaCrO<sub>4</sub> (Hauff et al. 1983), and siwakaite, Ca<sub>6</sub>Al<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O (Juroszek et al. 2020).  
64 Selenium is being incorporated into selenides (Se<sup>2-</sup>) (Sokol et al. 2014) and selenates (SeO<sub>4</sub><sup>2-</sup>)  
65 (Juroszek et al. 2020). Calcium, the classic lithophile element, forms sulfides – oldhamite CaS and  
66 dzierżanowskite, CaCu<sub>2</sub>S<sub>2</sub> (Galuskina et al. 2017). Other mineralogical highlights include oxides,  
67 such as grossite, CaAl<sub>4</sub>O<sub>7</sub>, discovered simultaneously in the Hatrurim Formation and within  
68 calcium-aluminium inclusions (CAI) of carbonaceous chondrites (Weber and Bischoff 1994);  
69 perovskite-supergruop minerals: vapnikite – the double perovskite CaCaUO<sub>6</sub> (Galuskin et al. 2014),  
70 shulamitite Ca<sub>3</sub>TiFe<sup>3+</sup>AlO<sub>8</sub> (Sharygin et al. 2013), cubic oxygen-deficient perovskite  
71 Ca(Ti,Si,Cr)O<sub>3-δ</sub> (Britvin et al. 2022c), and aluminate garnet priscillagrewite-(Y), (Ca<sub>2</sub>Y)Zr<sub>2</sub>(AlO<sub>4</sub>)<sub>3</sub>  
72 (Galuskina et al. 2021b).

73 Pyrometamorphic rocks of the Hatrurim Formation are enriched in phosphorus (e.g., Al-  
74 Ajarmeh and Khoury 2018), which can appear in the form of phosphides – rare minerals containing  
75 this element in a negative oxidation state (Britvin et al. 2015). To date, twelve phosphide minerals,

76 including nine new species, were recognized in Israel and Jordan. In the course of an ongoing  
77 research of phosphide assemblages, the authors of the present paper have discovered a suite of  
78 natural phosphates genetically related to phosphides (Britvin et al. 2021a). We herein introduce the  
79 reader with the most abundant representative of this mineralization – a new oxyphosphate  
80  $\text{CaFe}^{3+}_2(\text{PO}_4)_2\text{O}$ . The mineral was named crocobelonite, from Greek κρόκος (saffron) and βελόνα  
81 (needle), for the orange-red colour and prismatic to acicular habit of its crystals. Both the mineral  
82 and the name have been approved by the Commission on New Minerals, Nomenclature and  
83 Classification (CNMNC) of the International Mineralogical Association (IMA 2020-005). Since the  
84 IMA approval of crocobelonite, it was found that the mineral could form two polymorphic  
85 modifications. The originally described polymorph (IMA 2020-005) crystallizes in the orthorhombic  
86 symmetry. The subsequently discovered monoclinic dimorph was proposed by the authors and  
87 submitted for voting to CNMNC as a distinct species (IMA 2021-038). However, based on the  
88 topological similarity of the crystal structures of both polymorphs (Nickel and Grice 1998),  
89 CNMNC has decided to leave the same root name (i.e., crocobelonite) for both polymorphic  
90 modifications. According to the CNMNC decision based on voting results, the orthorhombic  
91 dimorph (IMA 2021-038) was named crocobelonite-2*O*, whereas its monoclinic counterpart has got  
92 the name crocobelonite-1*M*. According to the Strunz classification (Strunz and Nickel 2001),  
93 crocobelonite belongs to the group 8.AC - anhydrous phosphates with additional anions, and with  
94 medium-sized and large cations. Within the Dana's system of mineralogy (Gaines et al. 1997),  
95 crocobelonite is related to the group 38.05 (anhydrous phosphates, etc with miscellaneous  
96 formulae). The holotype specimens of crocobelonite-2*O* (registration number 5559/1) and  
97 crocobelonite-1*M* (5683/1) are deposited in the collections of the Fersman Mineralogical Museum of  
98 the Russian Academy of Sciences, Moscow, Russia.

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## Geological setting and occurrence

101 The outcrops of pyrometamorphic rocks belonging to the Hatrurim Formation are sporadically  
102 exposed over the area of 150×200 km<sup>2</sup> surrounding the Dead Sea basin, and to the north, along the  
103 Jordan River valley to the Jordan-Syria-Israel border junction (Fig. 1). From a tectonic point of  
104 view, this area belongs to the Dead Sea Transform fault system (Garfunkel and Ben-Avraham 1996;  
105 Ben-Avraham et al. 2008). The reviews in geology and stratigraphy of this region can be found  
106 elsewhere (Burg et al. 1992; Fleurance et al. 2013; Abzalov et al. 2015). The sediments subjected to  
107 pyrometamorphic processes were represented by chalky-marly sequences of late Cretaceous to  
108 Eocene age. A brief stratigraphic overview and relationships between the sequences in Israel and  
109 Jordan can be found in Britvin et al. (2022b). The geological dating of combusted rocks gave  
110 controversial results, from 16 Ma to 250 Ka (Gur et al. 1995; Kolodny et al., 2014); the former value  
111 is approximately coincident with the onset of tectonic activity at the Dead Sea Transform Fault. The  
112 wide range of age dating may evidence for multiple pyrometamorphic events occurred in the region.  
113 The temperatures during combustion processes could attain 1450 °C (Sharygin et al. 2016), that lead  
114 to the calcination and even fusion of sedimentary beds, with formation of varicoloured marbles,  
115 hornfels and the so-called paralava – fused counterparts of igneous rocks (Vapnik et al. 2007). There  
116 is an overall consensus that pyrometamorphic processes were driven by the combustion of organic  
117 matter, but the definition and the origin of this organic substance remains obscure, varying from  
118 bitumen (e.g., Kolodny and Gross 1974) to oil gas (methane) (Novikov et al. 2013). The possible  
119 initial event that could trigger combustion processes over such a vast area is also obscure (Britvin et  
120 al. 2021b, 2022c).

121 The known enrichment of pyrometamorphic rocks of the Mottled Zone in phosphorus can be  
122 relied upon the entrapment of underlying phosphorite beds, which are widespread in this area  
123 (Nathan et al. 1979; Abzalov et al. 2015; Khoury 2019). Phosphorite xenoliths of black colour,

124 partially assimilated by varicoloured hornfels, can be found in phosphorite and stone quarries, which  
125 tip the hills belonging to the Hatrurim Formation in the Daba-Siwaqa complex, West Jordan (Fig.  
126 2ab). A deeper metamorphic transformation of entrapped phosphorites resulted in the emergence of  
127 fine-grained fluorapatite (e.g., Al-Ajarmeh and Khoury 2018). The latter has an intense blue-green  
128 to emerald-green colour due to the trace amounts of  $\text{Cr}^{3+}$  in its composition (Fig 2c). Fluorapatite is  
129 considered a likely source of phosphorus, which was required for phosphides formation (Britvin et  
130 al. 2015, 2021a).

131 The type locality for crocobelonite-2O is a small abandoned quarry formerly operated for  
132 phosphorites, located at the Daba-Siwaqa complex in the Jizah District, Amman Governorate,  
133 Jordan ( $31^{\circ} 21' 52''$  N,  $36^{\circ} 10' 55''$  E) (Fig. 1 and 2a). In this quarry, phosphide-phosphate  
134 assemblages containing crocobelonite are comprised by diopside paralava and appear as nests and  
135 schlieren up to 30 cm in size situated in brown to red-colored hornfels (Fig. 2a). Macroscopically,  
136 the paralava nests have pale-brown colour, whereas the areas enriched in phosphates are colored in  
137 greenish-brown hues (Fig. 3a). The paralava consists of random to radial aggregates of colorless  
138 long-prismatic diopside crystals up to  $0.2 \times 3$  mm in size, cemented by late hydrothermal calcite and  
139 hydrous calcium silicates (Fig. 3b,c). Diopside composition is close to pure  $\text{CaMgSi}_2\text{O}_6$ , with Fe and  
140 Al impurities of less than 0.1 wt.%. Phosphates, including crocobelonite, form bubble-like  
141 segregations of brown color up to 1 cm size, disseminated in paralava. In thin sections, these  
142 bubbles exhibit very inhomogeneous interior (Fig 3d). They are filled with aggregates of round  
143 grains 0.05-0.5 mm in size, whose internal texture (Fig. 3e) resembles that of radial and  
144 cryptocrystalline chondrules of chondritic meteorites (e.g., Kurat 1969; Grossman et al. 2000). The  
145 droplets are composed of calcium silico-phosphate glass and unidentified anhydrous calcium silico-  
146 phosphates; the mesostasis between the droplets has the similar composition. The peripheral rims of  
147 centimeter-sized bubbles are composed of microcrystalline hematite, phosphides – murashkoite  $\text{FeP}$

148 (Britvin et al. 2019b), zuktamrurite  $\text{FeP}_2$  (Britvin et al. 2019a), barringerite  $\text{Fe}_2\text{P}$  and transjordanite  
149  $\text{Ni}_2\text{P}$  (Britvin et al. 2020a), halamishite  $\text{Ni}_5\text{P}_4$ , negevite  $\text{NiP}_2$  (Britvin et al. 2020b,c) and a variety of  
150 anhydrous phosphates (Fig. 3f), of which crocobelonite is the most abundant.

151 Crocobelonite-1M was primarily recognized in phosphide-phosphate assemblages  
152 encountered in detrital blocks of diopside paralava collected at the Halamish wadi, the Hatrurim  
153 Basin, Negev desert, Israel. The detailed description of this locality was recently reported by Britvin  
154 et al. (2022b). The specimens from the Hatrurim Basin do not contain bubble-like phosphate-  
155 phosphide aggregates, but in other terms are very similar to the samples from the Jordan locality.  
156 Subsequent investigations have revealed that both polymorphic modifications of crocobelonite occur  
157 together in the samples collected in Jordan and Israel.

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### Analytical Methods

#### *Electron microprobe analysis (EMPA) and electron backscatter diffraction (EBSD)*

160 Determinations of the chemical composition were carried out on polished and carbon-coated  
161 sections using a Hitachi S-3400N scanning electron microscope equipped with an INCA WAVE 500  
162 WDX spectrometer (20 kV, 10 nA), using the following standards ( $K\alpha$  series lines): diopside (Ca,  
163 Si), rutile (Ti), chromite (Cr), V metal (V), hematite (Fe), trevorite (Ni), gehlenite (Al), and  
164 chlorapatite (P). EBSD phase determination and mapping was performed on the same polished  
165 sections, after reactive ion etching (RIE) with  $\text{Ar}^+$  by means of an Oxford Instruments IonFab-300  
166 instrument (500 V, 2.4 mA  $\text{cm}^{-2}$  flow current). EBSD patterns were obtained using an Oxford  
167 Instruments Nordlys-HKL EBSD detector (20 kV, 1.5 nA, focused beam mode, 70° tilted stage)  
168 attached to a Hitachi S-3400N scanning electron microscope. Phase identification was carried out  
169 using the atomic coordinates obtained from X-ray structural refinements.

171



172 ***Powder X-ray diffraction (PXRD) and Rietveld refinement***

173 PXRD patterns were obtained by means of a Rigaku RAXIS Rapid II diffractometer. The instrument  
174 was equipped with a rotating anode ( $\text{CoK}\alpha$ , 40 kV, 15 mA), microfocus mirror monochromator and  
175 semi-cylindrical imaging plate detector ( $r = 127.4$  mm). The images were acquired in a Debye-  
176 Scherrer geometry. A plate-to-profile data conversion was carried out using osc2xrd software  
177 ([Britvin et al. 2017](#)). The unit-cell parameters refinement and calculation of theoretical patterns was  
178 performed with Stoe WinXPOW software (Stoe and Cie GmbH). Rietveld refinement of PXRD  
179 profile of crocobelonite-2O was carried out with Bruker TOPAS v.5.0 software (Bruker AXS).

180 ***Single-crystal X-ray diffraction (SCXRD) and crystal structures***

181 SCXRD studies were carried out for both crocobelonite polymorphs. Data collection for  
182 crocobelonite-2O was performed using a Bruker Kappa APEX DUO CCD diffractometer  
183 (microfocus tube,  $\text{MoK}\alpha$  radiation). Data collection for crocobelonite-1M was carried out with a  
184 Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer equipped with a microfocus X-ray  
185 tube ( $\text{MoK}\alpha$ ) and HyPix-6000 hybrid photon counting detector. Data processing and integration  
186 routines were completed using Rigaku Oxford Diffraction CrysAlisPro program suite ([Rigaku](#)  
187 [Oxford Diffraction 2018](#)). The crystal structures were solved and refined with the *SHELX*-2018  
188 package ([Sheldrick 2015](#)) via Olex2 graphical user interface ([Dolomanov et al. 2009](#)). The details of  
189 data collection and structure refinement for both crocobelonite polymorphs can be retrieved from  
190 crystallographic information files (CIF) in Supplementary Data. The SCXRD CIF file consists of  
191 two datablocks. The first block contains the best SCXRD refinement results obtained for  
192 crocobelonite-2O; these data were used as an input model for the Rietveld refinement of  
193 crocobelonite-2O. The third datablock contains SCXRD refinement results for crocobelonite-1M.  
194 Rietveld refinement results for crocobelonite-2O are given in the separate CIF file.

195

196 ***Raman spectroscopy***

197 Raman spectra for both polymorphic modifications of crocobelonite were obtained from the X-ray  
198 checked crystals, using a Horiba Jobin-Yvon LabRam HR800 spectrometer equipped with an Ar-ion  
199 laser (5 mW,  $\lambda = 514$  nm) and an Olympus BX41 microscope, using a 50 $\times$  confocal objective.

200

201 **Appearance and physical properties**

202 Crocobelonite occurs as irregular dense segregations up to 0.5 mm, intergrown with diopside,  
203 anorthite, hematite, phosphate-silicate glass and other phosphate minerals (Fig. 3f). Phosphides, in  
204 general murashkoite FeP, zuktamrurite FeP<sub>2</sub>, and the minerals belonging to the join barringerite  
205 Fe<sub>2</sub>P - transjordanite Ni<sub>2</sub>P, occur in the same areas. In the rarely found microcavities, crocobelonite  
206 forms prismatic to acicular crystals reaching 30 $\times$ 150  $\mu$ m in size (Fig. 4). The mineral has a saffron-  
207 red (crocoite-like) colour in dense aggregates, whereas single crystals exhibit distinct dichroism  
208 from pink-red to deep-red. Crocobelonite gives an orange strike and has a vitreous to greasy colour.  
209 It is brittle and shows a perfect cleavage in two directions (crocobelonite-2O) and in one direction  
210 (crocobelonite-1M), parallel to crystals elongation. Mohs hardness 4. The density, calculated based  
211 on the empirical formula and unit-cell parameters, is 3.555 g cm<sup>-3</sup> (2O polymorph) and 3.604 g cm<sup>-3</sup>  
212 (1M polymorph). Crocobelonite-2O and crocobelonite-1M are visually indistinguishable from each  
213 other, neither in macrosamples nor in thin sections. Moreover, they may occur in the same  $\mu$ m-sized  
214 assemblages and even to form mutual intergrowths (Fig. 5). The most reliable method to distinguish  
215 the polymorphs is the X-ray study. In polished thin sections, the 2O and 1M modifications can be  
216 distinguished using electron backscatter diffraction (EBSD) (Fig. 5). Optical properties of  
217 crocobelonite, measured in AsBr<sub>3</sub>-S immersion liquids, are provided in Table 1.

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## Chemical composition

221 Crocobelonite shows rather uniform composition; chemical zoning has never been observed. EMPA  
222 data for holotype material of both polymorphic modifications are summarized in [Table 2](#). Iron is  
223 calculated as Fe<sup>3+</sup> according to charge balance, taking into account the absence of water (Raman  
224 spectroscopy results) and crystal structure determinations which require the presence of 9 oxygen  
225 atoms per formula unit. The empirical formula of holotype crocobelonite-2*O* from Jordan  
226 (calculated on the basis of 9 O *apfu*) is Ca<sub>1.02</sub>(Fe<sup>3+</sup><sub>1.94</sub>Mg<sub>0.05</sub>Al<sub>0.02</sub>)<sub>2.01</sub>(P<sub>1.98</sub>Si<sub>0.02</sub>)<sub>2.00</sub>O<sub>9.00</sub>; holotype  
227 crocobelonite-1*M* from Israel has the empirical formula  
228 Ca<sub>0.99</sub>(Fe<sup>3+</sup><sub>1.85</sub>Ni<sub>0.04</sub>Ti<sub>0.04</sub>Al<sub>0.03</sub>V<sup>3+</sup><sub>0.02</sub>Cr<sub>0.01</sub>Mg<sub>0.01</sub>)<sub>2.00</sub>P<sub>2.01</sub>O<sub>9.00</sub>. The ideal formula of crocobelonite is  
229 CaFe<sup>3+</sup><sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>O. The comparison of compositions reveals slightly elevated contents of transition  
230 metal impurities (Ni, V, Cr, Ti) in crocobelonite-1*M* from Israel. However, the presence of these  
231 impurities can not be considered as a factor which determines stabilization of monoclinic polymorph  
232 of crocobelonite. EMPA data obtained on the intergrowths of 2*O* and 1*M* polytypes show that they  
233 are indistinguishable by the chemical composition.

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235

## Crystal structure and powder diffraction

236 X-ray single-crystal study of crocobelonite-2*O* showed that this polymorphic modification is  
237 isotopic with synthetic oxyphosphates of trivalent vanadium AV<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>, where A = Cd, Ca, Sr  
238 ([Boudin et al. 1994, 1995, 1996](#)) ([Table 3](#)). However, the attempts of obtaining high quality SCXRD  
239 data for this polymorph were unsuccessful, due to the crystal splitting manifested by the appearance  
240 of electron density phantoms ( $\geq 3 e \text{ \AA}^{-3}$ ) on the difference Fourier maps. In order to inspect the  
241 validity of SCXRD model, we have performed Rietveld refinement of powder diffraction profile of  
242 crocobelonite-2*O* ([Fig. 6](#) and CIF file in Supplementary Information). The refinement has confirmed  
243 that this is a Fe<sup>3+</sup> analogue of synthetic compound CaV<sup>3+</sup><sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub> ([Boudin et al. 1994](#)). Contrary to

244 the orthorhombic polymorph, crocobelonite-1*M* forms perfect crystals, which allowed conducting  
245 single-crystal structure solution and refinement. This polymorphic modification has no direct  
246 structural analogues, among neither natural nor synthetic phosphates. The crystal structures of both  
247 polymorphs show almost the same topology, with the same coordination of cation sites (Fig. 7,  
248 Table 4). Similar to synthetic phosphates  $AV_2O(PO_4)_2$  (Boudin et al. 1996), crystal structures of  
249 crocobelonite-2*O* and -1*M* can be described as tridimensional frameworks  $[Fe_2P_2O_9]^\infty$  composed of  
250 two kinds of structural subunits. The infinite chains (rods) of edge-sharing  $Fe(1)O_6$  octahedra,  
251 propagating along the *b*-axis in both polymorphs (Fig. 7), have the same topology as  $[TiO_6]$  rods in  
252 the rutile structure and hence are known as “rutile-like chains” (e.g., Baur 2007). The second type of  
253 subunit is comprised by the infinite chains  $[Fe(2)PO_8]$ , also running along the *b*-axis and composed  
254 of corner-sharing  $Fe(2)O_6$  octahedra and  $PO_4$  tetrahedra. Calcium atoms occupy the *b*-axis channels  
255 in the  $[Fe_2P_2O_9]$  framework. The  $P(1)O_4$  tetrahedron shares common edge with  $Fe(1)O_6$  octahedron  
256 and common corners with  $Fe(2)O_6$  octahedron. The  $P(2)O_4$  tetrahedron is corner-sharing with two  
257  $Fe(1)O_6$  octahedra,  $Fe(2)O_6$  octahedron and Ca-polyhedron (Fig. 8). The structural relationship  
258 between the polymorphs can be considered a type of “unit-cell twinning”, well known in some  
259 silicate systems (e.g., Ito 1950; Yau and Peacor 1986). The differences between the unit-cell  
260 stacking in crocobelonite-2*O* and crocobelonite-1*M* are illustrated in Fig. 9. X-ray powder  
261 diffraction data for crocobelonite polymorphs are presented in Tables 5 and 6. The low- to mid-  
262 range regions of powder XRD profiles (Fig. 10) can be used to distinguish crocobelonite-2*O* from  
263 crocobelonite-1*M*.

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265

### Raman spectroscopy

266 The Raman spectra of crocobelonite are shown in Fig. 11. The fingerprint regions (Fig. 11a) contain  
267 the groups of bands characteristic of inorganic orthophosphates (Table 7) (Nakamoto 2008, 2009).

268 The absence of bands in the O–H stretching region (3800–3000 cm<sup>-1</sup>) and bending modes of  
269 molecular H<sub>2</sub>O (1630–1670 cm<sup>-1</sup>) (Fig. 11b) evidences for the absence of water in the mineral  
270 composition, in accordance with the chemical, structural and optical data.

271

### 272 **Implications: crocobelonite and the new type of phosphate mineralization**

273 Crocobelonite, CaFe<sup>3+</sup><sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>O, is an example of natural oxyphosphate (oxophosphate) – the  
274 mineral whose chemical formula contains the so-called “additional” oxygen atom(s) (e.g.,  
275 Krivovichev 2008). Of more than 600 mineral species belonging to the phosphate class  
276 (Krivovichev 2021), oxyphosphates without other anions were, up to date, represented by three  
277 minerals: staněkite (Fe<sup>3+</sup>,Mn<sup>2+</sup>,Fe<sup>2+</sup>,Mg)<sub>2</sub>(PO<sub>4</sub>)O (Keller et al. 1997), grattarolaite Fe<sup>3+</sup><sub>3</sub>(PO<sub>4</sub>)O<sub>3</sub>  
278 (Cipriani et al. 1997), and joosteite Mn<sup>2+</sup>(Mn<sup>3+</sup>,Fe<sup>3+</sup>)(PO<sub>4</sub>)O (Keller et al. 2007). In contrast, the  
279 number of their nearest analogues – oxyarsenates (oxoarsenates) – approaches 20 minerals (Davis et  
280 al. 1965; Moore and Araki 1978; Vergasova et al. 2000; Roberts et al. 2001; Mills et al. 2010; Pekov  
281 et al. 2018, 2019a,b, 2021a,b; Shablinskii et al. 2018). The family of oxyarsenate minerals owes its  
282 diversity to a specific type of mineralization connected to arsenic-rich volcanic fumaroles, whose  
283 environment favours the formation of high-temperature anhydrous oxysalts (Pekov et al. 2018).  
284 However, the very first discoveries of natural oxyarsenates were confined to other mineralization  
285 type – the arsenide ores that underwent dry oxidation at high temperatures, the process known in ore  
286 mineral processing as pyrolytic oxidation (roasting) (e.g., Dunn and Chamberlain 1997). These  
287 assemblages represent, in fact, the combustion products of ores containing nickeline NiAs,  
288 skutterudite (Co,Ni)As<sub>3</sub>, safflorite CoAs<sub>2</sub>, and rammelsbergite NiAs<sub>2</sub>. The first described mineral in  
289 this family was aerugite Ni<sub>18.5</sub>(AsO<sub>4</sub>)<sub>2</sub>AsO<sub>8</sub> (Bergemann 1858; Davis et al. 1965; Fleet and Barbier  
290 1989), followed by a discovery of paganoite NiBiAsO<sub>5</sub> (Roberts et al. 2001). The origin of these

291 assemblages, also containing other anhydrous Ni-Co arsenates and bunsenite (natural NiO), was  
292 discussed by [Kampf et al. \(2020\)](#).

293 Taking into account the chemical proximity of arsenic and phosphorus, one could expect that  
294 the processes similar to high-temperature roasting of arsenide ores could also occur within natural  
295 phosphide assemblages. The combination of factors, which would allow the onset and maintenance  
296 of such processes, is quite exotic: it must involve the presence of phosphides (which are very rare in  
297 nature), highly oxidative conditions and high temperatures. The synthetic  $V^{3+}$  analogue of  
298 crocobelonite-2O ([Boudin et al. 1996](#)) was obtained at temperature 1100 °C - the level that can be  
299 used for the estimation of crocobelonite formation conditions. This value looks reasonable as it lies  
300 in between the assumed formation temperatures of natural Fe-Ni phosphides – 800–900 °C ([Britvin](#)  
301 [et al. 2020ab, 2021b, 2022a](#)) and the temperatures of at least 1450 °C which took place during  
302 solidification of rock-forming mineral assemblages in the Hatrurim Formation ([Sharygin et al.](#)  
303 [2016](#)). This value is considerably higher than the range of 500-750 °C assumed for the formation of  
304 volcanic fumarolic arsenates ([Pekov et al. 2018](#)). Such unusual formation environment was realized  
305 during the pyrometamorphic processes occurred in the Hatrurim Formation, that resulted in the  
306 emergence of a new type of phosphate mineralization ([Britvin et al. 2021a](#)), in which crocobelonite  
307 represents the first oxyphosphate species.

308

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317

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558 **List of figure captions**

559

560 **Figure 1.** The territory of the Middle East. The fields of the pyrometamorphic rocks belonging to  
561 the Hatrurim Formation (the Mottled Zone) are indicated by red areas and circles, with two localities  
562 of crocobelonite (the Hatrurim Basin in Israel and Daba-Siwaqa complex in Jordan). Adapted from  
563 [Britvin et al. \(2021a\)](#).

564

565 **Figure 2.** The phosphorite quarry in the Daba-Siwaqa complex – the type locality for crocobelonite-  
566 2O. (a) The overview of the outcrop containing crocobelonite. (b) The black xenolith of partially  
567 assimilated phosphorite within the olive-coloured hornfel. (3) The veinlets of bluish-green  
568 fluorapatite in a block of varicolored hornfel.

569

570 **Figure 3.** Crocobelonite in phosphate-phosphide assemblages from the phosphorite quarry at the  
571 Daba-Siwaqa complex, Jordan (the type locality). (a) The overview of a typical sample of  
572 phosphate-bearing paralava. (b) Diopside crystals filling up the paralava. Thin section, transmitted  
573 light, XPL. (c) Diopside clumps within the same paralava sample. Thin section, PPL. (d) Cross-  
574 section of a typical phosphate-phosphide bearing bubble within paralava. Red areas are  
575 crocobelonite aggregates. Thin section, scattered light. (e) Chondrule-like segregations of calcium  
576 silicophosphates (indicated as Ch within the bubble in Fig. 3d). Thin section, transmitted light (f)  
577 The detail of crocobelonite-bearing area shown in Fig. 3d. Abbreviations: Di – diopside, Ph –  
578 phosphides, Hem – hematite, Ch – hondrules, Ccb – crocobelonite.

579

580 **Figure 4.** Crocobelonite crystals in the paralava microcavities. (a) Aggregates of prismatic crystals  
581 intergrown with hematite (black) and diopside (white). (b) Prismatic crocobelonite crystal.  
582 Phosphorite quarry, Daba-Siwaqa complex, Jordan.

583

584 **Figure 5.** Two polymorphic modifications of crocobelonite in a complex phosphate assemblage.  
585 Nahal Halamish, Hatrurim Basin, Negev Desert, Israel. (a) Phosphate-bearing nest;  
586 photomicrograph of a polished section in scattered light. (b) The same field in reflected light. (c)  
587 SEM BSE image of the area. The highlighted rectangle outlines the area subjected to EBSD  
588 mapping. (d) EBSD crocobelonite phase map of an area highlighted in (c), superimposed onto BSE  
589 image. The red patches denote clinocrocobelonite; the yellow ones correspond to crocobelonite. (e)  
590 EBSD IPF (inverse pole figure) map. The different colours correspond to different orientations of  
591 crocobelonite crystals. Legend: M –crocobelonite-1M; O – crocobelonite-2O; Ald – unnamed  
592 alluaudite-group phosphate; Hm – hematite; Glass – Ca-Si-P-O glass.

593

594 **Figure 6.** Rietveld refinement plot for crocobelonite-2O.

595

596 **Figure 7.** Crystal structure of crocobelonite, in projection that emphasizes structural similarity of  
597 both polymorphs. The unit-cell axes of crocobelonite-2O are shown in blue; the axes of  
598 crocobelonite-1M are black. A three-dimensional framework composed of two types of structural  
599 subunits. The first one is represented by the infinite “rutile-like” chains (rods) of edge-sharing  
600 Fe(1)O<sub>6</sub> octahedra, propagating along the *b*-axis in both polymorphs. The second type of subunit is  
601 comprised by the infinite chains [Fe(2)PO<sub>8</sub>], also running along the *b*-axis and composed of corner-  
602 sharing Fe(2)O<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra. The rods are connected into a framework via the

603 inter-rod [FeO<sub>6</sub>] octahedra and [PO<sub>4</sub>] tetrahedra together with [CaO<sub>7</sub>] polyhedra (the latter are not  
604 shown for clarity). Legend: [FeO<sub>6</sub>] – red; [PO<sub>4</sub>] – yellow.

605

606 **Figure 8.** Fragment of crocobelonite structure showing the linkages between tetrahedral [PO<sub>4</sub>] and  
607 octahedral [FeO<sub>6</sub>].

608

609 **Figure 9.** Structural relationship between crocobelonite polymorphs. Projections onto {010}. (a)  
610 Crocobelonite-1*M*. The unit cell is highlighted by gray colour. (b) Crocobelonite-2*O*. The unit cell is  
611 highlighted by blue colour. Stacking of building sub-layers in crocobelonite-2*O* can be expressed as  
612 the “unit-cell twinning” of crocobelonite-1*M* cells, where the “twinned” 1*M* cells are related by the  
613 mirror plane {100} and half-cell translation along the *c*-axis (in orthorhombic setting). Legend:  
614 [FeO<sub>6</sub>] – red; [PO<sub>4</sub>] – yellow.

615

616 **Figure 10.** The mid-angle ranges of powder X-ray diffraction patterns of crocobelonite-1*M* and  
617 crocobelonite-2*O*. Note the substantial differences in the patterns due to the differences in the crystal  
618 structures and lattice geometries.

619

620 **Figure 11.** Raman spectra of crocobelonite polymorphs. (a) The fingerprint region. (b) The high-  
621 frequency part beyond 1500 cm<sup>-1</sup>. The absence of vibrations in the OH-stretching region indicates  
622 for the lack of hydroxyl water.

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**Table 1.** Optical properties of crocobelonite

	Crocobelonite-2 <i>O</i>	Crocobelonite-1 <i>M</i>
Colour	brownish-orange	
Pleochroism	very strong; <i>X</i> and <i>Y</i> – pale-yellow, <i>Z</i> – deep brownish-orange	
$\alpha$	1.885(5)	1.835(5)
$\beta$	1.885(5)	1.935(5)
$\gamma$	1.950(5)	1.955(5)
2 <i>V</i> (°)	~ (+)10 (meas.)	(–)44 (calc.)
Compatibility <sup>a</sup>	–0.041 (good)	–0.031 (excellent)

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<sup>a</sup> The Gladstone-Dale compatibility index ([Mandarino 1976](#)).

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**Table 2.** Chemical composition of crocobelonite

	Crocobelonite-2O <sup>a</sup>			Crocobelonite-1M <sup>b</sup>		
	Mean	Range ( <i>n</i> = 7)	2σ	Mean	Range ( <i>n</i> = 8)	2σ
CaO	16.03	15.80 – 16.26	0.18	15.56	15.42 – 15.78	0.13
MgO	0.56	0.40 – 0.77	0.13	0.16	0.00 – 0.31	0.10
NiO		b.d.l. <sup>c</sup>		0.78	0.50 – 0.97	0.17
Fe <sub>2</sub> O <sub>3</sub>	43.37	43.10 – 43.79	0.25	41.28	40.52 – 42.03	0.56
Al <sub>2</sub> O <sub>3</sub>	0.33	0.24 – 0.44	0.08	0.45	0.34 – 0.56	0.07
V <sub>2</sub> O <sub>3</sub>		b.d.l.		0.42	0.25 – 0.51	0.09
Cr <sub>2</sub> O <sub>3</sub>		b.d.l.		0.23	0.00 – 0.32	0.10
TiO <sub>2</sub>		b.d.l.		0.79	0.49 – 1.18	0.24
SiO <sub>2</sub>	0.32	0.26 – 0.38	0.04		b.d.l.	
P <sub>2</sub> O <sub>5</sub>	39.45	38.82 – 39.80	0.39	39.94	39.71 – 40.13	0.15
Total	100.06			99.61		

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<sup>a</sup> Holotype material: phosphorite quarry, Daba-Siwaqa complex, Jizah District, Amman Governorate, Jordan. <sup>b</sup> Holotype material: Halamish Wadi, Hatrurim Basin, Negev Desert, Israel. <sup>c</sup> b.d.l. – below detection limit.

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642 **Table 3.** Crystallographic data for crocobelonite polymorphs and synthetic  $\text{CaV}_2\text{O}(\text{PO}_4)_2$

	Crocobelonite-2O SCXRD	Crocobelonite-2O Rietveld refinement	Synthetic <sup>a</sup> $\text{CaV}_2\text{O}(\text{PO}_4)_2$	Crocobelonite-1M SCXRD
Chemical formula	$\text{CaFe}^{3+}_2(\text{PO}_4)_2\text{O}$	$\text{CaFe}^{3+}_2(\text{PO}_4)_2\text{O}$	$\text{CaV}^{3+}_2(\text{PO}_4)_2\text{O}$	$\text{CaFe}^{3+}_2(\text{PO}_4)_2\text{O}$
Structure type	$\text{CdV}^{3+}_2(\text{PO}_4)_2\text{O}^b$	$\text{CdV}^{3+}_2(\text{PO}_4)_2\text{O}^b$	$\text{CdV}^{3+}_2(\text{PO}_4)_2\text{O}^b$	New
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>	<i>P2<sub>1</sub>/m</i>
<i>a</i> (Å)	14.2392(8)	14.2757(1)	14.192(1)	7.2447(2) [ $\sim c(2O)$ ]
<i>b</i> (Å)	6.3632(3)	6.3832(1)	6.424(1)	6.3832(1)
<i>c</i> (Å)	7.2880(4) [ $\sim a(1M)$ ]	7.3169(1) [ $\sim a(1M)$ ]	7.317(1)	7.3993(2)
$\beta$ (°)				106.401(2)
<i>Z</i>	4	4	4	2
<i>V/Z</i> (Å <sup>3</sup> )	160.09	166.69	166.77	164.13
<i>D<sub>x</sub></i> (g cm <sup>-3</sup> ) <sup>c</sup>	3.60	3.56	3.46	3.62

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<sup>a</sup> Boudin et al. (1995). <sup>b</sup> Boudin et al. (1994). <sup>c</sup> Densities calculated for ideal formulae.

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**Table 4.** Selected bond lengths (Å) and bond-valence sums (BVS, v.u.) for crocobelonite <sup>a</sup>

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Bond	Crocobelonite-2O SCXRD	Crocobelonite-2O Rietveld refinement	Crocobelonite-1M SCXRD
Ca–O1	2.416(5) ×2	2.393(2) ×2	2.4259(14) ×2
Ca–O2	2.491(8)	2.475(3)	2.433(2)
Ca–O4	2.431(8)	2.444(3)	2.479(2)
Ca–O5	2.899(8)	2.918(4)	2.711(2)
Ca–O7	2.331(5) ×2	2.339(1) ×2	2.3452(15) ×2
< Ca–O >	2.474	2.472	2.452
BVS	1.95	1.97	1.97
Fe1–O1	1.993(5) ×2	2.033(2) ×2	2.0007(14)
Fe1–O2	2.238(8)	2.226(3)	2.262(2)
Fe1–O3	1.904(8)	1.861(4)	1.894(2)
Fe1–O4	2.068(7)	2.114(3)	2.056(2)
Fe1–O5	1.890(7)	1.870(4)	1.887(2)
< Fe1–O >	2.014	2.023	2.017
BVS	3.15	3.12	3.15
Fe2–O5	1.991(4) ×2	2.018(2) ×2	2.0341(12)
Fe2–O6	2.058(5) ×2	2.067(2) ×2	2.0525(12)
Fe2–O7	2.018(5) ×2	2.009(2) ×2	2.0233(13)
< Fe2–O >	2.022	2.031	2.037
BVS	2.95	2.88	2.83
P1–O2	1.538(9)	1.558(3)	1.531(2)
P1–O4	1.536(8)	1.535(3)	1.555(2)
P1–O7	1.534(5) ×2	1.543(1) ×2	1.5399(14) ×2
< P1–O >	1.536	1.545	1.541
BVS	4.81	4.70	4.74
P2–O1	1.525(5) ×2	1.526(2) ×2	1.5290(14) ×2
P2–O3	1.476(8)	1.547(4)	1.496(2)
P2–O6	1.556(8)	1.564(4)	1.559(2)
< P2–O >	1.521	1.541	1.528
BVS	5.03	4.75	4.92

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<sup>a</sup> Site labelling corresponds to synthetic CaV<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>O (Boudin et al. 1995). Bond-valence parameters were taken from Brese and O'Keefe (1991), assuming that Fe sites are populated with Fe<sup>3+</sup>.



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**Table 5.** X-ray powder diffraction data ( $d$  in Å) for crocobelonite-2O

$I_{\text{meas}}$	$d_{\text{meas}}$	$I_{\text{calc}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{meas}}$	$d_{\text{meas}}$	$I_{\text{calc}}$	$d_{\text{calc}}$	$hkl$
5	7.17	4	7.14	200	4	1.717	1	1.719	810
16	6.54	16	6.51	101			1	1.716	712
26	5.12	28	5.11	201			3	1.716	332
3	4.824	3	4.811	011	5	1.703	1	1.703	603
3	4.567	3	4.558	111			6	1.703	423
7	3.997	4	3.989	301	5	1.673	6	1.673	721
		4	3.989	211	2	1.662	2	1.662	531
8	3.664	10	3.658	002	2	1.646	3	1.646	613
		2	3.569	400	4	1.628	5	1.628	404
100	3.549	100	3.544	102	10	1.604	13	1.603	523
7	3.259	7	3.256	311	9	1.596	10	1.596	040
50	3.200	27	3.208	401	5	1.587	5	1.587	024
		37	3.192	020			2	1.586	630
2	3.103	2	3.098	112	1	1.565	1	1.564	703
19	2.912	14	2.914	220	1	1.557	1	1.558	820
		9	2.900	302	1	1.549	1	1.550	901
40	2.869	14	2.866	411	1	1.504	2	1.503	623
		30	2.866	121	4	1.4550	3	1.455	142
9	2.709	8	2.707	221	2	1.431	1	1.433	822
21	2.662	24	2.660	501			2	1.429	441
6	2.556	7	2.555	402	3	1.419	4	1.419	912
16	2.493	18	2.492	321	3	1.397	3	1.398	533
7	2.457	7	2.455	511			2	1.393	10.1.0
8	2.406	5	2.405	022	4	1.368	3	1.368	541
		4	2.404	103			2	1.366	732
10	2.376	3	2.379	420	2	1.330	1	1.3296	633
		8	2.372	122			1	1.3295	143
6	2.282	6	2.279	222	2	1.3244	2	1.3241	922
		1	2.278	013	1	1.2516	2	1.2507	443
20	2.264	3	2.263	601	3	1.2019	3	1.2012	932
		19	2.262	421	2	1.1858	1	1.1858	244
4	2.173	4	2.170	213			2	1.1855	10.3.0
2	2.055	2	2.055	313	1	1.1353	1	1.1356	126
6	2.040	6	2.039	230	1	1.1087	1	1.1083	10.1.4
4	2.014	5	2.014	403	1	1.0638	1	1.0639	060
3	1.995	3	1.994	602	1	1.0605	1	1.0604	11.3.2
5	1.921	3	1.920	413	1	1.0516	1	1.0519	345
		2	1.920	123			1	1.0518	13.0.2
7	1.908	6	1.908	620			1	1.0516	553
2	1.855	2	1.854	503	1	1.0190	1	1.0195	925
2	1.845	3	1.846	621			2	1.0189	162
5	1.829	5	1.829	004	1	1.0092	1	1.0098	461
3	1.795	4	1.795	323	1	1.0092	1	1.0087	11.3.3
8	1.783	3	1.784	800	1	0.9973	1	0.9973	12.0.4
		7	1.781	513	1	0.9973	1	0.9972	844
3	1.773	3	1.773	431	1	0.9946	2	0.9948	10.3.4
		2	1.772	204					

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**Table 6.** X-ray powder diffraction data ( $d$  in Å) for crocobelonite-1M

$I_{\text{meas}}$	$d_{\text{meas}}$	$I_{\text{calc}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{meas}}$	$d_{\text{meas}}$	$I_{\text{calc}}$	$d_{\text{calc}}$	$hkl$
5	7.13	6	7.10	001	3	1.9528	5	1.9540	-303
17	6.98	25	6.95	100	1	1.9212	1	1.9249	-321
6	4.72	>1	4.75	011			1	1.9147	131
		6	4.70	110	5	1.9021	9	1.9015	023
22	4.40	34	4.39	101	5	1.8696	11	1.8685	-313
3	4.33	3	4.32	-111	2	1.8416	4	1.8407	-322
8	3.614	5	3.617	111	1	1.8260	1	1.8252	032
		6	3.600	-102			1	1.8239	-231
100	3.547	100	3.542	-201	5	1.8108	7	1.8106	-401
21	3.485	31	3.477	200	2	1.7769	5	1.7757	004
50	3.195	47	3.192	020	7	1.7368	11	1.7370	123
5	3.138	8	3.136	-112	3	1.7040	5	1.7059	132
2	3.102	1	3.103	012			3	1.6996	231
1	3.059	1	3.054	210	12	1.6667	26	1.6665	-323
16	2.935	30	2.931	-202	2	1.6384	5	1.6386	-403
23	2.910	20	2.911	021	11	1.5959	19	1.5958	040
		12	2.901	120	2	1.5849	3	1.5826	033
38	2.855	44	2.854	102	4	1.5750	8	1.5748	-421
30	2.804	39	2.803	-121	1	1.5670	2	1.5656	114
2	2.668	>1	2.664	-212	2	1.5507	3	1.5517	024
12	2.607	19	2.606	112			2	1.5484	-422
8	2.464	14	2.463	-103	5	1.5209	12	1.5216	322
2	2.412	3	2.413	-301	1	1.4984	2	1.4998	141
33	2.389	48	2.388	-122	1	1.4621	2	1.4632	303
15	2.352	22	2.351	220	4	1.4549	6	1.4549	-241
2	2.304	2	2.298	-113	2	1.4395	5	1.4392	-333
3	2.262	1	2.257	-311	2	1.4301	5	1.4303	-215
11	2.195	21	2.195	202	1	1.4010	3	1.4015	-242
1	2.175	1	2.179	310	4	1.3923	8	1.3929	142
3	2.160	4	2.159	-222			3	1.3927	214
10	2.126	7	2.128	122	1	1.3406	4	1.3428	332
		8	2.125	-312			5	1.3392	-143
1	2.074	2	2.076	212	1	1.3148	2	1.3155	-521
9	2.039	4	2.041	301	1	1.2907	3	1.2907	242
		8	2.038	031					

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**Table 7.** Raman frequencies ( $\text{cm}^{-1}$ ) and band assignments for crocobelonite

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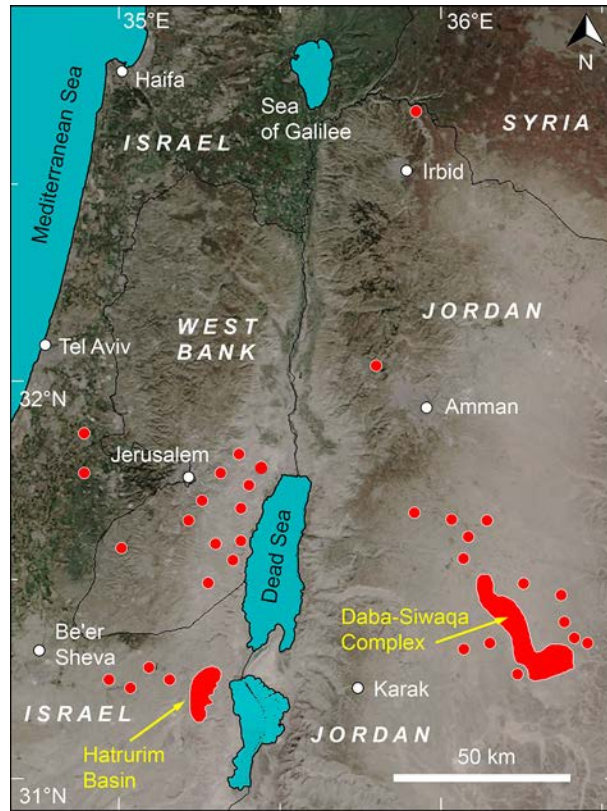
Crocobelonite-2O	Crocobelonite-1M	Assignment
106, 147, 179, 239	131, 174, 191, 204, 237, 269, 339	M–O bonds and lattice modes
437, 471	379, 407, 431, 470	Symmetric bending O–P–O
508, 551, 570, 600, 640, 687, 805, 856	519, 532, 598, 630, 647	Asymmetric bending O–P–O
956, 989	951, 978	Symmetric stretching O–P–O
1022, 1083, 1143	1019, 1034, 1089, 1143	Asymmetric stretching O–P–O

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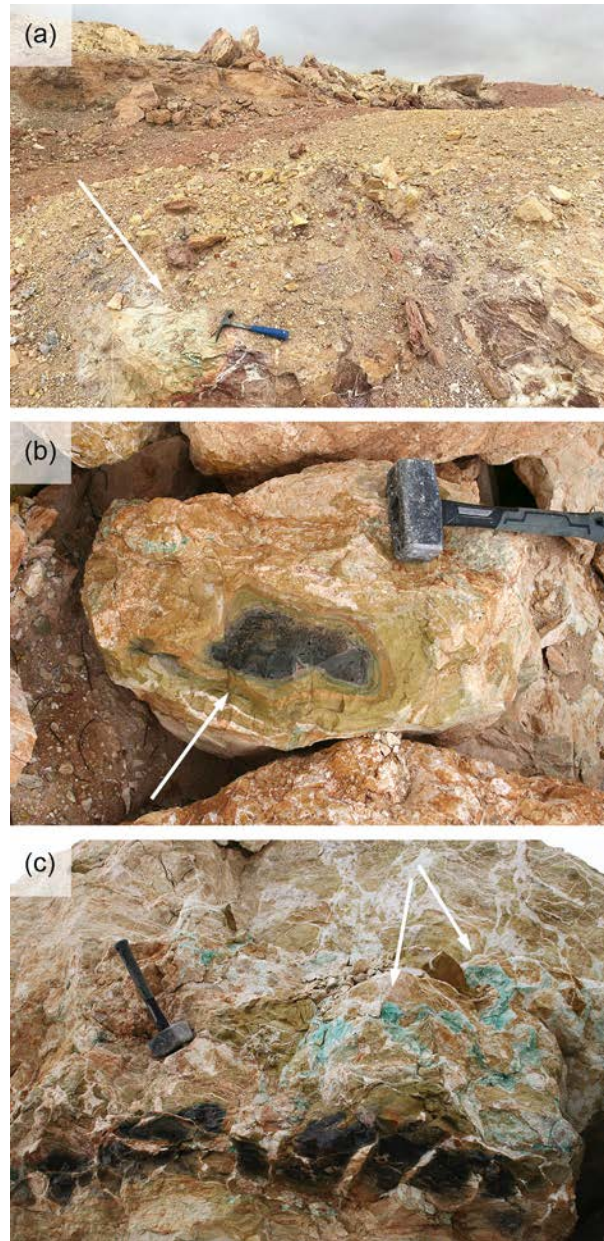
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**Figure 1**

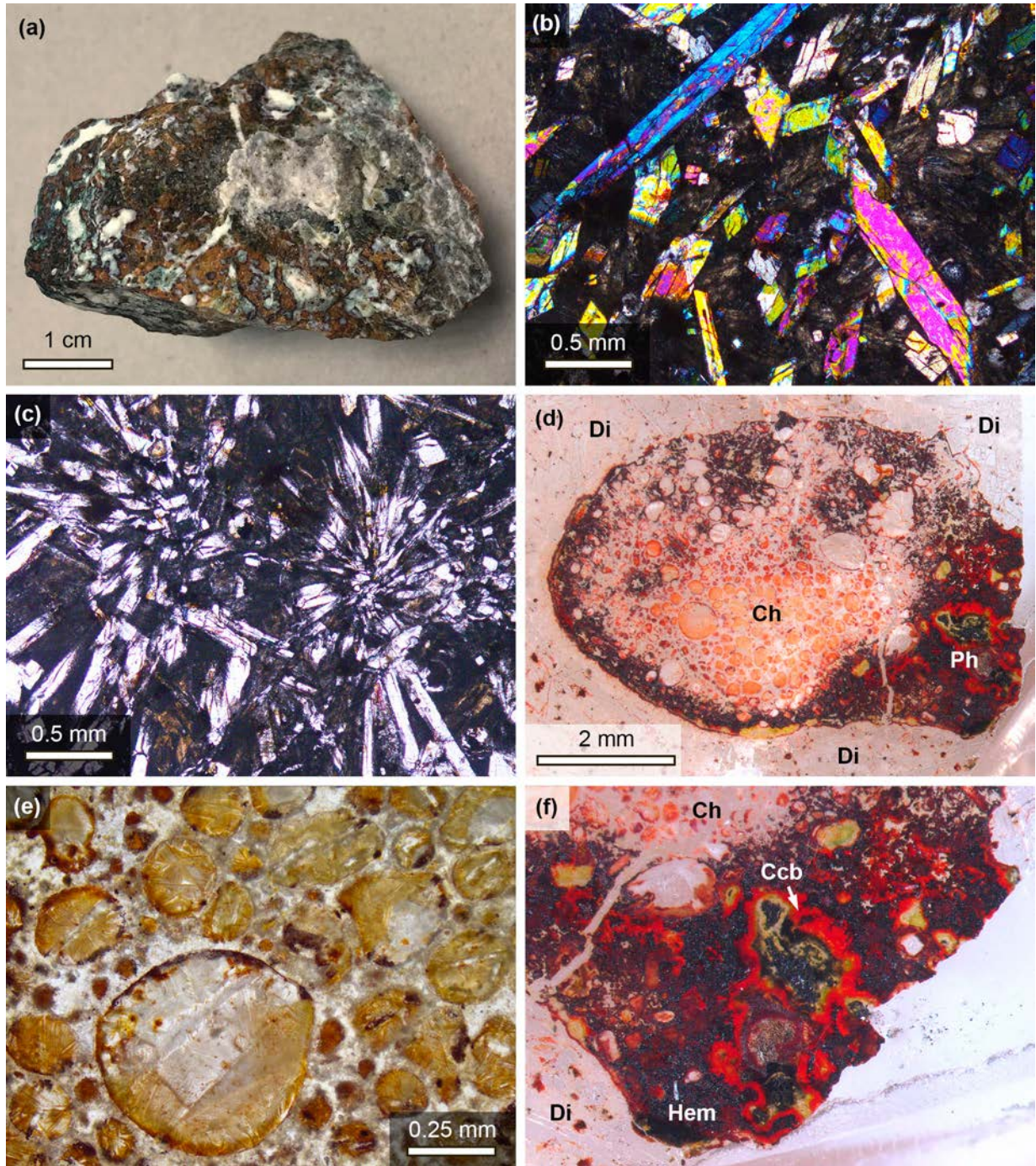


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**Figure 2**



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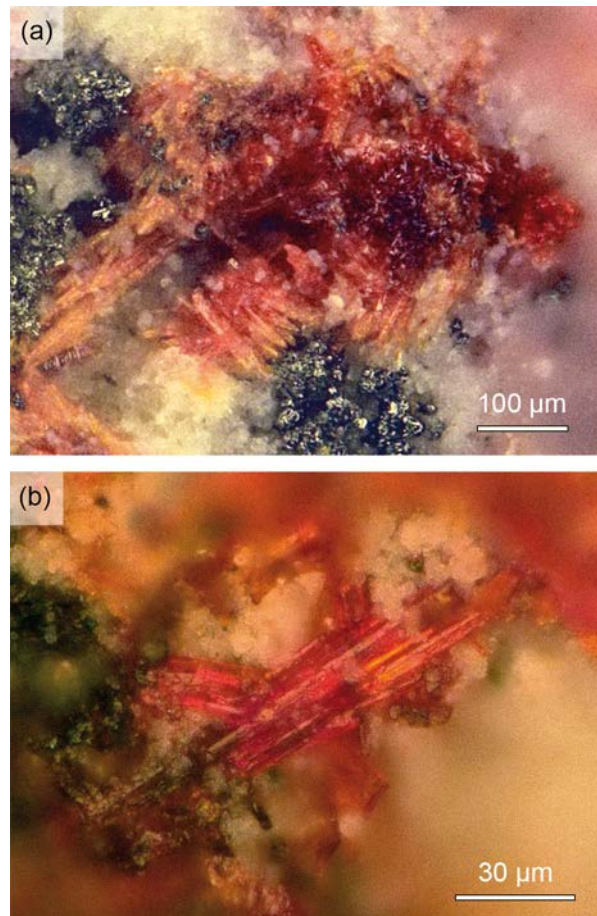
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**Figure 3**

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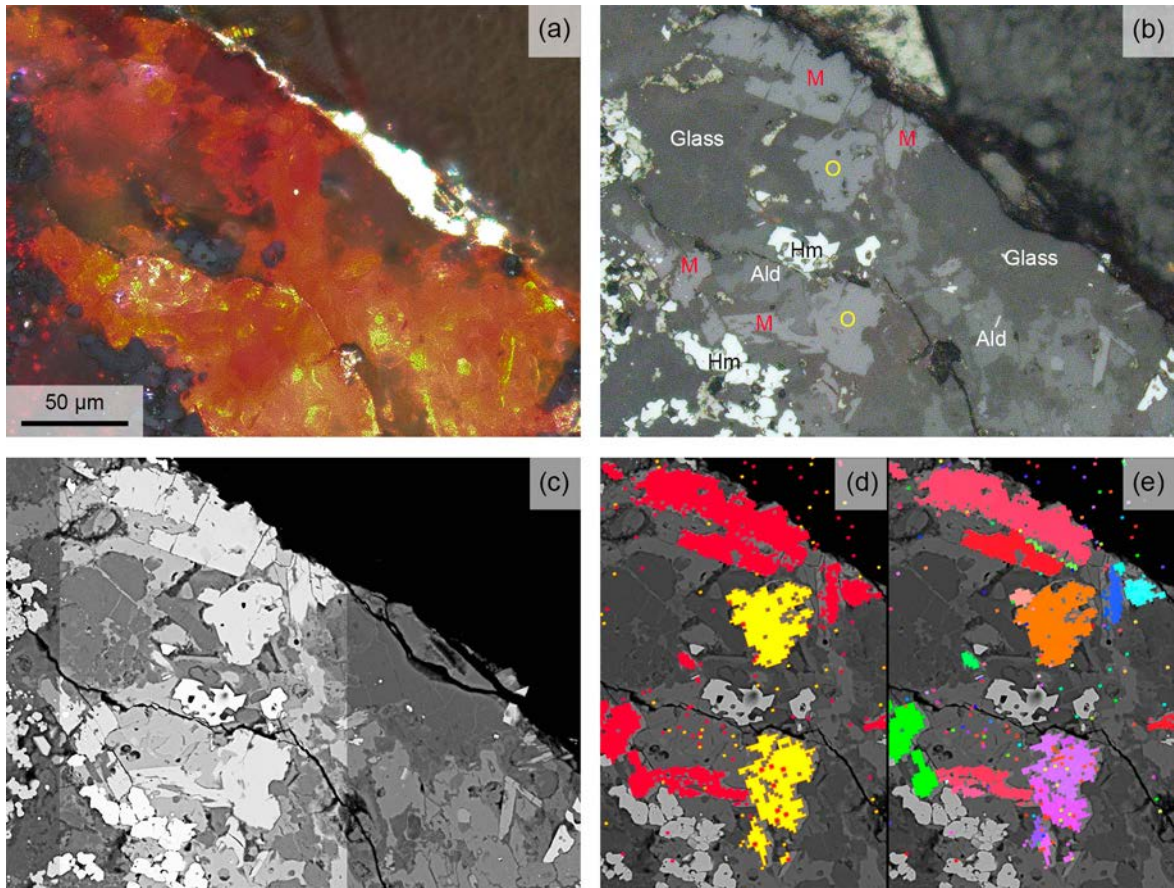
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**Figure 4**

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**Figure 5**



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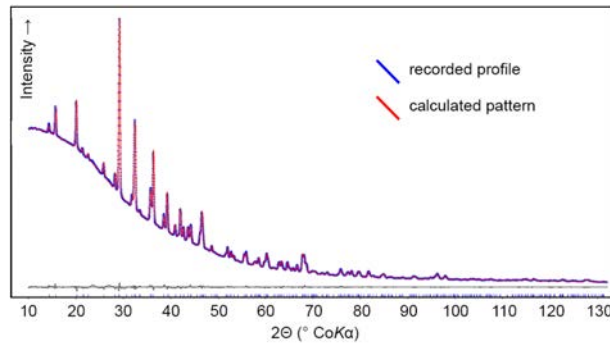
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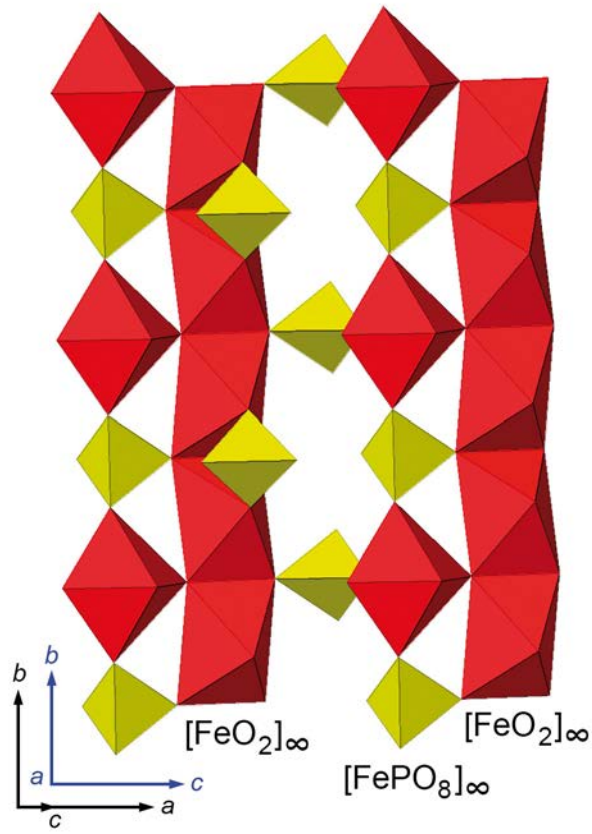
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**Figure 6**

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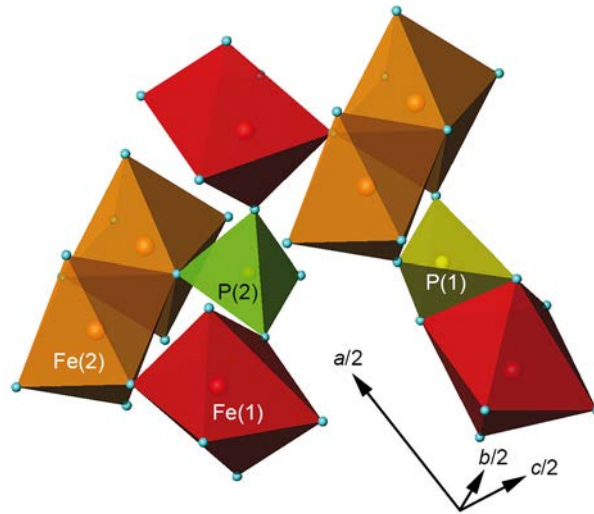
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**Figure 7**

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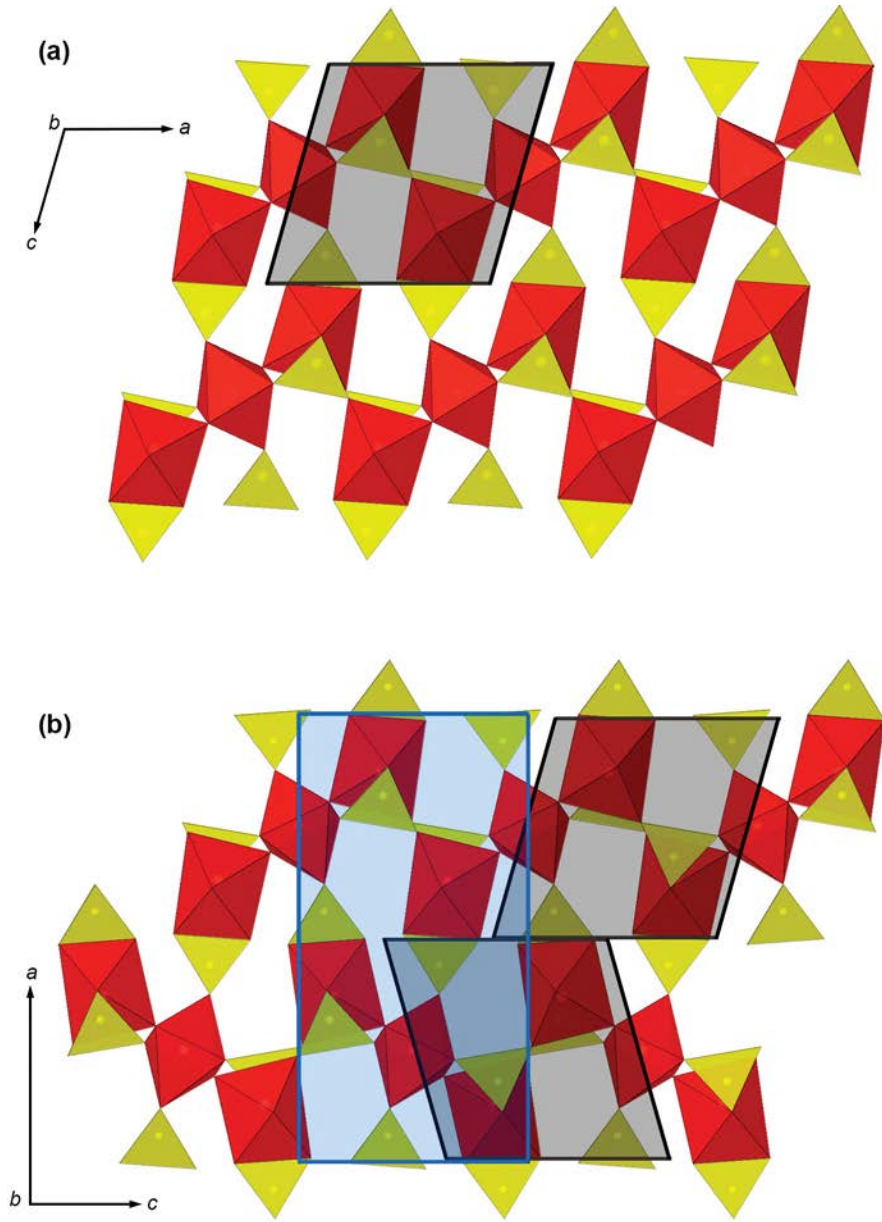
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**Figure 8**

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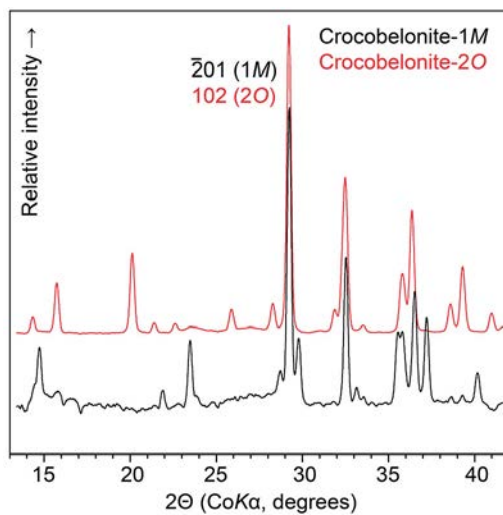
**Figure 9**

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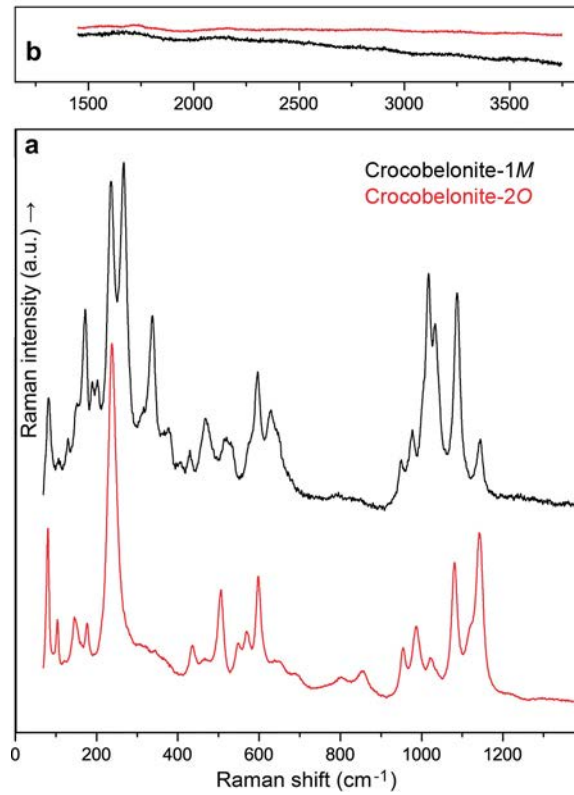
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**Figure 10.**

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**Figure 11**