

1 Revision 1

2 Discreditation of bobdownsite and the establishment of criteria for the identification of minerals
3 with essential monofluorophosphate (PO_3F^{2-})

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33 **Abstract**

34 Bobdownsite, IMA number 2008-037, was approved as a new mineral by the Commission on
35 New Minerals, Nomenclature and Classification (CNMNC) as the fluorine endmember of the
36 mineral whitlockite. The type locality of bobdownsite is in Big Fish River, Yukon Canada, and
37 bobdownsite was reported to be the first naturally occurring mineral with essential
38 monofluorophosphate (PO_3F^{2-}). The type specimen of bobdownsite has been reinvestigated by
39 electron probe microanalysis (EPMA), and our data indicate that fluorine abundances are below
40 detection in the mineral. In addition, we conducted detailed analysis of bobdownsite from the
41 type locality by gas chromatography isotope ratio mass spectrometry, Raman spectroscopy,
42 EPMA, and NMR spectroscopy. These data were compared with previously published data on
43 synthetic monofluorophosphate salts. Collectively, these data indicate that bobdownsite is
44 indistinguishable from whitlockite with a composition along the whitlockite-merrillite solid
45 solution. Bobdownsite is therefore discredited as a valid mineral species. An additional mineral,
46 krásnoite, has been purported to have monofluorophosphate components in its structure, but
47 reexamination of those data indicate that F^- in krásnoite forms bonds with Al, similar to OH^-
48 bonded to Al in perhamite. Consequently, krásnoite also lacks monofluorophosphate groups, and
49 there are currently no valid mineral species with monofluorophosphate in their structure. We
50 recommend that any future reports of new minerals that contain essential monofluorophosphate
51 anions be vetted by abundance measurements of fluorine, vibrational spectroscopy (both Raman
52 and FTIR), and where paramagnetic components are permissibly low, NMR spectroscopy.
53 Furthermore, we emphasize the importance of using synthetic compounds containing
54 monofluorophosphate anions as a point of comparison in the identification of minerals with
55 essential monofluorophosphate. Structural data that yield satisfactory P-F bond lengths
56 determined by X-ray crystallography, coupled with direct chemical analyses of fluorine in a
57 material do not constitute sufficient evidence alone to identify a new mineral with essential
58 monofluorophosphate anions.

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68 **Introduction**

69 Phosphate minerals such as apatite, merrillite, and whitlockite are of importance to a
70 wide variety of fields, from Earth science to life science, material science, and planetary science
71 (Chew and Spikings, 2015; Harlov, 2015; Hawthorne, 1998; Hughes et al., 2006; Hughes et al.,
72 2008; Hughes and Rakovan, 2015; Jolliff et al., 2006; McCubbin and Jones, 2015; McCubbin et
73 al., 2014; Rakovan and Pasteris, 2015; Shearer et al., 2015; Webster and Piccoli, 2015).
74 Phosphates are the major source of P on Earth and their uses range from fertilizers to detergents
75 to insecticides. Synthetic phosphates have been used for ceramics and coatings, and have even
76 been used for the production of fuel cells (i.e., Kendrick et al., 2007; Lin et al., 2007; Pietak et
77 al., 2007). Phosphates have a propensity for concentrating rare earth elements (Jolliff et al.,
78 1993; Prowatke and Klemme, 2006; Shearer et al., 2011), which are used pervasively for
79 deciphering sedimentary, igneous, and metamorphic petrogenesis. Furthermore, their ability to
80 accommodate the radioisotopes used for dating makes them important to geochronological
81 studies of rocks (Chew and Spikings, 2015).

82 At present, there are 586 unique phosphate mineral species that have been identified
83 (Hazen et al., 2015; IMA list of minerals updated as of January 2017). Of these, the phosphate
84 anion is most typically represented by phosphate (PO_4^{3-}), where phosphorus is bonded to 4
85 oxygens; however, there is a subset of phosphate minerals totaling 58 individual mineral species
86 that have OH^- or F^- substituents for O^{2-} on the phosphate molecule. These substituents consist of
87 either hydrogen phosphate anions ($\text{PO}_3\text{OH}^{2-}$) or monofluorophosphate anions (PO_3F^{2-}). Minerals
88 with protonated phosphate groups constitutes 57 of the 58 individual mineral species. The most
89 common of these species is the mineral whitlockite (Fron del, 1941; Hughes et al., 2008),

90 although other examples include brushite, monetite, newberyite, and groatite (Cooper et al.,
91 2009; Duff, 1971; Frost et al., 2011; Terpstra, 1937). Only one mineral species (bobdownsite) is
92 reported to have an essential monofluorophosphate component (PO_3F^{2-}) in its structure.

93 Bobdownsite was approved as a new mineral by the International Mineralogical
94 Association in 2008 (IMA number 2008-037), and it was described in detail by Tait et al. (2011).
95 The type locality of bobdownsite is in Big Fish River, Yukon Canada. Bobdownsite is also
96 reported to occur at a number of other localities on Earth (e.g., Tip Top Mine, South Dakota
97 USA), and it has been reported in martian meteorites (Gnos et al., 2002; Tait et al., 2011). In
98 addition to bobdownsite, the mineral krásnoite is reported to contain fluorophosphate groups
99 (Mills et al., 2012), but, unlike bobdownsite, the validity of krásnoite as a species is not
100 predicated on the assignment of fluorine to fluorophosphate groups. Although only two naturally
101 occurring fluorophosphate compounds have been reported, there is a wide array of synthetic
102 fluorophosphate compounds that have many versatile uses from additives in toothpaste (Sten,
103 1964) to treatments for osteoporosis (Balena et al., 1998; Kleerekoper, 1998; Lems et al., 2000).
104 In the present study, we provide in-depth structural and chemical characterization of
105 bobdownsite from the type locality in Big Fish River, Yukon Canada to reassess whether or not
106 fluorine is present, and if so, how it is bonded within the structure. The results of this study will
107 be compared and contrasted with previous studies of bobdownsite, krásnoite, as well as a number
108 of well-characterized synthetic monofluorophosphate salts. The aim of our study is to establish
109 minimum criteria for identifying and classifying minerals with an essential monofluorophosphate
110 structural component.

111 **Methods**

112 *Samples analyzed in the present study*

113 Bobdownsite samples from the type locality in Big Fish River, Yukon Canada were
114 obtained from a number of sources: Samples of bobdownsite were personally collected by
115 coauthor KTT in July, 2012 at the same locality that the bobdownsite type sample was collected
116 at Rapid Creek, Yukon, Canada. The mineral was not found *in situ*, but collected in the talus
117 slope below the original find (samples identified as Bobdownsite_Tait); bobdownsite specimens
118 were purchased from Rod Tyson of Tysons' Fine Minerals Inc. (samples identified as
119 bobdownsite_A); and we also obtained the type specimen of bobdownsite from Robert Downs at
120 the University of Arizona (sample number R050109). In addition, Robert Downs provided us
121 with a sample of bobdownsite from the Tip Top Mine in South Dakota, USA (sample number
122 R070654). Finally, we purchased a sample that was described as whitlockite from Steve Covey
123 of Amethyst Galleries' Mineral Gallery from Big Fish River, Yukon Canada (samples identified
124 as Yukon phosphate) that is identical in appearance to the bobdownsite from the same locality.
125 We suspect that the material is the same as the other material from this locality, which is
126 supported by the fact that the whitlockite specimen was purchased in 2009, prior to the
127 publication of Tait et al. (2011) describing bobdownsite for the first time.

128 In addition to using the natural samples described above, we also synthesized whitlockite
129 ($\text{Ca}_9\text{Mg}[\text{PO}_3\text{OH}][\text{PO}_4]_6$) (sample identified as MGS-008) to use as a F- and Fe-free standard to
130 compare with the natural bobdownsite samples. The whitlockite synthesis was conducted using
131 the methods of Adcock et al. (2013; 2014), which are optimized after Hughes et al. (2008) and
132 Gopal et al. (1974). A solution containing 90 ml of high-purity (18.2M Ω) water, 1.00 g of
133 laboratory-grade hydroxylapatite (Spectrum, reagent grade) and 0.30 g magnesium nitrate
134 hexahydrate (J.T. Baker, ACS grade) is created in a 125 ml Parr acid digestion vessel (Parr 4748)
135 with an acid-washed polytetrafluoroethylene liner. Once the solution is mixed, it is acidified to a

136 pH of 2.6–2.8 using concentrated phosphoric acid (Alfa Aesar, ACS grade). The vessel is then
137 sealed and incubated in an oven at 240 °C for 7 days. At the end of 7 days, the vessel is removed
138 from the oven and quenched in a water bath in an effort to prevent any further reaction. After
139 cooling, the vessel is opened and the solution decanted leaving the solids. Solid material is rinsed
140 from the vessel using ethanol, allowed to air dry for 24 h, weighed and inspected by optical
141 microscopy for preliminary phase identification. Additional phases can form during synthesis,
142 typically hydroxylapatite ($\text{Ca}_5[\text{PO}_4]_3\text{OH}$) and monetite (CaHPO_4), but are primarily confined to
143 the <75 μm fraction. Output masses are therefore brush sieved on a 200 mesh screen to remove
144 the <75 μm size fraction. The methods have been shown to consistently and reliably produce
145 high-purity Mg-endmember whitlockite (Adcock et al., 2013; Adcock et al., 2017; Hughes et al.,
146 2008), although a few wt.% of merrillite may occur within the whitlockite (Adcock et al., 2017;
147 Hughes et al., 2008).

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149 *Electron probe microanalysis (EPMA)*

150 All of the natural phosphate specimens (Bobdownsite_A, Yukon phosphate,
151 Bobdownsite_Tait, R050109, and R070654) were analyzed using the JEOL 8200 electron
152 microprobe at the Institute of Meteoritics at the University of New Mexico using Probe for
153 EPMA™ (PFE) software. An accelerating voltage of 15 kV, a nominal probe current of 20 nA,
154 and a beam diameter of 5 μm were used during each analysis. We analyzed for the elements Si,
155 Al, Fe, Mn, Mg, Ca, Na, P, F, and Cl. F was analyzed using a light-element LDE1 detector
156 crystal, and Cl was analyzed using a PET detector crystal. The standards used were as follows;
157 for Ca and P, Durango apatite (Jarosewich et al., 1980) was used as the primary standard, and a
158 natural fluorapatite from India (Ap020 from McCubbin et al., 2012) was used as a secondary

159 check on the standardization. A synthetic SrF₂ crystal from the Taylor multi element standard
160 mount (C. M. Taylor) was used as the primary F standard, and Ap020 was used as an additional
161 check on the F standardization. We have demonstrated previously that SrF₂ is a reliable fluorine
162 standard for the analysis of fluorine in both glasses and apatite (McCubbin et al., 2016;
163 McCubbin et al., 2015b). A synthetic sodalite crystal from Sharp et al. (1989) was used as a
164 primary Cl standard, and scapolite from the Smithsonian Institution (NMNH R6600-1) was used
165 as a secondary check on the Cl standardization. Spessartine, albite, and quartz from the Taylor
166 multi element standard mount (C.M. Taylor) were used as primary standards for Mn, Na, and Si,
167 respectively. Pyrope from the Taylor multi element standard mount (C.M. Taylor) was used for
168 Mg and Al. Ilmenite from the Smithsonian Institution (NMNH 133868) was used as a primary
169 standard for Fe.

170 The synthetic Mg-whitlockite (MGS-008) was analyzed using a JEOL JXA-8900 at the
171 EMiL facility within the University of Nevada, Las Vegas. An accelerating voltage of 15 kV, a
172 nominal probe current of 10 nA, and a beam diameter of 10 μm were used during each analysis.
173 We analyzed for the elements Si, Fe, Mn, Mg, Ca, Na, P, S, and Cl. Cl was analyzed using a
174 PETJ detector crystal. Standards included apatite for Ca from the Smithsonian Institution
175 (NMNH 104021) (Jarosewich, 2002) and San Carlos olivine for Mg and Si. Fe and Mn were
176 standardized using ilmenite sample NMNH 96189. Kakanui anorthoclase was used as a standard
177 for Na, and scapolite NMNH R6600 was used for Cl. P was standardized using Micro-Analysis
178 Consultants Ltd. Apatite from Yates Mine, Quebec (MAC EMS 80095-MINA apatite). S was
179 standardized using Micro-Analysis Consultants Ltd. pyrite, also from Yates Mine, Quebec
180 (MAC EMS 80095-MINA pyrite).

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182 *Carbon reduction Gas-chromatography–isotope ratio mass spectrometry*

183 Gas chromatography isotope-ratio mass spectrometry (GC-IRMS) was used to quantify
184 water contents in Bobdownsite_A and Yukon phosphate samples, and H isotopic values were
185 also determined for the Yukon phosphate sample. Measurements were made in the Center for
186 Stable Isotopes in the Department of Earth and Planetary Sciences at the University of New
187 Mexico, using the technique and apparatus previously described in detail by Sharp et al. (2001).
188 Briefly, the technique involves reduction of structural OH components in the phosphate samples
189 to H₂ gas by reaction with glassy carbon at 1450°C in a helium carrier gas. Product gases are
190 separated in a gas chromatograph and analyzed in a mass spectrometer configured to make
191 hydrogen isotope analyses in continuous flow mode. In the present study, the phosphate samples
192 were wrapped in silver foil and dropped into the furnace using a commercially available
193 autosampler (e.g., Carlo Erba AS 200-LS) mounted directly over the reduction tube. We used
194 sample sizes of about 5–11.5 mg, which produced a sufficient volume of H₂ to quantitatively
195 determine the abundances of H₂O in the phosphates. The detection limits for H₂O during our
196 session were determined by running empty silver foil buckets that were used to wrap the
197 phosphate samples, which yielded a detection limit of approximately 300 ppm H₂O, which is
198 equivalent to approximately 0.006 µl H₂O that we attribute to adsorbed surface water on the
199 silver. This base level amount of adsorbed surface water is consistent with the blank H₂O
200 contents from other investigations using this laboratory (McCubbin et al., 2012). This technique
201 was also used to determine δD values using standard correction procedures, which produced
202 results identical to those obtained conventionally with a precision of 4‰ (2σ) for hydrous
203 minerals that have at least 0.1 µl H₂O (Sharp et al., 2001) (equivalent to 5000 ppm H₂O in the
204 phosphate samples that were analyzed). Throughout our analysis routine, we checked the

205 reproducibility of the column using several H₂O standards including NBS 30 biotite (Sharp et al.,
206 2001), water canyon biotite (USGS sample number 3149-11), and BUD biotite (Bindeman and
207 Serebryakov, 2011). For each phosphate sample, we analyzed four to seven separate aliquots of
208 sample to test for homogeneity in our phosphate grains. Water contents for the phosphate
209 samples are presented in Table 1. The 2 σ uncertainty reported in Table 1 refers to the standard
210 deviation of the mean water contents among all analyses for each sample, which was larger than
211 the analytical uncertainty. Total time of analysis is less than two minutes for a single hydrogen
212 and δ D analysis.

213

214 *Raman Spectroscopy*

215 Raman spectra of Bobdownsite_A and Yukon phosphate were collected using a Witec α -
216 Scanning Near-Field Optical Microscope (SNOM) confocal Raman spectrometer. Both samples
217 were prepared as polished mounts. The excitation source is a frequency-doubled solid-state YAG
218 laser (532 nm) operating between 0.3 and 1 mW output power (dependent on objective), as
219 measured at the sample using a laser power meter. Objective lenses included a x100 LWD and a
220 x20 LWD with a 50 μ m optical fiber acting as the confocal pin hole. Spectra were collected on a
221 Peltier-cooled Andor EMCCD chip, after passing through a f/4 300 mm focal length imaging
222 spectrometer typically using a 600 lines/mm grating. The lateral resolution of the instrument is as
223 small as 360 nm in air when using the x100 LWD objective, with a focal plane depth of ~800
224 nm.

225 We employed this instrument to collect single spectra of the Bobdownsite_A and Yukon
226 phosphate samples. Single spectra mode allows the acquisition of a spectrum from a single spot
227 on the target. Average spectra are produced using integration times of 30 seconds per

228 accumulation and 10 accumulations to allow verification of weak spectral features. A cosmic ray
229 reduction routine was used to reduce the effects of stray radiation on Raman spectra.

230

231 *Nuclear Magnetic Resonance (NMR) spectroscopy*

232 NMR spectra were collected on Bobdownsite_A, Yukon phosphate, and the synthetic
233 Mg-whitlockite sample, MGS-008. The ^{19}F single-pulse (SP) spectra were collected on a
234 500 MHz (11.7 T) Varian InfinityPlus spectrometer operating at 470.179 MHz, using a
235 Varian/Chemagnetics T3-type probe assembly configured for 3.2 mm (O.D.) rotors. The 90°
236 pulse width was $5\mu\text{s}$, and 170 transients were collected at a relaxation delay of 100s. Longer
237 relaxation delays produced nominal increases in signal, however the NMR lineshapes did not
238 change at relaxation delays up to 600s. Chemical shifts were measured relative to neat CFCl_3 set
239 to $\delta_{\text{F}} = 0$ ppm. The MAS rate was 20 kHz. Additional spectra were acquired after a small
240 amount of NaF was added to each sample, corresponding approximately to one F per formula
241 unit (i.e., an F:P ratio of 1:7). The ^1H SP/MAS spectra were collected on a 400 MHz (9.4T)
242 Varian Inova spectrometer operating at 399.895 MHz. A probe assembly modified for low ^1H
243 background and configured 4 mm (O.D.) rotors was used, with the samples contained in ZrO_2
244 rotors having Kel-F tips, and PTFE spacers. The MAS rate was 10 kHz. The 90° pulse width was
245 $5\mu\text{s}$ with a pulse delay of 30 seconds, and 128 transients were collected. Chemical shifts were
246 measured relative to hydroxylapatite set to $\delta_{\text{H}} = 0.2$ ppm. The ^{31}P NMR spectra were acquired
247 with the 500 MHz spectrometer and a T3-type probe fitted with 4 mm spinning assembly and at
248 a 15 kHz spinning rate. The single-pulse spectra were collected with $4\mu\text{s}$ pulses, where the 90°
249 pulse width was $5\mu\text{s}$. For the synthetic samples, spectra collected fully relaxed as a single

250 acquisition after overnight equilibration did not differ significantly from spectra acquired with a
251 300 s relaxation delay. The ^{31}P chemical shifts are referenced to 85% H_3PO_4 , set to $\delta_{\text{P}} = 0$ ppm.

252

253 **Results**

254 *Chemical and isotopic composition of phosphates*

255 The compositions of all the phosphates analyzed in the present study are provided in
256 Table 1, and the H_2O abundances of samples Bobdownsite_A and Yukon phosphate are also
257 provided in Table 1. All of the phosphates from Big Fish River, Yukon, Canada have similar
258 compositions with some variations in Na, Mg, and Fe (Table 1). Sodium abundances in these
259 samples range from 0.61 to 1.00 wt.% Na_2O , which corresponds to 0.21–0.34 structural formula
260 units of Na (sfu) per 28 oxygens. Fe and Mg abundances in the samples from Big Fish River are
261 inversely correlated and range from 1.08 to 1.43 wt.% FeO and 2.63 to 2.88 wt.% MgO. These
262 abundances correspond to 0.16 to 0.21 sfu Fe and 0.69 to 0.73 sfu Mg per 28 oxygens. The sum
263 of Fe and Mg per 28 oxygens ranges from 0.90 to 0.94 sfu. Although H_2O abundances were only
264 measured in the samples Bobdownsite_A and Yukon phosphate, they yielded similar results of
265 0.71 and 0.70 wt.% H_2O , respectively. These abundances of H_2O correspond to 0.83 to 0.86 sfu
266 OH per 28 oxygens. Fluorine was not detected in any of the phosphates analyzed in the present
267 study, so the chemistry of the phosphates indicate that they are whitlockite with compositions
268 that lie along the whitlockite-merrillite solid solution.

269 The sample from the Tip Top mine, South Dakota, USA (R070654) was distinctly
270 different from the samples from Big Fish River, Yukon, Canada given the paucity of FeO, lower
271 abundance of Na, and elevated abundance of Mg (Table 1). We did not detect any fluorine within
272 sample R070654, so it is also likely a phase that lies along the whitlockite-merrillite solid

273 solution; however direct analysis of H₂O is required to definitively identify the sample as either
274 whitlockite or merrillite. The synthetic sample MGS-008 is an endmember Mg-whitlockite and
275 does not have detectable Fe or Na (Table 1).

276 In addition to elemental abundances, we measured the H-isotopic composition of the
277 sample Yukon phosphate. Isotopic compositions are traditionally expressed in delta notation
278 according to the following equation:

279

$$280 \quad \delta^M X = \left[\frac{\text{Heavy}^M X_{\text{Measured}} \times \text{Light}^M X_{\text{Standard}}}{\text{Light}^M X_{\text{Measured}} \times \text{Heavy}^M X_{\text{Standard}}} - 1 \right] \times 1000 \quad (1)$$

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282 where $\frac{\text{Heavy}^M X_{\text{Measured}}}{\text{Light}^M X_{\text{Measured}}}$ is the isotopic ratio of the measured sample, $\frac{\text{Light}^M X_{\text{Standard}}}{\text{Heavy}^M X_{\text{Standard}}}$ is the isotopic
283 ratio of the standard, and $\delta^M X$ is the delta value of the isotope expressed in per mil. The standard
284 for D/H is Vienna Standard Mean Ocean Water with D/H of 1.5576×10^{-4} (Coplen, 1994). The H
285 isotopic composition of the sample Yukon phosphate has a D value of $-200 \pm 12\%$, which is
286 similar to meteoric waters in northern Yukon Canada where the samples originated (e.g., Tondu
287 et al., 2013), and it is distinct from meteoric waters in Albuquerque, NM where the samples were
288 analyzed and stored prior to analysis (e.g., Yapp, 1985).

289

290 *Raman Spectroscopy*

291 We analyzed the samples Bobdownsite_A and Yukon phosphate by Raman spectroscopy,
292 and Raman spectra for samples R050109 and R070654 were reported by Tait et al. (2011).
293 Spectra from all four samples are displayed in Figure 1. All spectra exhibit the same patterns,
294 consistent with being comprised of similar material. Peaks in the range of 900 to 1180 cm⁻¹ are

295 associated with P-O vibrations (Socrates, 2001). The most prominent peak in this region is
296 represented by the symmetric P-O stretch (ν_1) in phosphate at $\sim 970\text{ cm}^{-1}$. The broad weak peaks
297 in the range of $1070\text{--}1120\text{ cm}^{-1}$ are representative of the asymmetric P-O stretching (ν_3) in
298 phosphate. The sharp medium to weak intensity peak at approximately $923\text{--}925\text{ cm}^{-1}$ is in the
299 region that has been attributed to the symmetric stretching mode (ν_1) of HPO_4^{2-} in whitlockite
300 (Jolliff et al., 2006). We observe no peaks in the region of the symmetric P-F stretching mode
301 (ν_1) of $776\text{ to }840\text{ cm}^{-1}$ range (highlighted in gray in Figure 1) reported previously for the P-F
302 symmetric stretch (ν_1) in PO_3F^{2-} from monofluorophosphate salts (Baran and Weil, 2009; Weil et
303 al., 2015; Weil et al., 2007).

304

305 *^{19}F and ^1H NMR*

306 ^{19}F is the second most sensitive naturally occurring stable nuclide for NMR spectroscopy,
307 with a detection limit estimated to be of the order $100\text{ }\mu\text{g F g}^{-1}$, but no ^{19}F MAS/NMR signal was
308 detected from the Bobdownsite_A, Yukon phosphate, and synthetic whitlockite (MGS-008)
309 samples. To check this result, additional spectra were acquired after addition of small amounts of
310 NaF (4.5–6 wt. percent), equivalent to approximately one F per formula unit (i.e., an F:P ratio of
311 1:7). Spectra acquired after addition of the NaF contain a central peak at $\delta_{\text{F}} = -220\text{ ppm}$ and
312 associated spinning sidebands (Fig. 2), but no other signals. This chemical shift is in good
313 agreement with previous reports for NaF (Stebbins and Zeng, 2000). Previous ^{19}F NMR studies
314 of inorganic fluorophosphate compounds show spectra containing wide spinning sideband
315 manifolds with distinct center band doublets for the fluorophosphate F. The ^{19}F chemical shifts
316 for the fluorophosphate group range from -52.5 ppm for BaPOF_3 to -75 ppm for $\text{Na}_2\text{PO}_3\text{F}$ (Jantz
317 et al., 2016; Stoeger et al., 2013; Weil et al., 2004; Weil et al., 2007; Zhang et al., 2007). No

318 signal in this chemical shift range (shaded region of Fig. 2) occurs in the spectra of the
319 Bobdownsite_A and Yukon phosphate samples from Big Fish River, Yukon Canada.

320 The synthetic whitlockite sample yields a well-resolved, relatively narrow ^1H NMR peak
321 near $\delta_{\text{H}} = +10$ ppm (Fig. 3), consistent with the presence of a single hydrogen phosphate group in
322 the crystal structure. Additional minor signals occur near +7 ppm and +12 ppm, possibly from
323 unidentified impurities. The ^1H NMR spectra of the natural Bobdownsite_A and Yukon
324 phosphate samples also contain a major peak centered near +10 ppm, although the peaks are
325 significantly broader and exhibit substantially more spinning sideband intensity than the
326 synthetic whitlockite. The broader resonances likely result from minor concentrations of
327 paramagnetic ions in the mineral specimens (e.g., Begaudeau et al., 2012; Oldfield et al., 1983),
328 consistent with the 1.1 to 1.4 wt.% FeO in these samples (Table 1). An additional minor peak
329 occurs in the synthetic whitlockite near +0.2 ppm that can be attributed to an impurity phase,
330 possibly hydroxylapatite based on its similar chemical shift (Yesinowski and Eckert, 1987).

331

332 ^{31}P NMR

333 The ^{31}P MAS/NMR spectra of the Bobdownsite_A and Yukon phosphate specimens
334 contain broad, poorly resolved centerbands centered near +0.6 ppm, 5.5 ppm FWHM (Fig. 4). In
335 contrast, the synthetic whitlockite (MGS-008) sample yields well-resolved centerbands
336 exhibiting sharp peaks at 2.3, 1.4, and -0.2 ppm plus shoulders at +0.7 and -0.8 ppm. Minor
337 additional peaks occur at -3.4 and -4.3 ppm that could arise from impurity phases. Qualitatively,
338 the centers of gravity of the Bobdownsite_A and Yukon phosphate spectra coincide with that of
339 the synthetic whitlockite (MGS-008). This result suggests that peak broadening by paramagnetic
340 substituents present in the natural samples, similar to that discussed for the ^1H results above,

341 prevents resolution of distinct sites. However, the spectrum of the natural Yukon phosphate
342 sample does appear to exhibit an asymmetry that suggests the presence of at least two peaks at
343 positions similar to those for the main peaks for the synthetic sample, namely at +2.3
344 and -0.2 ppm. The chemical shifts for the main peaks observed for these samples lie well within
345 ranges reported previously for orthophosphate groups in general, and Ca- and Mg-
346 orthophosphates in particular (Belton et al., 1988; Rothwell et al., 1980; Turner et al., 1986).

347 The spectrum of the synthetic whitlockite (MGS-008) is consistent with the presence of
348 three crystallographically distinct P positions in a 3:1:3 ratio plus additional signals arising from
349 merrillite-like local environments (Calvo and Gopal, 1975). A more complete report of the
350 NMR spectra of whitlockite and assignment of the resolved features will be presented in a
351 separate paper.

352 **Discussion**

353 *Discreditation of bobdownsite*

354 Based on the similarities in chemical composition and the nearly identical Raman spectra
355 among all phosphate samples analyzed from Big Fish River, Yukon Canada, we infer that all
356 samples from this locality are comprised of the same mineral phase. Consequently, we refer to
357 all of these samples collectively as “bobdownsite” throughout the discussion except in cases
358 where we refer to a specific sample, in which case the sample name is used.

359 Three of the primary lines of evidence that supported the identification of bobdownsite
360 require reassessment based on differences in results between the present study and the initial
361 description of this mineral (i.e., Tait et al., 2011). These include the absence of OH⁻ in the
362 samples inferred by thermogravimetric analysis (TGA), the assignment of a Raman peak at 923
363 cm⁻¹ to symmetric stretching in PO₃F²⁻, and the abundance of fluorine determined by EPMA. We

364 will first compare data from Tait et al. (2011) and the present study and then use NMR results
365 from the present study to resolve any remaining discrepancies.

366

367 H abundance of “bobdownsite”

368 Samples of “bobdownsite” heated to 1100 °C by Tait et al. (2011) did not exhibit weight
369 loss that could be attributed to the presence of OH in the structure. However, in the present
370 study, “bobdownsite” was heated to 1450 °C and H was liberated from the sample, yielding
371 approximately 0.7 ± 0.05 wt.% H₂O with an H isotopic composition of -200 ± 12 ‰. The
372 abundance of H₂O fills the equivalent of at least 83% of the OH⁻-site in whitlockite with OH⁻.
373 The presence of OH⁻ in the “bobdownsite” structure is confirmed by our observation of ¹H NMR
374 signals for a hydrogen phosphate group in samples from the Big Fish River, Yukon Canada
375 locality.

376

377 Vibrational spectroscopy of “bobdownsite”

378 The fluorophosphate group occurs in a number of inorganic salts for which crystal
379 structures and vibrational spectra have been reported (Baran and Weil, 2009; Heide et al., 1985;
380 Jantz et al., 2016; Weil et al., 2015; Weil et al., 2004; Weil et al., 2007; Zeibig et al., 1991).
381 Owing to a lack of significant bonding of fluorine beyond the P-F bond in most of these
382 compounds, the P-F stretching frequency is typically observed to vary only slightly from its
383 value for aqueous fluorophosphate ion, 795 cm^{-1} (Siebert, 1966). A small variation in the
384 symmetric P-F stretching mode has been observed, ranging from 776 cm^{-1} to 840 cm^{-1} that in
385 some cases appears to relate to the P-F bond distance (Baran and Weil, 2009; Heide et al., 1985;
386 Jantz et al., 2016; Weil et al., 2015; Weil et al., 2004; Weil et al., 2007; Zeibig et al., 1991). The

387 wavenumber range of stretching modes attributed to P-F bonds in fluorophosphate salts falls
388 outside that typical for the symmetric P-O stretch in phosphate and hydrogen phosphate. In
389 contrast, Tait et al. (2011) analyzed bobdownsite by Raman spectroscopy, assigning a peak at
390 923 cm^{-1} to the P-F ν_1 mode in PO_3F^{2-} . However, 923 cm^{-1} falls outside the range reported for P-
391 F symmetric stretching modes exhibited by synthetic fluorophosphate salts (Baran and Weil,
392 2009; Heide et al., 1985; Jantz et al., 2016; Weil et al., 2015; Weil et al., 2004; Weil et al., 2007;
393 Zeibig et al., 1991). Our analyses of bobdownsite_A and Yukon phosphate match those of Tait et
394 al. (2011) for samples R050109 and R070654, which supports the argument that a
395 fluorophosphate group attributed to “bobdownsite” is misidentified (Figure 1), despite the fact
396 that the refined P-F bond distance from the XRD results of Tait et al. (2011) falls within the
397 range of crystalline fluorophosphate salts (although substantially longer than previous reports for
398 all except $\text{NaK}_3(\text{PO}_3\text{F})_2$; Durand et al., 1975). Finally, the Raman spectra of the purported
399 “bobdownsite” specimens are strikingly similar to those reported for a whitlockite specimen
400 from the Palermo type locality (R080052) in Tait et al. (2011), which also exhibits a peak at
401 about 923 cm^{-1} . Peaks in vibrational spectra near 923 cm^{-1} have been attributed in previous
402 studies to the P-O stretch for the hydroxyl oxygen in the hydrogen phosphate group (e.g., Jolliff
403 et al., 2006; Socrates, 2001). Assignment of the 923 cm^{-1} peak to the P-O(H) vibration is
404 consistent with our observation of ^1H NMR signals for a hydrogen phosphate group in samples
405 from these localities.

406

407 F abundance of “bobdownsite”

408 Although Tait et al. (2011) reported fluorine abundances by EPMA in samples R050109
409 and R070654 of 1.9 and 1.5 wt.% F, respectively, fluorine was below detection (detection limit

410 was approximately 0.05 wt.% F) in our EPMA analyses of R050109 and R070654 as well as the
411 other phosphate samples from Big Fish River, Yukon Canada that we analyzed. To accurately
412 measure fluorine by EPMA, a synthetic multilayer crystal with a large d-spacing (e.g., LDE-1,
413 OV-60, PC0) is typically preferred over the more classically used and widely available thallium
414 acid phosphate (TAP) crystal because the intensity of the F $K\alpha$ peak using the multilayer crystal
415 is approximately 14 times higher than with TAP (Potts and Tindle, 1989; Raudsepp, 1995; Reed,
416 2005). This enhanced intensity in the F $K\alpha$ line renders the interference from a third order P $K\alpha$
417 line (and all other third order or greater interferences) on the F $K\alpha$ line insignificant, which was
418 one of the primary problems with analyzing F in apatite using a TAP crystal (Potts and Tindle,
419 1989; Raudsepp, 1995; Reed, 2005). Furthermore, the primary difference in the EPMA routines
420 between our study and that of Tait et al. (2011) is our use of an LDE-1 crystal to measure
421 fluorine X-ray counts versus use by Tait et al. (2011) of a TAP crystal (Robert Downs Pers.
422 Comm.); this may explain the differences between our results. We further investigated whether
423 or not F was present in the “bobdownsite” using ^{19}F MAS/NMR spectroscopy, which confirmed
424 that F was below detection (~ 100 ppm F) in the “bobdownsite” samples, consistent with our
425 EPMA results.

426

427 Whitlockite from Big Fish River, Yukon Canada

428 The mineral “bobdownsite” is differentiated from whitlockite based on the presence of a
429 monofluorophosphate group (PO_3F^{2-}) rather than a protonated phosphate group ($\text{PO}_3\text{OH}^{2-}$). We
430 were unable to detect fluorine in any of the phosphate specimens from Big Fish River, Yukon
431 Canada, including the type specimen R050904. Furthermore, measured H_2O abundances were at

432 a level consistent with a whitlockite along the whitlockite-merrillite join. Consequently, we
433 regretfully conclude that the mineral bobdownsite must be discredited.

434

435 **Implications for structural accommodation of fluorine in krásnoite**

436 The mineral krásnoite $[\text{Ca}_3\text{Al}_{7.7}\text{Si}_3\text{P}_4\text{O}_{22.9}(\text{OH})_{13.3}\text{F}_2 \cdot 8\text{H}_2\text{O}]$ is reported to be the fluorine
437 analog of the mineral perhamite (Mills et al., 2011). In a follow-up manuscript describing the
438 mineral krásnoite, Mills et al. (2012) concluded that the fluorine was substituting for OH^- on a
439 hydrogen phosphate anion ($\text{PO}_3\text{OH}^{2-}$), forming a fluorophosphate group rather than substituting
440 for one of the other OH^- sites available in the mineral. Although krásnoite is a valid species
441 regardless of the structural accommodation mechanism of fluorine, we have examined the
442 assignment of fluorine to a monofluorophosphate component given the paucity of such molecular
443 groups in other minerals as exemplified by the discreditation of bobdownsite. There are two
444 primary lines of evidence used by Mills et al. (2012) to support the occurrence of
445 monofluorophosphate groups in krásnoite, including vibrational (Raman and IR) spectroscopic
446 data and ^{19}F MAS NMR data. We compare the data in Mills et al. (2012) with those published on
447 synthetic monofluorophosphate salts to further elucidate the structural role of F in krásnoite.

448 Mills et al. (2012) also reported both Raman and FTIR data for krásnoite. They assigned
449 a Raman peak at 920 cm^{-1} to the P-F symmetric stretching mode in PO_3F based on the same
450 assignment in bobdownsite from Tait et al. (2011); however, this peak position falls outside the
451 range of the F-P ν_1 mode in PO_3F from fluorophosphates salts (Baran and Weil, 2009; Heide et
452 al., 1985; Jantz et al., 2016; Weil et al., 2015; Weil et al., 2004; Weil et al., 2007; Zeibig et al.,
453 1991), instead falling within the range of stretching and bending modes attributed to P-O or P-
454 O(H) groups (Jolliff et al., 2006; Socrates, 2001). Therefore, the 920 cm^{-1} Raman peak is likely

455 not indicative of a monofluorophosphate group in krásnoite. A peak at 820 cm^{-1} within the FTIR
456 spectrum of krásnoite was also assigned to a fluorophosphate group by Mills et al. (2012). The
457 position of the P-F ν_1 modes for fluorophosphate salts ranges from 727 to 824 cm^{-1} (Baran and
458 Weil, 2009; Jantz et al., 2016; Weil et al., 2015; Weil et al., 2004; Weil et al., 2007), so the
459 assignment of a P-F ν_1 mode to the 820 cm^{-1} in krásnoite is permissive; nevertheless, the lack of
460 a corresponding Raman peak to corroborate this assignment does not lend confidence to the
461 interpretation, especially given overlaps in the 820 cm^{-1} region with a number of other peaks
462 related to Al-O or Si-O vibrational modes (Socrates, 2001). Consequently, the vibrational
463 spectroscopic data do not provide sufficient evidence that krásnoite contains
464 monofluorophosphate groups within its structure.

465 Mills et al. (2012) reported ^{19}F MAS NMR results for krásnoite that were interpreted to
466 verify the presence of F in the mineral structure. Because chemical shifts reported by Mills et al.
467 (2012) were relative to CaF_2 , we have converted their values relative to CFCl_3 , the conventional
468 standard for ^{19}F NMR spectral comparisons (e.g., Huve et al., 1992). The chemical shift of ^{19}F in
469 CaF_2 relative to CFCl_3 is -110 ppm (Wang and Grey, 1998), which corresponds to a new primary
470 peak at a chemical shift of -130 ppm with minor peaks at chemical shifts of -110 ppm , -140 ppm ,
471 and -150 ppm . The ^{19}F chemical shifts for the monofluorophosphate groups in fluorophosphate
472 salts ranges from -52.5 ppm for BaPOF_3 to -75 ppm for $\text{Na}_2\text{PO}_3\text{F}$ (Jantz et al., 2016; Stoeger et
473 al., 2013; Weil et al., 2004; Weil et al., 2007; Zhang et al., 2007), which are substantially
474 displaced from the observed ^{19}F chemical shifts for krásnoite (Mills et al., 2012). Consequently,
475 the ^{19}F MAS NMR data in Mills et al. (2012) do not support assignment of F in krásnoite to
476 monofluorophosphate groups. Furthermore, the ^{19}F NMR peak for monofluorophosphate should
477 be represented by a doublet owing to the strong scalar coupling between ^{19}F and ^{31}P nuclei (e.g.,

478 Stoeger et al., 2013). In addition, Mills et al. (2012) attributed the peak at a chemical shift of -
479 150 ppm to a minor fluorapatite impurity, whereas ^{19}F NMR spectra of fluorapatite exhibit a
480 chemical shift near -103 ppm (e.g., Braun et al., 1995; Mason et al., 2009; McCubbin et al.,
481 2008), which is not exhibited by the ^{19}F NMR spectra for krásnoite. To further elucidate the role
482 of F in the structure of krásnoite, we have interpreted the ^{19}F NMR spectra accordingly and show
483 that the chemical shifts observed at -130, -140, and -150 ppm can be ascribed to Al-F groups
484 (Chupas et al., 2003; Kao and Chen, 2003; Kiczinski and Stebbins, 2002; Zhang et al., 2002),
485 indicating that F^- likely substitutes for OH^- bonded to Al in perhamite (i.e., Mills et al., 2006).

486

487 **Proposed criteria for identification of minerals with a monofluorophosphate (PO_3F^{2-}) anion**

488 We recommend that future reports of new minerals containing essential
489 monofluorophosphate anions be vetted by abundance measurements of fluorine, vibrational
490 spectroscopy (both Raman and FTIR), and where paramagnetic components are permissibly low,
491 NMR spectroscopy. Furthermore, the previous reports of bobdownsite and krásnoite highlight
492 the importance of using synthetic compounds containing monofluorophosphate anions as a point
493 of comparison in the identification of minerals with essential monofluorophosphate. Given that
494 fluoride is a common substituent for hydroxyl in many phosphates and occupies crystallographic
495 sites in phosphates that are not bonded directly to phosphorus, a concerted effort should also be
496 made to verify that a proposed new monofluorophosphate mineral contains PO_3F molecular
497 groups, or at minimum, P-F bonds. Although not a shortcoming of the bobdownsite and
498 krásnoite studies (Mills et al., 2012; Tait et al., 2011), it must be emphasized that structural data
499 that yield satisfactory P-F bond lengths determined by X-ray crystallography, coupled with direct

500 chemical analyses of fluorine in a material, do not constitute sufficient evidence alone to identify
501 a new mineral having essential monofluorophosphate anions.

502

503 **Implications**

504 The preponderance of data collection on whitlockite from Big Fish River, Yukon Canada
505 has highlighted the potential utility of this material as a phosphate standard for H abundance and
506 H-isotopic analysis by secondary ion mass spectrometry (SIMS). Given the heightened interest
507 in the analysis of hydrogen abundances and hydrogen isotopes in phosphates from planetary
508 materials (i.e., Barnes et al., 2013; Barnes et al., 2014; Barrett et al., 2016; Boctor et al., 2003;
509 Boyce et al., 2012; Boyce et al., 2010; Greenwood et al., 2008; Greenwood et al., 2011; Jones et
510 al., 2014; Jones et al., 2016; Mane et al., 2016; McCubbin et al., 2012; McCubbin et al., 2014;
511 McCubbin et al., 2010; Robinson et al., 2016; Robinson and Taylor, 2014; Sarafian et al., 2014;
512 Sarafian et al., 2013; Tartèse et al., 2013; Tartèse et al., 2014a; Tartèse et al., 2014b; Treiman et
513 al., 2014), the identification of whitlockite with consistent inter- and intra-granular H₂O
514 abundances and an isotopically light H isotope composition is unique among available phosphate
515 SIMS standards (c.f., McCubbin et al., 2015a, and references therein). Given that many of the
516 SIMS analyses of merrillite in planetary samples have been conducted using apatite standards
517 (Mane et al., 2016; McCubbin et al., 2014), a whitlockite standard will provide a better matrix
518 match for future SIMS studies of merrillite or whitlockite in Earth and planetary materials.

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Tables

Table 1. Average electron microprobe analyses of phosphates analyzed in present study

Oxide	Yukon					
	Bobdownsite_A	phosphate	Bobdownsite_Tait	R050109	R070654	MGS-008
P ₂ O ₅	45.52 (71)	46.6 (2)	46.94 (39)	47.07 (29)	46.03 (52)	46.98 (66)
SiO ₂	0.09 (3)	0.00 (0)	0.10 (10)	0.00 (0)	0.00 (0)	0.00 (0)
Al ₂ O ₃	0.37 (12)	0.34 (14)	0.30 (15)	0.01 (1)	0.00 (0)	n.d.
FeO	1.09 (11)	1.10 (19)	1.43 (40)	1.33 (10)	0.01 (1)	0.00 (0)
MnO	0.02 (1)	0.01 (1)	0.02 (2)	0.02 (1)	0.02 (3)	0.00 (0)
MgO	2.87 (8)	2.88 (13)	2.63 (19)	2.77 (11)	3.53 (8)	3.75 (10)
CaO	47.19 (50)	46.5 (2)	47.04 (40)	47.46 (21)	47.88 (19)	47.65 (36)
Na ₂ O	0.51 (22)	1.00 (31)	0.72 (29)	0.61 (18)	0.19 (0.04)	0.00 (0)
H ₂ O	0.71 (4)	0.70 (5)	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
SO ₃	0.00 (0)	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.16 (9)
F	0.00 (0)	0.00 (0)	0.00 (0)	0.00 (0)	0.00 (0)	n.d.
Cl	0.00 (0)	0.00 (0)	0.01 (1)	0.00 (0)	0.00 (0)	0.01 (1)
-O ≡ F	0	0	0	0	0	-
-O ≡ Cl	0	0	0	0	0	0
Total	98.37	99.2	99.20	99.26	97.65	99.41
<i>N</i>	78	54	66	101	102	10
<i>Structural formulae based on 28 oxygens</i>						
P	6.92	7.01	7.01	7.03	6.97	6.99
Si	0.02	0.00	0.02	0.00	0.00	0.00
Al	0.08	0.07	0.06	0.00	0.00	-
Fe	0.16	0.16	0.21	0.20	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.77	0.76	0.69	0.73	0.94	0.98
Ca	9.09	8.86	8.90	8.98	9.18	8.98
Na	0.18	0.34	0.25	0.21	0.07	0.00
S	0.00	-	-	-	-	0.02
∑ Cations	17.22	17.21	17.14	17.14	17.16	16.95
F	0.00	0.00	0.00	0.00	0.00	-
Cl	0.00	0.00	0.00	0.00	0.00	0.00
∑ Anions						
OH	0.86	0.83	0.85*	0.85*	0.85*	1.00 [‡]

N – number of analyses

- signifies that a value was not computed

n.d. – abundance was not determined

*Value is based on the average OH from Bobdownsite_A and Yukon phosphate to aid in accurate structural formula determination

[‡]Value is assumed based on stoichiometry and used to calculate an appropriate structural formula

Parenthetical values represent the uncertainty in the reported abundance

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Figure Captions

834 **Figure 1.** Raman spectra of Yukon phosphate, Bobdownsite_A, bobdownsite type specimen R050109,
835 and bobdownsite from Tip top Mine, South Dakota, USA (R070654). The sample names denoted with an
836 asterisk indicate the data were reported in Tait et al. (2011). The region that is characteristic of P-F
837 symmetric stretching modes in fluorophosphate salts is indicated by the shaded area (Baran and Weil,
838 2009; Heide et al., 1985; Jantz et al., 2016; Weil et al., 2015; Weil et al., 2004; Weil et al., 2007;
839 Zeibig et al., 1991).

840

841 **Figure 2.** ^{19}F MAS/NMR spectra of Bobdownsite_A (top) and Yukon phosphate (bottom) samples with
842 the indicated amounts of added NaF, which approximate one F atom per formula unit (seven P). Shaded
843 region corresponds to chemical shift range for previous reports of compounds containing fluorophosphate
844 groups (see text). Spectra acquired by direct excitation with a 100 s relaxation delay and a spinning rate of
845 20 kHz. Asterisks denote spinning sidebands.

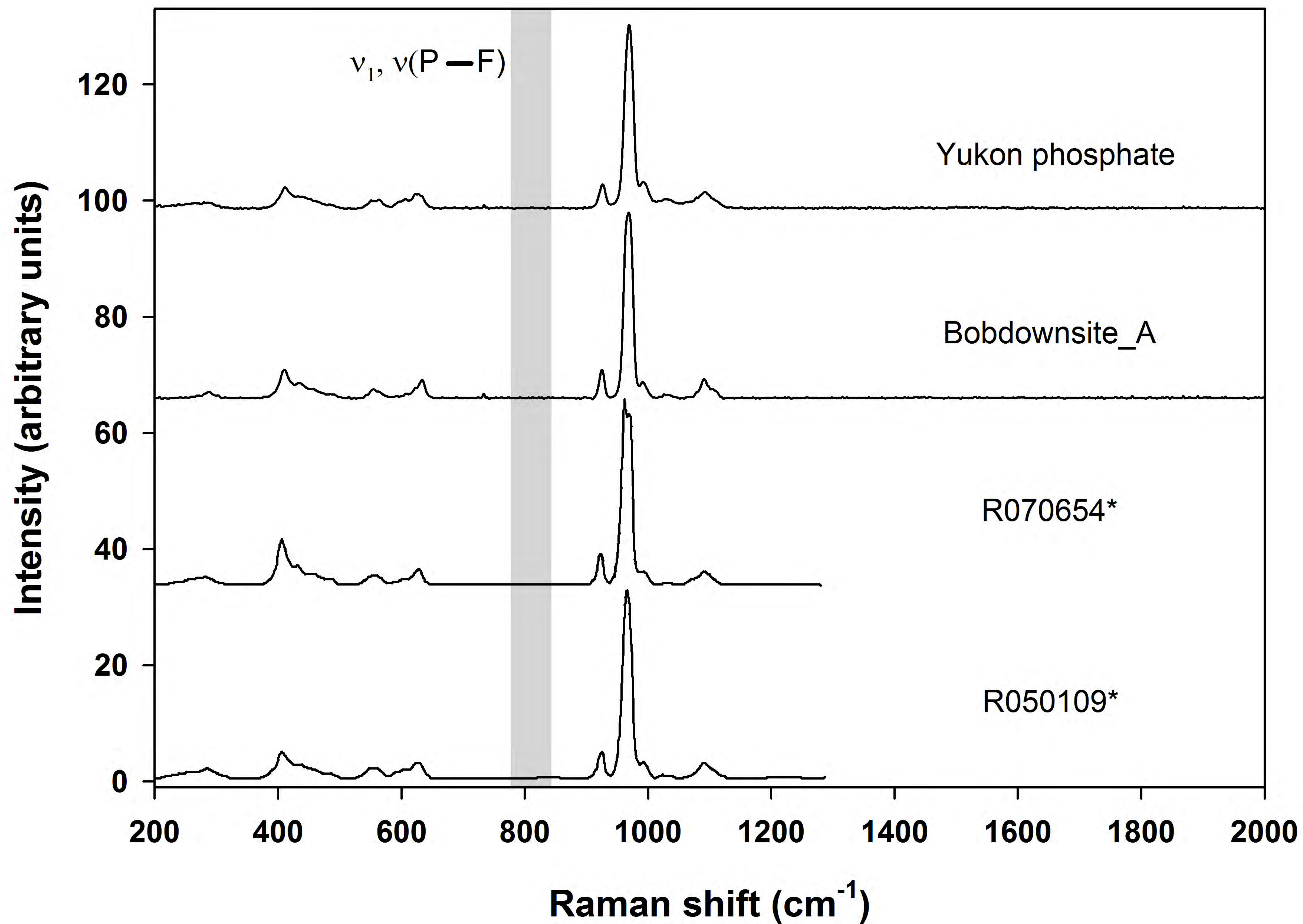
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847 **Figure 3.** Comparison of the center band region of ^1H MAS/NMR spectra of Bobdownsite_A (top) and
848 Yukon phosphate (middle) specimens and synthetic whitlockite sample MGS-008 (bottom). Spectra
849 acquired by direct excitation with a 30 s relaxation delay at a spinning rate of 10 kHz. Spinning sidebands
850 are denoted by asterisks and for the natural phosphate samples extend for at least four more orders owing
851 to broadening by paramagnetic ions.

852

853 **Figure 4.** Comparison of ^{31}P SP-MAS NMR spectra of Bobdownsite_A (top) and Yukon phosphate
854 (middle) specimens and synthetic whitlockite sample MGS-008 (bottom). Spectra were acquired with
855 direct excitation (single-pulse) with a 300 s relaxation delay at a spinning rate of 15 kHz. Spinning
856 sidebands fall outside the displayed spectral region. Highly resolved spectra for synthetic samples result
857 from absence of paramagnetic substituents.

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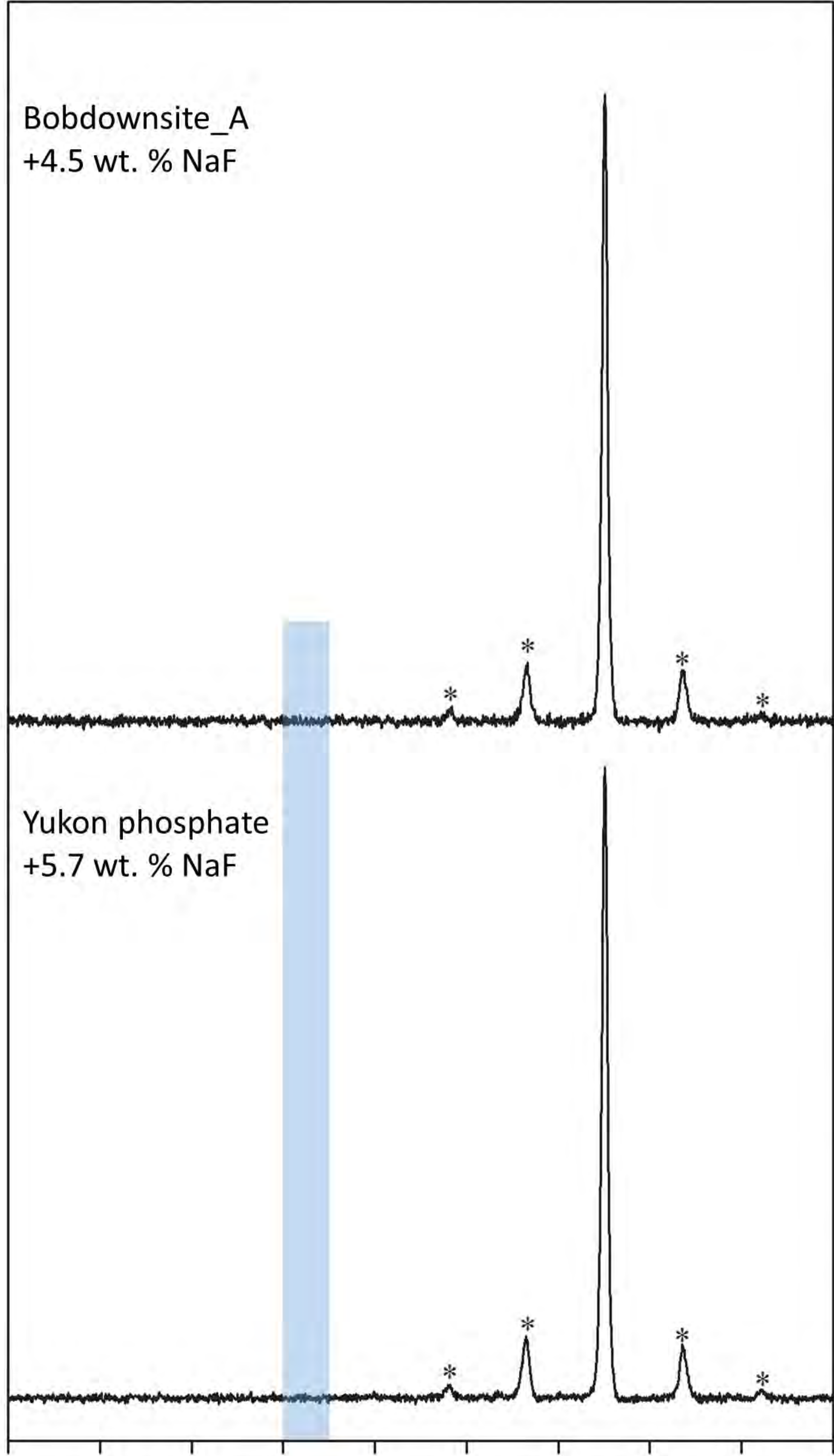
Bobdownsite_A
+4.5 wt. % NaF

Yukon phosphate
+5.7 wt. % NaF

Intensity (arb.)

100 50 0 -50 -100 -150 -200 -250 -300 -350

^{19}F Chemical Shift [ppm]



Intensity (arb.)

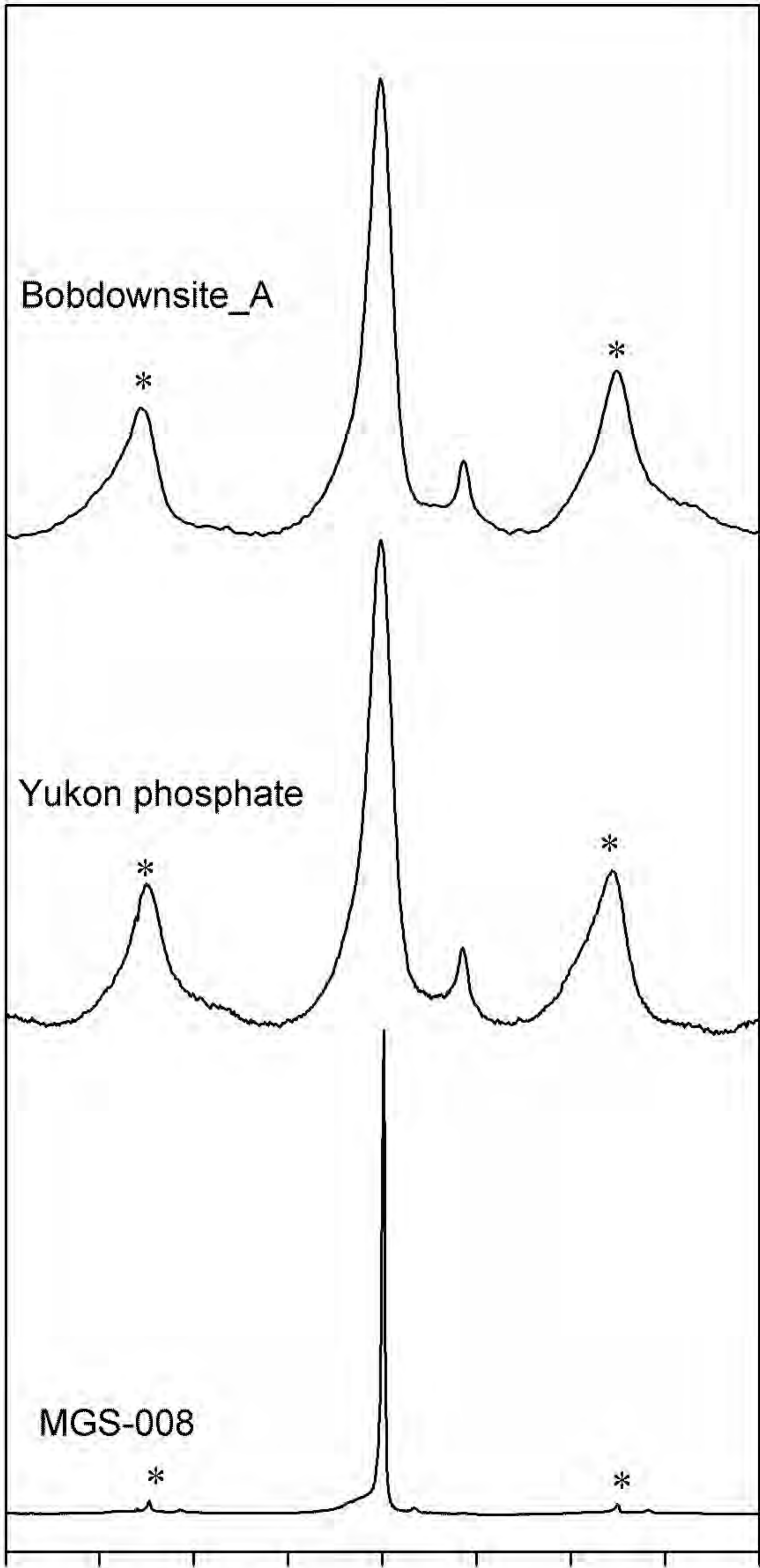
Bobdownsite_A

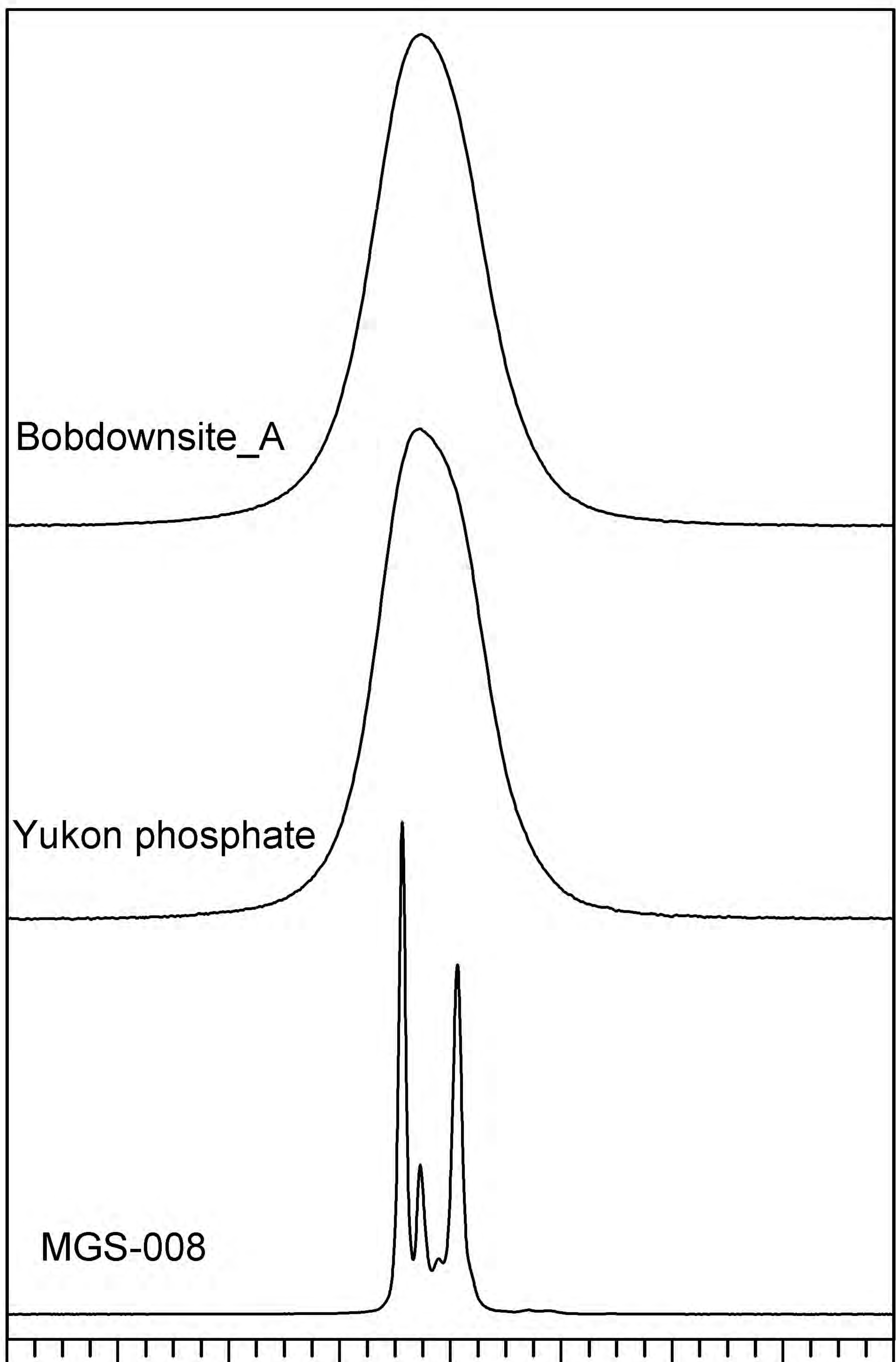
Yukon phosphate

MGS-008

50 40 30 20 10 0 -10 -20 -30

^1H Chemical Shift [ppm]





Bobdownsite_A

Yukon phosphate

MGS-008

Intensity (arb. units)

20 15 10 5 0 -5 -10 -15 -20

^{31}P chemical shift (ppm)