

1 Extreme reduction: Vanadium melts in mantle-derived oxide xenoliths

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16 Abstract

17 Coarse-grained xenoliths of hibonite + grossite + Mg-Al-V spinel from Cretaceous
18 pyroclastic rocks on Mt Carmel, N. Israel, and from Sierra de Comechingones,
19 Argentina, include spherules, rods and dense branching structures of native
20 vanadium and V-Al alloys. The microstructures suggest that vanadium melts
21 became immiscible with the host Ca-Al-Mg-Si-O melt, which was already depleted in
22 Fe and Si by the immiscible separation of Fe-Si-C silicide melts, and nucleated as
23 droplets on the surfaces of the oxide phases, principally hibonite. Many extended
24 outward into rods or branching structures as the host oxide crystal grew. The
25 stability of V⁰ implies oxygen fugacities ≥ 9 log units below the Iron-Wustite buffer,
26 suggesting a hydrogen-dominated atmosphere. This is supported by wt%-levels of
27 hydrogen released by crushing hibonite grains, by Raman spectroscopy on the
28 hibonite, and by the presence of VH₂, the first natural hydride, among the vanadium
29 balls. The oxide assemblage formed at 1400-1200 °C; the solution of hydrogen in
30 the metal could lower the melting point of V⁰ to these temperatures. These
31 assemblages probably resulted from reaction between differentiated mafic melts and
32 mantle-derived CH₄+H₂ fluids near the crust-mantle boundary, and their *f*O₂ record
33 the most reducing magmatic conditions yet documented on Earth.

34 35 Introduction

36 Vanadium is a mildly incompatible, refractory but lithophile transition element; it also
37 can be mildly siderophile, and may have partitioned into Earth's core at high
38 pressure and low oxygen fugacity (fO_2 ; Huang et al., 2015). Vanadium forms >200
39 minerals (Liu et al., 2018), and is a minor element on Earth and cosmic materials. Its
40 valence states (+5 to +2) represent a wide range of fO_2 . At 1500°C the V^{5+}/V^{4+}
41 transition occurs at fO_2 5 log units above the Iron-Wustite buffer ($\Delta IW+5$), and the
42 V^{3+}/V^{2+} transition at $\Delta IW-6$; native vanadium (V^0) becomes stable at *ca* $\Delta IW-9$,
43 conditions similar to the early solar nebula (Grossman et al., 2008). However, natural
44 V^0 has been reported previously only from sublimates in volcanic fumaroles
45 (Ostrooumov and Taran, 2016), and associated with chromitites from the Othrys
46 ophiolite, Greece (Ifandi et al., 2018).

47 Here we describe V^0 and V-Al alloys trapped as melts in hibonite ($CaAl_{12}O_{19}$)
48 and grossite ($CaAl_4O_7$) crystallizing in a super-reduced melt-fluid system in northern
49 Israel (Griffin et al., 2019), and similar material from Argentina. Sampling and
50 analytical methods are described in the Supplementary Data.

51

52 **Background**

53 Most of the material described here comprises xenoliths from the pyroclastic
54 ejecta of Cretaceous (99-85 Ma) intraplate basaltic volcanoes exposed on Mt
55 Carmel, in northern Israel (Fig.SD1; Griffin et al., 2016, 2018a, 2019, references
56 therein). At least eight of these volcanoes erupted over an area of *ca* 150 km², and
57 their xenoliths provide snapshots of similar melt-fluid systems, sampled at different
58 stages of their evolution. Aggregates of skeletal corundum crystals (Carmel
59 Sapphire™) occur as xenoliths in the tuffs, or re-deposited in nearby alluvial placers,
60 mainly in the Kishon River. Melt pockets trapped within and between these rapidly-
61 grown corundum crystals contain mineral assemblages requiring high T (>1450-1200
62 °C), moderate P (*ca* 1 GPa) and extremely low fO_2 (see below).

63 Paragenetic studies (Griffin et al., 2018a, 2019; Xiong et al., 2017) suggest
64 that both the low fO_2 and the crystallization of skeletal corundum reflect the
65 interaction of differentiated mafic magmas with CH_4+H_2 at high fluid/melt ratios.
66 These fluid-melt systems were sampled by eruption of the host basalts, but were not
67 directly genetically related to them; they represent much shallower, pre-existing
68 systems.

69 The earliest paragenesis in the melt pockets of these xenoliths is corundum +
70 tistarite (Ti_2O_3) + carmeltazite ($\text{ZrAl}_2\text{Ti}_4\text{O}_{11}$; Griffin et al., 2018b) + Mg-Al-Ti spinel in
71 a Ca-Mg-Al-Si-O glass. The crystallization of these Ti^{3+} -bearing phases requires $f\text{O}_2$
72 at least 6 log units below the Iron-Wustite buffer ($\Delta\text{IW-6}$; Griffin et al., 2016). The
73 original silicate melts were depleted in Fe and Si by the exsolution of immiscible Fe-
74 Ti-C-silicide melts, which also occur abundantly as inclusions in the corundum; these
75 melts crystallized moissanite (SiC), TiB_2 , TiN and khamrabaevite (TiC); the Ti^{2+} -
76 bearing phases suggest still lower $f\text{O}_2$ (Griffin et al., 2016, 2018a). The metal-silicide
77 melts efficiently scavenged Fe and heavier transition elements, so that no Fe-
78 bearing oxides or silicates are found in the melt pockets. The assemblages
79 described here thus formed from residual melts after extensive crystal fractionation
80 and sequential immiscibility, which enriched these melts in minor elements (REE, Zr,
81 Ti, V, Mn, Sc), Ca and Al. Hibonite appears late in the crystallization sequence,
82 together with corundum, carmeltazite, Mg-Al spinel, TiN, Fe-Ti silicides, TiC and
83 glass.

84 Coarser-grained (to cm-sized crystals; Fig. 1) intergrowths of hibonite,
85 grossite and spinel also occur as grains up to 2.5 cm across in placers of the Kishon
86 and Yoqneam Rivers that drain Mt Carmel. They suggest that hibonite-bearing melts
87 like those trapped in the corundum aggregates evolved even further beneath some
88 volcanic centres. In these xenoliths, V^0 and V-Al alloys occur as spherical, rod-like
89 and branching inclusions, mainly in hibonite.

90 At Mt Carmel, the late crystallization of dmisteinbergite (a polymorph of
91 anorthite) in the melt pockets reflects the peritectic reaction $\text{Liq} + \text{Crn} \rightarrow \text{An}$,
92 equivalent to the incongruent melting of anorthite ($\text{An} \rightarrow \text{Liq} + \text{Crn}$). This well-studied
93 reaction is constrained experimentally to pressures (P) >0.9 GPa and temperatures
94 (T) of ca 1450 °C (Goldsmith, 1980). However, thermodynamic modelling in the
95 $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system (Ottonello et al., 2013) suggests that grossite may not be
96 stable at $P >1$ GPa, and is definitely not present at $P =2$ GPa. The same modelling
97 shows that the melt-pocket glasses, which clearly were crystallizing corundum
98 (Griffin et al., 2016, 2018a), cannot be in equilibrium with corundum at $P <1$ GPa.
99 Finally, some samples contain the assemblage hibonite+krotite (CaAlO_4)+gehlenite,
100 suggesting $P \geq 1$ GPa (Ottonello et al., 2013). These P - T estimates place the
101 proposed site of fluid-melt interaction in the uppermost mantle, near the crust-mantle

102 boundary in the area, geophysically estimated at 25-30 km depth (Segev and
103 Rybakov, 2011). Comparisons of mineral parageneses in the melt pockets with
104 experimental studies suggest that T decreased from $>1450^{\circ}\text{C}$ to ca 1200°C as $f\text{O}_2$
105 dropped from $\Delta\text{IW}-6$ to $\Delta\text{IW}\leq-9$ (Griffin et al., 2018a; references therein).

106

107 **Petrography**

108 The petrography and parageneses of the coarse intergrowths from Mt Carmel
109 are described in detail elsewhere (Griffin et al., 2019). Resorbed remnants of
110 corundum in hibonite (Mt Carmel) document the peritectic reaction $\text{Crn} + \text{Liq} \rightarrow \text{Hbn}$.
111 The latest paragenesis (Fig. 2a) is grossite + spinel + krotite (CaAl_2O_4) + fluorite \pm
112 the undescribed oxyfluoride phase $\text{Ca}_4\text{Al}_6\text{F}_2\text{O}_{12} \pm$ fluorine-rich perovskite
113 ($\text{CaTi}(\text{O},\text{F})_3$).

114 Very similar assemblages have been found in an as-yet undocumented
115 locality in the Sierra de Comechingones, Argentina. The xenoliths comprise platy
116 cm-sized crystals of V-rich hibonite, in a matrix of grossite, dellagiustaitite ($\text{Al}_2\text{V}^{2+}\text{O}_4$
117 spinel, Cámara et al. 2018), and other phases including $\text{Ca}_4\text{Al}_6\text{F}_2\text{O}_{12}$ (Fig. 2b,c).

118 In the Mt Carmel xenoliths, vanadium occurs mainly as spheroidal to
119 amoeboid balls up to mm size in hibonite crystals; some balls show exsolution of Al-
120 rich vs Mn-rich vanadium alloys. More commonly, V^0 forms droplets on (0001)
121 planes, or rods normal to (0001); these rods commonly are necked down to produce
122 linear trains of droplets normal to (0001) (Figs 2a). The inclusions are zonally
123 distributed in some crystals (Fig. 3). In the Sierra de Comechingones samples, V^0
124 also forms elongate inclusions in hibonite, normal to (0001), necked down at
125 irregular intervals; some are partially empty (Fig. 4; Fig. SD2). Spheroidal to
126 amoeboid rods up to 0.1-0.2 mm across are mantled by dellagiustaitite or $\text{V}^{3+}/\text{V}^{2+}$ -rich
127 spinel (Fig. 5). Some examples contain tiny precipitates of Cu, and larger inclusions
128 (Fig. 5b,c) can be vesicular, attesting to the presence of volatiles.

129 In the Mt Carmel material, some spherical V^0 inclusions develop (Fig. 6; Fig.
130 SD3) into “dense branching structures” (Goldenfeld, 1989). These grow roughly
131 normal to (0001) of the host hibonite crystal, and each filament terminates in a single
132 dendritic crystal. Clusters of fine branches terminate at planes parallel to (0001),
133 suggesting pauses in the growth of the hibonite crystal. Some branches continued
134 to grow when crystal growth resumed, but new droplets of V^0 also nucleated on the

135 new crystal plane and grew independently of the older branches. In the example
136 shown in Fig. 6, this stop-start process occurred at least four times. The 3D- μ CT
137 images (Fig. SD3) show that the outer parts of many filaments contain no solid
138 phases, even where they terminate well below the present crystal face, and that
139 these “empty” portions are continuous with the vanadium-filled branches. Analysis of
140 the 3D images indicates that the voids make up approximately 3% of the total
141 volume of the illustrated branching structures. Some hibonite crystals with V^0
142 inclusions also contain hexagonal plates of apparently amorphous carbon (i.e. no
143 Raman signal), 50 μ m across but thin enough to be transparent.

144 In the Mt Carmel material, small bulbous protuberances on the sides of some
145 spheroidal V^0 inclusions enclosed in grossite have proven to be the phase VH_2 ,
146 representing the first discovery of a naturally-occurring metal hydride (Bindi et al.,
147 2019).

148

149 **Mineral Chemistry**

150 The smallest V^0 inclusions in hibonite from Mt Carmel contain 0.5-2.0% Si and
151 1.5-2.5% Mn (the oxide matrix assures that Si is in the alloy). Most larger inclusions
152 have less Si, 1-2% Cr, 0.5-3.5% Mn, and up to ca 4 wt% Al (V_9Al ; Table 1). Irregular
153 balls included in grossite are the latest to form, and contain up to 15 wt% Al (V_4Al ;
154 Table 1). Many of the EMP analyses total <100%. The discovery of vanadium
155 dihydride (VH_2 ; Bindi et al. 2019) among these balls suggests that the deficit could
156 be due to hydrogen in solid solution.

157 EBSD imaging and single-crystal X-ray diffraction studies confirm that
158 V^0 in the larger inclusions is cubic, and a TEM diffraction pattern matches the <110>
159 zone axis of V (James and Straumanis, 1960). Three inclusions of Al-rich vanadium
160 analysed by single-crystal XRD have space group $Im-3m$, consistent with the Al-V
161 phase diagram (Kroupa et al., 2017). The unit cell increases from 3.032 Å to 3.068
162 Å as Al increases from ca 2 at.% to >20 at.% (Fig. 7).

163 Vanadium in the Sierra de Comechingones hibonite contains almost no Al, but
164 has Si contents similar to the Mt Carmel examples (0.5-2.2 wt%), and many
165 analyses have low analytical totals (95-98 wt%). The Cr contents are clearly higher
166 than in the Mt Carmel material. Vanadium-oxide phases (Fig. 5) analysed by single-
167 crystal XRD yielded either a tetragonal or a monoclinic cell, corresponding to two

168 polymorphs of synthetic $V_{14}O_6$: a β -phase (space group $I4/mmm$), and a γ -phase,
169 monoclinic (space group $C2/m$) with ordered vacancies. The coexistence of these
170 two phases constrains the temperature to <1350 °C (Davydov and Rempel, 2009).
171 These oxides suggest an fO_2 somewhat higher than in the Mt. Carmel rocks, but the
172 presence of V^{2+} in spinel (dellagiustaite) requires $fO_2 = \Delta IW$ between -6 and -9.

173

174 **Analysis of included fluids**

175 To evaluate the composition of fluids that might be enclosed in the observed
176 voids associated with the vanadium rods and branching structures, four large (2-3
177 mm) grains of the hibonite-grossite aggregates from Mt Carmel were analysed for H,
178 C, N, and S contents by ignition in an O_2 -He atmosphere at ca 1150 °C, followed by
179 chromatographic analysis (see Supplementary Data). For comparison, four grains of
180 the corundum aggregates from Mt Carmel also were analysed. Contents of H, C, S
181 and N are given in Table 2. The hibonite samples all contain significant levels of
182 carbon and hydrogen, averaging 1120 ppm C and 2800 ppm H_2 by weight. This is 4-
183 5 times the concentrations found in the corundum aggregates, even though the
184 observed void space in the corundum aggregates appears to be greater than in the
185 hibonite crystals. However, in both cases the included fluids are comprised of >95
186 at.% hydrogen, assuming that oxygen is at most a minor constituent, as consistent
187 with the required low fO_2 .

188

189 **Raman Spectroscopy**

190 Raman spectra of hibonite from both localities (Fig. 8) show good peaks in the
191 range $0-1000$ cm^{-1} , indicating that the hibonite is well-crystallized, in contrast to most
192 meteoritic hibonite (e.g., Ma, 2010). Peak positions are in very good agreement with
193 those observed by Hofmeister et al. (2004) for synthetic hibonite (Table 3). We
194 observe a strong polarization effect on particular Raman shifts. Changes in the
195 Raman shift and intensity of the bands can be ascribed to the small amount of V in
196 the hibonite structure. A broad band at ca 1470 cm^{-1} is present only in N-S
197 orientation of the crystals, along with two shoulders at 1256 and 1588 cm^{-1} . These
198 are difficult to attribute, as plausible groups are ν_3 modes of CO_3 groups, but these
199 are usually very weak in carbonates. Another plausible assignment is to $-CH_2$ and $-$
200 CH_3 deformations. Interesting features are observed in the $3000-4150$ cm^{-1} spectral

201 range, where we observe Raman shifts corresponding to the stretching of O-H bonds
202 that are also polarized. This implies the presence of H in a nominally anhydrous
203 phase. However, the bonding is not well ordered and the bands are rather broad.
204 Bands are also observed in hibonite from Mt. Carmel but at different Raman shifts.
205 The only mode observed in hibonite from both localities is the Raman shift at ca
206 3950 cm^{-1} , which should correspond to one OH bond with the hydrogen far from any
207 donor oxygen. In the Mt. Carmel hibonite, the band at 3819 cm^{-1} is very strong and
208 this points to a higher content of H diffused within the lattice and defects in the
209 hibonite. This is consistent with the chromatography measurements reported above.
210 The intensity of the bands changes across the crystal, suggesting that the H is
211 related to the degassing of V^0 and VH_2 inclusions, yielding empty spaces by volume
212 reduction, as seen in the 3D μ -tomography images (Figs SD-2, SD-3), and diffusing
213 the H across the hibonite host.

214

215 **Discussion and Conclusions**

216 Native vanadium has been reported previously from fumaroles on a Mexican
217 volcano (Ostrooumov and Taran, 2016), where it forms platy crystals, never
218 intergrown with other minerals. It also has been found in heavy-mineral concentrates
219 from chromitites in the Othrys ophiolite, Greece (Ifandi et al., 2018), where it appears
220 to be related to serpentinisation processes. In contrast, the structures shown in
221 Figures 2-6 clearly suggest the coexistence of immiscible metallic melts and a low-
222 α_{SiO_2} silicate melt that was crystallizing Ca-Al oxides and spinel. They are best
223 explained by the nucleation of drops of molten vanadium on the faces of oxide
224 crystals exposed to the silicate melt. Many of these drops apparently attracted more
225 V^0 as the crystal grew, producing larger and elongated inclusions, continuously in
226 contact with the surrounding mixture of immiscible melts. These inclusions are thus
227 analogous in many ways to the cylindrical, CO_2 -filled inclusions of sulphide melts in
228 clinopyroxene megacrysts from some alkali basalts (Andersen et al., 1987).

229 The dense branching structures shown in Figure 4 appear to evolve in a
230 different way. They are not crystallographically controlled, but radiate outwards from
231 initial melt droplets; some even grow in spiral patterns (Fig. 6a). The formation of
232 such dendritic, or dense branching, structures typically reflects diffusion-controlled
233 interface motion such as the growth of a crystal into a fluid under conditions of mild

234 to strong supercooling (Goldenfeld, 1989). Since each branch of the dendrite would
235 need to be growing against a fluid, these structures probably grew rapidly from the
236 initial ball on a crystal surface, out into the melt surrounding the hibonite crystal, only
237 to be encased by hibonite as the crystal surface advanced further out into the melt.
238 The obvious planes in Figures 2 and 6b thus could represent stages where the
239 hibonite overgrew and terminated some parts of the expanding dendrite, but
240 presented a stable surface for the nucleation of new V^0 droplets. These structures
241 thus reflect an interplay between the growth rates of the V^0 dendrites and the
242 hibonite crystal, involving diffusion of several chemical species. Fluctuations in the
243 removal of latent heat of crystallization from the advancing crystal surface, rather
244 than the diffusion of elements in the silicate melt, may have controlled dendrite
245 growth.

246 Inclusions of V^0 occur mainly in hibonite, to a lesser extent in grossite and
247 spinel, and rarely in corundum mantled by hibonite; the metallic melt apparently
248 began separating from the parental oxide melt near the temperature of the
249 corundum-hibonite peritectic, driven by the continuing decrease in fO_2 ($V^{2+} \rightarrow V^0$).
250 Vanadium melts at $>1900^\circ\text{C}$; experimental data in binary systems suggest that the
251 observed levels of Al, Si, Mn and Cr might lower the melting temperature by $<100^\circ\text{C}$
252 (Table 1). Since the estimated temperature of the Cor +L \rightarrow Hib peritectic is close to
253 1300°C in the CaO-Al₂O₃-MgO-SiO₂ system (de Aza et al., 2000; Jung, 2010), any
254 immiscible V-dominated melt would be expected to freeze upon unmixing, which
255 apparently did not happen.

256 However, the fO_2 required for the presence of a V^0 melt ($\leq \Delta IW -9$) implies a
257 hydrogen-rich environment, equivalent to the early solar nebula in which hibonite-
258 bearing Calcium Aluminum Inclusions formed (Grossman et al., 2008). From the
259 analyses of the included gasses (Table 2), it is clear that they are dominated by
260 hydrogen, consistent with the inferred low oxygen fugacity and the evidence of
261 hydrogen defects in the Raman spectra of hibonite. The presence of hydrogen is
262 further supported by the recognition of grains of VH₂ (the first natural metal hydride)
263 among the V^0 balls in a sample similar to that in Figure 1 (Bindi et al., 2019). The
264 hibonite from both localities discussed here also contains inclusions of carbon or
265 graphite. At least some of the hydrogen thus may have been produced by the partial

266 oxidation of methane, with the deposition of carbon and the liberation of $H_2 + CO_2$
267 (Griffin et al., 2016).

268 In a hydrogen atmosphere, the melting point of vanadium can be lowered by
269 $>1000^\circ C$ as several wt % H_2 dissolves in the melt; solubility increases dramatically
270 with increasing pressure. H_2 is expelled during solidification of the melt, but the solid
271 V^0 phase can retain significant levels of hydrogen in solution to temperatures below
272 $1000^\circ C$ (Fukai, 2012). The consistently low analytical totals of the V^0 balls from
273 both localities may reflect this solid solution. The outer portions of many dendrite
274 branches (Mt Carmel) and some rods (Argentina) contain no solid phases, even
275 though the empty branches clearly are continuous with the vanadium-filled ones.
276 Furthermore, some of the larger droplets in the dendrites now comprise an irregular
277 lump of V^0 within a subspherical void (Figures 6, SD3). We suggest that these void
278 spaces reflect the exsolution of H_2 from the solidifying V^0 melts in the inner parts of
279 the structures. This could lead to the remelting and expulsion of V^0 from the outer
280 parts of the branches, closer to the front of hibonite nucleation, and perhaps to
281 production of the observed VH_2 phase. Similarly, the vesicles observed in some V^0
282 grains in the hibonites from Sierra de Comechingones (Fig. 5b) may represent the
283 exsolution of H_2 from a cooling melt. As noted above, some of the liberated
284 hydrogen in the Mt Carmel appears to have diffused into the surrounding hibonite,
285 producing the strong Raman band at 3819 cm^{-1} .

286 The petrographic and paragenetic similarities between the assemblages from
287 Mt Carmel and Sierra de Comechingones strongly suggest similar conditions of
288 formation. At present more constraints are available on the Mt Carmel xenoliths,
289 which are interpreted to have crystallized late in the pre-eruption evolution of fO_2 in
290 magma-fluid systems. This evolution ultimately led to the most reducing conditions
291 yet found on Earth, with free hydrogen as the fluid phase. The observed abundance
292 of carbon in the assemblages suggests an important role for CH_4 in this process. At
293 Mt Carmel, such conditions existed for at least 10 m.y. over an area of ca 150 km^2 ,
294 in the uppermost part of a thin mantle lithosphere, and high fluid/rock ratios would be
295 required to maintain such reduced volumes within the mantle. This suggests the
296 derivation of abundant $CH_4 \pm H_2$ fluids from the deeper mantle, which in turn seems to
297 imply that the sublithospheric mantle beneath this area was metal-saturated (i.e. fO_2
298 = IW), such that any C-O-H fluid issuing from it was dominated by $CH_4 \pm H_2$. This

299 conclusion has implications for understanding melting and metasomatic processes in
300 the mantle (Griffin et al., 2018).

301 As discussed elsewhere (Xiong et al., 2017; Griffin et al., 2018) there is a
302 significant, if scattered, body of evidence in the published literature that similar
303 reducing conditions may exist elsewhere on Earth, in connection with several types
304 of explosive volcanism. Finally, the Al-rich late-forming V⁰ melts reported here
305 represent the first *in situ* observation of Al alloys on Earth, and may add credence to
306 reports of Al⁰ in many other localities (cf. Dekov et al., 2009).

307

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420 **Figure Captions**

421
 422 Fig. 1. Combined phase map and backscattered electron (BSE) image of typical hibonite-
 423 grossite-spinel assemblage from Mt Carmel, with drop-like inclusions of native vanadium
 424 (V⁰).

425
 426 Fig. 2. (a) Transmitted-light photo (plane polars) of hibonite-grossite-spinel aggregate from
 427 Mt Carmel, showing inclusions of V⁰ in platy hibonite crystals (ca 5 mm across). Note

428 alternating layers with abundant or scarce inclusions, elongation of some inclusions parallel
429 to c-axis, and necking down of inclusions. (b) Hibonite from Sierra de Comechingones, with
430 vanadium rods normal to (0001) in (c) a grossite- $\text{Ca}_4\text{Al}_6\text{F}_2\text{O}_{12}$ matrix with skeletal F-rich
431 perovskite and dellagiustaite ($\text{V}^{3+}/\text{V}^{2+}$ spinel), some rimming V_{14}O_6 . Each figure is 1.7 mm
432 wide.

433

434 Fig. 3. BSE image of hibonite crystal from Mt Carmel (blue prism shows orientation from
435 EBSD), with zonal distribution of V^0 inclusions.

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437 Figure 4. (a) 3D- μCT image of hibonite fragment (length 600 μm) from Sierra de
438 Comechingones, showing necking-down of cylindrical rods of V^0 . (b) false-coloured image of
439 (a) showing that some V^0 rods (red) are partially empty (green) and some are rimmed by
440 dellagiustaite.

441

442 Fig. 5. (a) Reflected-light image of a polished rock chip from Sierra de Comechingones,
443 showing a V_{14}O_6 inclusion rimmed by dellagiustaite. Red arrow points to a very thin grain of
444 $\text{V}^{3+}_{1.78}\text{Al}_{0.21}\text{V}^{2+}_1\text{O}_4$; the composition of the dellagiustaite rim is $\text{Al}_{1.04}\text{V}^{3+}_{0.96}\text{V}^{2+}_{0.92}\text{Mg}_{0.08}\text{O}_4$. (b)
445 BSE image of V^0 inclusion with abundant fluid inclusions (Table 1, analysis #14). (c) BSE
446 image of V^0 inclusion (Table 1, analyses 2,3) with Cu precipitates, rimmed by euhedral Ti-
447 rich dellagiustaite.

448

449 Figure 6. (a) Transmitted-light and BSE images of a spiral dendritic growth of V^0 in hibonite.
450 (b) 3D- μCT image of vanadium “dendrites” in a hibonite crystal from Mt Carmel; each
451 cluster is ca 1 mm high and grows normal to the (0001) face of the hibonite. Red-orange
452 colours show V^0 , while green colours represent voids.

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454 Figure 7. Al content vs unit cell dimension of inclusions of Al-bearing vanadium in grossite.

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456 Figure 8. Raman spectra of hibonite from Sierra de Comechingones and Mt Carmel.

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Table 1. Mean major-element compositions of vanadium phases, Mt Carmel.

Table 1. EMP Analyses of vanadium phases

wt%	vanadium		V ₉ (Mn,Al)		V ₄ Al	
	EMP		EMP		EMP	
	n=5	stdev	n=5	stdev	n=7	stdev
Si	0.42	0.22	0.52	0.11	0.38	0.04
Zr			0.01	0.01		
Ti	0.01	0.02	0.15	0.11	0.20	0.03
Al	0.32	0.5	3.94	1.27	11.58	0.25
Cr	1.6*		0.71*		0.44	
V	95.2	3.23	79.83	6.86	83.37	0.76
Fe	0.03	0.01	0.01	0.01		
Mn	1.21	0.63	12.20	6.55	2.09	0.07
Ca	0.09	0.06	0.41	0.35	0.21	0.17
	98.9		97.78		98.28	

* EDS data

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Table 2. Gas analyses of hibonite and corundum aggregates from Mt Carmel.

Table 2. Analyses of included gasses, Mt Carmel hibonite and corundum

	sample	N [ppm]	C [ppm]	H [ppm]	S [ppm]
hibonite xl	982	60	1041	1572	73
hibonite aggregate	982	41	1165	2360	64.3
hibonite	1124B	122	1165	3293	113.1
	1124B-				
hibonite	dup.	43	1196	3925	228.7
corundum semi-	1124	156	329	554	166

transparent					
corundum-brecciated	1124	21	152	63	22.6
corundum with glass	1124	26	415	677	115.7
corundum	1124	226	347	667	222.5

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480 **Table 3.** Observed Raman shifts in hibonite from Sierra di Comechingones (Argentina) and

481 Mt. Carmel (Israel)

482 **Table 3.** Observed Raman shifts in hibonite from Sierra di Comechingones and Mt. Carmel

Synthetic (Hofmeister et al. 2004)	Sierra de Comechingones	Sierra de Comechingones	Mt Carmel
<i>Orientation</i> ν (cm ⁻¹)	lath E-W ν (cm ⁻¹)	lath N-S ν (cm ⁻¹)	lath N-S ν (cm ⁻¹)
		85	84.3
			102.1
	130.8	130.8	127
193.7	205.4	205.4	208.9
209.4p			
250.5p			
274.0	268.6	275.8	273.9
331.9	318.9	323.7	
	358.3	345.7	349.6
399.4			
449.5		438	
457.8	457	453.8	451.9
489.1	485.4	485.4	485.4
529.5	522	531	534.7
564.5	576.3		
		593.6	
624.5			
640.4		643.7	643.3
683.8	685.6	681.6	678.9
	726.3		
741.0	744.9		
773.9	767		762.6
795.8		804.3	808
837.3		838.	837.4
872.9	870	871.7	875.7
910.0	905.6	909.9	902.4
		3314	
			3437

			3497
	3640	3623	
	3682	3681	
			3819
		3945	3954
			4063

483 *bold = stronger bands

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489 **Appendix.** Sampling and analytical methods

490 *Sampling*

491 The Shefa Yamim exploration project is aimed at the discovery of economically viable
492 placer deposits of gemstones (mainly sapphire, ruby, hibonite, moissanite) and other
493 commodities within the drainage basin of the Kishon River. Over >10 years, the project has
494 sampled the Cretaceous pyroclastic centers on Mt Carmel (Fig. SD1: Rakefet, Har Alon, Bat
495 Shelomo, Muhraka and Beit Oren complexes) and adjacent areas (Ein Ha-Shofet), and minor
496 and major drainages in the Yaz'rael Valley. Samples range in size from several kg to >1000
497 tonnes. All samples were run through a static grizzly screen to remove pieces larger than
498 100mm in diameter. Rock samples from the vents were coarsely crushed and then treated
499 in the same way as alluvial samples. The <100mm fraction was washed in a scrubber that
500 breaks up any clods. The <0.5mm component is suspended in the wash water and pumped
501 to settling ponds; fractions larger than 25 mm are used to backfill exploration pits. Samples
502 in the +8mm-16mm and +16mm-24mm size fractions are sorted by hand on a picking belt.
503 The +0.5 -8mm component of the sample is washed and classified into 5 fractions: 0.5-
504 0.7mm, 0.7-1mm, 1-2mm, 2-4mm, 4-6mm, 6-8mm. These fractions are transferred to a
505 pulsating jig plant for gravity separation. Samples in the 2mm-8mm size fractions are
506 visually inspected after the jiggling process and sorted in the recovery laboratory. The three
507 smallest size fractions are jiggled separately. The heavy concentrate in the center of the jig
508 pan is collected and dried; material on the outer part of the jig pan is discarded. The sorters
509 in the laboratory have demonstrated their efficiency in identifying and recovering a wide
510 range of mineral species, including garnet (pyrope), ilmenite, spinel, chrome-diopside,

511 diamond, moissanite, sapphire, ruby, Carmel Sapphire™, hibonite, rutile and zircon. The
512 material described here is dominated by samples from the Rakefet Magmatic Complex, and
513 the alluvial deposits of the Kishon River mid-reach, because these localities have been most
514 thoroughly bulk-sampled, providing abundant material.

515 The unprocessed heavy mineral concentrates of several samples were hand-picked
516 under a binocular microscope in the CCFS laboratories. Several rock samples also have been
517 processed by SelFrag (electrostatic disaggregation) techniques at CCFS, sieved and hand-
518 picked after magnetic and heavy-liquid separation.

519

520

521 *Analytical Techniques*

522 *SEM, EMP*

523 Samples were mounted in epoxy blocks, polished and coated with carbon. A Zeiss
524 EVO MA15 scanning electron microscope (SEM) at the Geochemical Analysis Unit (GAU),
525 Macquarie University, Sydney, Australia was used to capture Backscattered Electron (BSE)
526 images and Energy Dispersive X-ray spectrometry (EDS) was used to map the elemental
527 composition of the samples, and to analyze phases of interest. An accelerating voltage of 15
528 keV and a beam current of 1 nA was used.

529 Major and minor elements were determined by electron microprobe (EMP) using a
530 CAMECA SX100 equipped with five wavelength-dispersive spectrometers at the Macquarie
531 University GeoAnalytical (MQGA; formerly GAU), Macquarie University, Sydney, Australia.
532 Analyses were performed using a focused beam (1-2 μm) with an accelerating voltage of 15
533 keV and a beam current of 20 nA. Standards were a suite of natural and synthetic minerals.
534 Peak counting varied between 10 – 20 s, and background was counted for 5 – 10 s on either
535 side of the peak. Oxygen and carbon were measured directly; matrix corrections were
536 carried out by the ZAF software.

537 Major and minor elements also were determined by electron microprobe (EMP)
538 using a JEOL 8530F electron microprobe equipped with five wavelength dispersive
539 spectrometers at the Centre for Microscopy Characterisation and Analysis (CMCA), The
540 University of Western Australia, Perth, Australia. Analyses were performed using a fully
541 focussed beam with an accelerating voltage of 15 keV, a beam current of 15 nA. Standards
542 were a suite of natural and synthetic minerals. On-peak counting times were 30 seconds for

543 all elements. X-ray intensity data was corrected for Time Dependent Intensity (TDI) loss (or
544 gain) using a self-calibrated correction for Si $k\alpha$, Ti $k\alpha$, Mn $k\alpha$, Na $k\alpha$, K $k\alpha$ and mean atomic
545 number (MAN) background corrections were used throughout (Donovan & Tingle, 1996;
546 Donovan et al., 2016). Unknown and standard intensities were corrected for deadtime.
547 Oxygen was measured, matrix corrections and ZAF correction were applied throughout.

548

549 *Transmission Electron Microscopy*

550 FIB foils from the region of interest were prepared for TEM using a dual-beam FIB
551 system (FEI Nova NanoLab 200). High Angle Annular Dark Field Scanning Transmission
552 Electron Microscopy (HAADF-STEM) imaging and element mapping were carried out using
553 an FEI Titan G2 80-200 TEM/STEM with ChemiSTEM Technology operating at 200 kV at the
554 Centre for Microscopy Characterisation and Analysis (CMCA), The University of Western
555 Australia, Perth, Australia. The element maps were obtained by energy dispersive X-ray
556 spectroscopy using the Super-X detector on the Titan with a probe size ~ 1 nm and a probe
557 current of ~ 0.25 nA. Total acquisition times of 20-30 minutes were used to obtain good
558 signal-to-noise ratios. Electron diffraction was carried out using a field limiting aperture that
559 selected an area approximately 400nm in diameter.

560

561 *3D- μ CT (add method for SdC material)*

562 For X-ray micro-computed tomography (μ CT) at the CMCA, the grain was mounted
563 on a finger of rigid PVC plastic with double-sided tape and a separate tomogram was
564 collected for each grain using a μ CT system (Versa 520 XRM, Zeiss) running Scout and Scan
565 software (v11.1.5707.17179, Zeiss). Samples were scanned at 50 kV and 77 μ A with the
566 source detector positions set to -17.7 and 117 mm, respectively. An LE1 source filter was
567 applied to screen out low energy X-rays. A 0.4X objective lens was used together with 2x
568 camera binning to achieve an isotropic voxel resolution of 9 μ m. Each scan comprised 2501
569 projections through 360 $^\circ$ with an exposure of 3s for each projection. Raw data were
570 reconstructed using XMReconstructor software (v11.1.5707.17179, Zeiss) following a
571 standard centre shift and beam hardening correction. The standard 0.7 kernel size recon
572 filter setting was also used. The visualization and analysis of data generated from μ CT scans
573 were performed using Avizo (v8.1.1, FEI) software.

574

575 *Released-Gas Analysis*

576 H, C, N, and S contents were obtained using a vario EL cube elemental analyzer
 577 (Elementar, Langensfeld, Germany). Aliquots of finely powdered sample, weighing
 578 between 80 and 120 mg, were mixed with WO₃ flux (sample:flux ratio between 1:1.2 and
 579 1:1.5), packed in Sn-foils, hand pressed, and then ignited in an O₂-He gas atmosphere
 580 furnace at around 1150 °C. The produced gases were trapped and sequentially released into
 581 a set of chromatographic columns for the analysis of N (no trapping), then C, H, and S. Each
 582 sample was measured for 9 min, and released gases were sequentially analyzed with a
 583 thermal conductivity detector. Reference materials JP-1, BE-N, PM-S and BAM-U110, were
 584 repeatedly measured in the same analytical conditions and yielded average values (Table
 585 SD-1) well within error of accepted or published values as tabulated in the GeoReM
 586 database (<http://georem.mpch-mainz.gwdg.de/>).

587 **Table SD-1.** Reference materials for CHNS analyzer.

588

	H TCD	C TCD	N TCD	S TCD	S IR
JP-1 Peridotite massif (JGS)					
<i>n</i>	4	12	14	14	14
Average (µg g ⁻¹) ± SD	3195 ± 170	763 ± 82	91 ± 23	27 ± 14	26 ± 7
RSD %	5	11	26	51	27
BHVO-2 Basalt, Hawaiian Volcanic Observatory (USGS)					
<i>n</i>	5	16	12	12	8
Average (µg g ⁻¹)	181 ± 45	316±60	219 ± 34	191 ± 41	179 ± 42
RSD %	25	19	15	21	23
PM-S Microgabbros (SARM)					
<i>n</i>	25	26	24	26	22
Average (µg g ⁻¹)	689 ± 70	992±55	154 ± 38	1128 ± 51	1165 ± 119
RSD %	10	6	15	5	10
BE-N Altered Basalts (SARM)					
<i>n</i>	14	20	17	21	8
Average (µg g ⁻¹)	2771 ± 534	2301 ± 147	197 ± 42	301 ± 37	298 ± 23
RSD %	19	6	21	12	8
BAM-U110					
<i>n</i>	13	18	18	17	–
Average (µg g ⁻¹)	12,258 ± 1758	72,340 ± 2640	4237 ± 165	9114 ± 1082	–
RSD %	14	4	4	12	–

589 *n* denotes the number of measurements performed; average is the arithmetic means of the *n* values
 590 measured and SD is the related standard deviation; RSD % is relative standard deviation expressed in
 591 %; TCD: Thermal Conductivity Detector; IR: Infra Red detector.

592

593 *Raman Spectroscopy*

594 Raman spectra were collected with and Horiba LabRAM HR Evolution microscope with a
595 Sincerity OE detector, using 532-nm laser the Department of Earth Sciences, University of
596 Milan. Reflected and transmitted light optics were used to select analysis locations. Hibonite
597 from Sierra di Comechingones was studied from a polished thin section. Hibonite from Mt.
598 Carmel was studied using a raw fragment. The analysis was performed using a 100x
599 objective and 600 (500 nm) grating. Laser power was attenuated to 50% of the power To
600 maximize the signal-to-noise ratio, two spectra were collected using an exposure time of 30
601 s, and then merged together at the end of the acquisition. Spectra were taken at two
602 polarizations at right angles to check for changes in intensity of the raman shifts. The system
603 was calibrated using the 520 cm^{-1} Raman line of metallic silicon. Spectra were processed
604 using LabSpec v.6 (Horiba[®]). Peak positions were obtained by fitting Gaussian peaks.
605 Observed peaks are reported in Table 3 and compared with Raman peaks reported by
606 Hofmeister et al. (2004) for synthetic hibonite. Two spectral ranges are reported in Figures
607 3a (50-1000 cm^{-1}) and 3b (3000-4150 cm^{-1}). Raw Raman spectra have been deposited as
608 supplementary material.

609

610

611 **Supplementary Figures**

612 Fig. SD1. Location maps showing the location of the Mt Carmel volcanic field. (a) Regional
613 setting; box shows Mt Carmel area; (b) Geological map indicating location of Cretaceous
614 volcanic centers.

615

616 Figure SD2. Animated 3D image of 6b.

617

618 Figure SD3. 3D animation showing successive slices through the structures shown in Figure
619 6b (rotated 90°). Left, grey-scale image; V^0 appears as bright tones, and voids in black.
620 Right, image from Fig. 6b, to show correlation of voids with green colours. Note that some
621 large vanadium “drops” in the middle parts of the structures actually are comprised of voids
622 (green) surrounding an irregular fragment of V^0 (yellow).

623