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2	The new mineral crowningshieldite: a high-temperature NiS polymorph
3	found in a type IIa diamond from the Letseng mine, Lesotho
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13	Abstract

Crowningshieldite is the natural analogue of the synthetic compound α-NiS. It has a NiAs-type structure and is the high-temperature polymorph relative to millerite (β-NiS), with an inversion temperature of 379 °C. Crowningshieldite is hexagonal, space group  $P6_3/mmc$ , with a = 3.44(1)Å, c = 5.36(1) Å, V = 55.0(2) Å<sup>3</sup>, Z = 2. It has an empirical formula (Ni<sub>0.90</sub>Fe<sub>0.10</sub>)S and  $d_{calc} = 5.47(1)$  g/cm<sup>3</sup>. The five strongest lines in the powder X-ray diffraction data are [ $d_{meas}$  in angstroms (I) (hkl)]: 1.992 (100) (102), 1.718 (55) (110), 2.978 (53) (100), 2.608 (35) (101), 1.304 (17) (202). Crowningshieldite was found as part of a multiphase inclusion in a gem-

21	quality, colorless, type IIa (containing less than approximately 5 ppm N) diamond from the
22	Letseng mine, Lesotho. The inclusion contains crowningshieldite along with magnetite-
23	magnesioferrite, hematite, and graphite. A fracture was observed that extended from the
24	inclusion to the diamond exterior, meaning that fluids, possibly kimberlite-related, could have
25	penetrated into this fracture and altered the inclusion. Originally, the inclusion might have been a
26	more reduced, metallic Fe-Ni-C-S mixture made up of cohenite, Fe-Ni alloy and pyrrhotite, akin
27	to the other fracture-free, pristine inclusions within the same diamond. Such metallic Fe-Ni-C-S
28	primary inclusions are a notable recurring feature of similar type IIa diamonds from Letseng and
29	elsewhere that have been shown to originate from the sublithospheric mantle.
30	The discovery of crowningshieldite confirms that the $\alpha$ -NiS polymorph occurs in nature. In this
31	case, the reason for its preservation is unclear, but the relatively iron-rich composition
32	(Fe/(Fe+Ni) = 0.1) or the confining pressure of the diamond host are potential factors impeding
33	its transformation to millerite. The new mineral name honors G. Robert Crowningshield (1919-
34	2006)(IMA2018-072).
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36	Keywords: crowningshieldite, alpha-NiS, inclusion, type IIa diamond, Letseng
37	
38	Introduction
39	Nickel monosulfide (NiS) has two known polymorphs. Millerite, or $\beta$ -NiS, with the trigonal

40 space group R3m, is the polymorph more familiar to geologists. The second form is  $\alpha$ -NiS, with

41 the hexagonal space group  $P6_3/mmc$ , with so-called NiAs-type structure, which is the stable form

42 above 379 °C for pure NiS (Kullerud and Yund 1962; Sowa et al. 2004). Here, we describe the

43 first known natural occurrence of  $\alpha$ -NiS, the new mineral named crowningshield ite, with an 44 empirical formula ( $Ni_{0.90}Fe_{0.10}$ )S. It was found as part of a multiphase inclusion assemblage in a diamond from the Letseng mine, Lesotho. This inclusion is likely altered from its primary 45 46 mineralogy. The diamond was investigated previously for its (unaltered) metallic Fe-Ni-C-S 47 inclusions and belongs to a newly recognized variety of sublithospheric diamonds called 48 CLIPPIR diamonds (Smith et al. 2016; Smith et al. 2017). Many occurrences of natural millerite appear to have formed in relatively low temperature 49 50 geological settings, during hydrothermal alteration, and develop a prominent acicular habit. 51 However, some examples of massive NiS in magmatic sulfides, at Norilsk, Russia, and 52 Temagami, Canada, for instance, are suspected to have formed originally as crystals of  $\alpha$ -NiS 53 (crowningshieldite) that inverted to millerite upon cooling (Borovskii et al. 1959; Kullerud and 54 Yund 1962). Synthetic  $\alpha$ -NiS can be quenched to room temperature, but it is metastable and 55 transforms to  $\beta$ -NiS, typically over months depending on temperature and composition (Kasper 56 et al. 2000; Wang et al. 2006). Interestingly, this  $\alpha$ -NiS to  $\beta$ -NiS transition is of concern for the 57 glass industry, because float glass can contain inclusions of NiS particles. Heat treatment and 58 rapid cooling to produce tempered or toughened glass can quench these inclusions as  $\alpha$ -NiS. 59 Later, after cooling, stresses arising as  $\alpha$ -NiS inverts to the ~3% larger  $\beta$ -NiS phase may lead to 60 localized micro-cracking that initiates spontaneous glass failure (Barry and Ford 2001; Swain 61 1981).

The new mineral is named in honor of G. Robert Crowningshield (1919–2006). He was a central
figure in research at the Gemological Institute of America (GIA) for more than 50 years, helping
it to become a place of unique research opportunities such as the present mineral discovery.

Crowningshield advocated for the use of spectroscopy as a valuable tool in gemology and
meticulously recorded the absorption patterns of many transparent gems by hand, ultimately
publishing them as a key reference for gem mineral identification. In 1956 he described a reliable
spectroscopic method to identify yellow irradiated diamonds and discriminate them from
naturally-colored yellow diamonds, thereby resolving a serious concern in the gem trade at the
time (Crowningshield 1957-1958).

The mineral and the name crowningshieldite have been approved by the Commission on New Minerals, Nomenclature and Classification (IMA2018-072). The holotype specimen described herein has been deposited at the Mineralogical Museum of the University of Padova, Italy (catalog number: MM 20501). A second, smaller piece of the original specimen is deposited in the collections of the Gemological Institute of America Museum, Carlsbad, California, USA (catalog number: 41800).

### 77 Occurrence

78 The Letseng mine in Lesotho has a kimberlite eruption age of 85.5±0.3 Ma, based on U-Pb 79 dating of groundmass perovskite (Stamm et al. 2018). The diamond in which crowningshieldite 80 was discovered (Figure 1) was studied previously by Smith et al. (2016) under the sample name 81 Letseng 889 (here shortened to sample 889). It is a 2.14 carat (0.428 g) inclusion bearing offcut, 82 trimmed from a larger type IIa (no detectable nitrogen in infrared spectroscopy; less than about 5 83 ppm) colorless rough diamond during the gem manufacturing process. The size of the larger 84 parental rough diamond is unknown, but probably had dimensions exceeding 1 cm  $\times$  1 cm  $\times$  1 85 cm and a weight greater than 10 carats, based on the size of the offcut (Figure 1). Remnant rough 86 surfaces on the offcut are strongly resorbed and suggest an irregular morphology, as opposed to a 87 symmetrical octahedral or dodecahedral diamond habit. These features are typical of the type IIa

88 gem diamonds regularly found at Letseng (Bowen et al. 2009), as well as of other high quality 89 type IIa diamonds recovered globally. Such diamonds are collectively termed CLIPPIR 90 diamonds (Cullinan-like, Large, Inclusion Poor, Pure, Irregular, Resorbed). This sample, 889, is 91 part of a larger suite of diamonds that was used to investigate the geologic origin of CLIPPIR 92 diamonds (Smith et al. 2016; Smith et al. 2017). 93 In the previous investigations (Smith et al. 2016; Smith et al. 2017), which sought to document 94 inclusions in CLIPPIR diamonds, the focus was on the nature of their recurring metallic Fe-Ni-95 C-S melt inclusions that are predominantly made up of cohenite ((Fe,Ni)<sub>3</sub>C), Fe-Ni alloy, and 96 pyrrhotite. The average bulk composition is estimated as (Fe<sub>60-80</sub>Ni<sub>8-15</sub>C<sub>10-16</sub>S<sub>4-14</sub>)(Smith et al. 97 2016). These are the most abundant kind of inclusions in CLIPPIR diamonds, with the metallic 98 melt being observed in 67 of 83 inclusion bearing diamonds (Smith et al. 2017). Inclusions of 99 brevite (CaSiO<sub>3</sub>) plus other Ca-silicates, together interpreted as the breakdown products of 100 former CaSiO<sub>3</sub>-perovskite, along with inclusions of majoritic garnet indicate that CLIPPIR 101 diamonds are sublithospheric (super-deep) in origin, derived from a depth of about 360–750 km 102 (Smith et al. 2016; Smith et al. 2017). 103 The offcut studied here (sample 889) contained more than 10 primary metallic Fe-Ni-C-S

104 inclusions (see Figure 1c) of varying size, two of which were shown to contain the cohenite, Fe-

105 Ni alloy, and pyrrhotite assemblage (Smith et al. 2016; Smith et al. 2017). These metallic

106 inclusions have methane (CH<sub>4</sub>), detectable with Raman spectroscopy, that is trapped at the walls

107 between the solid inclusion and the surrounding diamond host (Smith et al. 2016). The methane

- 108 confirms these inclusions are fully enclosed in the diamond. Any fracture reaching from the
- 109 inclusion to the diamond exterior would allow the methane to leak out. It is important to note that

110	these pristine metallic Fe-Ni-C-S inclusions do not have any reddish iron-oxide staining
111	associated with them.

112 In contrast, the largest inclusion in sample 889 had a large, reddish, iron-oxide stained fracture 113 extending between the inclusion and the exterior surface of the diamond (Figure 1c). Based on 114 the fracture, it is strongly suspected that this inclusion has been exposed to fluids that have 115 altered its primary mineralogy, possibly during the time of kimberlite eruption. It was in this 116 largest inclusion that crowningshieldite was discovered, by X-ray diffraction analysis. 117 Crowningshieldite occurs as part of a multiphase assemblage along with magnetite-118 magnesioferrite, hematite, and graphite. Given the reddish stained fracture, the 119 crowningshieldite-bearing inclusion is interpreted to be an altered, partly oxidized version of the 120 metallic Fe-Ni-C-S melt inclusions described above. The as-received diamond offcut (sample 121 889) was already mostly broken open along the large fracture, such that the fracture surface was 122 mostly exposed and the crowningshield ite-bearing inclusion was also partly exposed along its 123 side (Figure 1b). The surface of the exposed inclusion was tested with a multimeter and found to 124 be electrically conductive, suggesting graphite interconnectivity.

125 The original 2.14 carat offcut (Figure 1) has been trimmed down further for other ongoing

studies of the Fe-Ni-C-S inclusions. The remaining diamond fragment shown in Figure 2 is the

127 holotype sample for crowningshieldite, from which high quality diffraction data was collected,

128 and from which the composition was measured on a flat surface. All analytical work presented

here focuses on this holotype sample (Figure 2).

130 The multiphase inclusion in sample 889 (Figure 2) is reasonably flat and smooth because it sits

- 131 flush with the polished surface of the adjacent diamond host. This flat exposed surface, still
- 132 embedded within its diamond host, is shown in secondary electron (SE) and backscattered

133 electron (BSE) images in Figure 3. Crowningshieldite occurs as small grains, 10–20 µm, along 134 with magnesioferrite and graphite. Due to the fine-grained and fractured nature of the 135 crowningshieldite it was not possible to isolate a single crystal for measurement of optical and 136 physical properties. Also, the inclusion material could not be safely removed from the diamond 137 host to polish it separately, due to its rarity and probable fragility. Therefore, a well-polished 138 crowningshieldite surface was not available for reflected-light microscopy. A nickel sulfide phase was also found within a second Letseng diamond (sample Letseng 893) 139 140 by SEM-EDS during a prior preliminary investigation. This nickel sulfide is presumed to be 141 crowningshieldite, but diffraction data could not be obtained to confirm its crystal structure, so it 142 is not discussed further. Again, a fracture connected this particular inclusion to the diamond's 143 exterior surface and, accordingly, it had no detectable methane fluid jacket in Raman 144 spectroscopy. 145 It is proposed that when cracks develop in the host diamond, connecting metallic Fe-Ni-C-S 146 inclusions to the exterior of the diamond, they allow fluids to interact with the inclusion and alter 147 it to a variable assemblage including iron oxides, iron bearing nickel sulfide, and graphite. It is 148 unclear when alteration of the original inclusion occurred, but kimberlite volcanism and eruption 149 is considered the most likely timing, when the diamond would have been subject to stresses that 150 may have caused cracking and also exposed to volatiles/fluids at elevated temperatures. 151 Graphite geothermometry, while more often used for determining peak metamorphic 152 temperatures of carbonaceous rocks, may provide a sense of the temperature conditions during 153 the formation of this crowningshieldite-bearing assemblage. Using Raman spectroscopy to assess 154 graphite crystallinity affords an estimate of the peak temperature that graphite was exposed to 155 (Beyssac et al. 2002). It is not an ideal tool for this purpose, but given the simplicity of the

156 approach, graphite geothermometry is applied here as a qualitative indicator under the 157 assumption that graphite and crowningshieldite formed at comparable conditions (during a single 158 episode of alteration). Graphite associated with crowningshieldite has a Raman spectrum (Figure 159 4) with D1, G and D2 peak area ratios corresponding to a temperature of  $357\pm50$  °C, according 160 to the geothermometer of Beyssac et al. (2002). In an iron free system, the NiS inversion 161 temperature between  $\beta$  (millerite) and  $\alpha$  (crowningshieldite) ranges from 379 °C for 162 stoichiometric NiS down to 282 °C for more nickel deficient compositions, Ni<sub>1-x</sub>S with x 163 reaching 0.09 (Kullerud and Yund 1962). Taken qualitatively, the graphite geothermometry for 164 this crowningshieldite-bearing inclusion suggests alteration took place at a temperature a few 165 hundred degrees or more above ambient surface temperatures, which is consistent with the 166 interpretation that alteration occurred prior to the complete cooling of the kimberlite after 167 emplacement. However, although the temperature overlaps the experimental stability field for  $\alpha$ -168 NiS (crowningshieldite) formation, it does not provide an independent confirmation that 169 alteration in this assemblage occurred at a higher temperature than the millerite stability field. 170 In general, the crowningshield te-bearing inclusion still retains its proposed original iron-, 171 nickel-, carbon-, and sulfur-rich composition but is more oxidized, from cohenite-Fe-Ni alloypyrhhotite to magnesioferrite-hematite-graphite-crowningshieldite. This latter mineral 172 173 association may be the typical outcome for metallic inclusions with surface-reaching cracks in 174 CLIPPIR diamonds. If such particular circumstances are needed for the formation of 175 crowningshieldite, it is understandable that it has not been found previously. CLIPPIR diamonds 176 are rare, making up only about 1% of gem diamonds worldwide, and often carry a high gem 177 value, so they are challenging to access for research and have only recently been examined in 178 detail (Smith et al. 2016; Smith et al. 2017).

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### 180 **Physical properties**

181 Crowningshieldite is opaque, with a metallic luster, and bronze yellow color. Its occurrence as 182 small anhedral grains in the only available sample (Figure 3) prohibited direct determination of some properties. The calculated density of crowningshieldite is 5.47(1) g/cm<sup>3</sup>, based on the 183 184 empirical formula and refined unit-cell, which is slightly greater than the 5.38 g/cm<sup>3</sup> density of 185 millerite, something predicted from the more compact structure of crowningshieldite compared 186 to millerite. Crowningshieldite is predicted to have a hardness, between 3 and 3.5 on the Mohs 187 scale, similar to millerite, based on the crystal-chemical similarity between crowningshieldite 188 and millerite.

189 Attempts to measure the Raman spectrum of crowningshieldite proved unsuccessful. The spectra 190 recorded were that of millerite, even at minimal laser power and long integration times, despite 191 the fact that no traces of millerite were found by X-ray diffraction analysis of this multiphase 192 inclusion assemblage. The unavoidably poor surface polish on the crowningshieldite, as it is still 193 embedded in diamond, could be a reason for the Raman observations. Mechanical polishing of 194 ore minerals has been shown to affect Raman spectra, in some cases leading to loss of 195 crystallinity in the surface layer to perhaps tens of nanometers deep (Libowitzky et al. 2011). 196 Another possible explanation is that the laser excitation caused inadvertent localized, surficial 197 transformation of crowningshieldite to millerite at the point of analysis. The Raman spectrum of 198 Bishop et al. (1998) that is reportedly for synthetic  $\alpha$ -NiS (crowningshieldite), which is the only 199 published spectrum for  $\alpha$ -NiS, also appears to suffer from this problem where all major spectral 200 features essentially correspond to millerite and do not coincide with calculated  $\alpha$ -NiS Raman

modes (Goel et al. 2019). Raman analysis of millerite alone shows even modest laser power can
degrade the sample surface, causing broadening and shifting of Raman bands (Guillaume et al.
2008). Laser induced changes like this are a relatively common difficulty encountered for Raman
spectroscopy of opaque materials susceptible to oxidation or structural transformation (e.g. de
Faria et al. 1997).

206

### 207 Chemical composition

208 Given that an ideally polished crowningshieldite surface could not be prepared without risking 209 its destruction, it was not possible to perform quantitative electron microprobe analysis. 210 However, the surface sitting flush to the polished diamond surface was sufficiently flat and 211 smooth to permit semi-quantitative analysis by EDS (energy-dispersive X-ray spectroscopy). 212 Crowningshieldite grains in Figure 3 were examined using a CamScan MX3000 electron 213 microscope equipped with a LaB<sub>6</sub> source, four-quadrant solid state back-scattered electron (BSE) 214 detector and an EDAX EDS system for micro-analysis, at the Department of Geosciences at the 215 University of Padova. Analysis was performed with a 20 kV accelerating voltage, ~13 nA 216 filament current, and 27 mm working distance. The non-ideal crowningshieldite surface is the 217 largest source of uncertainty, which cannot be rectified with the use of standards. However, this 218 instrumental setup has shown accurate results, compared to known compositions, for analysis of 219 other minerals with poorly-polished surfaces and relatively simple compositions, like NiS. 220 Figure 5 shows the EDS spectrum of crowningshieldite, constituted only by Ni, Fe and S. No 221 other elements were detected. Cobalt, which is often present as a minor component in millerite, 222 was not detected, even with extended counting times. Although the crystal size is limited, the

relatively simple nature of the chemical composition permitted its reliable determination by

EDS, based on four spot analyses (Table 1). The empirical formula calculated from EDS data on

225 the basis of one sulfur atom per formula unit is  $(Ni_{0.90}Fe_{0.10})S$ . The simplified formula is NiS,

requiring 64.67 wt% nickel and 35.33 wt% sulfur.

227

### 228 X-ray diffraction

229 The crystal structure of crowningshieldite was determined using X-ray powder diffraction 230 methods, in-situ, due to the nature of the sample. Single-crystal diffraction was not possible due 231 to its limited crystal size and micro-texture. The instrumentation consisted of a Rigaku-Oxford 232 Diffraction Supernova single-crystal diffractometer (Kappa-geometry) equipped with an X-ray 233 micro-source (Mo $K\alpha$ ) with 120 µm beam spot, operating at 50 kV and 0.8 mA, and a 200K 234 Pilatus detector (Dectris), at the Department of Geosciences at the University of Padova. Data 235 were collected in powder diffraction mode. The multiphase inclusion (Figure 3), exposed to air, 236 was centered under the X-ray beam and X-ray data were collected in phi scan mode. The X-ray 237 data were converted to a format readable by HighScore Plus software (Panalytical) to examine 238 and plot the data.

Figure 6 shows the X-ray diffraction results, indicating that a polycrystalline mixture of phases make up the inclusion. The pattern was subsequently evaluated by Rietveld methods (Table 2), which made it possible to quantify the relative amount of each phase present in the analyzed inclusion volume: magnesioferrite 57%, crowningshieldite (labeled NiS) 28%, graphite 10% and hematite 6%. No traces of millerite were recorded. To emphasize the clear differences between

crowningshieldite and millerite, Figure 7 shows the X-ray diffraction pattern again, with only the
labels for crowningshieldite and added reference peaks for millerite.

246 Rietveld analysis for crowningshieldite (Table 3), using the starting model given by Rost and

Haugsten (1969), gave reasonable values of  $R_{Bragg} = 2.34\%$  and an  $R_{WP} = 4.21\%$ . The simple

248 structure of crowningshieldite permitted refinement of B<sub>iso</sub>, but attempts to refine the

249 occupancies failed as the X-ray scattering power of Ni and Fe are virtually the same (Table 4).

250 Overlap between the peaks of crowningshieldite and other phases prohibits a reliable estimation

251 of standard deviation for refined occupancies and B<sub>iso</sub> values. Therefore, occupancies were fixed

252 based on EDS chemical analyses and  $B_{iso}$  values were fixed to 0.5 Å<sup>2</sup>. Considering the low  $R_{Bragg}$ 

253 obtained, such a chemical constraint appears to be reliable, which reinforces the conclusion that

the composition obtained by EDS analysis is robust. Table 5 lists the *d*-spacings of

255 crowningshield ite and, for comparison, the published *d*-spacings of miller and synthetic  $\alpha$ -NiS

are given in Table 6.

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#### 258 **Crystal structure of crowningshieldite**

Crowningshieldite follows the archetype structure of nickeline, NiAs (Wyckoff 1963). A CIF is on deposit. Each Ni atom is bound to six S atoms, with a bond length of 2.397(2) Å. Its unit cell is shown in Figure 8 along with a visualization of NiS<sub>6</sub> octahedra, which share faces along the *c* axis. Crowningshieldite and nickeline have a similar unit-cell volume, 55.0(2) Å<sup>3</sup> and 56.3 Å<sup>3</sup>, respectively, but their unit cell parameters are significantly different owing to the different ionic radius of S compared to As (Table 7). In crowningshieldite the two groups of six S – S distances

are somewhat similar, being 3.443(3) Å and 3.336(4) Å, whereas in nickeline, the two groups of

six As – As distances are more dissimilar, being 3.602 Å and 3.255 Å. Their orientations with respect to the *a* and *c* axes cause a longer *a* axis for crowningshieldite and a longer *c* axis for nickeline.

Compared to crowningshieldite, where the Ni atoms are 6-coordinated, millerite has Ni atoms
that are 5-coordinated, and the space group changes to *R3m*. The 5-coordinated Ni in millerite is
relatively uncommon in nature.

272

#### 273 Discussion

274 Based on experiments, quenched samples of  $\alpha$ -NiS (crowningshieldite) are metastable and 275 eventually tend to revert to β-NiS (millerite). For this reason, the long-term stability of the 276 holotype specimen is somewhat uncertain. For example, Wang et al. (2006) observed that a 277 stoichiometric pure synthetic crowningshieldite stored for six months at room temperature 278 exhibited 3-4% transformation to millerite. As suggested by Kullerud and Yund (1962), massive 279 millerite in some magmatic sulfide deposits is suspected to have crystallized initially as 280 crowningshieldite ( $\alpha$ -NiS) and subsequently inverted to millerite during cooling. It is therefore 281 noteworthy that crowningshield in the present sample has remained preserved on a geological 282 timescale, although the precise mechanism for its preservation is not understood. Potential 283 factors are discussed below.

The possibility that the observed crowningshieldite might have been generated during sample preparation as a result of heat, by transforming millerite above approximately 379 °C, is ruled out for two reasons. Firstly, the crowningshieldite-bearing multiphase inclusion was not exposed to any such high temperatures. The sample surface in Figure 2 has been lightly polished after the

288 diamond was cut, which may have led to some limited local heating at the interface, but the 289 crowningshieldite occurs throughout the bulk of the inclusion, most of which was protected by 290 diamond during these processes (Figure 1). The second reason is that the polishing and 291 preparation work was actually completed two years prior to the present analyses. The fact that no 292 traces of millerite were detected after this period (Figures 3, 7) reinforces the notion that this 293 crowningshieldite is reasonably stable. Two potential factors that might contribute to the 294 apparent stability are composition and confining pressure. In terms of composition, it is possible 295 that there is some trace element not detected in EDS that stabilizes the structure. Another 296 possible compositional effect could stem from the Fe content in this crowningshieldite, 297  $Ni_{0.9}Fe_{0.1}S$  (5 at% Fe). This Fe content is relatively high compared to typical millerite Fe 298 contents, with the maximum measured in synthetic millerite being 5.5 at% at 230 °C and in 299 natural millerite being below 1.6 at% (Misra and Fleet 1973). Substantial incorporation of Fe 300 into crowningshieldite is not unexpected, given that, in the NiAs-type structure, there is complete 301 solid solution between Fe<sub>1-x</sub>S and Ni<sub>1-x</sub>S (i.e. monosulfide solid solution, or MSS) above 302 approximately 400 °C (Misra and Fleet 1973; Ueno et al. 2000). The evident maximum Fe 303 content of millerite, however, might suggest a limit to the ease with which Fe can be 304 accommodated during the  $\alpha$ -NiS to  $\beta$ -NiS transition, which involves structural reorganization as 305 the Ni coordination changes from sixfold to fivefold, respectively (Wang et al. 2006). 306 Experiments clearly demonstrate that even small amounts of Fe slow the kinetics of the 307 transformation of  $\alpha$ -NiS (crowningshieldite) to  $\beta$ -NiS (millerite)(Kasper et al. 2000; Yousfi et al. 308 2010). Further work is needed to assess the effect of Fe to slow or perhaps present an energy 309 barrier for the transformation of  $\alpha$ -NiS (crowningshieldite) to  $\beta$ -NiS (millerite).

310	An alternative factor that may be relevant for the preservation of the examined crowningshieldite
311	has to do with the confining pressure of the host diamond. Some inclusions in diamond have
312	substantial remnant confining pressure, for example in the case of diamond containing
313	ringwoodite with a residual pressure of approximately 2 GPa that has prevented its inversion to
314	olivine (Pearson et al. 2014). Experiments show that with increasing pressure, the temperature
315	stability field of $\alpha$ -NiS increases (Sowa et al. 2004), suggesting that pressure may help stabilize
316	crowningshieldite. The actual pressure within the examined crowningshieldite-bearing inclusion
317	(prior to being exposed by any cutting) is not known, but might not have been particularly high
318	due to its relatively large size and the large natural fracture around it. Nevertheless, pressure
319	within the inclusion may be a relevant consideration for crowningshieldite preservation.
320	Ultimately, the factors that have inhibited crowningshieldite from transforming to millerite are
321	not known in this case, but these conditions are likely rare in nature.

### 322 Implications

323 With the ongoing study of Fe-Ni-C-S inclusions in CLIPPIR diamonds, further examples of altered inclusion assemblages containing crowningshieldite may yet be found. The present 324 325 finding illustrates not only that the  $\alpha$ -NiS polymorph occurs in nature, but also that particular 326 circumstances can permit its long-term preservation. Inclusions in diamonds are unique among 327 geological materials accessible at Earth's surface. Several otherwise exotic minerals, such as 328 ringwoodite (Pearson et al. 2014) and CaSiO<sub>3</sub>-perovskite (Nestola et al. 2018), have been found 329 preserved within them. The discovery of crowningshieldite shows even altered inclusions can 330 host unexpected phases.

331

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### 419 Figure captions

420 Figure 1. As-received 2.14 carat diamond offcut sample (sample 889). a) This piece contains 421 multiple metallic Fe-Ni-C-S inclusions with black graphitic fractures (Smith et al. 2016) and a 422 larger inclusion containing crowningshieldite. **b**) A close-up of the largest inclusion, which 423 contains crowningshieldite. c) Another view of the 2.14 carat offcut, with key features colored and labelled to compare with (a). Note that the large inclusion is associated with a surface-424 425 reaching fracture, which would have connected the inclusion to the diamond exterior. The 426 fracture surface shows reddish iron oxide staining. This larger inclusion has a related 427 composition (with Fe, Ni, C, and S) but different mineralogy compared to the smaller ones, 428 which is consistent with the visual evidence that it has been altered by fluids that penetrated 429 along the fracture and interacted with the inclusion.

430

Figure 2. Holotype sample, a cut fragment of the as-received diamond offcut shown in Figure 1, with a portion of the crowningshieldite-bearing multiphase inclusion circled. The inclusion in this region was used for compositional analysis because it is reasonably flat and polished, as it sits flush with the polished surface of the adjacent diamond host. Black inclusions fully enclosed in the center of the diamond are primary metallic Fe-Ni-C-S inclusions (Fig. 1c), with a Ramandetectable thin jacket of fluid methane (Smith et al. 2016).

437

438 Figure 3. Electron microscope images of the polished region of the crowningshieldite-bearing

439 multiphase inclusion (Fig. 2). a) Secondary electron (SE) image. b) Backscattered electron

440	(BSE) image. c) Enlargement of region outlined in (b) showing individual crowningshieldite
441	grains.

442

443	Figure 4. Raman s	pectrum of graphite	associated with o	crowningshieldite.	The recorded spe	ectrum
	0			0		

- 444 is shown in red. The fitted curve shown in in blue is based on deconvolution into the three
- graphite peaks D1, G and D2, shown in green. Relative peak areas were used to asses
- 446 crystallinity and gauge the temperature of crystallization (Beyssac et al. 2002).

447

- 448 Figure 5. Energy dispersive X-ray spectrum (EDS) of crowningshieldite composition. Only Ni,
- 449 Fe, and S were detected.

450

- 451 Figure 6. X-ray diffraction pattern collected from multiphase inclusion shown in Figure 3
- 452 (sample 889). Identified phases are color coded: magnesioferrite in orange (ICSD code: 96-900-
- 453 3583); crowningshieldite in green (nickel sulfide; ICSD code: 646334); hematite in blue (ICSD
- 454 database: 96-210-1168); graphite in purple (ICSD database code: 96-901-1578). The red curve
- 455 below the X-ray diffractogram shows the difference between the observed and fitted
- 456 diffractogram, which is relatively small.

- 458 Figure 7. X-ray diffraction pattern from Figure 6, showing only the reference peaks for
- 459 crowningshieldite (C) in red along with millerite (M) in black (ICSD code: 98-006-1032) for
- 460 comparison. The experimental diffractogram in red is overlain by the fitted one in blue, while the
- 461 background is shown in green at the bottom. No millerite was detected.

### 462

463	Figure 8. Hexagonal crystal structure of crowningshieldite. The unit cell (left) is shown with Ni
464	in grey and S in yellow. Each Ni atom is bound to 6 S atoms, making a NiS <sub>6</sub> octahedron ( <b>right</b> ).
465	The NiS <sub>6</sub> octahedra share faces along the $c$ axis. Modeled with VESTA (Momma and Izumi
466	2011).

467

470

# 468 Tables

469 Table 1. Crowningshieldite EDS analyses (wt%)

Element	Spot 1	Spot 2	Spot 3	Spot 4	Average
Ni	58.25	58.04	58.1	59.61	58.50±0.75
Fe	5.16	6.16	7.29	4.96	5.89±1.07
S	36.59	35.79	34.62	35.43	35.61±0.82

471 Table 2. Rietveld refinement and relative proportions of phases

Phase	a (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$V(\text{\AA}^3)$	$R_{Bragg}$ (%)	wt%
<sup>a</sup> magnesioferrite	8.40(2)	8.40(2)	8.40(2)	593(1)	0.72%	57(5)
<sup>b</sup> crowningshieldite	3.44(1)	3.44(1)	5.36(1)	55.0(2)	2.34%	28(3)
chematite	5.06(4)	5.06(4)	13.7(1)	304(4)	3.4%	6(1)
dgraphite	2.4(2)	2.4(2)	6.74(8)	34(3)	1.0%	10(3)

472 Notes: References for structural data are <sup>a</sup>(Antao et al. 2005), <sup>b</sup>(Rost and Haugsten 1969),

473 <sup>c</sup>(Maslen et al. 1994), <sup>d</sup>(Trucano and Chen 1975)

## 474

## 475 Table 3. Crowningshieldite Rietveld refinement details

Space group	P6 <sub>3</sub> /mmc
<i>a</i> (Å)	3.44(1)
<i>c</i> (Å)	5.36(1)
$V(\text{\AA}^3)$	55.0(2)
Z	2
$R_{Bragg}$ (%)	2.34
R <sub>WP</sub> (%)	4.21

477

476

478 Table 4. Fractional atomic coordinates for crowningshieldite verified by Rietveld analysis using

479	the structural	model by	Rost and	Haugsten	(1969)
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Atom	Wyckoff positions	s.o.f.	Х	У	Z	$B(Å^2)$	
S	2c	1.00	0.333333	0.666667	0.25	0.5	
Ni	2a	0.90	0.000000	0.000000	0	0.5	
Fe	2a	0.10	0.000000	0.000000	0	0.5	
Bond le	ngths						
Ni-S	2.397(2) Å × 6	S-S	3.336(4) Å × 6				
			3.443(3) Å × 6				

480

## 482 Table 5. List of *d*-spacings (in angstroms, Å) with relative intensities and *hkl* indices for

Imeasured	$d_{\text{measured}}$	<i>I</i> <sub>calculated</sub>	$d_{\text{calculated}}$	hkl	
<sup>a</sup> 53	2.978	55	2.979	100	
17	2.693	6	2.680	002	
35	2.608	27	2.604	101	
100	1.992	100	1.992	102	
55	1.718	45	1.720	110	
5	1.532	5	1.532	103	
<sup>a</sup> 3	1.486	7	1.490	200	
7	1.453	6	1.448	112	
-	-	4	1.435	201	
7	1.332	6	1.340	004	
17	1.304	23	1.302	202	

483 crowningshieldite obtained by X-ray powder diffraction

Note: <sup>a</sup>Intensity estimated due to the peak overlap with coexisting phases.

- 485 Table 6. List of *d*-spacings (in angstroms, Å) with relative intensities and *hkl* indices for millerite
- 486 and for synthetic  $\alpha$ -NiS.

<sup>a</sup> Millerite (β-NiS)			bS	<sup>b</sup> Synthetic α-NiS				
Imeasured	$d_{\text{measured}}$	hkl	Imeasured	$d_{\text{measured}}$	hkl			
74	4.803	1 1 0	60	2.978	100			
45	2.940	101	3	2.676	002			
100	2.773	300	50	2.602	101			
65	2.508	2 0 -1	100	1.990	102			
11	2.402	220	50	1.720	110			
50	2.223	211	8	1.530	103			
81	1.860	3 1 -1	4	1.489	200			
31	1.816	410	1	1.446	112			
33	1.734	401	6	1.435	201			
12	1.631	321	4	1.338	004			
20	1.601	330	16	1.302	202			
16	1.544	10-2	1	1.220	104			

- 487 Notes: <sup>a</sup>(Grice and Ferguson 1974), natural sample from Marbridge Mine Malartic, Quebec, with
- 488 a composition of  $(Ni_{0.981}Fe_{0.016}Co_{0.004})S$  and *d*-spacings reported down to 1.544 Å; <sup>b</sup>(Trahan et al.
- 489 1970), *d*-spacings were reported down to 1.306 Å.
- 490
- 491 Table 7. General comparison between crowningshieldite and related species. Information for
- 492 nickeline from Wyckoff (1963) and millerite from Sowa et al. (2004).

	Crowningshieldite		Nickeline		Millerite	
Chemical formula	Ni <sub>0.9</sub> Fe <sub>0.1</sub> S		NiAs		NiS	
Crystal system	Hexagonal		Hexagonal		Trigonal	
Space group	$P6_3/mmc$		$P6_3/mmc$		R3m	
Unit-cell parameters (Å)	a = 3.44(1)		<i>a</i> = 3.603		<i>a</i> = 9.611	
	c = 5.36(1)		c = 5.009		<i>c</i> = 3.151	
Unit-cell volume (Å <sup>3</sup> )	55.0(2)		56.3		252.1	
Density (calc.)( $g/cm^3$ )	5.47		7.88		5.38	
Three main <i>d</i> -spacings (Å) (rel. intensity)	1.99 1.72 2.98	(100) (55) (53)	2.65 1.95 1.80	(100) (41) (24)	1.86 2.77 4.80	(100) (89) (56)















