1	Revision 2
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3	Nixonite, Na ₂ Ti ₆ O ₁₃ , a new mineral from a metasomatized mantle garnet
4	pyroxenite from the western Rae Craton, Darby kimberlite field, Canada
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19 Abstract

Nixonite (IMA 2018-133), ideally Na₂Ti₆O₁₃, is a new mineral found within a heavily-20 metasomatized pyroxenite xenolith from the Darby kimberlite field, beneath the west central Rae 21 Craton, Canada. It occurs as microcrystalline aggregates, 15 to 40 µm in length. Nixonite is 22 23 isostructural with jeppeite, K₂Ti₆O₁₃, with a structure consisting of edge- and corner-shared titanium-centered octahedra that enclose alkali-metal ions. The Mohs hardness is estimated to be 24 between 5 and 6 by comparison to jeppeite and the calculated density is 3.51(1) g/cm³. Electron 25 microprobe wavelength-dispersive spectroscopic analysis (average of 6 points) yielded: Na₂O 26 6.87, K₂O 5.67 CaO 0.57, TiO₂ 84.99, V₂O₃ 0.31, Cr₂O₃ 0.04, MnO 0.01, Fe₂O₃ 0.26, SrO 0.07, 27 28 total 98.79 wt%. The empirical formula, based on 13 0 atoms. is: 29 $(Na_{1,24}K_{0,67}Ca_{0,06})_{\Sigma_{1,97}}(Ti_{5,96}V_{0,023}Fe_{0,018})_{\Sigma_{6,00}}O_{13}$ with minor amounts of Cr and Mn. Nixonite is monoclinic, space group C2/m, with unit-cell parameters a = 15.3632(26) Å, b = 3.7782(7) Å, 30 c = 9.1266(15) Å, $\beta = 99.35(15)^{\circ}$ and V = 522.72(1) Å³, Z = 2. Based on the average of seven 31 integrated multi-grain diffraction images, the strongest diffraction lines are $[d_{obs}$ in Å (I in %) 32 (h k l)]: 3.02 (100) (3 1 0) , 3.66 (75) (1 1 0), 7.57 (73) (2 0 0), 6.31 (68) (2 0 -1), 2.96 (63) 33 (3 1 – 1), 2.96 (63) (2 0 – 3) and 2.71 (62) (4 0 2). The five main Raman peaks of nixonite, in 34 order of decreasing intensity, are at: 863, 280, 664, 135 and 113 cm⁻¹. Nixonite is named after 35 Peter H. Nixon, a renowned scientist in the field of kimberlites and mantle xenoliths. Nixonite 36 occurs within a pyroxenite xenolith in a kimberlite, in association with rutile, priderite, 37 perovskite, freudenbergite and ilmenite. This complex Na-K-Ti rich metasomatic mineral 38 assemblage may have been produced by a fractionated Na-rich kimberlitic melt that infiltrated a 39 mantle-derived garnet pyroxenite and reacted with rutile during kimberlite crystallization. 40

Keywords: nixonite, new mineral, crystal structure, jeppeite, mantle xenolith, kimberlite, Rae
Craton.

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Introduction

44 The Darby kimberlite field, located ~ 200 km southwest of the community of Kugaaruk, 45 Nunavut, Canada, provides an opportunity to study mantle xenoliths from beneath the western portion of the central Rae Craton. To date, the Darby kimberlite field contains nine bodies, of 46 47 which eight are kimberlitic (Counts 2008). The kimberlite eruption age is estimated from a Rb-Sr isochron to be 542.2 ± 2.6 Ma (Harris et al. 2018). Further details about lithosphere depletion, 48 the mantle geotherm and crustal/lithosphere thickness across the Rae Craton are found in Harris 49 50 et al. (2018), which provides compositional and geochronological information on mantle xenoliths and kimberlite-derived mineral concentrates from the Darby kimberlite field. 51 Six garnet pyroxenites erupted by the Darby kimberlites and studied in detail in Harris et 52 al. (2018) contain a variety of rare Ti-rich minerals, including jeppeite, K₂Ti₆O₁₃, as discrete 53 grains or reaction rims on rutile. In particular, one mantle-derived, plagioclase-free garnet 54 55 pyroxenite xenolith, sample M-2B-3A, contains rutile with a complex reaction rim (Figure S1) 56 comprised of the minerals priderite, K(Ti,Fe)₈O₁₆, perovskite, CaTiO₃, freudenbergite, $Na_2(Ti,Fe)_8O_{16}$, ilmenite, FeTiO₃, and nixonite, $Na_2Ti_6O_{13}$ (Figure 1). Nixonite is the first natural 57 occurrence of $Na_2Ti_6O_{13}$, and is the Na-rich analogue of jeppeite, which occurs as a groundmass 58 mineral in lamproites (Pryce et al. 1984; Grey et al. 1998; Jaques 2016). Previously, Na₂Ti₆O₁₃ 59 was only known as a synthetic material (Andersson and Wadsley 1962) and has been suggested 60 for potential use in batteries (e.g., Cech et al. 2017). 61 Here we describe the new mineral nixonite in terms of its physical, chemical, optical and 62

63 structural properties, and suggest a possible mechanism of formation. Nixonite is named after

64	Peter H. Nixon (b. 1935), who was Professor of Mantle Geology at Leeds University, UK, and is
65	now retired. In addition to a lifetime of work on kimberlites and their mantle- and deep crustal-
66	derived xenoliths, he named knorringite, the high-Cr garnet end-member with the formula
67	Mg ₃ Cr ₂ (SiO ₄) ₃ (Nixon and Hornung 1968). Nixon also discovered the Letseng kimberlite during
68	his Ph.D., now a world-famous source of large high-quality diamonds, and described the second
69	occurrence of yimengite (Nixon and Condliffe 1989), a potassium-chromium oxide of the
70	magnetoplumbite group that occurs in the mantle as a metasomatic mineral. Peter Nixon was a
71	visionary who brought the scientific community's attention to the growing evidence of
72	orogenically-emplaced mantle rocks from the diamond stability field, providing the first strong
73	evidence for this process in the form of graphitized diamonds from the Beni Bousera peridotite
74	massif (Pearson et al. 1989). Nixonite has been approved by the Commission on New Minerals,
75	Nomenclature and Classification with the code IMA 2018-133, and the holotype material is
76	deposited at the Royal Ontario Museum (Canada), under catalogue number M59224.

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Experimental methods

78 Scanning Electron Microscopy – Energy Dispersive Spectroscopy

In order to verify the distribution of Na over the nixonite area (Figure 1e), we used a
CamScan MX3000 electron microscope equipped with a LaB₆ source, a four-quadrant solid-state
backscattered-electron detector and an EDAX EDS system for micro-analysis installed at the
Department of Geosciences of the University of Padova. The measurement conditions were:
accelerating voltage, 20 kV; filament emission, ~ 13 nA; working distance, 27 mm.
The EBSD pattern (Figure 1f) collected on this same area was indexed in the same crystal
system as jeppeite, confirming that the nixonite grain was the Na-dominant analogue of jeppeite.

EBSD analyses were performed at CNR-ICMATE in Padova, using a Quanta 200F FEG-ESEM system operating in high-vacuum mode with an accelerating voltage of 30 kV, emission current of 174 μ A and beam spot of 4.5 μ m, without any conductive coating. EBSD patterns were collected at a working distance of 10 mm and a specimen tilt of 75° using an EDAX DigiView EBSD system. The instrument was controlled by the OIMTM 5.31 software, which contains a large EBSD pattern database.

92 Electron probe microanalysis

Nixonite was analyzed by electron probe microanalysis (EPMA) on a CAMECA SX100 93 instrument at the Department of Earth and Atmospheric Sciences, University of Alberta. The 94 95 analyses were conducted using wavelength dispersive spectroscopy (WDS) and an accelerating voltage of 20 kV, probe current of 20 nA, and a fully focused beam (< 1 μ m) for the oxides SiO₂, 96 TiO₂, Al₂O₃, V₂O₃, Cr₂O₃, MnO, Fe₂O₃, MgO, CaO, Na₂O, K₂O, SrO, Nb₂O₅ and BaO. The 97 precision for the major elements is better than 1 %. Lower limits of detection were calculated in 98 the Probe for EPMA software (Donovan et al. 2015) at the 99% confidence limit to be (in ppm, 99 100 rounded to the nearest 10, or 100 ppm for Ba): Nb 360, Si 80, Ti 180, Al 80, V 160, Cr 190, Fe 101 110, Mn 110, Mg 90, Ca 60, Sr 280, Ba 1200, Na 150, K 80. The elements Mg, Al, Si, Nb, and 102 Ba were not found above the limits of detection. Oxide abundances and standards used for the 103 elements above the limit of detection are listed in Table 1.

104 Synchrotron X-ray diffraction

No single-crystal diffraction study was possible because of the microcrystalline nature of
 nixonite (Figure 2) coupled with the fact that the sample is in a thick section embedded in resin,
 mounted on a glass slide. Unfortunately, this remains the only example of nixonite available for

108	study. The sample was characterized by angle-dispersive synchrotron X-ray diffraction carried
109	out at the experimental station GSECARS 13-BM-C of the Advanced Photon Source (APS),
110	Argonne National Laboratory. The X-ray beam was monochromated with a silicon (311) crystal
111	to a wavelength of 0.434 Å (28.6 keV) with 1 eV energy bandwidth. A Kirkpatrick-Baez mirror
112	system was used to focus the beam to 20 μm (vertical) by 15 μm (horizontal) in full width at
113	half-maximum at the sample position. A MAR165 charge-coupled device (CCD) detector
114	(Rayonix) was used to collect the diffraction patterns. A NIST LaB ₆ powder standard was used
115	to calibrate the sample-detector distance and tilting angle (Zhang et al. 2017).

116 Micro-Raman spectroscopy and laser-stimulated fluorescence

117 Micro-Raman and fluorescence spectroscopy measurements were carried out at the Department of Earth and Planetary Sciences, Northwestern University, using a custom-built 118 confocal optical system consisting of an Olympus BX microscope with 100× Mitutoyo M Plan 119 Apo long working distance objective (numerical aperture 0.7, working distance 6.0 mm), focused 120 into an Andor Shamrock 303i spectrograph (30-cm focal length) with Andor Newton DU970 121 CCD camera cooled to 188 K. For both Raman and fluorescence measurements, a 458 nm solid-122 state diode laser with 250 mW output was used as the excitation source (Melles Griot model BLS 123 124 85-601). A neutral-density filter was used to reduce the laser-power at the sample to ~ 6 mW. Raman spectra were recorded for 10 s, averaged over six accumulations from 0–4000 cm⁻¹ shift 125 126 using a holographic 1800 l/mm grating. Laser-stimulated fluorescence spectra were collected from 450–1100 nm using a 300 l/mm grating. The black dots in Figure 1, labelled R1 through 127 R5, show where the Raman spectra were collected. Fluorescence spectra were recorded at spot 128 129 R2

130

Results

131Appearance, physical and optical properties

Nixonite occurs as aggregates, between 15 to 40 µm in length (Figure 1), of
 microcrystalline grains whose domain size is not more than a few micrometers, based on the

134 spotty diffraction rings that were observed in 2D synchrotron X-ray diffraction patterns collected

with a $15 \times 20 \,\mu\text{m}$ focused beam (Figure 2). This micro-domain size prevented the determination

136 of color, streak, cleavage, parting, tenacity and fracture properties. However, we can assume the

137 cleavage and tenacity to be similar to those of the K-analogue jeppeite, which is brittle and

cleaves along the (100) plane. No luster was observed but probably it is submetallic based on the

analogy with jeppeite and the assumed mean refractive index (see below).

Although the density of nixonite was not measured because of the small size of the mineral grains, the density was calculated to be 3.51(1) g/cm³, based on the unit-cell volume determined

142 by X-ray diffraction and the chemical composition determined by electron probe microanalysis.

143 The hardness was not determined because of the character of the material available. However,

nixonite is the Na-analogue of jeppeite, ideally $K_2Ti_6O_{13}$, which has a hardness between 5 and 6

on the Mohs scale. As synthetic $K_2Ti_6O_{13}$ has a density of 3.56 g/cm³ (Cid-Dresdner and Buerger

146 1962) and nixonite has a calculated density of 3.51(1) g/cm³, it is reasonable to expect that they

147 have similar hardness. The micro-hardness could not be measured because of the very-fine

 $(\sim \mu m)$ grain size and very limited amount of sample, precluding destructive measurements.

149 Instead we sought to maximize the amount of archived material.

The small crystal size and finely-intergrown texture also prevented the measurement of the optical properties of nixonite. However, the optical properties of its K-analogue, jeppeite, can

152	provide guidance as to the mean refractive index of nixonite based on the compatibility index
153	(Mandarino 1979, 1981). Jeppeite has α , β and γ refractive indices of 2.13, 2.21 and 2.35,
154	respectively, with average refractive index: $[(\alpha + \beta + \gamma)/3] = 2.23$ (Pryce et al. 1984). Nixonite
155	should have an average refractive index in the same range as that of jeppeite, based on the
156	similarity of the densities of their synthetic end-members (Na ₂ Ti ₆ O ₁₃ has density $d = 3.51$ g/cm ³
157	and $K_2Ti_6O_{13}$ has density $d = 3.56$ g/cm ³). Alternatively, the average refractive index of nixonite
158	can be computed (using the Gladstone-Dale constants together with its composition and
159	calculated density) to be 2.27, which is very similar to the assumed value of 2.23 above.
160	Calculation of the Gladstone-Dale relationship yields a compatibility index, $1-(K_P/K_C) = 0.03$,
161	rated as 'excellent' (Mandarino 1981).

Chemical composition 162

163 The empirical formula of nixonite, calculated from the EPMA data in Table 1, on the

164 basis of 13 oxygens atoms per formula unit (apfu) is:

 $[Na_{1,24}K_{0.67}Ca_{0.06}]_{\Sigma 1.97}$ $[Ti_{5,96}V_{0.023}Fe_{0.018}]_{\Sigma 6.00}O_{13}$, with minor amounts of Cr and Mn. 165

- The simplified formula is $(Na,K)_2Ti_6O_{13}$, and the ideal formula is $Na_2Ti_6O_{13}$, which 166
- requires Na₂O 11.45 wt% and TiO₂ 88.55 wt%. Elemental maps for K, Na, Ti, Ca and Fe were 167
- acquired to outline zones of interest for characterization by X-ray diffraction (Figure 1e, Figure 3 168
- and Figure S2). The nixonite and freudenbergite reaction rim is clearly shown by the Na 169
- elemental abundance map (Figure 3b). 170

171 X-ray crystallography

The black squares in Figure 1, labelled D1 through D7, show where the multi-grain 172 diffraction patterns were collected. As a result of the small grain size and the sample having to be 173 174 measured in a thick section – with the likelihood of additional phases underlying the nixonite 175 grains – multiple phases (mostly rutile and priderite) were observed along with the nixonite 176 diffraction pattern (Figure 4). Our procedure for dealing with multi-grain, multi-phase diffraction data is outlined below in order to extract crystallographic data for nixonite. 177 We first masked out rutile and priderite diffraction signals from the raw diffraction 178 image, and then the masked diffraction image was integrated with the DIOPTAS software 179 (Prescher and Prakapenka 2015). Individual peak positions (*d*-spacings are reported in Table 2) 180 were fitted with the Gaussian peak shapes from the integrated diffraction pattern, and the 181 UnitCell program (Holland and Redfern 1997) was used to determine unit-cell parameters 182 183 (Figure 5). Rietveld refinement was carried out on the pseudo-powder diffraction patterns generated by averaging seven integrated multi-grain diffraction patterns using the GSAS 184 program (Toby and Von Dreele 2013). Our starting model of nixonite was revised from the 185 Na₂Ti₆O₁₃ structure determined by Andersson and Wadsley (1962) with space group C2/m on a 186 synthetic material. In the Rietveld refinement, the cell parameters from UnitCell were fixed, 187 whereas the atomic coordinates of the (Na,K) position and the three Ti positions were refined 188 189 (the atomic coordinates of the oxygen positions were not refined). Our diffraction data are consistent with the previously published structure models for synthetic Na₂Ti₆O₁₃ (Andersson 190 191 and Wadsley 1962) and K₂Ti₆O₁₃ (Cid-Dresdner and Buerger 1962), although the R-factor for 192 the model is ~ 57 % due to poorly constrained intensities from the microcrystalline diffraction patterns. The refined unit-cell parameters are: a = 15.3632(26) Å, b = 3.7782(7) Å, 193 c = 9.1266(15) Å, $\beta = 99.35(15)^{\circ}$ and V = 522.72(1) Å³ (Z = 2). The *a:b:c* ratio calculated from 194

unit-cell parameters is 4.0663:1:2.4155. For a comparison of nixonite with synthetic Na₂Ti₆O₁₃ and other related species see Table S2.

197 Crystal structure

198 A complete crystal structure refinement could not be carried out due to the micro-199 crystalline nature of the sample (see Figure 2); the diffraction patterns are neither single-crystal 200 nor powder, and contain multiple phases, along with being mounted on a glass slide. In light of 201 the limited nature of the data (not powder, not single-crystal, and not a lot of observables), a high-quality Rietveld refinement of the proportions of the different phases was not realistic. The 202 203 best approach was therefore to average all seven background-corrected diffraction patterns and 204 remove the peaks from the other phases. Whereas the peak intensities were not well constrained for Rietveld refinement, the peak positions produced reliable unit cell parameters and confirmed 205 the structural identity of this material. 206

It was not possible to refine the atomic coordinates of the oxygen atoms, as unrestricted refinement yielded inappropriate interatomic distances; however, refinement of the (Na,K) position, and the three Ti positions yielded atomic coordinates that compare favorably with the models of Andersson and Wadsley (1962) for Na₂Ti₆O₁₃, and Cid-Dresdner and Buerger (1962) for K₂Ti₆O₁₃. In the refinement of the data for nixonite, the occupancy of the Na1 site was fixed to Na 0.666, K 0.334, based on the EPMA data.

Nixonite is isostructural with jeppeite, ideally $K_2Ti_6O_{13}$, and consists of three chains of distorted, edge-sharing Ti-centered octahedra that extend along the *c*-axis. Two of the chains are connected by sharing corner along the *b*-axis, and the third chain links the first two by sharing edges with both. In this way, the structure can also be thought of as a zig-zag chain of three Ticentered octahedra edge-sharing along *b*. The alkali cations fit into tunnels formed by the Ti-

octahedral framework, lying in a distorted cube coordination with eight oxygen. (Figure 6). The
axes of the Ti-centered octahedra are parallel to the two-fold *b*-axis (Figure 6d).

220 Vibrational spectroscopy

221	The micro-Raman spectra collected on nixonite are shown in Figure 7 (black), where they
222	are compared to the spectrum of $Na_2Ti_6O_{13}$ (red), synthesized at 800 °C to 1200 °C by
223	Bamberger and Begun (1987). We did not observe any Raman peaks above 1000 cm^{-1} (see
224	Supplementary Material). The five main peaks of nixonite, in order of decreasing intensity, are
225	(in cm ^{-1}): 863, 280, 664, 135 and 113. Lower intensity peaks are evident in the 171–250 cm ^{-1}
226	and in the 332–618 cm^{-1} regions; two more peaks are centered at 97 and 747 cm^{-1} , respectively.
227	The list of Raman peaks and their assignments is given in Table S1. The laser-stimulated
228	fluorescence spectrum collected on nixonite is reported in Figure 8. The gap in signal at around
229	900 nm of Figure 8 is due to double-diffraction from the 458 nm notch filter. The peaks observed
230	between 450 and 500 nm in Figure 8 are Raman peaks and used to confirm that the fluorescence
231	spectra are associated with nixonite.

232

Discussion

233 Occurrence and paragenesis

- $(\sim 1 \text{ cm} \times 1 \text{ cm} \times 0.5 \text{ cm}, \text{Figure S1})$ from the Darby kimberlite field, located $\sim 200 \text{ km}$
- southwest of the community of Kugaaruk, Nunavut, Canada, beneath the west central Rae Craton
- $(67^{\circ}23'56.6"N 93^{\circ}21'13.9"W)$. This xenolith contains rutile, TiO₂, up to 200 μ m in size, with a
- complex and thin reaction rim that consists of priderite, K(Ti,Fe)₈O₁₆, perovskite, CaTiO₃,

239	freudenbergite, Na ₂ (Ti,Fe) ₈ O ₁₆ , ilmenite, FeTiO ₃ , and nixonite, Na ₂ Ti ₆ O ₁₃ (Figure 1). Jeppeite
240	was not recorded in the same reaction rim on rutile as nixonite, but was found in other thin
241	sections from the same xenolith (Harris et al. 2018). Rutile is observed in a variety of mantle
242	xenocrysts and xenoliths but is most commonly found in eclogitic (Smith and Dawson 1975;
243	Carswell 1990; Sobolev et al. 1997; Sobolev et al. 2000) or mantle-metasomatic assemblages
244	(e.g., MARID associations; Dawson and Smith 1977; Haggerty 1991). Priderite, freudenbergite
245	and jeppeite have been observed in a range of metasomatized mantle material (Jones et al. 1982;
246	Mitchell and Lewis 1983; Haggerty et al. 1994; Giuliani et al. 2012). Jeppeite has been
247	previously reported most commonly in lamproites, as a late-crystallizing groundmass phase
248	(Pryce et al. 1984; Grey et al. 1998; Jaques 2016).

249 Relationship to other species

Nixonite can be compared to its K-analogue, jeppeite, and to the only other known
natural sodium–titanium oxides: freudenbergite and kudryavtsevaite.

Nixonite has the same structure as jeppeite, synthetic $Na_2Ti_6O_{13}$ and synthetic $K_2Ti_6O_{13}$. However, jeppeite and its synthetic analogue $K_2Ti_6O_{13}$ have slightly larger unit-cell volumes, whereas synthetic $Na_2Ti_6O_{13}$ has a slightly smaller unit-cell volume. As one would expect among structural analogues, the positions of their main diffraction peaks are similar, whereas their intensities are different (Table S2).

Freudenbergite and kudryavtsevaite are the only other known natural sodium–titanium oxides (Ishiguro et al. 1978; Anashkin et al. 2013). Freudenbergite has the same space group as nixonite, but its unit-cell parameters are significantly different, as are the positions of its main diffraction peaks, with the exception of the main peak (located at 3.63 Å), which is close to the second-most intense peak of nixonite (located at 3.66 Å, Table S2). Kudryavtsevaite, in contrast,

is orthorhombic and has a much larger unit-cell volume and very different diffraction peak-

263 positions than nixonite; these two minerals can therefore be distinguished without ambiguity.

264

Implications

The first natural occurrence of nixonite is observed here to co-exist within a single assemblage of freudenbergite, perovskite and priderite within a pyroxenite xenolith from the Darby kimberlite field. These other minerals, together with jeppeite, are also found in six mantlederived garnet pyroxenites within a metasomatic mineral suite that surrounds rutile grains and/or occurs as discrete grains in the case of jeppeite (Harris et al. 2018).

Freudenbergite and priderite have previously reported in metasomatized peridotites 270 271 sampled by kimberlites from southern Africa and North America (Jones et al. 1982; Mitchell and Lewis 1983; Haggerty et al. 1994; Giuliani et al. 2012). Jeppeite is most commonly found as a 272 late-crystallizing groundmass phase in lamproites (Haggerty, 1987) but has also been recorded in 273 metasomatized mantle peridotites within the Prarie Creek lamproite (Mitchell and Lewis 1983). 274 Jeppeite has also been noted as a reaction rim on priderite (Mitchell and Bergman 1987). Hence, 275 these K-Ba-Ti-rich metasomatic phases characteristically form in highly alkaline, relatively Ti-276 277 rich melts such as the ground mass of lamproites. The occurrence of jeppeite and nixonite in the reaction rims around rutile grains in the Darby pyroxenite xenolith seem to be mutually exclusive 278 though there is a ready source of Ti, in addition to any input from the metasomatic melt. The lack 279 of association of nixonite and jeppeite is consistent with their formation in different chemical 280 environments: jeppeite (and priderite) form in ultrapotassic environments from fluids rich in K, 281 282 Ba and Ti (very high K/Na), whereas nixonite and freudenbergite appear to form in Na-rich, Bapoor environments. Despite extensive searching, nixonite was not observed in any of the other 283 284 numerous jeppeite occurrences around rutile grains within this pyroxenite, whereas jeppeite is

285	absent from the assemblage containing nixonite. This may reflect small-scale variations in the
286	relative K and Na contents of the metasomatic melt, or different stages in the evolution of the
287	metasomatic melt. Freudenbergite, a Na-rich mineral, only occurs in the reaction rim containing
288	nixonite in this rock, with whatever K was present being accommodated by priderite in this
289	assemblage. The textural relationships between nixonite and priderite around the rutile in sample
290	M-2B-3A are complex (Figure 1), in places directly mantling rutile and in other places mantling
291	priderite. Without other grains from which to constrain these relations we cannot rule out the role
292	of sectioning effects in creating these spatial relationships.
293	Among the nine bodies that constitute the Darby kimberlite field, most are classified as
294	archetypal (or Group-I) kimberlites, but one is reported to be of "lamprophyre" affinity based on
295	initial diamond exploration studies. Moreover, Sarkar et al. (2018) have recently reported the
296	occurrence of intrusive rocks at Aviat, to the east of the Darby field, that are akin to orangeites
297	(previously also known as Group-II kimberlites), which have close mineralogical and
298	compositional similarities to lamproites. The occurrences of freudenbergite and the crichtonite-
299	magnetoplumbite series minerals in metasomatized peridotites derived from kimberlites of the
300	Kimberley area, South Africa, is notable because the K-Ba-Ti-rich MARID-like metasomatism
301	there has been proposed to be the source of orangeites (Giuliani et al. 2015). Such K-Ti mantle
302	metasomatism also was invoked for the formation of yimengite reaction rims around xenocrystic
303	spinel in Venezuelan kimberlites, by Nixon and Condliffe (1989).
304	A mantle origin for the garnet pyroxenites containing nixonite and jeppeite was
305	established using the approach of Hardman et al. (2018). Hence, the complex Na-K-Ti rich
306	metasomatic mineral assemblages recorded beneath the Darby kimberlite field could reflect

traces of an unusual metasomatic melt that percolated into the lithospheric mantle. Giuliani et al.

(2012) have suggested that such complex titanium oxides, also found with alkali salts within
 Kimberley mantle xenoliths, originate from alkali-carbonate melts that percolate through
 cratonic lithospheric mantle.

311 There are other alternatives to consider. The Darby kimberlites and their host peridotites 312 and eclogites have been subject to intense later-stage serpentinisation (Harris et al. 2018). However, there are no records of the Na-K-Ti rich assemblage reported here being related to late 313 stage alteration in the crust. This, and the lack of these assemblages around rutile in other Darby 314 pyroxenites that are similarly altered/serpentinised, gives us confidence that the nixonite and 315 other minerals in the rutile reaction rim of sample M-2B-3A did not form as a result of low 316 temperature alteration. Nonetheless, this does not preclude metasomatic alteration taking place 317 during magma infiltration into the pyroxenite during kimberlite sampling, transport and 318 319 crystallization. This option is very difficult to differentiate from metasomatism of the pyroxenite 320 by passing metasomatic melts while the pyroxenite was still residing in the mantle lithosphere beneath the Darby kimberlite field, prior to kimberlite sampling, because of the lack of 321 determined phase relations for jeppeite and nixonite at geologically meaningful conditions. 322 Transport by the host kimberlite and the subsequent evolution of an alkali-rich melt during 323 324 kimberlite crystallization, as documented by Giuliani et al. (2017), producing a Na-rich melt 325 could have invaded the pyroxenite and caused alteration of the rutile. This melt infiltration could have been responsible for the generation of the complex assemblage of Na-K-Ti rich minerals 326 observed here, with Ti being derived from the pre-existing rutile. 327 328 The late groundmass crystallization of jeppeite in lamproites, together with its previously

The late groundmass crystallization of jeppeite in lamproites, together with its previously observed reaction-relationship with priderite, has been used to infer a low-pressure origin for this mineral (Chakhmouradian and Mitchell 2001). By inference, a low-pressure origin for nixonite,

332 metasomatic origin, until the stability relations of the jeppeite – nixonite series are determined.

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Figure captions 465

Figure 1. a) Backscattered image of rutile grain with complex reaction rim containing nixonite 466

(in 5 locations), priderite, freudenbergite, ilmenite, and perovskite; **b**) and **c**) portions of the rutile 467

grain; d) nixonite area in which e) a Na EDS map and f) an EBSD pattern were collected. The 468

EBSD pattern acquired from the Na-rich area was indexed in the same crystal system as jeppeite, 469

470 confirming that nixonite is the Na-dominant form of jeppeite. Black dots and black squares

indicate where Raman spectra and diffraction patterns were collected, respectively. 471

Figure 2. Example 2D X-ray diffraction image of nixonite collected at spot D2 in Figure 1 and 472

corresponding to diffraction pattern DB2 in Figure 4. The diffraction pattern was collected with 473

monochromatic synchrotron radiation ($\lambda = 0.434$ Å) focused to a spot size of 20 µm (vertical) by 474

15 µm (horizontal) at beamline 13-BMC (GSECARS) of the Advanced Photon Source, Argonne 475

- National Lab. The spotty nature of the 2D diffraction pattern in this configuration suggests the 476
- 477 nixonite grain size is on the order of $1-2 \mu m$.

Figure 3. False-color (16 shades) X-ray intensity maps. a) K map showing priderite, nixonite,
and freudenbergite; b) Na map displaying nixonite and freudenbergite in the reaction rim. Dark
red shows the zone where nixonite is the most abundant.

481 Figure 4. a) X-ray diffraction patterns of nixonite at positions D1-D7, shown in Figure 1, before

background correction and subtraction of other phases (N = nixonite, P = priderite, R = rutile); **b**)

483 X-ray diffraction patterns of nixonite at positions D1-D7, shown in Figure 1, after background

484 correction and subtraction of other phases.

Figure 5. a) The average of seven nixonite diffraction patterns after background correction is 485 shown in black, while the blue pattern is the sum of all peaks that could be indexed as nixonite. 486 487 This diffraction pattern was used to refine the unit cell parameters of nixonite reported in the text; b) Comparison between calculated nixonite diffraction pattern (green) and the sum of all 488 peaks that could be indexed as nixonite (blue). The calculated diffraction pattern was produced 489 by refining the lattice parameters from the masked diffraction pattern and a starting structure 490 revised from synthetic Na₂Ti₆O₁₃ (space group C2/m); c) Comparison between the calculated 491 nixonite pattern (green), the average of DB1-DB7 after applying background correction (black) 492 and the reference patterns of rutile: calculated from PowderCell (Kraus and Nolze 1996) using 493 494 the structure from Swope et al. 1995, red; and of priderite: calculated from PowderCell using the 495 structure from Post et al. 1982, purple. All of the peaks can be indexed by nixonite, rutile, and priderite. 496

Figure 6. Crystal structure of nixonite a) viewed obliquely down the *b* axis, showing the corrugated chains of (3-wide) edge-shared octahedra that extend along the *b* axis; b) viewed along the *a* axis; c) viewed along the *b* axis; d) viewed along the *c* axis. Oxygen atoms are represented in red, titanium-centered octahedra in blue, and sodium and potassium in yellow and purple, respectively. In **d**) it is evident that chains of Ti-centered octahedra are parallel to the baxis.

Figure 7. Raman spectra of nixonite (black) at five different positions labelled R1-R5 in Figure 1, and the spectrum of $Na_2Ti_6O_{13}$ (red), synthesized at 800 °C to 1200 °C by Bamberger and Begun (1987).

Figure 8. Fluorescence spectrum of nixonite acquired at position R2 (Figure 1), excited by the 458 nm laser used for Raman spectroscopy. The extinction of light at around 900 nm is due to second-order diffraction by the 458 nm holographic notch filter and is thus an artifact of the spectroscopic system. The observed peaks below 500 nm correspond to Raman scattering.

510 **Figure S1.** Thick section of the pyroxenite showing the location of rutile with nixonite under **a**)

transmitted and **b**) oblique light; **c**) and **d**) are close ups of the rutile grain under incident light.

512 Figure S2 False-color (16 shades) X-ray intensity maps. a) Ti map showing rutile host and rare

513 Ti minerals surrounding it; b) Ca map highlighting perovskite and the alteration rim on rutile; c)

514 Fe map highlighting ilmenite and the alteration rim on rutile.

Oxide	Wt%	Stand. Dev.	Range	Probe Standard
Na ₂ O	6.87	0.68	5.93-7.60	NaAlSi ₃ O ₈ 131705
K ₂ O	5.67	1.25	4.11-7.33	KAlSi ₃ O ₈ Itrongay
CaO	0.57	0.36	0.30-1.26	CaMgSi ₂ O ₆ Wakefield
TiO ₂	84.99	0.50	84.08-85.34	TiO ₂ MTI
V_2O_3	0.31	0.08	0.15-0.39	V Alfa
Cr_2O_3	0.04	0.03	0-0.07	Cr ₂ O ₃ Alfa
MnO	0.01	0.01	0-0.02	(Mn,Fe) ₃ Al ₂ Si ₃ O ₁ Navegadora Mine
Fe ₂ O ₃	0.26	0.08	0.17-0.37	FeTiO ₃ 96189
SrO	0.07	0.03	0.04-0.11	SrTiO ₃ MTI
Total	98.79	0.70	97.55-99.57	

516 **Table 1:** WDS chemical analyses (wt%) carried out on nixonite and based on the average of six 517 analysis points. Data have been rounded to the nearest 0.01 wt% oxide.

519	Table 2: L	ist of	d-spa	cings	(in Å),	relative	intensities	and <i>hkl</i>	indices	for r	nixonite	obtained	by
			T T D							1:00	. •		

pseudo-powder XRD, obtained by averaging seven "multi-grain" 2D diffraction patterns (seeFigure 2).

No.	Iobs	d _{obs} (Å)	I _{calc}	d _{calc} (Å)	h	k	l
1	73	7.57	100	7.58	2	0	0
2 3	68	6.31	67	6.33	2	0	-1
	4	4.18	4	4.18	2	0	-2
4	8	3.77	2	3.79	4	0	0
5	75	3.66	80	3.67	1	1	0
6	5 7	3.34	1	3.35	1	1	1
7	7	3.28	2	3.31	4	0	1
8	100	3.02	79	3.03	3	1	0
9	63	2.96	65	2.96	3 2	1	-1
10	63	2.96	44	2.96	2	0	-3
11	39	2.79	17	2.79	1	1	2 2
12	62	2.71	27	2.69	4	0	2
13	22	2.54	18	2.54	6	0	-1
14	51	2.09	43	2.09	4	0	-4
15	29	2.06	29	2.06	6	0	2
16	25	1.99	19	1.98	5	1	-3
17	48	1.89	42	1.89	0	2	0
18	25	1.74	15	1.74	5	1	-4
19	12	1.65	11	1.65	7	1	2
20	47	1.59	26	1.59	2	2	-3
21	21	1.56	20	1.55	7	1	-4
22	24	1.54	21	1.55	4	2	-4 2 5
23	15	1.53	9	1.53	4	0	5
24	10	1.52	13	1.52	6	2	-1
25	17	1.51		1.51	-10	0	2
26	15	1.50	8 5 8	1.50	0	0	2 6
27	23	1.48	8	1.48	9	1	1
28	15	1.41	9	1.41	1	1	-6
29	61	1.40	20	1.40	4	2	-4

No.	I obs	d _{obs} (Å)	I calc	d _{calc} (Å)	h	k	l
1	73	7.57	100	7.58	2	0	0
2	68	6.31	67	6.33	2	0 -	-1
3	4	4.18	4	4.18	2	0 -	-2
4	8	3.77	2	3.79	4	0	0
5	75	3.66	80	3.67	1	1	0
6	5	3.34	1	3.35	1	1	1
7	7	3.28	2	3.31	4	0	1
8	100	3.02	79	3.03	3	1	0
9	63	2.96	65	2.96	3	1 -	-1
10	63	2.96	44	2.96	2	0 -	-3
11	39	2.79	17	2.79	1	1	2
12	62	2.71	27	2.69	4	0	2
13	22	2.54	18	2.54	6	0 -	-1
14	51	2.09	43	2.09	4	0 -	-4
15	29	2.06	29	2.06	6	0	2
16	25	1.99	19	1.98	5	1 -	-3
17	48	1.89	42	1.89	0	2	0
18	25	1.74	15	1.74	5	1 -	-4
19	12	1.65	11	1.65	7	1	2
20	47	1.59	26	1.59	2	2 -	-3
21	21	1.56	20	1.55	7	1 -	-4
22	24	1.54	21	1.55	4	2	2
23	15	1.53	9	1.53	4	0	5
24	10	1.52	13	1.52	6	2 -	-1
25	17	1.51	8	1.51	-10	0	2
26	15	1.50	5	1.50	0	0	6
27	23	1.48	8	1.48	9	1	1
28	15	1.41	9	1.41	1	1 -	-6
29	61	1.40	20	1.40	4	2 -	_4

	Wavenum	ber (cm ⁻¹)		
This study	Zeng et al. $(2013)^{a}$	Zhu et al. (2007) ^b	Bamberger and Begun (1987) ^c	Assignment
96	101	93	92	vibration of the Na–O–Ti bonds ^a
110		110	108	vibration of the Na–O–Ti bonds ^a
138	130	138	138	vibration of the Na–O–Ti bonds ^a
171	187		167	vibration of the Na–O–Ti bonds ^{a,d}
196		197	195	
226	216	224	224	vibration of the Na–O–Ti bonds ^a
250			251	
278	268	278	277	vibration of the Na–O–Ti bonds ^{a,d,e}
332	327			vibration of the Na–O–Ti bonds ^a
362 391	388	396	394	
408	404	414	410	pure framework Ti–O–Ti vibrations ^a
455	450			pure framework Ti–O–Ti vibrations ^a
	472	481	481	pure framework Ti–O–Ti vibrations ^a

508	515	526	526	Ti–O–Ti stretching in edge-shared TiO ₆ ^e
615	602		616	Ti–O–Ti stretching in edge-shared TiO ₆ ^a
668	671		658	Ti–O–Ti stretching in edge-shared TiO ₆ ^{a,d}
		681	681	vibration of the Na–O–Ti bonds ^b
758	732	745	745	Ti–O–Ti stretch in corner- shared TiO ₆ ^a
867	865	871	871	short Ti–O stretching vibration in distorted TiO ₆ ^a
Notes: ^d Li	u et al. (2010); ^e Kolen'k	o et al. (20	06).

	Nixonite	Jeppeite (Pryce et al. 1984)
Chemical formula	$(Na_{1.24}K_{0.67}Ca_{0.06})(Ti_{5.96}V_{0.023}Fe_{0.018})O_{13}$	(K,Ba) ₂ (Ti,Fe ³⁺) ₆ O ₁₃
Crystal system	Monoclinic	Monoclinic
Space group	C 2/m	C 2/m
Z	2	2
	a = 15.3632(26) Å,	a = 15.453 Å,
Unit-cell parameters	b = 3.7782(7) Å	b = 3.8368 Å,
and volume	c = 9.1266(15) Å, $\beta = 99.35(15)^{\circ};$	c = 9.123 Å, $\beta = 99.25^{\circ};$
	$V = 522.72(1) \text{ Å}^3$	$V = 533.9 \text{ Å}^3$

Seven main		
d-spacings	3.02(100), 3.66(75), 7.57(73), 6.31(68),	3.07(100), 2.99(100), 2.81(100),
(Å), relative	2.96(63), 2.96(63), 2.71(62)	1.92(80), 2.09(60), 2.07(60), 2.97(40)
intensity	2.90(03), 2.90(03), 2.71(02)	1.32(80), 2.03(00), 2.07(00), 2.37(40)
(% or s)		

Calculated		
density	3.51	3.98
(g/cm ³)		

Freudenbergite (Ishiguro et al. 1978)	Kudryavtsevaite (Anashkin et al. 2013)		
Na ₂ Fe ₂ Ti ₆ O ₁₆	Na ₃ (Mg,Fe ³⁺)Ti ₄ O ₁₂		
Monoclinic	Orthorhombic		
C 2/m	Pnma		
4	4		
a = 12.267(6) Å,	a = 27.714(1) Å,		
b = 3.823(5) Å,	b = 2.9881(3) Å,		
c = 6.483(3) Å, β = 107.16(5)°; V = 290.5 Å ³	c = 11.3564(6) Å, $\beta = 90^{\circ};$ $V = 940.5(1) Å^{3}$		

3.63(100), 1.91(63), 3.10(57),	7.17(100), 4.84(70), 2.45(70),		
2.06(55), 2.04(55), 2.72(48), 2.73(41)	2.84(50), 2.71(50), 2.54(50), 2.97(35)		

3.97

3.85

Na ₂ Ti ₆ O ₁₃ (Andersson and Wadsley 1962)	K ₂ Ti ₆ O ₁₃ (Cid-Dresdner and Buerger 1962)			
Na ₂ Ti ₆ O ₁₃	$K_2 Ti_6 O_{13}$			
Monoclinic	Monoclinic			
C 2/m	C2/m			
2	2			
a = 15.131(2) Å,	a = 15.582(6) Å,			
b = 3.745(2) Å,	b = 3.82(1) Å,			
c = 9.159(2) Å, $\beta = 99.30(5)^{\circ};$	c = 9.112(1) Å, $\beta = 99.764(8)^{\circ};$			
$V = 512.2 \text{ Å}^3$	$V = 534.5 \text{ Å}^3$			

7.47(s), 3.63(s) 1.87(s), 6.27(ms),	7.68(100), 3.06(73), 2.99(70),
2.99(ms), 2.97(ms), 2.93(ms)	2.96(59), 1.91(55), 6.40(54), 2.70(45)

3.51

3.56

nixonite

R4

d

D2

i R3

b

perovskite *

255

223

191

159

128

0

priderite



rutile

	20	10. µm BSE 20	. kV		U
b		LEGEND ■ nixonite ◆ priderite ◆ freudenbergite ※ ilmenite ▲ perovskite	255 223 191	 LEGEND nixonite priderite freudenbergite ilmenite perovskite 	













Intensity (arbitrary units)







Raman shift (cm⁻¹









