

THE VANADIUM-BEARING OXIDE MINERALS OF THE GREEN GIANT VANADIUM-GRAPHITE DEPOSIT, SOUTHWEST MADAGASCAR

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ABSTRACT

Rare vanadium-rich oxide minerals have been previously identified in graphite-bearing quartzo-feldspathic gneisses derived from shale protoliths. In this work, such minerals are described from the Green Giant vanadium-graphite property in southwest Madagascar. The vanadium-rich oxides include vanadium-bearing rutile ($2.88 \pm 1.75\% \text{ V}_2\text{O}_3$, $n = 18$), schreyerite, oxyvanite, and karelianite. These minerals have been previously identified together in the Sludyanka, Lake Baikal area. Green Giant is the second occurrence worldwide of oxyvanite, and within the oxyvanite–berdesinskiite solid solution series Green Giant oxyvanites are the closest to endmember, with an average calculated mineral formula of $(\text{V}^{3+}_{1.49}, \text{Cr}_{0.50}, \text{Fe}^{3+}_{0.01})_{\Sigma 2.00} \text{V}^{4+}_{1.00} \text{O}_5$. Also found in this study is an unknown vanadium-titanium oxide mineral, UK1, which has a calculated formula of $(\text{V}^{3+}_{1.67}, \text{Cr}^{3+}_{0.26}, \text{Al}_{0.06})_{\Sigma 1.99} (\text{V}^{4+}_{2.05}, \text{Ti}^{4+}_{1.94})_{\Sigma 3.99} \text{O}_{11}$ and may be related to the $\text{V}_2\text{Ti}_4\text{O}_{11}$ reported previously from the Lake Baikal area.

Keywords: vanadium, vanadium oxides, Madagascar, graphite, oxyvanite, Green Giant, schreyerite.

INTRODUCTION

The Green Giant vanadium-graphite deposit is located in southwest Madagascar (Fig. 1), 145 km southeast of the city of Toliara in the Tulear Region. The deposit is owned by NextSource Materials Inc., formerly Energizer Resources Inc. Green Giant, believed to be one of the largest known vanadium deposits in the world, is a graphite-bearing trend, and is separated by approximately 15 km from the Molo Graphite Project, also owned by NextSource Materials Inc. Vanadium deposits are of interest due to potential future use in large-scale energy storage applications.

In September 2011 a project began to investigate the mineralogy of the vanadium minerals present in the Green Giant lithologies. Although vanadium has been

known to be associated with graphite (e.g., Rose 1973), few localities of this type have been described. Vanadium-graphite localities known to date, such as the Kwale District, south of Voi, Kenya (Medenbach & Schmetzer 1976); the Sludyanka complex, Lake Baikal, Russia (Koneva 2002); Amstall, Lower Austria (Ertl *et al.* 2008); and black slates in the Okcheon Metamorphic Belt, Korea (Jeong 2006) typically host unusual vanadium-rich mineral assemblages, suggesting the possibility of similar findings at Green Giant. Typically, most vanadium deposits are Ti-rich magnetite in mafic intrusions (e.g., Maracás Menchen Mine, Brazil, Hammond 2016; Bushveld, South Africa, Maier *et al.* 2012); uranium-vanadium-enriched sandstone-hosted deposits (e.g., Colorado Plateau, USA; Wanty *et al.* 1990); and black/

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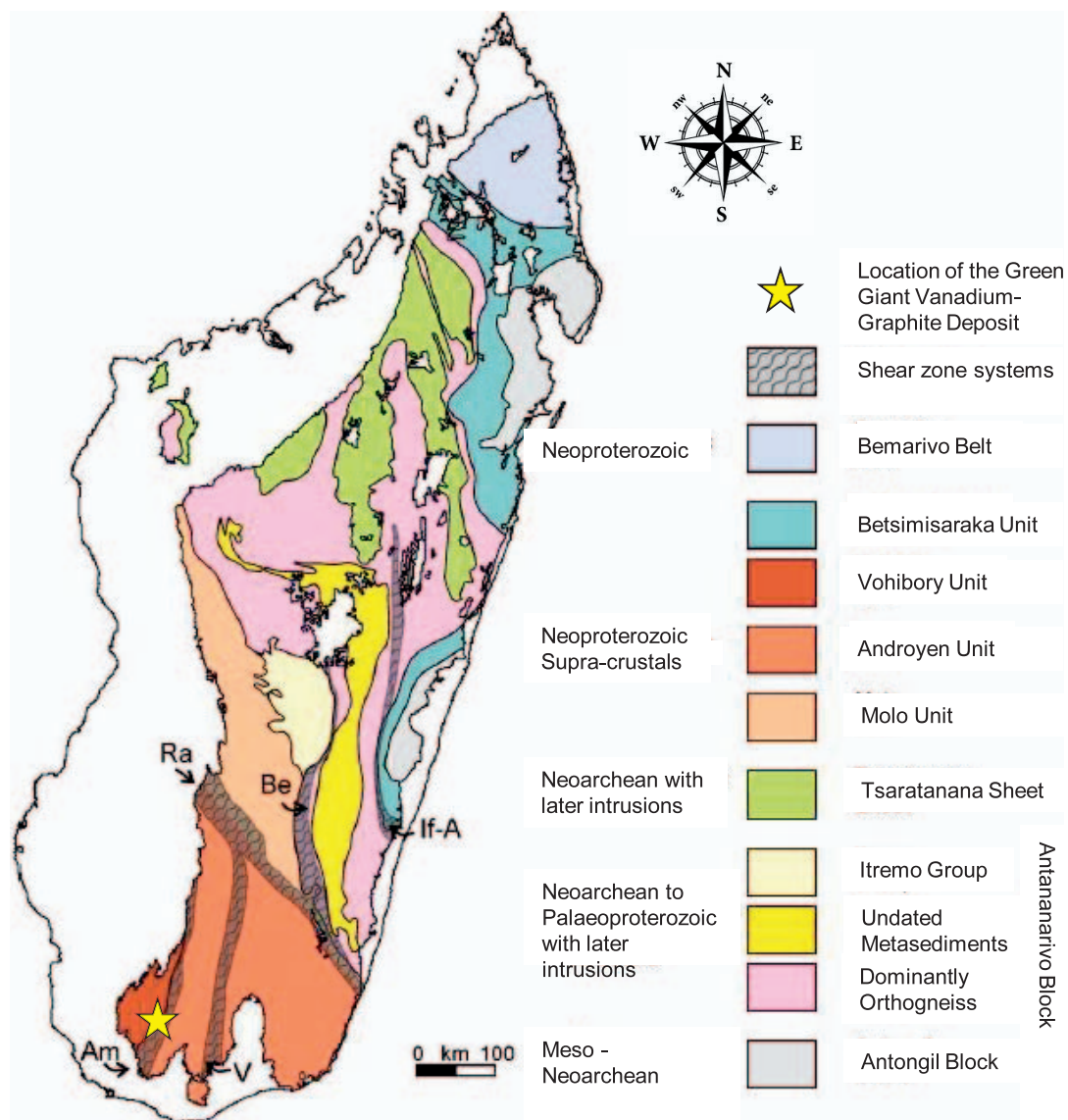


FIG. 1. Geological basement map of Madagascar (from Collins 2006) showing the location of the Green Giant vanadium-graphite deposit. Shear zone systems: Am – Ampanihy, Be – Betsileo, If-A – Ifanadiana-Angavo, Ra – Ranotsara, V – Vorokafotra.

variegated shales (e.g., Gibellini, Eureka, Nevada, USA; Rose 1973; Didaleusky *et al.* 2010).

Samples for mineralogical analysis were selected from a drill core from the Manga area (23°59'52.6231"S, 045°01'48.6590"E, Fig. 2), one of the major vanadium-bearing trends on the property. In this trend, the average V_2O_5 content is reported to be

0.67 ± 0.32 wt.% by NextSource Materials Inc. In this work, the vanadium-bearing oxide minerals of the Green Giant property are identified and their chemical compositions are documented through electron-microprobe analysis, allowing us to further describe the vanadium oxide minerals occurring in highly metamorphosed vanadium-graphite deposits.

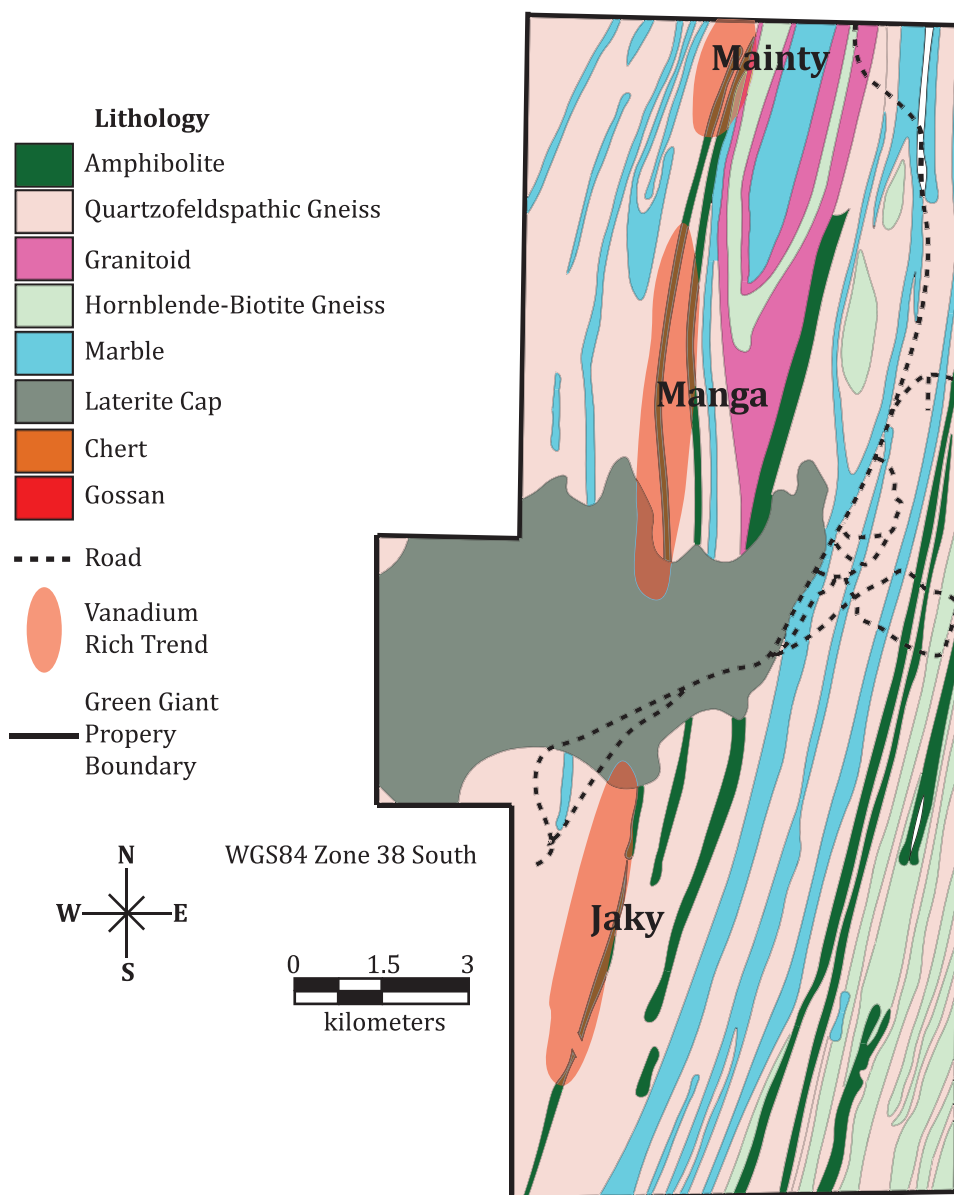


FIG. 2. Geology of the Green Giant vanadium-graphite property (after Energizer Resources Inc. 2011). Manga, Mainty, and Jaky are the names of subareas.

OCCURRENCE

The Green Giant vanadium-graphite property is located in the Vohibory unit, bordering the Androyen unit and within the Ampanihy transpressive shear zone (Fig. 1). Both units contain Neoproterozoic metasediments (Rakotovo *et al.* 2014). The Vohibory unit includes pelites, marbles, and amphibolites, deposited

in the Cryogenian (between 720 and 635 Ma) and metamorphosed at 642 ± 8 Ma (Collins 2012). This unit underwent the highest-grade metamorphism on the island, with peak conditions between 9 and 11.5 kbar and 750 and 850 °C (Nicollet 1990, Martelat *et al.* 1997, Collins 2006). It was subjected to a Pan-African deformation event at 530–580 Ma which produced vertical shear zones and is interpreted to be the result

TABLE 1. SAMPLES EXAMINED FOR VANADIUM-BEARING OXIDES AND THEIR RESPECTIVE DEPTHS DOWN CORE IN MANGA DRILL HOLE M-87 (VANADIUM-BEARING OXIDES PRESENT ARE LISTED)

Sample Number	Depth Down Core (m)	Rutile	Schreyerite	Oxyvanite	Karelianite	Unknown 1
UT117	192–192.4	X	X			
UT130	218–218.4				X	X
UT134	226–226.4	X	X			X
UT150	258–258.4	X	X		X	X
UT159	276–276.4	X	X	X		X

of east–west bulk horizontal shortening of the Precambrian crust, resulting in high-pressure, high-temperature metamorphic-grade rocks (Martelat *et al.* 1997, Lardeaux *et al.* 1999). These rocks in the western region of the Green Giant occurrence are predominantly present as quartzo-feldspathic gneisses (Energizer Resources Inc. 2011).

The Androyen unit includes metapelites, quartzites, and marbles, originally deposited as mudstones, sandstones, and limestones between 750 and 630 Ma (Collins 2006). This unit then underwent regional transpression and high-temperature metamorphism up to 800 °C, leading to peak amphibolite- to granulite-facies conditions between 645 and 545 Ma (Martelat *et al.* 1997, Collins 2006). The Androyen unit lies in the eastern part of the property and is predominantly amphibolite gneiss (Energizer Resources Inc. 2011).

The Molo graphite deposit, 15 km from the Green Giant property, occurs in the Androyen unit and consists of moderately to highly metamorphosed, sheared, graphitic quartzo-feldspathic schists and gneisses rich in biotite (annite), chlorite, and pyrope (de Bruin 2017). At this time, the Molo project has measured mineral resources of 23 MT grading 6.32% C with further indicated and inferred resources (de Bruin 2017). Complexly folded graphitic horizons are present with a surficially exposed strike length of over 2 km, and the vanadium mineralization occurs lining fractures (de Bruin 2017).

The Molo and Green Giant rocks typically form narrow, alternating bands trending NNE and dipping steeply to the WNW. The geology of the Green Giant property is shown in Figure 2 and mainly consists of quartzo-feldspathic gneisses, with bands of hornblende biotite gneiss, marble, granitoid, and amphibolite. The rocks containing the highest vanadium contents are sillimanite- and graphite-bearing quartzo-feldspathic gneisses with minor phlogopite, graphite, pyrite, muscovite, apatite, titanite, chalcocopyrite, hematite, and calcite. Identified using X-ray diffraction, electron microprobe analysis, and Raman spectroscopy, the vanadium host minerals in the suite are roscelite (up to 8.45% V_2O_5), rutile, schreyerite, oxyvanite, karelianite, an unknown vanadium-titanium bearing oxide,

pyrrhotite, pyrite, goldmanite, dravite, uvite, actinolite, and three unidentified vanadium-bearing sulfides. The vanadium-bearing oxides are discussed in detail in this paper.

ANALYTICAL METHODS

Polished thin sections were made of unweathered Manga drill core M-87 and divided into concentration categories using X-Ray Fluorescence (XRF) data provided by Energizer Resources Inc (2011). Five representative samples of high ($V_2O_5 > 0.5\%$) and medium ($0.2\% \leq V_2O_5 \leq 0.5\%$) concentration materials were analyzed to produce element X-ray maps. A list of these samples and their depths down core are given in Table 1. These maps were produced at the University of Windsor Great Lakes Institute for Environmental Research (GLIER) in Ontario, Canada using a FEI Quanta 200 Field Emission Gun (FEG) Environmental SEM equipped with EDAX Energy Dispersive Spectrometry (EDS). A 20 kV accelerating voltage was used and images were captured at 70× magnification. Maps were made for the elements Al, Ca, Cr, Fe, K, Si, S, Ti, U, V, Mg, Mn, and P. Using the photographic software ENVI, element maps were overlaid to isolate vanadium phases. These phases and surrounding material were examined at the Department of Geological Sciences and Geological Engineering at Queen's University in Ontario, Canada using a JEOL JXA-8230 Electron Probe Microanalyzer (EPMA). Oxides were analyzed with an accelerating potential of 15 kV and a fully focused static beam with a current of 30 nA and a spot size of 1 μm . The standards used were rutile (NMNH 120812, Ti), diopside (Si), synthetic CoNb_2O_6 (Nb), chromite (Al, Cr), synthetic V_2O_5 (V), hematite (Fe), and synthetic hausmannite (Mn). To determine if water was present, Raman spectra were collected using a Horiba Lab-RAM Aramis micro-Raman spectrometer at the Royal Ontario Museum in Toronto, Canada. A 532 nm 50 mW laser, focused to create a 1.3 μm spot, was used at 50% power to prevent damage to the samples. A 100 μm slit and 1200 gr/mm grating were used for data collection and the instrument was calibrated with Si

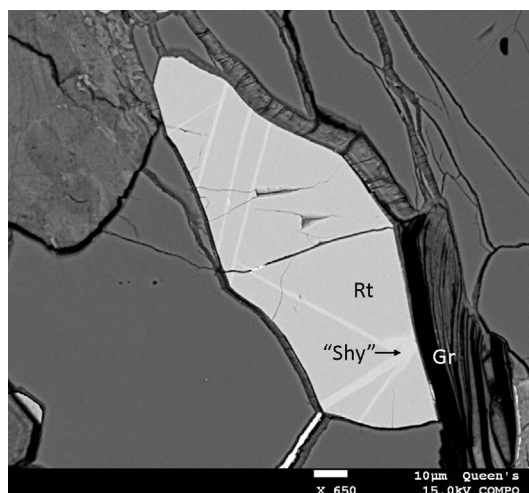


Fig. 3. A backscattered electron image of thin section UT117 showing schreyerite exsolving from vanadium-bearing rutile. Symbols: Rt – V-bearing rutile; “Shy” – schreyerite; Gr – graphite. Scale bar indicates 10 μm .

metal. It should be noted that the use of a 532 nm laser Raman to determine if a mineral is hydrated can sometimes reveal only broad OH stretching bands which may be difficult to resolve or can be below the detection limit of the instrument. Therefore, a negative result does not completely eliminate the possibility of hydration.

To isolate vanadium oxide grains for analysis by powder X-Ray Diffraction (XRD), a heavy mineral concentrate was obtained. Samples were crushed, passed through a 100 μm sieve, and separated using methylene iodide. A Frantz isodynamic magnetic separator, located at the Jack Satterly Geochronology Lab at the University of Toronto, was then used to separate mineral grains based on magnetic susceptibility.

To confirm the presence of vanadium-bearing oxide species, XRD was carried out on the mineral separates. A Bruker D8 Advance Diffractometer system was used, employing a two-circle goniometer setup and Cu radiation source at the Royal Ontario Museum in Toronto, Canada. The system was operated at 40 kV and 40 mA and data were collected using a Göbel mirror, 0.6 mm slit size, low background plate, and a LynxEye detector. Data were analyzed using the program DiffraC.Eva. Miller indices were determined by comparison to known powder diffraction files in the International Centre for Diffraction Data PDF-4+ database.

RESULTS

A list of samples examined, their depths down core, and the vanadium-bearing oxides identified are listed in Table 1. Weight percent oxides are reported here with $\pm 2\sigma$.

Rutile

The most common vanadium-bearing oxide species present is rutile. Eighteen grains of this mineral were examined by EPMA, ranging in size from 240 to 740 μm . The majority of the grains show exsolution of the vanadium-rich phase schreyerite (Fig. 3). On average, the rutile has a VO_2 content of 3.18 ± 1.93 wt.%, with a range of 2.21 to 6.61 wt.%. The calculated mineral formula based on two oxygen atoms is $(\text{Ti}_{0.96}\text{V}_{0.03})\text{O}_2$. The mean results of EPMA of the vanadium-bearing oxides are listed in Table 2.

Schreyerite

Schreyerite is present as intergrowths within rutile (Fig. 3) and in association with Unknown 1 (Fig. 4). Fifteen analyses of this mineral were performed by EPMA of grains ranging in size from 200 to 700 μm . This species has a mean V_2O_3 content of 34.73 ± 2.81 wt.%. It has a mean TiO_2 content of 61.35 ± 1.75 wt.% and contains minor amounts of Cr_2O_3 and Al_2O_3 (Table 2). The formula of schreyerite was calculated on the basis of nine oxygen atoms per formula unit using the average weight percent oxide data from Table 2 and was found to be $(\text{V}^{3+}_{1.88}\text{Cr}_{0.12}\text{Al}_{0.03})_{\Sigma 2.03}\text{Ti}_{3.01}\text{O}_9$, comparable to the ideal formula $\text{V}^{3+}_2\text{Ti}^{4+}_3\text{O}_9$ (Medenbach & Schmetzer 1976). The strongest lines in the X-ray powder diffraction files are (d (Å), I , ($h k l$)): 3.382, 100, (002); 1.698, 51, (422); 1.385, 45, (912); 4.092, 42, (111); 1.639, 34, (114).

Oxyvanite

Oxyvanite grains are located adjacent to pyrrhotite in sample UT159 (Fig. 5). Ten electron microprobe analyses were obtained from six grains ranging in size from 50 to 280 μm . The average V_2O_3 content of this mineral was calculated to be 47.58 ± 1.29 wt.%, and the average VO_2 content 35.10 ± 0.95 wt.%. Substantial chromium is also present, with an average Cr_2O_3 content of 16.02 ± 1.35 wt.%. When calculated on the basis of five oxygen atoms per formula unit, the ideal formula of oxyvanite at Green Giant is $(\text{V}^{3+}_{1.49}\text{Cr}^{3+}_{0.5})_{\Sigma 1.99}\text{V}^{4+}_{1.00}\text{O}_5$. The formula of oxyvanite is defined by Reznitsky *et al.* (2010) as $\text{V}^{3+}_2\text{V}^{4+}\text{O}_5$, and the calculated formula of the type specimen is $(\text{V}^{3+}_{1.70}\text{Cr}^{3+}_{0.30})_{\Sigma 2.00}(\text{V}^{4+}_{0.59}\text{Ti}_{0.41})_{\Sigma 1.00}\text{O}_5$. As discussed by Reznitsky *et al.* (2010), the

TABLE 2. THE MEAN RESULTS OF EMPA OF V-BEARING OXIDES

Mineral	Analyses	Total V expressed as V ₂ O ₃	V ₂ O ₃ *	VO ₂ *	TiO ₂	SiO ₂	Al ₂ O ₃
Rutile	<i>n</i> = 18	2.88 ± 1.75	-	3.18 ± 1.93	96.29 ± 4.36	0.01 ± 0.03	0.01 ± 0.01
Schreyerite	<i>n</i> = 15	34.73 ± 2.81	34.73 ± 2.81	-	61.35 ± 1.75	-	0.48 ± 0.30
Oxyvanite	<i>n</i> = 10	79.30 ± 2.15	47.58 ± 1.29	35.10 ± 0.95	0.12 ± 0.23	0.01 ± 0.02	0.09 ± 0.26
Karelianite	<i>n</i> = 5	91.27 ± 1.69	91.27 ± 1.69	-	0.42 ± 0.44	0.01 ± 0.02	0.27 ± 0.18
Unknown 1	<i>n</i> = 11	59.04 ± 5.70	26.57 ± 2.56	35.94 ± 3.47	32.66 ± 3.06	0.01 ± 0.02	0.70 ± 0.28

All values are reported in weight percent ± 2σ. The mineralogical formula of rutile is calculated on the basis of 2 (O); schreyerite is calculated on the basis of 9 (O); oxyvanite is calculated on the basis of 5 (O); and karelianite is calculated on the basis of 3 (O) per formula unit. * = calculated using the method of Reznitsky *et al.* (2010).

maximum content of Cr₂O₃ in oxyvanite is 20.82 wt.%, and the Green Giant oxyvanites are consistent with this constraint. The strongest lines in the X-ray powder diffraction patterns are (*d* (Å), *I*, (*h k l*)): 1.6308, 100, (131); 1.6315, 91, (314); 1.632, 68, (004); 1.625, 34, (114); 1.564, 34, (423). Differences between Green Giant oxyvanite and other known oxyvanites are discussed below.

Karelianite

Karelianite is located in contact with vanadium-bearing pyrrhotite (up to 2.99 wt.% V₂O₃), as shown in Figure 6. Five analyses of this species were obtained by EPMA of four grains ranging in size from 50 to 250 μm. When expressed as V³⁺ the

average V₂O₃ content was determined to be 91.27 ± 1.69 wt.%. Minor amounts of Cr₂O₃ were also present, averaging 2.15 ± 1.94 wt.%, and TiO₂ content is low at 0.42 ± 0.44 wt.%. When calculated on the basis of three oxygen atoms per formula unit, the average formula of karelianite at Green Giant is (V³⁺_{1.93}Cr³⁺_{0.04}Fe³⁺_{0.01}Al_{0.01})Σ1.99O₃. The calculated formula of the type specimen of karelianite is (V³⁺_{1.82}Fe³⁺_{0.08}Cr³⁺_{0.04}Mn_{0.01})Σ1.99O₃ (Long *et al.* 1963). Low total wt.% in EPMA data (*i.e.*, average of 94.46 ± 1.13 wt.%, *n* = 5) is noted when all vanadium is expressed as V₂O₃. There was no evidence of H₂O or OH in these samples, including broad OH-stretching bands, as determined by Raman spectroscopy. However, these peaks may be below

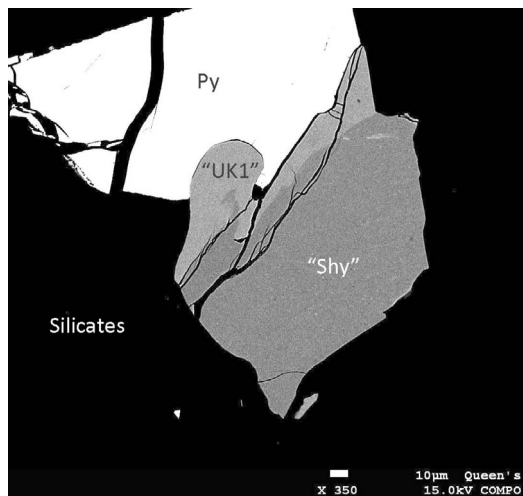


FIG. 4. A backscattered electron image of thin section UT134 where UK1 is shown replacing schreyerite. Symbols: "UK1" – unknown 1; "Shy" – schreyerite; Py – pyrite. Scale bar indicates 10 μm.

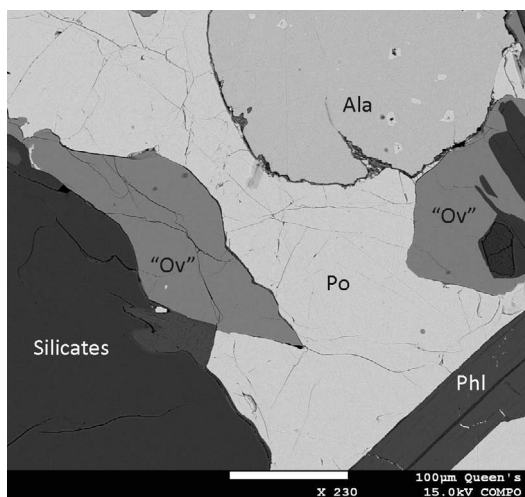


FIG. 5. A backscattered electron image of thin section UT159 where oxyvanite is shown adjacent to pyrrhotite and alabandite. Symbols: "Ov" – oxyvanite; Ala – alabandite; Po – pyrrhotite; Phl – phlogopite. Scale bar indicates 100 μm.

TABLE 2. CONTINUED.

Cr ₂ O ₃	Fe ₂ O ₃	MnO	Total	Calculated Average Mineral Formula
0.07 ± 0.17	0.01 ± 0.03	0.01 ± 0.02	100.27 ± 1.41	(Ti _{0.96} V _{0.03})O ₂
2.26 ± 2.91	0.09 ± 0.07	0.04 ± 0.04	98.97 ± 0.69	(V ³⁺ _{0.91} Cr ³⁺ _{0.06} Al _{0.02}) ₂ Ti _{3.01} O ₉
16.02 ± 1.35	0.24 ± 0.27	0.04 ± 0.02	99.19 ± 0.76	(V ³⁺ _{1.49} Cr ³⁺ _{0.50} Fe ³⁺ _{0.01})V ⁴⁺ _{1.00} O ₅
2.15 ± 1.94	0.35 ± 0.30	0.01 ± 0.01	94.46 ± 1.13	(V ³⁺ _{1.93} Cr ³⁺ _{0.04} Fe ³⁺ _{0.01} Al _{0.01})O ₃
4.12 ± 4.11	0.24 ± 0.27	0.04 ± 0.06	100.28 ± 0.61	(V ³⁺ _{1.67} Cr ³⁺ _{0.26} Al _{0.06})(V ⁴⁺ _{2.05} Ti ⁴⁺ _{1.94})O ₁₁

the detection limit of the instrument. Samples could not be isolated for powder XRD study.

Unknown 1

Unknown 1 (UK1, likely Ti₂V⁴⁺₂V³⁺₂O₁₁) is typically found replacing schreyerite (Fig. 4) and containing rutile (Fig. 6). Eleven analyses of this unknown material were obtained by EPMA of four different thin sections; the grains examined ranged in size from 50 to 300 µm. When expressed entirely as V³⁺ the average V₂O₃ content was determined to be 59.04 ± 5.70 wt.%, and the TiO₂ content to be 32.66 ± 3.06 wt.%. The Cr₂O₃ contents were variable, with mean concentration of 4.19 ± 4.11 wt.%. Ratios of V⁴⁺ and V³⁺ were determined using the method of Reznitsky *et al.* (2010), in which mineral formulae were calculated stoichiometrically using a varying number of oxygen atoms and ratios of V₂O₃ to VO₂ and were used to determine a formula for this species of (V³⁺_{1.67}Cr³⁺_{0.26}Al_{0.06})Σ_{1.99}(V⁴⁺_{2.05}Ti⁴⁺_{1.94})Σ_{3.99}O₁₁. There is no evidence of H₂O or OH in these samples, including broad OH-stretching bands, as determined by Raman spectroscopy. However, a possibility does still exist that OH stretching bands are broad enough to be below the detection limit of the instrument. Therefore, the formula may also be expressed as Ti₂V⁴⁺₂V³⁺₂O₁₀(OH)₂. Calculated formulae do not match that of kyzylkumite, Ti₄V³⁺₂O₁₀(OH)₂ (Reznitsky *et al.* 2012). Samples could not be isolated for powder XRD study. Material with the formula V₂Ti₄O₁₁ has been previously reported as an unnamed Ti-Cr-V oxide from the Lake Baikal region by Koneva (2002). Hence, it is likely that UK1 is related to this mineral or to kyzylkumite.

DISCUSSION

High vanadium contents have been reported for rutile from other localities (Table 3). Medenbach & Schmetzer (1978) list compositions of rutile associated with schreyerite from Voi, Kwale district, Kenya. For these rutiles, the mean composition is 1.79% V₂O₃,

therefore making the rutiles from Green Giant, containing 2.88% V₂O₃, more enriched in comparison. However, Reznitsky *et al.* (2016) list compositions of V-Nb-bearing rutiles from the Sludyanka Complex, Southern Baikal region, Russia, a region which shows many similarities in vanadium-bearing oxide minerals. These rutiles average 5.45% V₂O₃, as well as an average Nb₂O₅ composition of 20.40%. The highest average reported V₂O₃ content in rutile used as a comparison in this study is from Deadhorse Creek, Northwestern Ontario, Canada at 9.46% (Potter & Mitchell 2005). Deadhorse Creek is a volcanoclastic breccia complex in which the vanadium content was enriched by alkaline metasomatic fluids (Potter & Mitchell 2005).

Schreyerite is a rather rare mineral and has been previously identified from six localities (Medenbach & Schmetzer 1976, Zakrzewski *et al.* 1982, Höller & Gandhi 1997, Koneva 2002, Lu & Wang 2005, Spry &

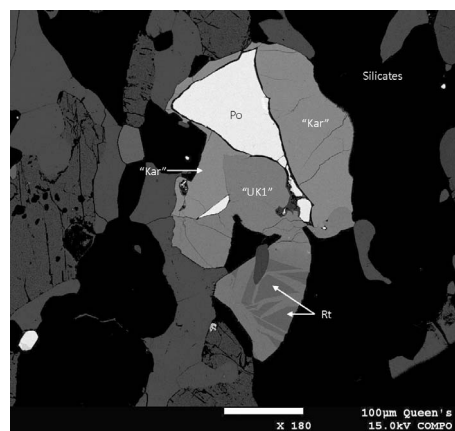


FIG. 6. A backscattered electron image of thin section UT150 with Unknown 2 in close proximity to pyrrhotite (containing 1.66 wt.% V) and Unknown 1 exsolving rutile (with 3.42 wt.% VO₂). Symbols: "UK1" – Unknown 1; "Kar" – karelianite; Rt – rutile; Po – pyrrhotite. Scale bar indicates 100 µm.

TABLE 3. A COMPARISON OF AVERAGE VANADIUM-BEARING RUTILE COMPOSITIONS FROM GREEN GIANT, MADAGASCAR

		TiO ₂	SiO ₂	Nb ₂ O ₅	Al ₂ O ₃	Cr ₂ O ₃	V ₂ O ₃	Fe ₂ O ₃	MnO	CaO
Green Giant, Madagascar	<i>n</i> = 18	96.29	0.01	0.69	0.01	0.07	2.88	0.01	0.01	n.d.
Sludyanka, Russia	<i>n</i> = 20	65.55	0.01	20.4	0.03	7.92	5.45	0.05	0.02	0.01
Voi, Kenya	<i>n</i> = 3	98.03	n.d.	0.06	n.d.	0.08	1.79	n.d.	0.02	n.d.
Namalulu, Tanzania	<i>n</i> = 6	97.28	0	n.d.	0	0.25	1.91	n.d.	n.d.	0.13
David Bell Mine, Canada	<i>n</i> = 12	87.46	0	0	0	0	3.83	0.5	n.d.	n.d.
Deadhorse Creek, Canada	<i>n</i> = 2	59.89	0.81	23.32	0.08	4.75	9.46	0.46	0.1	0.99

Sludyanka Complex, Russia (Reznitsky *et al.* 2016); Kwale District, Kenya (Medenbach & Schmetzer 1978); Namalulu, Tanzania (Feneyrol *et al.* 2012); David Bell Mine, Canada (Urban *et al.* 1992); and Deadhorse Creek, Canada (Potter & Mitchell 2005). n.d. = not detected.

Scherbarth 2006). Prior to this study, three papers had been published describing the chemical composition of schreyerite: Medenbach & Schmetzer (1978) on samples from Voi, Kenya; Zakrzewski *et al.* (1982) on samples from the Sättra (Doverstorp) pyrite deposit, Sweden; and Döbelin *et al.* (2006) on samples from Sludyanka, Lake Baikal, Russia. When compared to the previous studies (see Table 4), the compositions collected from Green Giant are most comparable to the material from the Sättra Mine, Sweden (Zakrzewski *et al.* 1982).

This is the second identified occurrence of oxyvanite. The type locality is in the Sludyanka Complex in the southern Baikal region of Russia (Armbruster *et al.* 2009, Reznitsky *et al.* 2010).

The low amount of TiO₂ in the samples from Green Giant means that the V⁴⁺ site, used to distinguish between oxyvanite and berdesinskiite, is nearly pure, making this endmember oxyvanite in the oxyvanite–berdesinskiite solid solution series (Fig. 7). While the V⁴⁺ site may be pure, the V³⁺ site contains a higher amount of Cr³⁺ than the type locality, approaching 25% occupancy of the V³⁺ site. This indicates that it is on a solid solution between oxyvanite (V³⁺₂V⁴⁺O₅) and the synthetic phase Cr₂³⁺Ti⁴⁺O₅ (Armbruster *et al.* 2009, Kamiya *et al.* 1979).

Comparison of the data from Green Giant and Sludyanka, Lake Baikal, Russia

The Cr-V-enriched rocks of the Sludyanka complex are described as alternating bands of quartz, diopside, and calcite-diopside in the Olkhon series which underwent high-temperature granulite-facies metamorphism and retrograde amphibolite-facies metamorphism, 477.6 ± 2 Ma (Salnikova *et al.* 1998, Reznitsky *et al.* 2010).

There are several similarities between the Green Giant deposit and the high-grade metamorphic rocks of the Sludyanka complex, Lake Baikal area, Russia. Both Green Giant and Sludyanka contain the vanadium-bearing accessory minerals dravite, goldmanite, rutile, schreyerite, oxyvanite, and karelianite (Koneva 2002). In addition, an unnamed V-Ti oxide, V₂Ti₄O₁₁, has been reported from the Sludyanka Complex, and is possibly related to UK1. The rocks of the western Lake Baikal coast are a folded sequence of interlayered metasediments, including quartzites, basic schists, marbles, and gneisses which have been metamorphosed to upper amphibolite and granulite facies (Koneva 2002). The rock types hosting the Green Giant location are similar to those at Lake Baikal, having also undergone upper amphibolite- to granulite-facies metamorphism. The rocks in the Lake Baikal region have high levels of Cr and V, few

TABLE 4. A COMPARISON OF THE AVERAGE COMPOSITIONS, DETERMINED BY EMPA, OF SCHREYERITE FROM GREEN GIANT (THIS STUDY)

Analysis	TiO ₂	SiO ₂	Nb ₂ O ₅	Ta ₂ O ₅	Al ₂ O ₃	Cr ₂ O ₃	V ₂ O ₃	Fe ₂ O ₃	MnO	MgO	Total
Green Giant Average	60.88	-	0.02	-	0.47	3.09	34.42	0.11	0.05	0.02	99.06
Voi, Kwale district, Kenya	61.07	-	-	0.03	0.43	2.23	36.41	0.12	0.02	0.11	100.40
Sludyanka Complex, Lake Baikal, Russia	51.91	0.12	-	-	0.04	3.06	43.26	0.75	0.11	0.04	99.30
Sättra Mine, Sweden	60.98	-	-	-	0.30	2.45	33.8	1.39	0.18	-	99.09

Voi, Kenya (Medenbach & Schmetzer 1978); Sludyanka Complex, Lake Baikal, Russia (Döbelin *et al.* 2006); and the Sättra Mine, Sweden (Zakrzewski *et al.* 1982).

TABLE 3. CONTINUED.

	WO ₃	Sb ₂ O ₃	Ta ₂ O ₅	MgO	ZnO	NiO	F	SrO	Total
Green Giant, Madagascar	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	99.96
Sludyanka, Russia	0.29	n.d.	0.13	0	0.01	0.01	0.12	n.d.	99.99
Voi, Kenya	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	99.98
Namalulu, Tanzania	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	99.57
David Bell Mine, Canada	3.75	3.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	98.56
Deadhorse Creek, Canada	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.21	100.05

modally significant concentrations of Cr-V bearing minerals, and are irregularly distributed in carbonate and quartzitic rocks (Koneva 2002). The distribution of V-bearing minerals at the Green Giant deposit is similar, although high concentrations of Cr have not been documented.

The principal Cr-V-bearing minerals of the Lake Baikal area are silicates (muscovite, diopside, tourmaline, and garnet), spinel, and Cr-V-oxides in graphitic schists (Koneva 2002). Mineral associations are similar between the two localities. Both have Cr-V oxides associated with rutile, as well as V-bearing muscovite, V-bearing tourmaline, V-bearing garnet, graphite, and sillimanite. The Cr-V-oxides at Lake Baikal include schreyerite, karelianite, eskolaite (Cr₂O₃), berdesinskiite, vourelainite (Mn²⁺V³⁺₂O₄), manganochromite (Mn²⁺Cr₂O₄), and olkhonskite (Cr₂Ti₃O₉) (Koneva 2002). The V-Ti-oxides are equivalent to those at Green Giant. However, the other oxides identified at Lake Baikal are more

chromium- and manganese rich than those at Green Giant. Rutiles from the two areas contain between 1.00 and 3.86 wt.% V₂O₃. However, like the other oxides, the Lake Baikal rutiles have higher Cr₂O₃ contents (0.46 to 1.93 wt.%). At Green Giant the average is 0.07 wt.% Cr₂O₃.

The similarities in petrographic description and mineralogy suggest that the mineral identifications made in this study are correct and that similar processes formed the Olkhon series of Lake Baikal and Green Giant. At Lake Baikal, schreyerite was most likely exsolved from V-Cr oversaturated rutile during retrograde metamorphism (Koneva 2002), which, based on similar mineralogy and morphology, is the likely method of formation at Green Giant. In the Olkhon series it was suggested that the Cr and V were preferentially associated with organic matter and clay minerals in precursor sediments (Koneva 2002). During prograde metamorphism these elements have extremely low mobility and original sedimentary

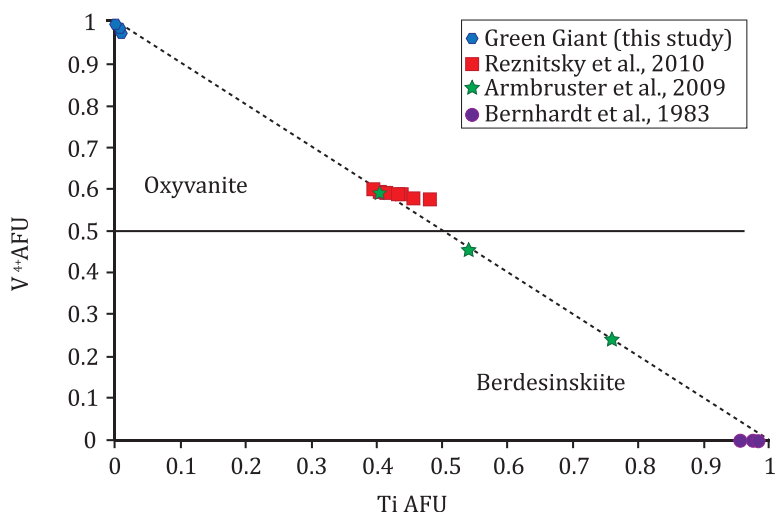


FIG. 7. Variation of molecular proportions of Ti vs. V⁴⁺ in the oxyvanite–berdesinskiite series. Data are included from Green Giant, the South Baikal region (Armbruster *et al.* 2009, Reznitsky *et al.* 2010), and Kenya (Bernhardt *et al.* 1983). The tie line between oxyvanite and berdesinskiite is 0.5 V⁴⁺:0.5 Ti (Reznitsky *et al.* 2010).

variations resulted in large variations in phase chemistry (Koneva 2002). This is likely also the cause of vanadium enrichment and the formation of V-Ti oxides at the Green Giant property.

CONCLUSIONS

As has been determined through SEM-EDS, XRD, and EPMA, the vanadium-bearing oxide phases in the Green Giant property are rutile, schreyerite, oxyvanite, karelianite, and the as yet unidentified oxide, UK1, likely $V_2(Ti,V)_4O_{11}$. The petrology and minerals identified at this locality are similar to those described by Koneva (2002) from the Sludyanka area in the Lake Baikal region, Russia. This is the second occurrence worldwide of oxyvanite, and it is near the endmember composition on the oxyvanite–berdesinskiite solid solution series.

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