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## Evaluation of rammelsbergite (NiAs<sub>2</sub>) as a novel mineral for <sup>187</sup>Re-<sup>187</sup>Os dating and implications for unconformity-related U deposits

Stepan Chernonozhkin, Julien Mercadier, Laurie Reisberg, Béatrice Luais, Catherine Zimmermann, Christophe Morlot, Lise Salsi, Andreï Lecomte, Olivier Rouer, Marc Brouand, et al.

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1 **Evaluation of rammelsbergite (NiAs<sub>2</sub>) as a novel mineral for <sup>187</sup>Re - <sup>187</sup>Os dating and implications**  
2 **for unconformity-related U deposits**

3

4 Stepan M. Chernonozhkin<sup>1,2</sup>, Julien Mercadier<sup>1\*</sup>, Laurie Reisberg<sup>2</sup>, Béatrice Luais<sup>2</sup>, Catherine  
5 Zimmermann<sup>2</sup>, Christophe Morlot<sup>1</sup>, Lise Salsi<sup>1</sup>, Andreï Lecomte<sup>1</sup>, Olivier Rouer<sup>1</sup>, Marc Brouand<sup>3</sup>, Amber  
6 Doney<sup>4</sup>, Patrick Ledru<sup>4</sup>

7

8 <sup>1</sup> Université de Lorraine, CNRS, CREGU, GeoRessources Lab, Campus Aiguillettes, Faculté des  
9 Sciences et Technologies, rue Jacques Callot, Vandoeuvre-lès-Nancy, F-54506, France

10 <sup>2</sup> Centre de Recherches Pétrographiques et Géochimiques (CRPG), CNRS, Université de Lorraine,  
11 UMR 7358, 15 rue Notre Dame des Pauvres, Vandoeuvre lès Nancy, F-54501, France

12 <sup>3</sup> Orano Mining, 1 place Jean Millier, 92400 Courbevoie, France

13 <sup>4</sup> Orano Canada Inc. 817 45th Street West, S7K 3X5 Saskatoon, Canada

14

15 \* Corresponding author: julien.mercadier@univ-lorraine.fr

16 Stepan M. Chernonozhkin ORCID ID: 0000-0003-4521-0805;

17

18 **Abstract**

19 Rammelsbergite (NiAs<sub>2</sub>) is often present in ore deposits worldwide in association with other arsenides, sulphides  
20 and sulfarsenides. This work demonstrates the value of the application of the Re-Os isotopic system to the dating  
21 of rammelsbergite. Using the example of the Cigar Lake uranium deposit (Athabasca Basin, Saskatchewan,  
22 Canada), our results show that rammelsbergite concentrates significant and variable amounts of Re when  
23 crystallizing, up to 1.6 µg g<sup>-1</sup>, while incorporating minimal common Os. Such characteristics make this mineral  
24 an ideal target for Re-Os isotopic dating, by both isochron and model age methods. Remarkable agreement of the  
25 Re-Os age of the rammelsbergite with the U-Pb age of the uranium oxide grains found inside one of the massive  
26 rammelsbergite veins confirms the applicability of the method. The selected rammelsbergite samples from the  
27 Cigar Lake uranium deposit yield a <sup>187</sup>Re-<sup>187</sup>Os isochron age of 1239 +33/-20 Ma. These results challenge a long-  
28 standing petrogenetic model which postulates contemporaneous U oxide and Ni-Co-arsenide deposition in  
29 unconformity-related uranium deposits. The new Re-Os age of rammelsbergite veins indicates that arsenide

30 crystallization postdated the deposition of the primary uranium oxides at 1461-1341 Ma, implying that uranium  
31 oxides and nickel arsenides, as well as other sulphides and sulfarsenides, were not precipitated contemporaneously  
32 during a single hydrothermal event as previously proposed. The  $^{187}\text{Re}$ - $^{187}\text{Os}$  data suggest that crystallization of  
33 rammelsbergite and co-genetic sulphides, arsenides and sulfarsenides was linked to the ca. 1270 Ma Mackenzie  
34 magmatic event, marked by the emplacement of mafic dikes throughout the Canadian Shield, including in the area  
35 of the Athabasca Basin. This study therefore suggests a new hypothesis for the origin of nickel, cobalt, sulfur and  
36 arsenic in unconformity-related U deposits of the Athabasca Basin. More broadly, the successful application of  
37 the  $^{187}\text{Re}$ - $^{187}\text{Os}$  rammelsbergite chronometer in this geological context suggests that its application in other ore  
38 deposit environments worldwide is likely to provide similar insights. In this respect, the  $^{187}\text{Re}$ - $^{187}\text{Os}$  chronometer  
39 applied to rammelsbergite, and potentially to other arsenides and sulfarsenides, represents a valuable complement  
40 to molybdenite dating because it can be used in systems that lack molybdenite.

41 Keywords:  $^{187}\text{Re}$ - $^{187}\text{Os}$ , rammelsbergite, arsenide, unconformity-related, uranium deposit, Cigar Lake,  
42 Mackenzie magmatic event

## 43 1. Introduction

44 The dating of mineral phases, including those of economic interest, is a key step for constraining their formation  
45 mechanisms and how these may have changed as the Earth evolved. Major progress has been made in the direct  
46 dating of metal-bearing phases (such as wolframite, cassiterite, columbite-tantalite or sulfides, notably  
47 molybdenite) in recent years, through both conventional and in-situ methods (Deng et al., 2019; Harlaux et al.,  
48 2018; Legros et al., 2019; Saintilan et al., 2017; Stein et al., 2001). Parallel to this improvement of dating ore-  
49 bearing minerals, there is growing interest in the so-called “critical metals”, because of their importance in  
50 communication technologies, and in the energy and transport transitions which will drive the 21<sup>st</sup> century. Nickel  
51 is one of these highly coveted metals so any new method allowing to temporally constrain Ni mineralization is a  
52 sought-after tool. Nickel sulfides and/or arsenides are particularly useful forms of economically exploitable Ni.  
53 Among these phases, rammelsbergite ( $\text{NiAs}_2$ , containing 28 % nickel and 72 % arsenic) is an uncommon mineral  
54 at a global scale, but is nevertheless formed in a wide range of geological settings (magmatic, metamorphic or  
55 hydrothermal) and is commonly found as disseminated grains or in the form of bulk veins in over 200 mining  
56 locations worldwide, including some world class districts. Rammelsbergite occurs as a minor component of  
57 nickeline–chromite ores in metaperidotite, *i.e.* Ni-Cr ores hosted in ultramafic rocks of the Beni Bousera massif  
58 of Morocco, or in the La Gallega and Los Jarales mines in Malaga province in Spain (Oen, 1973). Magmatic  
59 rammelsbergite is also described in nepheline-sodalite syenite plutonic rocks (naujaite) in the Ilimaussaq alkaline  
60 massif, South Greenland (Oen et al., 1977). Rammelsbergite, along with other arsenides and sulfarsenides, is a  
61 common mineral in metamorphosed Ni–Cu-PGE sulfide ores, such as the metamorphic-hydrothermal  
62 assemblages of disseminated Co-Ni-Cu ores of the Duluth Complex, Minnesota, USA (Raič et al., 2015), and  
63 Norilsk ore field (Gritsenko and Spiridonov, 2008). In this type of deposit, rammelsbergite and other arsenides  
64 co-crystallize from hydrothermal fluids that have reworked primary sulfides. Rammelsbergite is also a ubiquitous  
65 phase in several Ag-Bi-Ni-Co ore deposits of hydrothermal origin, in which it is found in association with other  
66 arsenides and sulfarsenides and with native silver and bismuth within carbonate veins. Typical examples of such  
67 associations include the Cobalt-Gowganda silver mining areas (Ontario, Canada) (Petruk, 1971), the five-element  
68 deposits of the Variscan belt (*e.g.* Jáchymov ore district, Czech Republic), deposits of the Odenwald and  
69 Niederschlema–Alberoda, Germany (Ondrus et al., 2003; Forster et al., 2004; Burisch et al., 2017), the Khovu-  
70 Aksy Co–Ni arsenide ores in Tuva, Russia (Bortnikova et al., 2012), and deposits of the Great Bear Lake region,  
71 Northwest Territories, Canada (Changkakoti and Morton, 1986). Rammelsbergite is also described in  
72 hydrothermal vein type Cu-Ni-Co-U deposits of the Anarak mining area in Central Iran (Bagheri, 2015). Finally,

73 rammelsbergite is often found in association with uranium in the world class unconformity-related U deposits of  
74 the Athabasca Basin (Saskatchewan, Canada; Jefferson et al., 2007; Kyser and Cuney, 2015), for example, at the  
75 Key Lake (Carl et al., 1992), Moore Lake (Annesley et al., 2000), Cigar Lake and Midwest deposits (Reyx and  
76 Rulhmann, 1993). For these deposits and for numerous other U occurrences throughout the Athabasca Basin,  
77 rammelsbergite is found in association with different arsenides and sulfarsenides within or in close vicinity to the  
78 uranium mineralization (Reyx and Rulhmann, 1993). Based on petrographic observations, rammelsbergite is  
79 suggested to be one of the primary arsenide minerals in a sequence of multiple arsenides and sulfarsenides, while  
80 nickeline, gesrdorfitte and cobaltite are considered to crystallize later but during the same global fluid event (Reyx  
81 and Rulhmann, 1993).

82 The widespread presence of rammelsbergite in many types of ore deposits makes this mineral an attractive target  
83 for Re-Os dating, compared to other arsenide minerals previously evaluated (Arne et al., 2001; Morelli et al.,  
84 2005; Morelli et al., 2007; Saintilan et al., 2017). Considering the example of unconformity-related Athabaskan  
85 U deposits, the conditions of crystallization of the uranium mineralization are currently not entirely known,  
86 leading to loosely constrained genetic models for this major ore province. Several dating approaches, based on  
87 different target minerals (uranium oxides and clays), have been attempted to determine the timing and duration of  
88 fluid circulation episodes within the last 1.6 Ga and their role in controlling the current shape of the uranium  
89 deposits. But the post-crystallization preservation of these phases and therefore of the isotopic systems used for  
90 dating is a recurrent problem leading to questionable results (Fryer and Taylor, 1984; Philippe et al., 1993; Fayek  
91 et al., 2002a; Martz et al., 2019b). In consequence, the links between tectono-thermal event(s), successive fluid  
92 circulations and potential episode(s) of metal deposition in the Athabasca Basin (Jefferson et al., 2007; Kyser and  
93 Cuney, 2015) are not fully established for this province, as for many other metalliferous provinces worldwide. In  
94 this study we evaluate the applicability of the  $^{187}\text{Re}$ - $^{187}\text{Os}$  rammelsbergite chronometer, using the example of the  
95 Cigar Lake U deposit, the archetype of unconformity-related U deposits. The new key temporal constraints  
96 provided by rammelsbergite dating for the formation and evolution of this deposit are used to demonstrate the  
97 potential utility of the rammelsbergite chronometer in the wide range of depositional environments in which this  
98 phase is found.

## 99 **2. Regional geology and geochronology of the Cigar Lake uranium deposit**

100 Detailed description of the geology at the regional, local and deposit scales and of the current metallogenic models  
101 for unconformity-related U deposits are provided in numerous publications, such as Reyx and Rulhmann (1993),  
102 Bruneton (1993), Pacquet and Weber (1993), Kotzer and Kyser (1995), Annesley et al. (2005), Jefferson et al.

103 (2007), Kyser and Cuney (2015), and Martz et al. (2017, 2019). Only a short summary is presented here and for  
104 more details the reader is referred to the papers above.

105 The Cigar Lake deposit is a world-class uranium deposit located close to the eastern edge of the Athabasca Basin,  
106 in northern Saskatchewan, Canada. The deposit is lens-shaped and elongated in the E-W direction over 1.9 km,  
107 and is 15 to 100 m wide and 10-20 m high. With 613,400 t of uranium reserves at an average grade of 16.2%  $U_3O_8$   
108 (Cameco, 2016), the Cigar Lake deposit is the world's second largest high-grade uranium deposit after McArthur  
109 River, also located in the Athabasca Basin 45 km to the south-west. The Cigar Lake deposit is classified as  
110 unconformity-related because the mineralization is located 410 to 450 m below the surface at the unconformity  
111 between an Archean to Paleoproterozoic basement and the unmetamorphosed Paleo- to Mesoproterozoic  
112 sedimentary basin (the Athabasca Basin). The deposit is almost entirely basin-hosted, and the basin in this area is  
113 composed of red-bed sandstones and conglomerates. The basin has been greatly eroded since the formation of the  
114 deposit, with a possible thickness of up to 5 km at the time of deposit formation (Pagel, 1975). The Cigar Lake  
115 deposit sits directly above a major E-W-oriented basement-hosted graphitic-rich structure called the "Cigar Main  
116 conductor", which is considered to be a key structure for the formation of the deposit (Bruneton, 1993; Martz et  
117 al., 2017). The deposition of uranium is associated with massive hydrothermal alteration in both basin and  
118 basement, dominated by the development of an illite-chlorite clay zone and major desilicification (Bruneton,  
119 1993). Large-scale circulations of NaCl- and  $CaCl_2$ -rich basinal brines at the basin-basement interface favoured  
120 massive fluid-rock interactions leading to the formation of the hydrothermal alteration and U mineralization  
121 (Derome et al., 2005; Mercadier et al., 2010; Richard et al., 2016; Martz et al., 2019a). The Cigar Lake uranium  
122 deposit is also marked by the presence in the U ore of arsenide and sulpharsenide minerals of potential economic  
123 importance as by-products: rammelsbergite ( $NiAs_2$ ), nickeline ( $NiAs$ ), maucherite ( $Ni_{11}As_8$ ), löllingite ( $FeAs_2$ ),  
124 skutterudite ( $NiAs_3$ ), gersdorffite ( $NiAsS$ ) and cobaltite ( $CoAsS$ ) (Reyx and Rulhmann, 1993; Kaczowka; 2017).  
125 The overall tonnage is estimated at 11 000 t for As, 7200 t for Ni and 1360 t for Co (Cameco, 2016). Although  
126 petrographic observations suggest that Ni-Co-Fe arsenides and sulfarsenides were emplaced into the Cigar Lake  
127 deposit after fracturing and brecciation of the primary uraninite (Kaczowka, 2017), neither the age of the Ni-Co-  
128 As-S episode nor the origin and type of the mineralizing fluids are known, and the exact conditions and mechanism  
129 of emplacement of Ni, Co, As and S remain unconstrained.

130 The Cigar Lake U deposit, like all the unconformity-related U deposits of the Athabasca Basin, is marked by a  
131 major post-crystallization alteration of the uranium oxides and associated minerals (clays), leading to  
132 remobilization of U and formation of secondary disseminated U ore-bodies (Alexandre and Kyser, 2005; Martz

133 et al., 2019b). Such alteration/remobilization resulted in resetting of the apparent isotopic ages, complicating  
134 accurate and precise U-Pb dating on uranium oxides, but also K-Ar or  $^{40}\text{Ar}/^{39}\text{Ar}$  dating on clays. Multiple  
135 approaches to dating the primary uranium mineralization event in the Cigar Lake deposit have been taken, and  
136 the resulting ages lie between  $1341 \pm 17$  (U-Pb TIMS analysis of uranium oxide mineral separates, Philippe et  
137 al., 1993) and  $1461 \pm 47$  Ma ( $\pm 1\sigma$ , in-situ SIMS U-Pb measurements of pure primary uraninite grains, Fayek et  
138 al., 2002). Subsequent fluid alteration episodes recrystallized younger generations of U minerals. Fayek et al.  
139 (2002) reported stage 2 ( $1176 \pm 9$ ) and stage 3 ( $876 \pm 14$  Ma) generations of U oxides, and Kaczowka (2017)  
140 resolved 3 generations of secondary U oxides at  $1270 \pm 10$  Ma,  $1163 \pm 25$  Ma and  $947 \pm 57$  Ma using U-Pb dating  
141 by LA-ICP-MS. The Rb-Sr isochron method provides an age of  $1477 \pm 57$  Ma for crystalline illites (Kotzer and  
142 Kyser, 1995). Philippe et al. (1993) reported K-Ar ages of  $1385 \pm 30$  and  $1390 \pm 33$  Ma for the  $< 2 \mu\text{m}$  fraction  
143 of clays from the alteration area of the deposit. An event of U remobilization with crystallization of new U oxides  
144 is reported at 320 Ma (Philippe et al., 1993).

### 145 **3. Materials and methods**

146 3.1 Sample selection and characterization. The rammelsbergite samples were taken from two exploration  
147 drillholes executed by Areva Resources Canada (currently Orano Canada). Most samples were taken from  
148 drillhole WC287 ( $58.07175^\circ$  N  $104.51813^\circ$  W) on the Cigar East mineralized extension of the main body while a  
149 single sample was taken from the Cigar North mineralized corridor (WC530; 457.2 m;  $58.04123^\circ$  N  $104.33593^\circ$   
150 W). The WC287 drillhole first crosscuts fine to medium grained fresh sandstone with rare medium grained grit  
151 layers and isolated clay clasts (down to 199.5 m), followed by fine to medium grained unaltered sandstone with  
152 regular pebbly/gritty intervals before reaching the unconformity with the basement at 424.5 m, underlain by  
153 chloritized and argillized graphitic gneiss/pegmatite basement lithologies. The 6.5 m immediately above the  
154 unconformity (418 to 424.5 m) are characterised by the presence of high-grade U mineralization and abundant  
155 nickel arsenides. Figure 1 A illustrates massive U oxide vein at 419.1 – 419.3 m depth. Massive veins of  
156 rammelsbergite are observed between 420.0 and 420.7 m of the drillhole. The association of massive U oxides  
157 and rammelsbergite veins at 419.9-420.1 m is shown in Figure 1 B. Three different samples from these massive  
158 veins of rammelsbergite were taken at the levels of 420.0, 420.1 and 420.7 meters, as shown in Figure 1 A,B,C.  
159 No disseminated arsenides were examined in this study. The sample from WC530 was taken from a 2.5 m  
160 chloritized and argillized zone (456.2-458.7) above the unconformity (458.7 m), characterized by medium  
161 uranium grade and abundant nickel arsenides. This zone is underlain by chloritized and argillized graphitic  
162 gneiss/pegmatite basement lithologies. The petrography of these rammelsbergite veins is identical to that

163 described earlier by Reyx and Rulhmann (1993) for the historical drillholes of Cigar Lake U deposits, as well as  
164 by Kaczowka (2017) in a recent study of this deposit.

165 The drillcores were specifically chosen because they present the most massive and freshest intercepts of  
166 rammelsbergite drilled during the last exploration campaigns. Due to its massive character, the rammelsbergite in  
167 these veins is easily separable from the uranium oxides and is identical to the rammelsbergite described in the  
168 main U mineralization by previous authors for the Cigar Lake U deposit (Reyx and Rulhmann, 1993; Kaczowka,  
169 2017), as well as for other U deposits of the Athabasca Basin (Carl et al., 1992; Annesley et al., 2000; Jefferson  
170 et al., 2007; Kyser and Cuney, 2015).

171 Thick sections were prepared from the samples and were first observed by optical and scanning electron  
172 microscopy. The samples are mainly (> 90%) composed of pure rammelsbergite, a few centimetres thick,  
173 contained in a matrix of Mg-Al clays, siderite, uranium oxide and/or calcite (Figure 2A). Small areas of  
174 gersdorffite (NiAsS) are occasionally observed at the borders between massive rammelsbergite and the  
175 clay/uranium oxide/carbonate matrix. The matrix of the three samples from WC287 also contains disseminated  
176 grains of gersdorffite, pyrite (often intergrown with gersdorffite) and chalcopyrite. Massive rammelsbergite from  
177 WC530 contains a zone with several 10-100  $\mu\text{m}$  euhedral uranium oxide grains in association with gersdorffite  
178 (Figure 3), co-genetic with or closely post-dating the rammelsbergite crystallization. Traces of sparse nickeline  
179 (NiAs) are sometimes observed at the edges of the rammelsbergite crystals (Figure 3).

180 Major and minor element contents of nickel arsenides and sulfarsenides (rammelsbergite and gersdorffite) were  
181 measured with a CAMECA SX100 electron microprobe (EMPA) at the Service Commun de Microscopies  
182 Electroniques et de Microanalyses of the GeoRessources laboratory (Vandoeuvre-lès-Nancy, France). A set of  
183 Co, Ni, Bi, Cu metal, and pyrite ( $\text{FeS}_2$ ), molybdenite ( $\text{MoS}_2$ ), clausthalite ( $\text{PbSe}$ ), stibnite ( $\text{Sb}_2\text{S}_3$ ) and gallium  
184 arsenide (GaAs) mineral standards was used, together with measurement parameters of 20 nA beam current and  
185 20 kV accelerating voltage with a beam diameter of 1  $\mu\text{m}$ . In spot analysis mode, the intensities of 10 elements  
186 were acquired at  $K_\alpha$  lines of S, Fe, Co, Ni, and Cu,  $L_\alpha$  lines of As, Se, Sb and Mo, and  $M_\beta$  line of Bi, with a 10 s  
187 on-peak acquisition time. An on-peak acquisition time of 200 ms and spacing of 2 – 8  $\mu\text{m}$  (depending on total  
188 mapped area, to limit the total mapping time) was used in mapping mode for Ni, As, Co, S and Se. BSE images  
189 in high-contrast mode were taken using the CAMECA SX100 electron microprobe during the same analytical  
190 session. Two-dimensional element distribution maps of the entire thick sections of the samples from 420.1 and  
191 420.7 m depth levels (drillhole WC287) were acquired using a Bruker M4 Tornado XRF instrument at the



192 GeoRessources laboratory (Figure 2A), equipped with a 30W Rh- anode X-ray source (50 kV operating voltage,  
193 150  $\mu$ A operating current) and a Be side-window. In this instrument, the X-rays are focused to a 25  $\mu$ m spot  
194 (measured for Mo  $K_{\alpha}$ ) using a polycapillary lens. The instrument is equipped with two silicon drift detector  
195 spectrometers (30  $\text{mm}^2$ , 145 eV energy resolution for Mn  $K_{\alpha}$ ), placed symmetrically relative to the sample.  
196 Measurements were performed under a vacuum of 20 mbar.

197 Rammelsbergite chips of 100-250 mg for Re-Os analysis were cut using a diamond wire saw from the massive  
198 vein samples of the WC530 core at 457.2 m and of the WC287 cores at 420.0 m, 420.1 m and 420.7 m and are  
199 referred to respectively as WC530 and WC287 (420.0), each composed of a single 200 mg sub-sample; WC287  
200 (420.1) A-F (six sub-samples); and WC287 (420.7) A-E (five sub-samples). Prior to acid digestion, the purity of  
201 representative rammelsbergite samples and the absence of any potential inclusions of other minerals (silicate,  
202 sulfides, *etc.*) and/or alteration phases were verified by observing their virtual 3D models (Fig. 2B) obtained by X-  
203 ray microtomography using the CT-Scan Nanotom S Phoenix (GE) equipment of the X-ray tomography platform,  
204 UMR 7359 GeoRessources Laboratory (Vandoeuvre-lès-Nancy, France). This instrument is equipped with a 180  
205 kV micro-focus X-ray tube/generator and Flat CMOS 5 Mpx system which enables high-definition X-ray  
206 projections. About 1500 projections of rammelsbergite samples were made, using parameters of 98 kV tension,  
207 98  $\mu$ A current, time exposure of 1000 ms, and about 200 mm distance to the X-ray source detector, with the latter  
208 parameter adjusted to obtain the best resolution to size ratio. The spatial resolution varies according to the sample  
209 size.

210 3.2 U-Pb SIMS analysis. The U/Pb and Pb/Pb isotopic compositions of the uranium oxide grains in the WC530  
211 sample were measured with a CAMECA IMS 1280 HR2 ion microprobe at the Centre de Recherches  
212 Pétrographiques et Géochimiques (CRPG-Nancy, France). The conditions for data acquisition and the isotope  
213 data processing protocols are identical to those described in Martz et al. (2019b) and references therein.

214 3.3 Re-Os reference materials and spikes. National Institute of Standards and Technology (NIST, USA) reference  
215 material 8599 Henderson molybdenite was used for quality control of Re and Os analysis and the model age  
216 measured (Markey et al., 2007). Isotope spikes of  $^{185}\text{Re}$  ( $\omega = 96.73\%$ ) and  $^{190}\text{Os}$  ( $\omega = 96.99\%$ ) were obtained  
217 from Oak Ridge National Laboratory (Tennessee, USA) and mixed at concentrations of  $4.72 \cdot 10^{-2} \text{ nmol g}^{-1} \text{ }^{190}\text{Os}$   
218 and  $1.72 \text{ nmol g}^{-1} \text{ }^{185}\text{Re}$  in high-purity 6 N HCl (Le Mignot et al., 2017).

219 3.4 Sample preparation and digestion protocols for Re-Os dating. All Re-Os isolation and measurements were  
220 carried out at the Centre de Recherches Pétrographiques et Géochimiques (CRPG) Nancy, France, under clean

221 laboratory conditions using high purity reagents and ultrapure water. Rammelsbergite is a metallic mineral, and  
222 bulk vein material cannot be crushed or powdered to a mesh size needed for homogenization using traditional  
223 approaches. The samples were thus digested in the form of 50-250  $\mu\text{g}$  fragments of pure rammelsbergite, after  
224 addition of weighed amounts of  $^{185}\text{Re}$ - $^{190}\text{Os}$  mixed isotope tracer (spike). Rammelsbergite appears to passivate in  
225 concentrated HCl, but dissolves in HCl –  $\text{HNO}_3$  mixtures. Thus to dissolve the rammelsbergite, 8 ml reversed  
226 *aqua regia* (6 ml 14 M  $\text{HNO}_3$  and 2 ml 12 M HCl) were added to the spiked rammelsbergite in 60 ml pre-cleaned  
227 quartz digestion vials. Several minutes were allowed before sealing the quartz vials as a precaution against  
228 potential vigorous dissolution. Although neither an instant effervescent reaction nor heating in the reversed *aqua*  
229 *regia* was observed, minor loss of Os as  $\text{OsO}_4$  at this stage cannot be fully excluded, potentially leading to scatter  
230 of the  $^{187}\text{Os}$  concentrations measured if this occurs prior to spike-sample equilibration. Though the absence of  
231 heating (and the consistency of the results, see below) suggests that this effect was minor to negligible, cooling  
232 the digestion vials during the process of adding the acid to the sample-spike mixtures might be a potential  
233 improvement of the analytical procedure to minimize any potential loss of Os. Just before sealing the vials 0.1 ml  
234 of  $\text{H}_2\text{O}_2$  were added to assure full oxidation. The sealed vials were then placed in a High-Pressure Asher HPA-S  
235 (Anton Paar, Austria) and heated at 280  $^\circ\text{C}$  and a pressure of 100 bars for 6 hours. This procedure not only  
236 permitted digestion of the samples, but also brought all of the Os to its highest oxidation state, essential to assure  
237 spike-sample equilibration.

238 3.5 Re-Os chemical separation procedure, isotope ratio measurements and data reduction protocols. Os extraction  
239 protocols were modified from Birck et al. (1997). After acid digestion, Os was selectively separated from the  
240 sample solution using solvent extraction into liquid bromine, while Re remained in the reversed *aqua regia*. After  
241 addition of HBr to promote Os reduction, the  $\text{Br}_2$  fraction was evaporated, and the Os was further purified by  
242 micro-distillation. Os isotopic compositions of the rammelsbergite samples, molybdenite standards and blanks  
243 were measured by negative thermal ionization mass spectrometry (N-TIMS; Creaser et al., 1991; Völkening et  
244 al., 1991). For this the purified Os concentrated in 1-2  $\mu\text{l}$  of HBr was loaded onto Re-free Pt filaments with  
245  $\text{Ba}(\text{OH})_2$  - NaOH as an emission activator. Isotope ratios of Os were measured as  $\text{OsO}_3^-$  ions in CRPG Nancy  
246 using a FinniganMAT 262 mass spectrometer operated in single-collection peak jumping mode using an ETP  
247 electron multiplier. An oxygen leak valve was used to maintain a source pressure of  $3\text{-}5 \cdot 10^{-7}$  mbar. The isotope  
248 ratios of Os are corrected off-line for heavy oxide, mass fractionation, common Os, and blank contributions,  
249 allowing calculation of  $^{187}\text{Os}$  concentrations by isotope dilution. Instrumental mass fractionation was corrected  
250 iteratively simultaneously with the oxide contribution, assuming that the true  $^{192}\text{Os}/^{188}\text{Os}$  ratio of the spiked sample

251 lies on a mixing line between the natural ( $^{192}\text{Os}/^{188}\text{Os} = 3.08271$ ) and the spike ( $^{192}\text{Os}/^{188}\text{Os} = 5.00736$ )  
252 composition. Radiogenic Os ( $^{187}\text{Os}^*$ ) was corrected for a contribution of common Os, assuming a  $^{187}\text{Os}/^{188}\text{Os}$  ratio  
253 of  $0.5 \pm 0.4$ , and the uncertainty on this ratio is included in the combined uncertainty on  $^{187}\text{Os}^*$ . The  $^{187}\text{Re}$  decay  
254 constant ( $\lambda^{187}\text{Re}$ ) used for the age calculation is  $1.666 \cdot 10^{-11} \text{ a}^{-1}$  (Smoliar et al., 1996).

255 Re was separated from the residual acidic solution remaining after Os extraction into liquid bromine. This solution  
256 was evaporated to dryness and re-dissolved in 0.4 M  $\text{HNO}_3$ . Re was extracted from the sample matrix by a simple  
257 anion exchange technique using 200-400 mesh AG1X8 resin (BioRad, USA). Re was adsorbed onto 0.6 ml resin  
258 in the 0.4 M  $\text{HNO}_3$  media, the matrix was eluted using 0.8 M  $\text{HNO}_3$ , and after that Re was collected with 8 M  
259  $\text{HNO}_3$ . Measurements of  $^{187}\text{Re}/^{185}\text{Re}$  ratios for isotope dilution calculations in rammelsbergite, the Henderson  
260 molybdenite reference material and blanks were carried out using an XSeriesII (Thermo Scientific, USA)  
261 quadrupole-based ICP-MS unit. Instrumental mass fractionation was corrected for with a sample-standard  
262 bracketing approach using a Re standard solution of natural isotopic composition (taken as  $^{187}\text{Re}/^{185}\text{Re} = 1.6738$ ).

263 Total procedural blanks were 0.08 - 3 pg for radiogenic  $^{187}\text{Os}^*$  and 0.01 - 0.5 ng for Re, representing less than 1%  
264 compared with the quantities of  $^{187}\text{Os}$  (0.47 – 5.6 ng) and Re (35 - 430 ng) analysed in the rammelsbergite samples  
265 (Table 2). The isotope data are corrected for the blank contribution, and the uncertainty on the blank contribution  
266 is included in the total combined uncertainty. These blank values are considerably higher than those typically  
267 encountered for non-radiogenic samples in the CRPG laboratory, arguing for some limited cross-contamination  
268 between these highly radiogenic, Re-rich samples. Based on repeated measurements of the instrumental blanks  
269 before and after every analytical session, it can be concluded that the major part of the Os blank is a result of  
270 memory effects within the source of the TIMS instrument, a consequence of high amounts of radiogenic Os found  
271 in the samples. Two analyses of the Henderson molybdenite reference material (NIST 8599) were performed,  
272 yielding ages of  $28.21 \pm 0.34 \text{ Ma}$  and  $27.98 \pm 0.31 \text{ Ma}$ , which are 0.5 - 0.8 % higher than that given in the detailed  
273 characterization of the Henderson reference material by Markey et al. (2007) ( $27.656 \pm 0.022 \text{ Ma}$ , 95% confidence  
274 interval). This could mean that the ages of the rammelsbergite obtained in our study are about 0.5 - 0.8 % (i.e., ~  
275 10 My) too high, but this will not change the relative ages of the various sample aliquots.

## 276 4. Results

277 4.1.  $\mu\text{XRF}$ ,  $\mu\text{-tomography}$  and EMPA results. Micro XRF 2D mapping of the entire 2.5 cm epoxy mounts with  
278 the embedded WC287 samples from the 420.1 and 420.7 m depth levels (Figure 2A) reveals inhomogeneous  
279 chemical areas within the rammelsbergite veins. These elemental variations are related to changes in the Co/Ni

280 ratio within the rammelsbergite, as also observed using BSE and element mapping modes of EMPA (Figure 4).  
281 The cobalt content varies mostly between 0.88 and 1.72 wt.% Co, with one exceptional analysis at 4.85 wt.% Co  
282 for WC287 420.1 and between 0.26 and 1.02 wt.% for WC287 420.7 (Table 1). The studied arsenides have low  
283 average Co ( $1.53 \pm 1.2$  wt% for WC287 420.1 and  $0.64 \pm 0.27$  wt% for WC287 420.7) and Fe ( $< 0.08$  wt%)  
284 contents, classifying them as rammelsbergite (see Table 1). Different fragments prepared for Re-Os analysis of  
285 rammelsbergite veins from the WC287 drill hole were separately analysed by micro X-ray tomography to  
286 characterize their homogeneity in 3D (Fig. 2B and the electronic supplementary materials). These fragments are  
287 homogeneous without any detectable inclusions of sulphides, other arsenides or other phases (silicates,  
288 carbonates) and do not show any trace of alteration, as demonstrated by the comparison with a fragment of  
289 rammelsbergite from drill hole CIG 259-1 (Cigar Lake U deposit, Fig. 2B). This impure fragment displays  
290 inclusions of gersdorffite (NiAsS), silicate matrix, and areas of co-existing rammelsbergite and gersdorffite easily  
291 detectable by micro X-ray tomography cross-section analysis.

292 4.2 U-Pb isotope data on the U oxides. The results of the U-Pb and Pb-Pb SIMS measurements of the U oxides  
293 embedded in the WC530 massive rammelsbergite vein (Fig. 3) are presented in Figure 5. An upper intercept  
294 discordia age of  $1255 \pm 71$  Ma ( $n = 15$ , MSWD = 12) was calculated using model 1 of Ludwig's Isoplot 3.7 (York,  
295 1966; Ludwig, 2008). All analyses display variable degrees of discordancy, indicating post-crystallization  
296 alteration as visible in Figure 3B. The discordia is interpreted to represent the age of crystallization of the uranium  
297 crystals at 1255 Ma, followed by a lead loss event at 242 Ma (calculated age for the lower intercept).

298 4.3 Re-Os isotope data. The results of ID-NTIMS Os measurements and ID-ICP-MS measurements of Re are  
299 presented in Table 2. Rammelsbergite contains high and variable amounts of Re, ranging from  $63 \text{ ng g}^{-1}$  to  $1.6 \mu\text{g}$   
300  $\text{g}^{-1}$ . The Os in rammelsbergite samples consists almost entirely of radiogenic  $^{187}\text{Os}$ , ranging from 0.8 to  $22 \text{ ng g}^{-1}$ ,  
301 while having minimal common Os (9 to  $42 \text{ pg g}^{-1}$  of  $^{188}\text{Os}$ , equivalent to  $^{187}\text{Os}/^{188}\text{Os}$  ratios of 94-3442).

302 4.4 Chronological interpretation of the  $^{187}\text{Re}$ - $^{187}\text{Os}$  isotope data. Figure 6 A shows  $^{187}\text{Os}^*$  plotted against  $^{187}\text{Re}$  for  
303 the 13 chips prepared from the 4 rammelsbergite samples (WC530, WC287 420, WC287 420.1 and  
304 WC287 420.7). The data plotted in a conventional  $^{187}\text{Os}/^{188}\text{Os}$  vs.  $^{187}\text{Re}/^{188}\text{Os}$  isochron diagram are presented in  
305 figure 6B. As these two approaches provide nearly identical ages, while the latter is associated with large  
306 propagated uncertainties due to low  $^{188}\text{Os}$  abundance and high blank contribution for this isotope, we only discuss  
307 the results calculated with  $^{187}\text{Os}^* - ^{187}\text{Re}$  diagram hereafter. This is in line with recommendation of Stein et al.  
308 (2001) for phases that are almost devoid of common Os. A well-defined linear correlation is observed, which if

309 interpreted as an isochron, yields a crystallization age for the rammelsbergite of  $1267 \pm 33$  Ma (2 sigma),  
310 calculated using York's regression, implemented as model 1 of Ludwig's Isoplot 3.7 (York, 1966; Ludwig, 2008).  
311 The scatter however greatly exceeds the levels that can be accounted for solely by the assigned analytical  
312 uncertainties, as the Mean Square of Weighted Deviation (MSWD) is equal to 138. Because the linearized  
313 probability plot for Re-Os model ages suggests that a normal distribution is questionable, the dataset was evaluated  
314 for the potential presence of outliers, using the generalized extreme Studentized many-outlier test (GESO test,  
315 Rosner, 1983). The test indicates that the rammelsbergite sub-sample «WC287 (420.7m) B», with a model age of  
316  $1347.6 \pm 5.2$  Ma, may be considered an outlier ( $G=2.608 > G_{crit}=2.462$ ) at the 95 % confidence level. Treating the  
317 «WC287 (420.7m) B» datapoint as an outlier and recalculating a York regression for the data set of 12 points  
318 yields an age of  $1252 \pm 16$  Ma with a smaller MSWD = 30.

319 However, at elevated levels of scatter, the assumption made in the isochron line-fitting algorithm of York's  
320 regression (York, 1966) that the weighing factors should be inversely proportional to the analytical uncertainties,  
321 is unlikely to be valid (Ludwig, 2008). Although assuming one datapoint as an outlier decreases the MSWD from  
322 138 to 30, this value is still quite large, suggesting that York's algorithm is not an appropriate choice for line  
323 fitting in this case. In situations of elevated scatter, with MSWD  $\gg 1$ , such as observed for the rammelsbergite,  
324 it is preferable to use a line fitting model free of arbitrary assumptions concerning the nature of the scatter, such  
325 as that provided by the "robust regression" option in Isoplot 3.70 (Ludwig, 2008). This algorithm calculates the  
326 slope as the median of all pairwise slopes (Theil, 1992), with errors calculated according to Rock and Duffy (1986)  
327 after Vugrinovich (1981). Using the "robust regression" option on 13 points provides a rammelsbergite  
328 emplacement age of  $1237 +34/-24$  Ma. If the WC287 (420.7m) B datapoint is excluded from the solution as an  
329 outlier, a very similar estimate of  $1239 +33/-20$  Ma is obtained. The model ages calculated for the 12 individual  
330 samples, presented in Table 2 and as a histogram in Figure 6, result in an average of  $1257 \pm 43$  Ma and median of  
331 1257.2, once the result of WC287 420.7 B is cancelled as an outlier.

332 When sub-samples of the WC287 rammelsbergite are evaluated for each of the 420.1 and 420.7 sampling depths  
333 individually, the robust regression solution yields  $1250 +650/-150$  Ma for 420.7 and  $1200 +78/-78$  Ma for 420.1  
334 sub-samples (solutions on 5 and 6 points respectively, no outliers confirmed using the GESO test).

## 335 **5. Discussion**

336 5.1 Applicability of Re-Os geochronology to rammelsbergite. This work presents, to our knowledge, the first  
337 application of the  $^{187}\text{Re}$ - $^{187}\text{Os}$  chronometer to rammelsbergite ( $\text{NiAs}_2$ ), and one of the few attempts to date

338 arsenides using this system. Concerning the other arsenide minerals,  $^{187}\text{Re}$ - $^{187}\text{Os}$  system was previously used to  
339 date löllingite ( $\text{FeAs}_2$ ) by Saintilan *et al.* (2017), arsenopyrite ( $\text{FeAsS}$ ) by Arne *et al.* (2001) and Morelli *et al.*  
340 (2005, 2007), and Co-arsenopyrite by Mikulski *et al.* (2005). The rammelsbergite from the Cigar Lake U deposit  
341 is specifically characterised by elevated and variable Re contents, up to nearly  $2 \mu\text{g g}^{-1}$ , and very little common  
342 Os (up to  $0.04 \text{ ng g}^{-1}$  of  $^{188}\text{Os}$ , see Table 2). The low abundance of common non-radiogenic Os, the large relative  
343 amounts of Re and its variable concentrations (Table 2) make rammelsbergite an excellent target for  $^{187}\text{Re}$ - $^{187}\text{Os}$   
344 dating. Compared to the other tested arsenide minerals, rammelsbergite is more suitable for  $^{187}\text{Re}$ - $^{187}\text{Os}$  dating  
345 than *e.g.* arsenopyrite or löllingite, which can contain large amounts of common Os (*e.g.* löllingite from the Broken  
346 Hill Pb-Zn-Ag deposit in Australia contains up to  $\sim 26 \text{ ng g}^{-1}$  of  $^{188}\text{Os}$ , calculated from data in Saintilan *et al.*  
347 (2017)) or be characterized by relatively low levels of parent Re (below  $12 \text{ ng g}^{-1}$ ); Arne *et al.* (2001) and Morelli  
348 *et al.* (2005, 2007)). We suggest that crystal lattice constraints of the rammelsbergite allow it to preferentially  
349 concentrate Re rather than Os during crystallization, leading over time to the accumulation of radiogenic  $^{187}\text{Os}^*$   
350 in quantities sufficient for high-precision isotopic analysis. In this respect rammelsbergite is analogous to  
351 molybdenite, the most widely used phase in Re-Os geochronometry (Stein *et al.*, 2001). The U oxide grains found  
352 in the WC530 massive rammelsbergite (Figure 3) are crystallized within the rammelsbergite, without clear  
353 relationship to specific fractures cross-cutting the rammelsbergite. These euhedral crystals of uranium oxide can  
354 be thus considered as co-genetic to the crystallization of the rammelsbergite, suggesting that the two phases  
355 crystallized during the same fluid circulation event. As such, the  $1255 \pm 71 \text{ Ma}$  U-Pb upper intercept discordia  
356 age (Figure 5) defined for these U oxides can be interpreted as the oldest temporal constraint for the  
357 rammelsbergite at the Cigar Lake U deposit. The fact that the U-Pb SIMS age coincides within error with the  $1254$   
358  $\pm 12 \text{ Ma}$  model age for the fragment of WC530 (Table 2) and with the Re-Os  $1239 +33/-20 \text{ Ma}$  isochron age  
359 calculated for the Cigar Lake rammelsbergite confirms the suitability of the Re-Os radioisotope decay couple for  
360 rammelsbergite dating. It also confirms that the rammelsbergite Re-Os isotope data array is not an accidental  
361 mixing line between two components.

362 The isotopic data for rammelsbergite plot very close to a straight line in  $^{187}\text{Os} - ^{187}\text{Re}$  space (Figure 6) whereas  
363 several hydrothermal fluid circulation events occurred in the Cigar Lake U deposits after the crystallization of the  
364 rammelsbergite (*ca.* 1170 Ma, *ca.* 900 Ma, *ca.* 320 Ma, *ca.* 250 Ma and *ca.* 40 Ma) and perturbed the isotopic  
365 systems of both uranium oxides (*e.g.* at 242 Ma, see Figure 5 and Martz *et al.*, 2019b) and clays (Fayek *et al.*,  
366 2002; Kaczowka, 2017; Philippe *et al.*, 1993). Such linearity indicates the resistance of rammelsbergite to gain or  
367 loss of Re or incorporation of common Os and/or radiogenic Os loss after its initial crystallization. Tests now need

368 to be done on rammelsbergite from other types of deposits, from the Athabasca Basin and elsewhere, including  
369 those formed under different conditions to confirm the global applicability of the Re-Os isotopic system for dating  
370 of this mineral and related Ni mineralization.

371 5.2 Chemical and isotopic heterogeneities of massive rammelsbergite.  $\mu$ XRF and EMPA elemental maps  
372 demonstrate that the tested rammelsbergite veins include intermixtures of domains with variable Co contents  
373 (Figures 2 and 4; table 1). The variability of the Re content measured in the different chips of rammelsbergite may  
374 be linked to this heterogeneity of the Co/Ni ratio within the massive rammelsbergite veins. The variable  
375 concentration of Re in the rammelsbergite at the time of crystallization is a key point for  $^{187}\text{Re}$ - $^{187}\text{Os}$  dating of this  
376 phase, allowing for construction of single-mineral  $^{187}\text{Re}$ - $^{187}\text{Os}$  isochrons as is classically done for molybdenite  
377 (Stein et al., 2000). The origin of these chemical variations is not currently known. This fine-scale heterogeneity  
378 of the massive rammelsbergite might be related to a subsolidus process occurring during slow cooling after the  
379 initial precipitation of the rammelsbergite, before sub-solidus diffusion is effectively closed. Alternatively, the  
380 structure of Co-rich and Co-poor domains of the rammelsbergite might develop during post-depositional thermal  
381 reequilibration events younger than  $1239 \pm 33/-20$  Ma, such as that responsible for formation of stage 3 at 876-  
382 947 Ma (Fayek et al., 2002; Kaczowka, 2017) or ca. 350 Ma (Philippe et al., 1993) uranium oxides for example.  
383 While both cases could contribute to the scatter in the  $^{187}\text{Re}$ - $^{187}\text{Os}$  isotope systematics, the effect of Re-Os  
384 redistribution in the latter case would be expected to be much stronger, since the events occurred several hundred  
385 millions of years after rammelsbergite crystallization, after substantial amounts of  $^{187}\text{Os}$  have had the chance to  
386 grow in. Such a process would not produce the obtained isochron. Thus, the protracted cooling period after the  
387 initial precipitation of rammelsbergite linked to subsolidus equilibration of Re and Co-Ni seems a much more  
388 likely explanation. A third possibility could be that the heterogeneous Co/Ni composition of massive  
389 rammelsbergite results from growth under changing conditions, at varying temperature, fluid compositions, and/or  
390 activities of Co and Ni. Common Os of variable isotopic composition could be incorporated into the nickel  
391 arsenide during this process, which could contribute to the scatter of the isochron. During our analytical procedure,  
392 common Os was measured and is later corrected for assuming a  $^{187}\text{Os}/^{188}\text{Os}$  ratio of  $0.5 \pm 0.4$ . However, if common  
393 Os with more radiogenic and/or more variable composition is incorporated into the sub-samples during  
394 crystallization of rammelsbergite, this would not be accounted for, and could introduce scatter. However, the fact  
395 that the y-intercept of the isochron in Figure 6 plots well within error of zero suggests that underestimation of the  
396 initial radiogenic Os component was not a generalized problem.

397 Finally, some of the scatter in the isochron diagram could result from the fact that Re and  $^{187}\text{Os}$  may not enter into  
398 the same structural sites in the crystal, resulting in spatial decoupling. This possibility was summarized for  
399 molybdenite in Stein and Hannah (2014). As shown by Takahashi et al. (2007),  $^{187}\text{Os}$  has a smaller radius and a  
400 lower valence than Re incorporated in the molybdenite structure, suggesting that newly formed radiogenic Os  
401 could diffuse more rapidly than Re and thus is more likely to enter into structural defects. It is possible that a  
402 similar process could cause spatial decoupling of radiogenic Os from its parent Re in the rammelsbergite.  
403 Radiogenic Os may have diffused out of (or into) the small sub-sample over time into more favourable sites in the  
404 surrounding crystal, thus leading to the scatter observed.

405 These different possibilities of scatter need to be constrained, but the first results on rammelsbergite clearly  
406 demonstrate that this mineral presents a high potential for use in Re-Os geochronometry. The diversity of  
407 geological contexts in which rammelsbergite can be found, from magmatic to hydrothermal conditions, and its  
408 possible future significance as a source of nickel, could allow a rapid development of its use to constrain geological  
409 models, as demonstrated below for the unconformity-related U deposits. In this context rammelsbergite could  
410 complement molybdenite as dating targets in deposit environments where molybdenite is not common.

### 411 5.3 Contribution of rammelsbergite Re-Os dating to the formation model for unconformity-related U deposits.

412 The best estimate for the age of emplacement of rammelsbergite in the Cigar Lake uranium deposit is  $1239 \pm 33/-$   
413  $20$  Ma (robust regression solution on 12 points, excluding sample WC287 (420.7m) B, figure 6). This age is the  
414 first obtained on sulphides, sulpharsenides or arsenides for the unconformity-related U deposits of the Athabasca  
415 Basin. It provides new key information about the formation of unconformity-related U deposits and fills several  
416 important gaps in our understanding of the genetic model of these world-class deposits.

417 The  $1239 \pm 33/-20$  Ma Re-Os age first demonstrates that rammelsbergite crystallized late compared to the earliest  
418 generation of uranium oxide. The age of primary deposition of uranium oxides in the Cigar Lake deposit is still  
419 debated, due to the susceptibility of the U-Pb system in uranium oxide to disturbance under post-crystallization  
420 conditions (Fayek et al., 2000; Alexandre and Kyser, 2005; Macmillan et al., 2016; Martz et al., 2019a), but the  
421  $1341 - 1461$  Ma age range is commonly interpreted to date the primary U oxide deposition event (Philippe et al.,  
422 1993; Fayek et al., 2002). Numerous U-Pb ages post-dating the first U deposition have been measured on uranium  
423 oxides in the Cigar Lake U deposit, as well as at a broader scale for the different unconformity-related U deposits  
424 of the Athabasca Basin. These ages cover a broad period of over a billion years, with different individualized  
425 statistical peaks (Cumming and Krstic, 1992; Philippe et al., 1993; Fayek et al., 2002a; Fayek et al., 2002b;



426 Alexandre et al., 2009; Cloutier et al., 2009; Cloutier et al., 2011). Among these peaks, the 1250-1270 Ma period  
427 is one of the most frequently defined within the Athabasca Basin. The similarity between the Re-Os age of  
428 rammelsbergite, the U-Pb ages of secondary uranium oxides within the Athabasca U province, and the age of the  
429 U oxides found within the WC530 rammelsbergite vein (figure 5) likely indicates that primary uranium oxides  
430 were strongly hydrothermally remobilized/perturbed during the emplacement of the arsenides, sulfides and  
431 sulpharsenides in these unconformity-related U deposits. Temporal distinction between the rammelsbergite and  
432 initial U oxide emplacement observed in this work is also in agreement with recently observed discrepancies in  
433 lateral distributions of U and Ni in a single pod of the Cigar Lake deposit (c.f. figure 2.21 of Kaczowka, 2017).

434 Another possibility is that the massive veins of rammelsbergite are secondary and do not represent rammelsbergite  
435 disseminated in the U ores, which might instead be contemporaneous with primary U mineralization at ca. 1341  
436 – 1461 Ma. Though we did not evaluate disseminated Ni arsenides in this study, such phases may have precipitated  
437 in the same event as the primary U oxides but then have been mobilized as primary uranium oxides in a subsequent  
438 1239 Ma event, which reset the  $^{187}\text{Re}$ - $^{187}\text{Os}$  system and crystallized massive rammelsbergite veins. This scenario  
439 is however not supported by the near-zero initial  $^{187}\text{Os}/^{188}\text{Os} = 0.8 \pm 6.6$  observed for the massive rammelsbergite  
440 (Fig. 6B). If the massive rammelsbergite veins were indeed formed by dissolution and remobilization of primary  
441 Ni arsenides, radiogenic initial Os is expected because in the intervening 100-220 Ma period the hypothetical  
442 primary Ni arsenides would acquire significant amounts of  $^{187}\text{Os}$  by radiogenic ingrowth. We cannot completely  
443 exclude a secondary origin for the massive rammelsbergite, because near-zero initial  $^{187}\text{Os}/^{188}\text{Os}$  could  
444 conceivably be explained by (i) elevated uncertainty on the intercept as a result of geological scatter, or (ii) an  
445 absence of Re in the hypothetical primary Ni arsenides, which would then have been introduced into the system  
446 only at 1239 Ma, or (iii) a potentially high distribution coefficient for Os in the fluid-mineral system, preventing  
447 any radiogenic Os from entering the rammelsbergite lattice. However in the absence of any evidence supporting  
448 these suggestions, the contemporaneous emplacement of U and Ni arsenides in the Cigar Lake deposit must be  
449 viewed as hypothetical.

450 Despite the elevated uncertainty on the  $^{187}\text{Re}$ - $^{187}\text{Os}$  age found for Cigar Lake rammelsbergite, our data strongly  
451 suggest that the endowment of Ni, Co, S and As in unconformity-related U deposits of the Athabasca Basin is  
452 linked to the Mesoproterozoic magmatic event responsible for the emplacement at 1269 Ma of the Mackenzie  
453 large igneous province (LIP) over a vast area of northern Canada and Russia (LeCheminant and Heaman, 1989).  
454 The Mackenzie LIP is represented by the mafic-ultramafic layered Muskox intrusion ( $1269 \pm 2$  Ma, Mackie et al.,  
455 2009) and the Coppermine basalts ( $1263 +20/-16$  Ma, Day et al., 2013). Both are located at the focal point of the

456 related giant swarm of Mackenzie diabase dikes ( $1267 \pm 2$  Ma to  $1268.5 \pm 1.5$  Ma, LeCheminant and Heaman,  
457 1989; Schwab et al., 2004), which radiate outwards over at least 2400 km, reaching the Athabasca Basin (Mackie  
458 et al., 2009). The focal point of the dike swarm is located approximately 1100 km north east of the Cigar Lake  
459 deposit and several mafic dykes have been described as crosscutting the Athabasca Basin and the U mineralization,  
460 for example at the Midwest and Centennial deposits (Alexandre et al., 2012; Reid et al., 2014). Our new  $^{187}\text{Re}$ -  
461  $^{187}\text{Os}$  age of  $1239 \pm 33/-20$  Ma for the rammelsbergite of the Cigar Lake U deposit demonstrates that nickel  
462 arsenide veins in the uranium deposit were either emplaced at the same time as the mafic dikes, or formed several  
463 millions to tens of millions of years after their emplacement, by fluid mobilization of elements (Ni, Co, As) derived  
464 from a probable mafic source. Presumably, the Mackenzie event provided both the material, in the form of Ni-As  
465 rich magmas, and potentially the energy needed for hydrothermal activity to transport the metals to the Athabasca  
466 Basin, where they are redeposited in the form of arsenides, sulfides and sulfarsenides in the uranium deposits. In  
467 this context Ni-Co-As mineral precipitation seems to be dependent on structural controls and reducing  
468 environments, likely resulting from hydrogen produced by the radiolysis of water, similar to those that drove  
469 earlier U reduction and deposition (Dargent et al., 2015; Truche et al., 2018) because there are no occurrences of  
470 Ni-Co-As independent from U deposits in the Athabasca Basin. The Mackenzie event thus deeply modified the  
471 initial characteristics of the unconformity-related U deposits, being likely responsible for remobilisation of the  
472 primary stage 1 uranium oxides in the deposit, with partial to total resetting of the U-Pb uraninite age and  
473 formation of stage 2 uranium oxides (as well as the U oxides found within the WC530 rammelsbergite vein), and  
474 for massive deposition of nickel, cobalt, sulfur and arsenic in the form of arsenides, sulphides and sulfarsenides.

475 The compositional spectrum of unconformity-related U deposits in the Athabasca Basin is currently described in  
476 terms of monometallic and polymetallic genetic models, on the basis of associated metals. Polymetallic ores, like  
477 that of the Cigar Lake U deposit, are characterized by anomalous concentrations of sulphides, sulpharsenides and  
478 arsenides containing significant amounts of Ni, Co, S, As, Cu, Pb, Zn and Mo, whereas monometallic ores, like  
479 that of the McArthur U deposit, contain only traces of metals other than U (Jefferson et al., 2007; Kyser and  
480 Cuney, 2015). Such mineralogical differences have been explained until now using two end-member genetic  
481 models for the unconformity-related U deposits in the Athabasca Basin, one for monometallic deposits and one  
482 for polymetallic deposits (Hoeve and Sibbald, 1978; Fayek and Kyser, 1997; Quirt, 2003; Jefferson et al., 2007;  
483 Kyser and Cuney, 2015). The major differences between these two end-member models is the involvement of a  
484 basement-derived reduced fluid to explain both U deposition and the source of Ni, Co, S, As, Cu and Zn in  
485 polymetallic deposits. Such a fluid is not considered to have been involved in monometallic deposits, which

486 instead are thought to have formed from oxidized and U-bearing basinal brines flowing into basement-rooted  
487 structures and interacting with reduced minerals (Hoeve and Sibbald, 1978; Kotzer and Kyser, 1995; Fayek and  
488 Kyser, 1997; Jefferson et al., 2007; Kyser and Cuney, 2015). These two genetic models which have guided the  
489 exploration of unconformity-related U deposits for years are based on the postulate that the U, Ni, Co, S and As  
490 ( $\pm$  Zn, Cu) are introduced simultaneously into the deposits. The clear differences in the timing of the initial  
491 deposition of the uranium and of the Ni-Co in the Athabasca Basin calls for reconsideration of the existing models.  
492 Our results suggest that the presence of nickel and cobalt, as well as associated elements such as S and As, in  
493 unconformity-related U deposits is directly linked to the local involvement of mafic dykes of MacKenzie age in  
494 the vicinity of some of these U deposits, including the Cigar Lake, Midwest and Centennial deposits. These dykes  
495 favoured specific and localized circulations of Ni- and Co-rich fluids at ca. 1250-1270 Ma leading to  
496 crystallization of arsenides, sulphides and sulfarsenides in the reduced environment of the uranium deposits and  
497 the perturbation/recrystallization of the uranium oxides. This scenario explains the formation of the polymetallic  
498 deposits. The U deposits of the Athabasca Basin in which geological and structural conditions have not allowed  
499 the local intrusion of dykes and related fluid circulation at ca. 1250-1270 Ma are not enriched in sulphides,  
500 sulfarsenides or arsenides, and have thus remained monometallic.

## 501 **6. Summary and conclusions**

502 This work presents the first tests of Re-Os dating on rammelsbergite ( $\text{NiAs}_2$ ), a rare mineral at a global scale but  
503 often present in ore deposits worldwide in association with other arsenides, sulphides and sulfarsenides. This study  
504 is one of the first published on the Re-Os dating of arsenides, minerals that may be of future economic interest  
505 due to their content in nickel or cobalt. The suitability of the Re-Os chronometer for dating rammelsbergite is  
506 demonstrated here for the unconformity-related uranium deposits of the Athabasca Basin (Canada), using the  
507 example of the world-class Cigar Lake deposit. The massive rammelsbergite veins found in this deposit display  
508 significant (up to  $1.7 \mu\text{g g}^{-1}$ ) and variable Re contents, coupled with a near absence of common Os, making this  
509 mineral an ideal candidate for  $^{187}\text{Re}$ - $^{187}\text{Os}$  dating, by both isochron and model age methods, comparable in this  
510 respect to molybdenite. Similarity of the Re-Os age of the rammelsbergite and the U-Pb age of the accessory  
511 uranium oxide grains found inside one of the massive rammelsbergite veins confirms the applicability of the  
512 method. Furthermore, the Re-Os isotopic system appears to be resistant to post-crystallization perturbation. The  
513  $^{187}\text{Re}$ - $^{187}\text{Os}$  isotope system applied to rammelsbergites from various economically important ore deposits  
514 throughout the world may thus serve as a powerful dating tool. This study demonstrates that the Re-Os

515 chronometer can be applied to rammelsbergite in ore deposits where molybdenite is rare or absent, and suggests  
516 that the pertinence of this system should also be evaluated in other arsenide minerals.

517 For the case of unconformity-related U deposits, rammelsbergite from the Cigar Lake deposit demonstrates the  
518 potential of new  $^{187}\text{Re}$ - $^{187}\text{Os}$  mineral proxies used in conjunction with traditional chronometers, to challenge long-  
519 established petrogenetic deposit models and to advance our understanding of the distribution of critical mineral  
520 resources. The 1239  $\pm$ 33/-20 Ma age calculated for the crystallization of the rammelsbergite in the Cigar Lake  
521 uranium deposit provides new first-order constraints on the formation and evolution of unconformity-related U  
522 deposits, and argues for a profound reconsideration of existing genetic models. This result first demonstrates that  
523 the massive precipitation of arsenides, sulphides and sulpharsenides post-dates the deposition of primary uranium  
524 oxides (1341 – 1461 Ma) and that the endowment of Ni-Co in the Athabasca Basin was disconnected in time from  
525 that of U. The similarity between the age of the rammelsbergite and a secondary age peak including many uranium  
526 oxides in Athabascan unconformity-related U deposits indicates that the primary uranium oxides were strongly  
527 perturbed and/or remobilized when rammelsbergite and related minerals crystallized. The massive emplacement  
528 of rammelsbergite is most probably genetically linked to the 1269 Ma Mesoproterozoic magmatic Mackenzie  
529 event. Presumably, this event activated regional hydrothermal activity, resulting in partial mobilisation of primary  
530 uranium oxides, resetting of the U-Pb system in the uraninite, mobilisation of Ni, Co and As from the ultramafic  
531 materials, and their precipitation in the deposit adjacent to uranium oxides. In favourable structural contexts this  
532 process led to the formation of the so-called “polymetallic deposits” of the Athabasca Basin. This study thus  
533 suggests a plausible new mechanism for the emplacement of nickel and cobalt in unconformity-related U deposits  
534 and represents a first step towards defining a new genetic model for these world-class deposits.

535

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791

		S wt %	Co wt %	Ni wt %	As wt %
WC287 rammelsbergite (420.7 m)	#1	<0.07	0.89 ± 0.11	28.51 ± 0.61	71.4 ± 1.4
	#2	<0.08	1.02 ± 0.12	27.97 ± 0.60	71.1 ± 1.4
	#3	<0.08	0.79 ± 0.11	28.01 ± 0.60	70.76 ± 1.4
	#4	<0.08	0.45 ± 0.10	27.92 ± 0.60	71.3 ± 1.4
	#5	<0.08	0.39 ± 0.10	27.98 ± 0.60	71.2 ± 1.4
	#6	<0.07	0.82 ± 0.11	27.83 ± 0.60	71.1 ± 1.4
	#7	<0.08	0.26 ± 0.09	28.04 ± 0.60	71.3 ± 1.4
	#8	<0.09	0.38 ± 0.09	28.48 ± 0.61	71.4 ± 1.4
	#9	<0.09	0.50 ± 0.10	28.52 ± 0.61	71.3 ± 1.4
	#10	<0.08	0.88 ± 0.12	27.65 ± 0.59	71.0 ± 1.4
<i>average 420.7 m</i>	-	<i>0.64 ± 0.27</i>	<i>28.09 ± 0.31</i>	<i>71.2 ± 0.21</i>	
WC287 rammelsbergite (420.1 m)	#11	<0.09	1.05 ± 0.12	27.36 ± 0.59	71.3 ± 1.4
	#12	0.08 ± 0.07	1.72 ± 0.14	27.33 ± 0.59	71.1 ± 1.4
	#13	<0.09	1.24 ± 0.12	27.22 ± 0.59	71.3 ± 1.4
	#14	<0.08	0.88 ± 0.12	27.16 ± 0.59	71.4 ± 1.4
	#15	0.08 ± 0.08	1.00 ± 0.12	27.05 ± 0.58	71.0 ± 1.4
	#16	0.09 ± 0.07	1.00 ± 0.12	27.25 ± 0.59	71.2 ± 1.4
	#17	<0.07	4.85 ± 0.21	23.04 ± 0.53	71.0 ± 1.4
	#18	<0.09	1.50 ± 0.13	27.13 ± 0.59	71.2 ± 1.4
	#19	<0.09	1.03 ± 0.12	26.66 ± 0.58	71.3 ± 1.4
	#20	<0.08	1.01 ± 0.12	26.72 ± 0.58	71.3 ± 1.4
<i>average 420.1 m</i>	-	<i>1.53 ± 1.2</i>	<i>26.69 ± 1.3</i>	<i>71.2 ± 0.14</i>	

793 **Table 1** Results of EMPA measurements of the rammelsbergite from 420.1 and 420.7 m depth levels (WC287  
794 drill hole, Cigar Lake U deposit, Saskatchewan, Canada). The locations of the analyses are shown in Figure 4.  
795 Uncertainty represents one standard deviation. All measurements for Fe, Se, Sb, Bi, Cu and Mo are below  
796 detection limits (0.08, 0.3, 0.2, 0.2, 0.1 and 0.2 wt % respectively).

	Sample weight, mg	Blank contribution on $^{187}\text{Os}^*$ radiogenic, %	$^{188}\text{Os}$ , pg g $^{-1}$	$^{187}\text{Os}/^{188}\text{Os}$	$^{187}\text{Re}/^{188}\text{Os}$	rho	$^{187}\text{Os}^*$ radiogenic, ng g $^{-1}$	Re, ng g $^{-1}$	$^{187}\text{Os}/^{187}\text{Re}$	Model age
WC530 (457.2m)	247	0.2	9.03 ± 0.17	94.0 ± 1.7	4443 ± 91	0.893	0.8465 ± 0.0077	63.48 ± 0.58	0.02112 ± 0.00020	1254 ± 12 Ma
WC287 (420.0m)	191	0.1	14.59 ± 0.22	169.8 ± 2.6	8110 ± 140	0.912	2.473 ± 0.010	187.1 ± 1.3	0.02092 ± 0.00014	1 242.6 ± 8.5 Ma
WC287 (420.1m) A	126	0.03	30.36 ± 0.33	431.5 ± 4.7	19590 ± 280	0.774	13.092 ± 0.016	941.2 ± 8.4	0.02201 ± 0.00010	1 307 ± 12 Ma
WC287 (420.1m) B	155	0.02	26.98 ± 0.98	554 ± 20	25910 ± 970	0.968	14.954 ± 0.027	1106 ± 10	0.02139 ± 0.00010	1 270 ± 12 Ma
WC287 (420.1m) C	140	0.03	29.54 ± 0.31	382.6 ± 4.0	18030 ± 200	0.921	11.295 ± 0.015	842.7 ± 3.7	0.021211 ± 0.000049	1 259.8 ± 5.8 Ma
WC287 (420.1m) D	141	0.04	8.90 ± 0.46	1038 ± 53	48600 ± 2500	0.997	9.231 ± 0.016	684.2 ± 2.4	0.021352 ± 0.000042	1 268.2 ± 5.0 Ma
WC287 (420.1m) E	107	0.02	36.36 ± 0.78	581 ± 12	28040 ± 610	0.976	21.129 ± 0.044	1613.2 ± 7.0	0.020727 ± 0.000050	1 231.4 ± 5.9 Ma
WC287 (420.1m) F	252	0.009	39.29 ± 0.73	565 ± 11	27330 ± 540	0.933	22.189 ± 0.040	1699 ± 12	0.020663 ± 0.000074	1 227.6 ± 8.8 Ma
WC287 (420.7m) A	139	0.05	4.68 ± 0.30	1690 ± 110	79300 ± 5100	0.993	7.895 ± 0.014	586.5 ± 4.4	0.021305 ± 0.000083	1 265.4 ± 9.8 Ma
WC287 (420.7m) B	136	0.04	8.26 ± 0.45	1077 ± 59	47300 ± 2600	0.998	8.892 ± 0.017	618.4 ± 2.2	0.022757 ± 0.000046	1 350.6 ± 5.5 Ma
WC287 (420.7m) C	188	0.07	10.00 ± 0.69	392 ± 27	18400 ± 1300	0.999	3.921 ± 0.012	290.95 ± 0.91	0.021327 ± 0.000047	1 266.7 ± 5.6 Ma
WC287 (420.7m) D	106	0.03	4.30 ± 0.43	3440 ± 340	165000 ± 16000	0.999	14.812 ± 0.024	1123.7 ± 3.9	0.020862 ± 0.000040	1 239.3 ± 4.8 Ma
WC287 (420.7m) E	143	0.05	5.63 ± 0.37	1227 ± 82	58400 ± 3900	0.997	6.904 ± 0.015	520.5 ± 2.4	0.020992 ± 0.000054	1 246.9 ± 6.4 Ma
Henderson a	73	0.2	3.6 ± 2.4	920 ± 610	2000000 ± 1300000	0.9999	3.350 ± 0.027	11280 ± 100	0.0004700 ± 0.0000028	28.21±0.34 Ma
Henderson b	118	0.1	2.2 ± 1.3	1490 ± 890	3200000 ± 1900000	0.9999	3.220 ± 0.018	10930 ± 110	0.0004663 ± 0.0000026	27.98±0.31 Ma

798 **Table 2.**  $^{187}\text{Re}$ - $^{187}\text{Os}$  isotope data and model ages of rammelsbergite for the 13 selected fragments of rammelsbergite from Cigar Lake uranium deposit, Athabasca Basin

799 (Saskatchewan, Canada).  $^{187}\text{Os}^*$  stands for radiogenic only  $^{187}\text{Os}$ , corrected for a contribution of common Os, assumed to have a  $^{187}\text{Os}/^{188}\text{Os}$  ratio of  $0.5 \pm 0.4$ . All uncertainties

800 are 2SE. All data are blank corrected and uncertainties include the uncertainties on the blank value and on the assumed common Os isotopic composition.

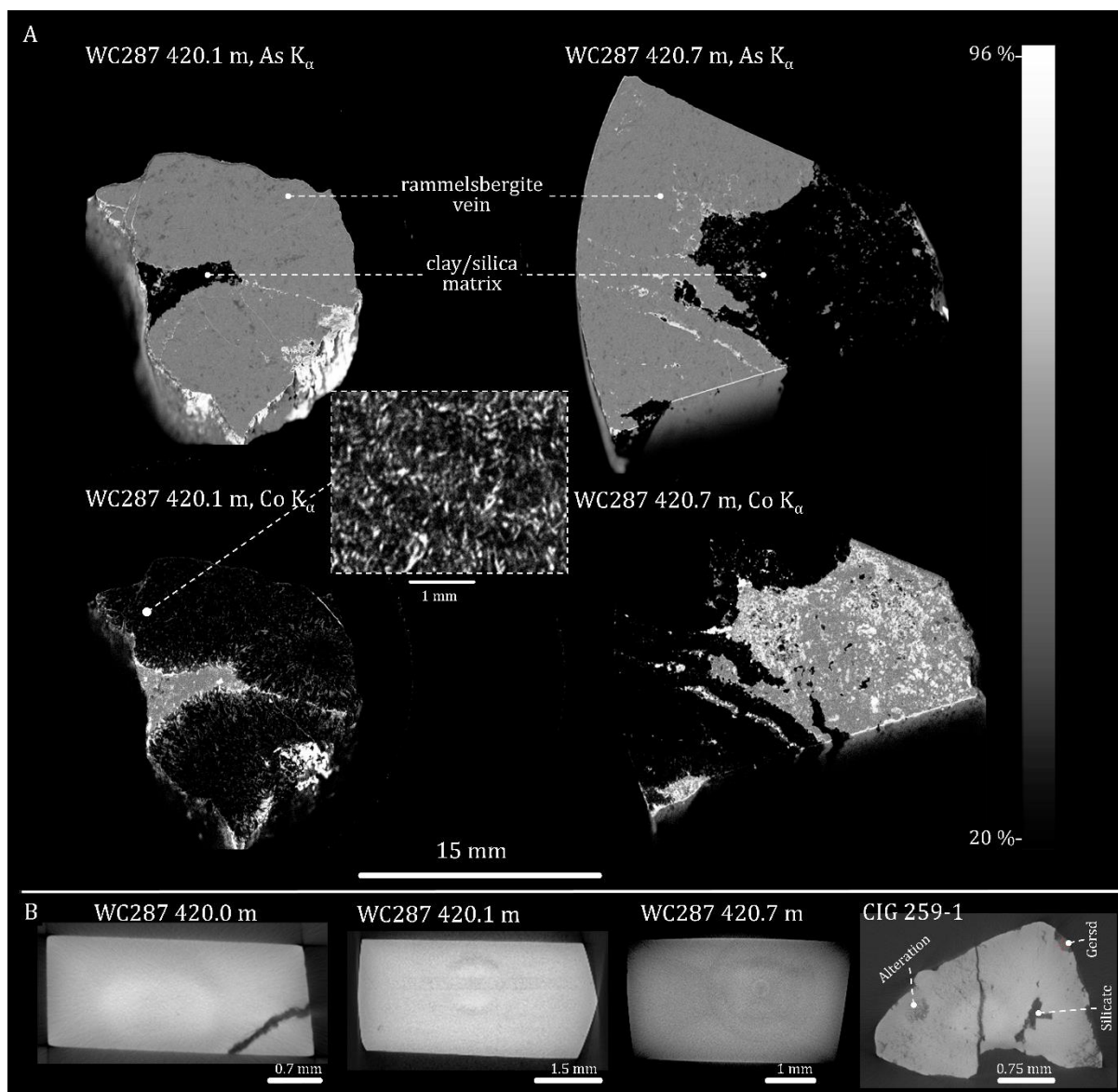
802 **Figures**



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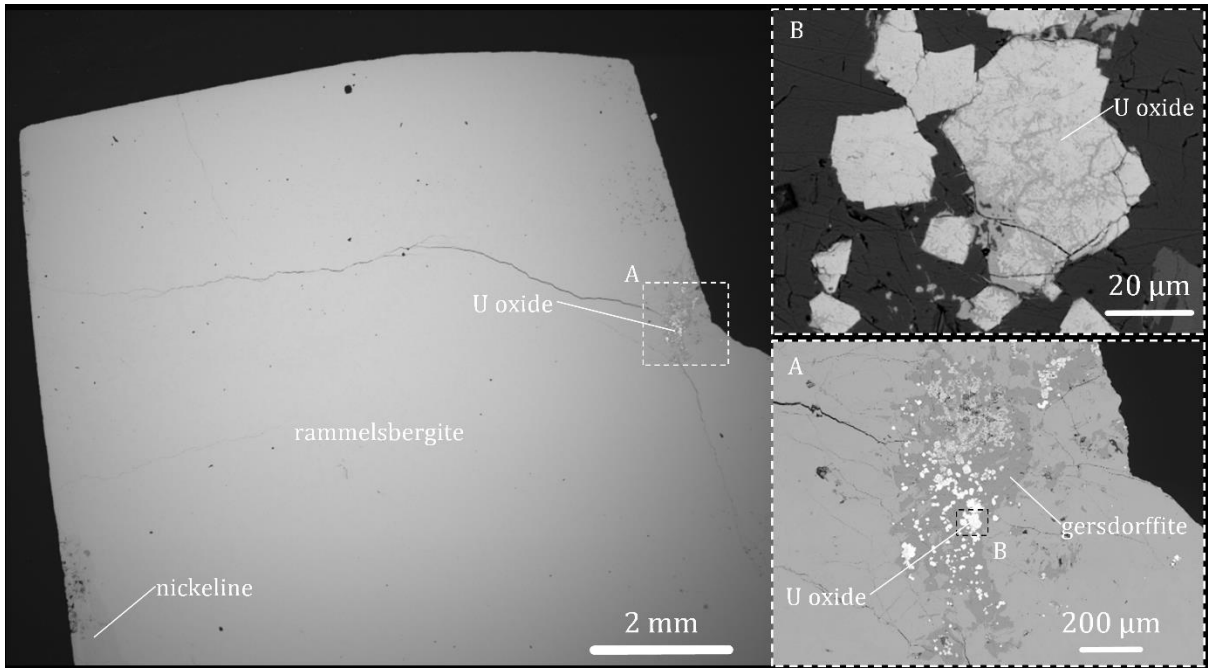
804 **Fig. 1** The 417.4 – 421.6 m section of the WC287 drill core, Cigar Lake U deposit (Saskatchewan, Canada). A)  
805 Massive U oxide and rammelsbergite vein at 419.1 – 419.3 m depth. B) Association of massive U oxides and  
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807 the locations of the three samples analysed (420.0, 420.1 and 420.7). The bottom part of the figure shows an  
808 expanded view of each of the three sampled intervals. The number given above each interval of 10 cm is the total  
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810 vein was taken from the WC530 drillhole in the Cigar Lake deposit area, at 457.2 m.





811

812 **Fig. 2** A)  $\mu$ XRF element distribution intensity maps of the two rammelsbergite samples from 420.1 m (left) and  
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 815 The insert shows an expanded Co  $K_{\alpha}$  intensity distribution map measured on a pure rammelsbergite area of sample  
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 818 the WC287 drill hole before their dating by Re-Os analysis. The X-ray tomography demonstrates the purity of the  
 819 dated fragments, which can be compared with an altered fragment of rammelsbergite compromised by silicates  
 820 and gersdorffite (Gersd) from another drill hole at the Cigar Lake U deposit (CIG 259-1).



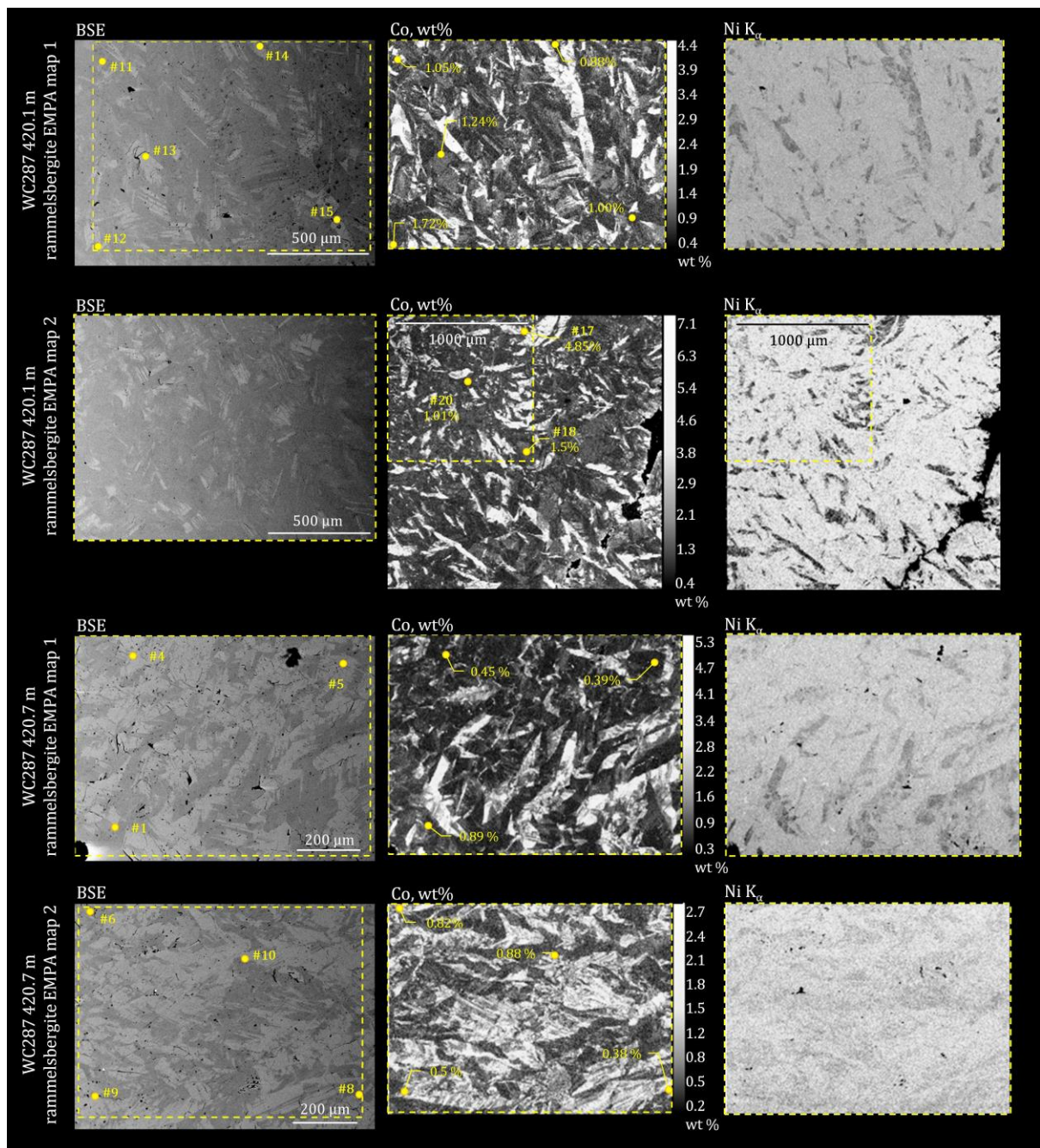
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822 **Fig. 3** SEM-BSE images of the massive rammelsbergite vein material from the WC530 borehole, 457.2 m depth,

823 Cigar Lake deposit (Saskatchewan, Canada). A – association of the rammelsbergite, gersdorffite and U oxide. B

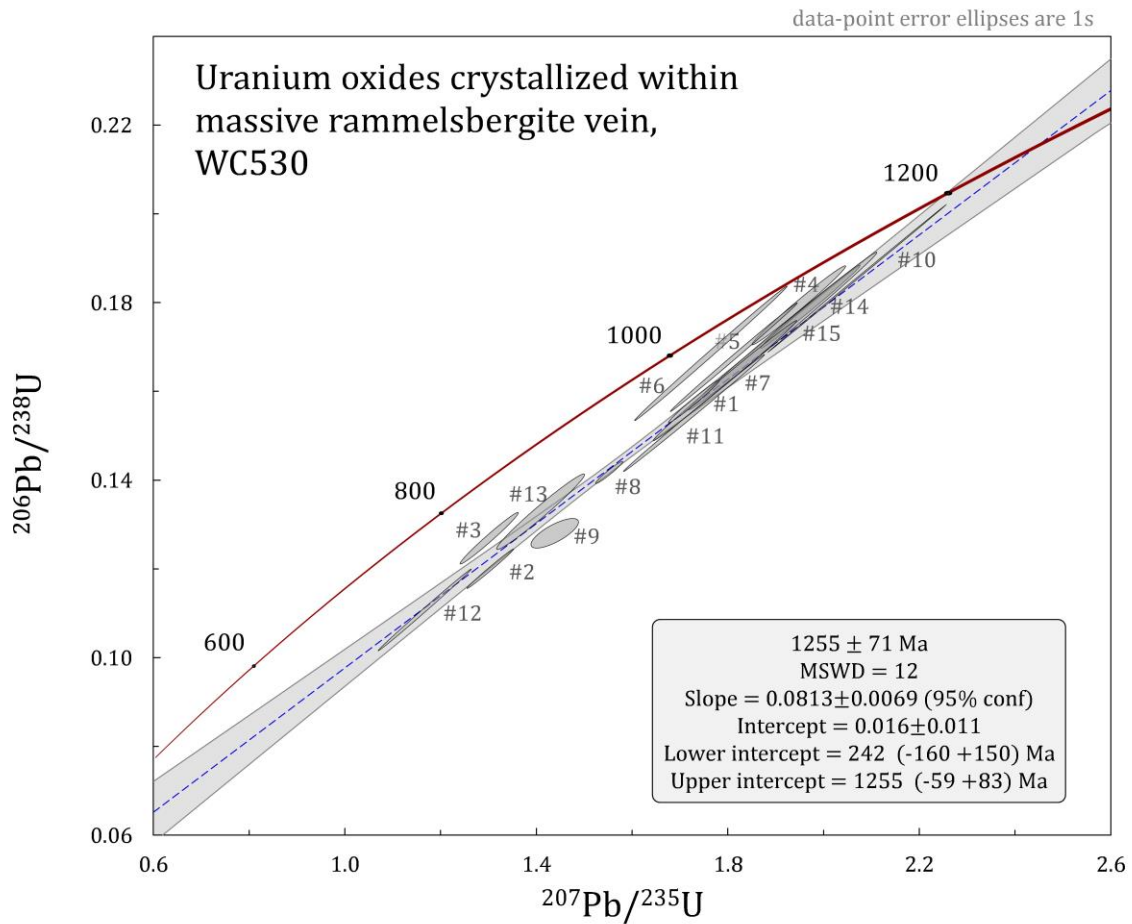
824 – euhedral U oxide grains. The darker areas within the U oxide correspond to the Pb loss event (c.f. Figure 5).

825



826

827 **Fig. 4** EMPA maps and chemical analyses of 4 different locations for two samples (WC287 420.1 and  
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 830 Ni) are highlighted with yellow rectangles. Ni  $K_{\alpha}$  intensity distribution maps are shown in the right column and  
 831 quantitative Co element distribution maps (in wt.%) of the same region in the middle column. The numbered spots  
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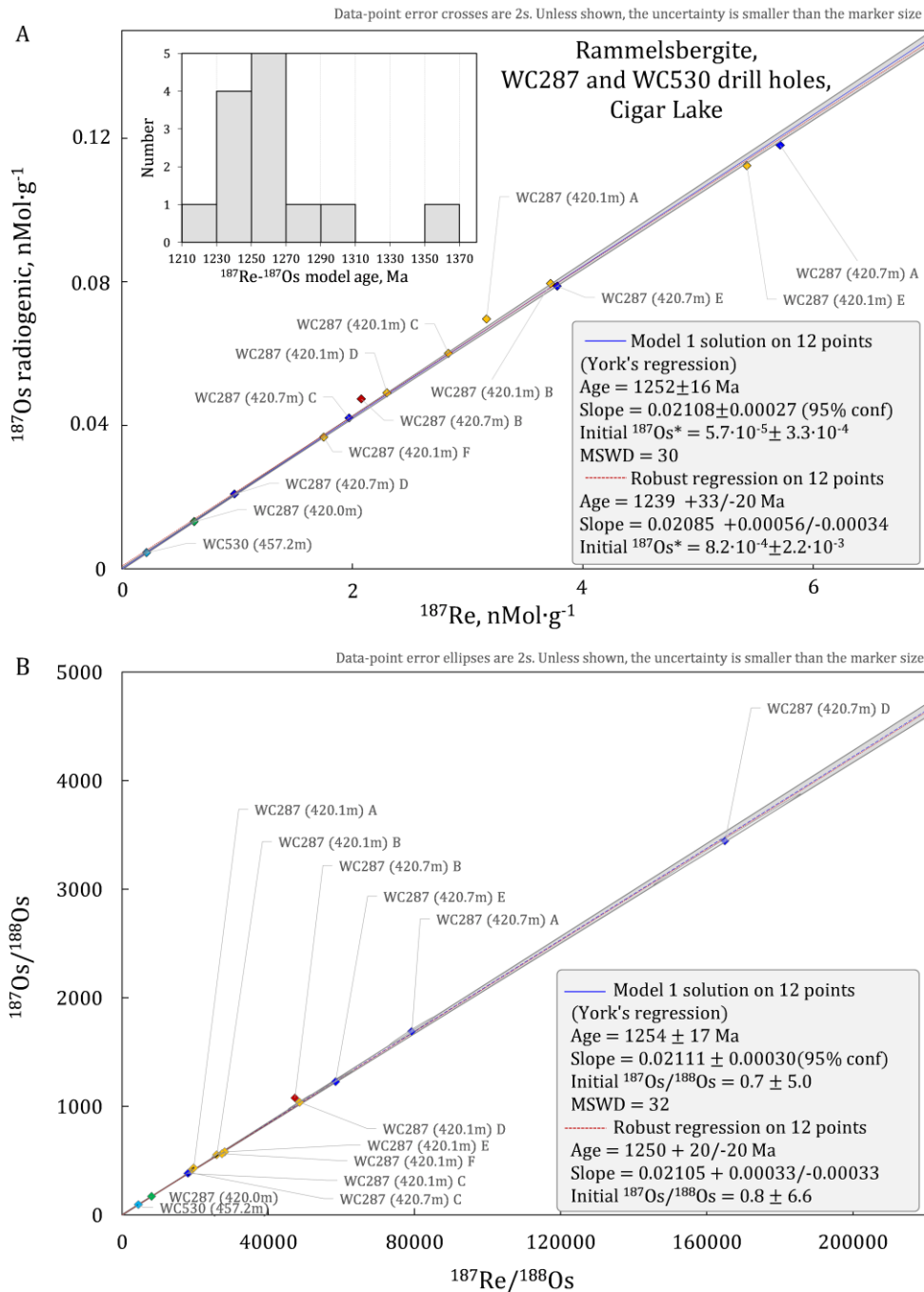
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835 **Fig. 5** Wetherill's Concordia diagram for 15 U-Pb analyses measured for the uranium oxides crystallized within

836 the massive rammelsbergite vein, Cigar Lake deposit (Saskatchewan, Canada), sample WC530, 457.2 m (c.f.

837 Figure 3).

838



839

840 **Fig. 6 A** –  $^{187}\text{Re}$  –  $^{187}\text{Os}$  isochron plot for the 13 fragments of rammelsbergite from WC287 and WC530 drillholes,  
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849 analytical uncertainties (MSWD = 30), a robust regression solution (dashed line) is preferred. B – when presented  
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851 uncertainties.

852 **Captions for tables and figures.**

853 **Table 1** Results of EMPA measurements of the rammelsbergite from 420.1 and 420.7 m depth levels (WC287  
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