

Evaluation of rammelsbergite (NiAs2) as a novel mineral for 187Re-187Os dating and implications for unconformity-related U deposits

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1	Evaluation of rammelsbergite (NiAs ₂) as a novel mineral for ¹⁸⁷ Re - ¹⁸⁷ Os dating and implications					
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17						
18	Abstract					
19	Rammelsbergite (NiAs ₂) 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 $1.6 \ \mu g \ g^{-1}$, 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

26 rammelsbergite veins confirms the applicability of the method. The selected rammelsbergite samples from the

Re-Os age of the rammelsbergite with the U-Pb age of the uranium oxide grains found inside one of the massive

27 Cigar Lake uranium deposit yield a ¹⁸⁷Re-¹⁸⁷Os isochron age of 1239 +33/-20 Ma. These results challenge a long-

standing petrogenetic model which postulates contemporaneous U oxide and Ni-Co-arsenide deposition in 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 ¹⁸⁷Re-¹⁸⁷Os 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 the ¹⁸⁷Re-¹⁸⁷Os rammelsbergite chronometer in this geological context suggests that its application in other ore 37 deposit environments worldwide is likely to provide similar insights. In this respect, the ¹⁸⁷Re-¹⁸⁷Os chronometer 38 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: ¹⁸⁷Re-¹⁸⁷Os, 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 21st 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 (NiAs₂, 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 Athabascan 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 this study we evaluate the applicability of the ¹⁸⁷Re-¹⁸⁷Os rammelsbergite chronometer, using the example of the 94 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

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

(2007), Kyser and Cuney (2015), and Martz et al. (2017, 2019). Only a short summary is presented here and formore 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, in northern Saskatchewan, Canada. The deposit is lens-shaped and elongated in the E-W direction over 1.9 km, 106 107 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 CaCl2-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 (NiAs₂), nickeline (NiAs), maucherite (Ni₁₁As₈), löllingite (FeAs₂), 124 skutterudite (NiAs₃), 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 accurate and precise U-Pb dating on uranium oxides, but also K-Ar or ⁴⁰Ar/³⁹Ar dating on clays. Multiple 134 135 approaches to dating the primary uranium mineralization event in the Cigar Lake deposit have been taken, and 136 the resulting ages lie between 1341 ± 17 (U-Pb TIMS analysis of uranium oxide mineral separates, Philippe et 137 al.,1993) and 1461 \pm 47 Ma (\pm 1 σ , 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 ± 10 Ma, 1163 ± 25 Ma and 947 ± 57 Ma using U-Pb dating 141 by LA-ICP-MS. The Rb-Sr isochron method provides an age of 1477 ± 57 Ma for crystalline illites (Kotzer and 142 Kyser, 1995). Philippe et al. (1993) reported K-Ar ages of 1385 ± 30 and 1390 ± 33 Ma for the $< 2 \,\mu m$ 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° N 104.51813° 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° N 104.33593° 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

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

The drillcores were specifically chosen because they present the most massive and freshest intercepts of rammelsbergite drilled during the last exploration campaigns. Due to its massive character, the rammelsbergite in these veins is easily separable from the uranium oxides and is identical to the rammelsbergite described in the main U mineralization by previous authors for the Cigar Lake U deposit (Reyx and Rulhmann, 1993; Kaczowka, 2017), as well as for other U deposits of the Athabasca Basin (Carl et al., 1992; Annesley et al., 2000; Jefferson 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 µm 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 (FeS₂), molybdenite (MoS₂), clausthalite (PbSe), stibnite (Sb₂S₃) 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 µm. In spot analysis mode, the intensities of 10 elements 186 were acquired at K_{α} lines of S, Fe, Co, Ni, and Cu, L_{α} lines of As, Se, Sb and Mo, and M_{β} line of Bi, with a 10 s 187 on-peak acquisition time. An on-peak acquisition time of 200 ms and spacing of $2 - 8 \mu m$ (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 μ A operating current) and a Be side-window. In this instrument, the X-rays are focused to a 25 μ m spot 194 (measured for Mo K_a) using a polycapillary lens. The instrument is equipped with two silicon drift detector 195 spectrometers (30 mm², 145 eV energy resolution for Mn K_a), 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 sufides, 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 µA 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.

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

214 <u>3.3 Re-Os reference materials and spikes.</u> 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 ¹⁸⁵Re ($\omega = 96.73$ %) and ¹⁹⁰Os ($\omega = 96.99$ %) were obtained 217 from Oak Ridge National Laboratory (Tennessee, USA) and mixed at concentrations of 4.72 10⁻² nmol g⁻¹ ¹⁹⁰Os 218 and 1.72 nmol g⁻¹ ¹⁸⁵Re in high-purity 6 N HCl (Le Mignot et al., 2017).

219 <u>3.4 Sample preparation and digestion protocols for Re-Os dating</u>. 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 µg fragments of pure rammelsbergite, after 224 addition of weighed amounts of ¹⁸⁵Re-¹⁹⁰Os mixed isotope tracer (spike). Rammelsbergite appears to passivate in 225 concentrated HCl, but dissolves in HCl - HNO₃ mixtures. Thus to dissolve the rammelsbergite, 8 ml reversed 226 aqua regia (6 ml 14 M HNO₃ 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 OsO_4 at this stage cannot be fully excluded, potentially leading to scatter 230 of the ¹⁸⁷Os 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 H₂O₂ 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 °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 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 µl of HBr was loaded onto Re-free Pt filaments with 245 Ba(OH)₂ - NaOH as an emission activator. Isotope ratios of Os were measured as OsO₃ 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 3-5 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 ¹⁸⁷Os concentrations by isotope dilution. Instrumental mass fractionation was corrected iteratively simultaneously with the oxide contribution, assuming that the true ¹⁹²Os/¹⁸⁸Os ratio of the spiked sample 250

251 lies on a mixing line between the natural ($^{192}Os/^{188}Os = 3.08271$) and the spike ($^{192}Os/^{188}Os = 5.00736$) 252 composition. Radiogenic Os ($^{187}Os^*$) was corrected for a contribution of common Os, assuming a $^{187}Os/^{188}Os$ ratio 253 of 0.5 ± 0.4, and the uncertainty on this ratio is included in the combined uncertainty on $^{187}Os^*$. The ^{187}Re decay 254 constant (λ ^{187}Re) used for the age calculation is 1.666 10⁻¹¹ 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 HNO₃. 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 HNO₃ media, the matrix was eluted using 0.8 M HNO₃, and after that Re was collected with 8 M HNO₃. Measurements of ¹⁸⁷Re/¹⁸⁵Re ratios for isotope dilution calculations in rammelsbergite, the Henderson 259 260 molybdenite reference material and blanks were carried out using an XSeriesII (Thermo Scientific, USA) quadrupole-based ICP-MS unit. Instrumental mass fractionation was corrected for with a sample-standard 261 bracketing approach using a Re standard solution of natural isotopic composition (taken as ${}^{187}\text{Re}/{}^{185}\text{Re} = 1.6738$). 262

Total procedural blanks were 0.08 - 3 pg for radiogenic ¹⁸⁷Os^{*} and 0.01 - 0.5 ng for Re, representing less than 1% 263 compared with the quantities of 187 Os (0.47 – 5.6 ng) and Re (35 - 430 ng) analysed in the rammelsbergite samples 264 265 (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 ± 0.34 Ma and 27.98 ± 0.31 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 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**

4.1. μXRF, μ-tomography and EMPA results. Micro XRF 2D mapping of the entire 2.5 cm epoxy mounts with
the embedded WC287 samples from the 420.1 and 420.7 m depth levels (Figure 2A) reveals inhomogeneous
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). The cobalt content varies mostly between 0.88 and 1.72 wt.% Co, with one exceptional analysis at 4.85 wt.% Co 281 282 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 ±1.2 wt% for WC287 420.1 and 0.64 ±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.

2924.2 U-Pb isotope data on the U oxides. The results of the U-Pb and Pb-Pb SIMS measurements of the U oxides293embedded in the WC530 massive rammelsbergite vein (Fig. 3) are presented in Figure 5. An upper intercept294discordia age of 1255 ± 71 Ma (n = 15, MSWD = 12) was calculated using model 1 of Ludwig's Isoplot 3.7 (York,2951966; Ludwig, 2008). All analyses display variable degrees of discordancy, indicating post-crystallization296alteration as visible in Figure 3B. The discordia is interpreted to represent the age of crystallization of the uranium297crystals at 1255 Ma, followed by a lead loss event at 242 Ma (calculated age for the lower intercept).

 $\frac{4.3 \text{ Re-Os isotope data}}{1000 \text{ Re are or sisotope data}}$ The results of ID-NTIMS Os measurements and ID-ICP-MS measurements of Re are presented in Table 2. Rammelsbergite contains high and variable amounts of Re, ranging from 63 ng g⁻¹ to 1.6 µg g⁻¹. The Os in rammelsbergite samples consists almost entirely of radiogenic ¹⁸⁷Os, ranging from 0.8 to 22 ng g⁻¹, while having minimal common Os (9 to 42 pg g⁻¹ of ¹⁸⁸Os, equivalent to ¹⁸⁷Os/¹⁸⁸Os ratios of 94-3442).

<u>4.4 Chronological interpretation of the ¹⁸⁷Re-¹⁸⁷Os isotope data</u>. Figure 6 A shows ¹⁸⁷Os* plotted against ¹⁸⁷Re for
the 13 chips prepared from the 4 rammelsbergite samples (WC530, WC287 420, WC287 420.1 and
WC287 420.7). The data plotted in a conventional ¹⁸⁷Os/¹⁸⁸Os vs. ¹⁸⁷Re/¹⁸⁸Os isochron diagram are presented in
figure 6B. As these two approaches provide nearly identical ages, while the latter is associated with large
propagated uncertainties due to low ¹⁸⁸Os abundance and high blank contribution for this isotope, we only discuss
the results calculated with ¹⁸⁷Os* - ¹⁸⁷Re diagram hereafter. This is in line with recommendation of Stein et al.
(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 ± 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 ± 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 >> 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 ± 43 Ma and median of 331 1257.2, once the result of WC287 420.7 B is cancelled as an outlier.

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

336 <u>5.1 Applicability of Re-Os geochronology to rammelsbergite.</u> This work presents, to our knowledge, the first
 337 application of the ¹⁸⁷Re-¹⁸⁷Os chronometer to rammelsbergite (NiAs₂), and one of the few attempts to date

arsenides using this system. Concerning the other arsenide minerals, ¹⁸⁷Re-¹⁸⁷Os system was previously used to 338 date löllingite (FeAs₂) by Saintilan et al. (2017), arsenopyrite (FeAsS) by Arne et al. (2001) and Morelli et al. 339 340 (2005, 2007), and Co-arsenopyrite by Mikulski et al. (2005). The rammelsbergite from the Cigar Lake U deposit is specifically characterised by elevated and variable Re contents, up to nearly 2 µg g⁻¹, and very little common 341 342 Os (up to 0.04 ng g⁻¹ of ¹⁸⁸Os, see Table 2). The low abundance of common non-radiogenic Os, the large relative amounts of Re and its variable concentrations (Table 2) make rammelsbergite an excellent target for ¹⁸⁷Re-¹⁸⁷Os 343 dating. Compared to the other tested arsenide minerals, rammelsbergite is more suitable for ¹⁸⁷Re-¹⁸⁷Os dating 344 345 than e.g. arsenopyrite or löllingite, which can contain large amounts of common Os (e.g. löllingite from the Broken Hill Pb-Zn-Ag deposit in Australia contains up to ~26 ng g^{-1} of ¹⁸⁸Os, calculated from data in Saintilan et al. 346 347 (2017)) or be characterized by relatively low levels of parent Re (below 12 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 ¹⁸⁷Os* 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 ± 71 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 Ma model age for the fragment of WC530 (Table 2) and with the Re-Os 1239 +33/-20 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.

The isotopic data for rammelsbergite plot very close to a straight line in 187 Os – 187 Re space (Figure 6) whereas several hydrothermal fluid circulation events occurred in the Cigar Lake U deposits after the crystallization of the rammelsbergite (ca. 1170 Ma, ca. 900 Ma, ca. 320 Ma, ca. 250 Ma and ca. 40 Ma) and perturbed the isotopic systems of both uranium oxides (*e.g.* at 242 Ma, see Figure 5 and Martz et al., 2019b) and clays (Fayek et al., 2002; Kaczowka, 2017; Philippe et al., 1993). Such linearity indicates the resistance of rammelsbergite to gain or loss of Re or incorporation of common Os and/or radiogenic Os loss after its initial crystallization. Tests now need to be done on rammelsbergite from other types of deposits, from the Athabasca Basin and elsewhere, including
those formed under different conditions to confirm the global applicability of the Re-Os isotopic system for dating
of this mineral and related Ni mineralization.

371 5.2 Chemical and isotopic heterogeneities of massive rammelsbergite. µXRF 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 ¹⁸⁷Re-¹⁸⁷Os dating of this phase, allowing for construction of single-mineral ¹⁸⁷Re-¹⁸⁷Os isochrons as is classically done for molybdenite 376 377 (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 occuring 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 +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 ¹⁸⁷Re-¹⁸⁷Os 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 ¹⁸⁷Os 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, common Os was measured and is later corrected for assuming a ${}^{187}\text{Os}/{}^{188}\text{Os}$ ratio of 0.5 ± 0.4 . However, if common 392 393 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.

Finally, some of the scatter in the isochron diagram could result from the fact that Re and ¹⁸⁷Os may not enter into 397 398 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), ¹⁸⁷Os 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.

These different possibilities of scatter need to be constrained, but the first results on rammelsbergite clearly demonstrate that this mineral presents a high potential for use in Re-Os geochronometry. The diversity of geological contexts in which rammelsbergite can be found, from magmatic to hydrothermal conditions, and its possible future significance as a source of nickel, could allow a rapid development of its use to constrain geological models, as demonstrated below for the unconformity-related U deposits. In this context rammelsbergite could 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.

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

417 The 1239 +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, sufides 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).

Another possibility is that the massive veins of rammelsbergite are secondary and do not represent rammelsbergite 434 435 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 1239 Ma event, which reset the ¹⁸⁷Re-¹⁸⁷Os system and crystallized massive rammelsbergite veins. This scenario 438 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 439 440 (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 primary Ni arsenides would acquire significant amounts of ¹⁸⁷Os by radiogenic ingrowth. We cannot completely 442 443 exclude a secondary origin for the massive rammelsbergite, because near-zero initial ¹⁸⁷Os/¹⁸⁸Os 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.

Despite the elevated uncertainty on the ¹⁸⁷Re-¹⁸⁷Os age found for Cigar Lake rammelsbergite, our data strongly suggest that the endowment of Ni, Co, S and As in unconformity-related U deposits of the Athabasca Basin is linked to the Mesoproterozoic magmatic event responsible for the emplacement at 1269 Ma of the Mackenzie large igneous province (LIP) over a vast area of northern Canada and Russia (LeCheminant and Heaman, 1989). The Mackenzie LIP is represented by the mafic-ultramafic layered Muskox intrusion (1269 \pm 2 Ma, Mackie et al., 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 ± 2 Ma to 1268.5 ± 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 ¹⁸⁷Re-461 ¹⁸⁷Os age of 1239 +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 (± 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 (NiAs₂), 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 μ g g⁻¹) and variable Re contents, coupled with a near absence of common Os, making this 509 mineral an ideal candidate for ¹⁸⁷Re-¹⁸⁷Os 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 ¹⁸⁷Re-¹⁸⁷Os isotope system applied to rammelsbergites from various economically important ore deposits throughout the world may thus serve as a powerful dating tool. This study demonstrates that the Re-Os 514

chronometer can be applied to rammelsbergite in ore deposits where molybdenite is rare or absent, and suggeststhat 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 ¹⁸⁷Re-¹⁸⁷Os 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 +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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792 Tables

		S wt %	Co wt %	Ni wt %	As wt%
	#1	< 0.07	0.89 ± 0.11	28.51 ± 0.61	71.4 ± 1.4
gite	#2	< 0.08	1.02 ± 0.12	27.97 ± 0.60	71.1 ± 1.4
erg	#3	< 0.08	0.79 ± 0.11	28.01 ± 0.60	70.76 ± 1.4
llsb n)	#4	< 0.08	0.45 ± 0.10	27.92 ± 0.60	71.3 ± 1.4
me 7 n	#5	< 0.08	0.39 ± 0.10	27.98 ± 0.60	71.2 ± 1.4
am 20.	#6	< 0.07	0.82 ± 0.11	27.83 ± 0.60	71.1 ± 1.4
7 7 (4)	#7	< 0.08	0.26 ± 0.09	28.04 ± 0.60	71.3 ± 1.4
58	#8	< 0.09	0.38 ± 0.09	28.48 ± 0.61	71.4 ± 1.4
AC VC	#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
average	420.7	-	0.64 ± 0.27	28.09 ± 0.31	71.2 ± 0.21
m					
	#11	< 0.09	1.05 ± 0.12	27.36 ± 0.59	71.3 ± 1.4
jite	#12	0.08 ± 0.07	1.72 ± 0.14	27.33 ± 0.59	71.1 ± 1.4
erg	#13	< 0.09	1.24 ± 0.12	27.22 ± 0.59	71.3 ± 1.4
dsl (r	#14	< 0.08	0.88 ± 0.12	27.16 ± 0.59	71.4 ± 1.4
n n 1	#15	0.08 ± 0.08	1.00 ± 0.12	27.05 ± 0.58	71.0 ± 1.4
20.	#16	0.09 ± 0.07	1.00 ± 0.12	27.25 ± 0.59	71.2 ± 1.4
7 ri (4)	#17	< 0.07	4.85 ± 0.21	23.04 ± 0.53	71.0 ± 1.4
58	#18	< 0.09	1.50 ± 0.13	27.13 ± 0.59	71.2 ± 1.4
AC VC	#19	< 0.09	1.03 ± 0.12	26.66 ± 0.58	71.3 ± 1.4
2	#20	<0.08	1.01 ± 0.12	26.72 ± 0.58	71.3 ± 1.4
average	420.1	_	1.53 ± 1.2	26.69 ± 1.3	71.2 ± 0.14
m					

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

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	Blank	¹⁸⁸ Os, pg g ⁻¹	¹⁸⁷ Os/ ¹⁸⁸ Os	¹⁸⁷ Re/ ¹⁸⁸ Os	rho	¹⁸⁷ Os [*] radiogenic,	Re, ng g ⁻¹	¹⁸⁷ Os/ ¹⁸⁷ Re	Model age
	weight,	contribution					ng g ⁻¹			
	mg	on ¹⁸⁷ Os*								
		radiogenic,								
		%								
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	$1\ 242.6\pm 8.5\ Ma$
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	$1~307\pm12~\mathrm{Ma}$
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	$1\ 270\pm12\ Ma$
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	$1\ 259.8\pm 5.8\ { m Ma}$
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	$1\ 268.2\pm 5.0\ Ma$
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	$1\ 231.4\pm 5.9\ Ma$
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	$1\ 227.6\pm 8.8\ Ma$
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	$1\ 265.4\pm9.8\ { m Ma}$
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	$1 350.6 \pm 5.5 \text{ Ma}$
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	$1\ 266.7\pm 5.6\ Ma$
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	$1\ 246.9\pm 6.4\ Ma$
Henderson a	73	0.2	3.6 ± 2.4	920 ± 610	2000000	0.9999	3.350 ± 0.027	11280 ± 100	0.0004700 ± 0.0000028	28.21±0.34 Ma
					± 1300000					
Henderson b	118	0.1	2.2 ± 1.3	1490 ± 890	3200000	0.9999	3.220 ± 0.018	10930 ± 110	0.0004663 ± 0.0000026	27.98±0.31 Ma
					± 1900000					

798 Table 2. ¹⁸⁷Re-¹⁸⁷Os 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 Os^{*} stands for radiogenic only 187 Os, corrected for a contribution of common Os, assumed to have a 187 Os/ 188 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



Fig. 1 The 417.4 – 421.6 m section of the WC287 drill core, Cigar Lake U deposit (Saskatchewan, Canada). A)
Massive U oxide and rammelsbergite vein at 419.1 – 419.3 m depth. B) Association of massive U oxides and
rammelsbergite veins at 419.9-420.1 m. C) Rammelsbergite vein at 420.6-420.8 m depth. Red stars correspond to
the locations of the three samples analysed (420.0, 420.1 and 420.7). The bottom part of the figure shows an
expanded view of each of the three sampled intervals. The number given above each interval of 10 cm is the total
counts per second of radioactivity measured by a hand scintillometer. The last sample of a massive rammelsbergite
vein was taken from the WC530 drillhole in the Cigar Lake deposit area, at 457.2 m.



Fig. 2 A) μ XRF element distribution intensity maps of the two rammelsbergite samples from 420.1 m (left) and 812 813 420.7 m (right) depth levels of the WC287 drill core, Cigar Lake U deposit (Saskatchewan, Canada). Arsenic K_{α} 814 intensity distribution maps are shown on top, and Co K_{α} intensity distribution maps are presented on the bottom. 815 The insert shows an expanded Co K_{α} intensity distribution map measured on a pure rammelsbergite area of sample 816 WC287 420.1, free of visible clay contamination, which demonstrates an inhomogeneous distribution of Co within 817 rammelsbergite. B) Micro X-ray tomography cross-sections of three different fragments of rammelsbergite from 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 gersdorfitte (Gersd) from another drill hole at the Cigar Lake U deposit (CIG 259-1).



821

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).



826

Fig. 4 EMPA maps and chemical analyses of 4 different locations for two samples (WC287 420.1 and WC287 420.7) of pure rammelsbergite from the WC287 drill core, Cigar Lake uranium deposit, Athabasca Basin (Saskatchewan, Canada). BSE images are shown to the left, and the areas corresponding to element maps (Co and Ni) are highlighted with yellow rectangles. Ni K_{α} intensity distribution maps are shown in the right column and quantitative Co element distribution maps (in wt.%) of the same region in the middle column. The numbered spots refer to the locations where quantitative *in situ* spot analyses were made (Table 1). To see this figure in colour, the reader is referred to the online version of the manuscript.



Fig. 5 Wetherill's Concordia diagram for 15 U-Pb analyses measured for the uranium oxides crystallized within
the massive rammelsbergite vein, Cigar Lake deposit (Saskatchewan, Canada), sample WC530, 457.2 m (c.f.
Figure 3).



839

Fig. 6 A - ¹⁸⁷Re - ¹⁸⁷Os isochron plot for the 13 fragments of rammelsbergite from WC287 and WC530 drillholes, Cigar Lake U deposit, Athabasca Basin (Saskatchewan, Canada). The WC287 samples from 420, 420.1 and 420.7 m are shown with green, yellow and blue diamonds respectively, and the WC530 sample with light blue. The insert in the upper left shows probability distribution histogram of the individual model ages, with a mean age of 1257 ± 43 Ma (12 individual ages, WC287 420.7 B considered as outlier). Error bars represent the total 2SE analytical uncertainty due to the isotopic measurements and blank corrections (see text for details). The isochron shown with the solid line and corresponding error envelope represents a solution on 12 points using regression of

- 847 York (1966) excluding one outlier (WC287 420.7 B, marked in red), (calculated using model 1 of Isoplot 3.7 848 (Ludwig, 2008)). Due to the scatter of the data, which greatly exceeds that which can be explained by the assigned 849 analytical uncertainties (MSWD = 30), a robust regression solution (dashed line) is preferred. B – when presented 850 in 187 Os/ 188 Os – 187 Re/ 188 Os isochron space, the data provide similar crystallization ages within associated
- uncertainties.

852 Captions for tables and figures.

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

Table 2. 187 Re- 187 Os isotope data and model ages of rammelsbergite for the 13 selected fragments of rammelsbergite from Cigar Lake uranium deposit, Athabasca Basin (Saskatchewan, Canada). 187 Os^{*} stands for radiogenic only 187 Os, corrected for a contribution of common Os, assumed to have a 187 Os/ 188 Os ratio of 0.5 ±0.4. All uncertainties are 2SE. All data are blank corrected and uncertainties include the uncertainties on the blank value and on the assumed common Os isotopic composition.

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