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▶ To cite this version:

Pierre Martz, Julien Mercadier, Julien Perret, Johan Villeneuve, Etienne Deloule, et al.. Post-crystallization alteration of natural uraninites: Implications for dating, tracing, and nuclear forensics. Geochimica et Cosmochimica Acta, 2019, 249, pp.138-159. 10.1016/j.gca.2019.01.025 . hal-02334117

HAL Id: hal-02334117 https://hal.science/hal-02334117

Submitted on 21 Oct 2021

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Version of Record: https://www.sciencedirect.com/science/article/pii/S0016703719300493 Manuscript a060ee5f51dec6ded45cf5c003108ca3

1 Post-crystallization alteration of natural uraninites: implications

2 for dating, tracing, and nuclear forensics

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13

14 Abstract

This study presents systematic chemical (U, Pb, Ca, Si, Fe) mapping coupled with *in situ* analyses of major, minor and trace elements, U/Pb, ²⁰⁷Pb/²⁰⁶Pb, and O isotopic compositions of natural uraninites (UO₂) from two samples of the high-grade uranium ore from the Cigar Lake unconformity-related uranium deposit (Athabasca Basin, Saskatchewan, Canada).

19 The studied uraninites are characterized by major chemical and isotopic heterogeneities 20 expressed at small scale (μ m to tens of μ m), from almost pristine zones to strongly altered 21 material. The ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U ratios of the different areas are widely spread and 22 depict two similar and well-defined Discordia, providing an upper intercept age of 23 crystallization at ca. 1300 Ma (1299 ± 4 and 1308 ± 14 Ma, respectively) and similar lower 24 intercepts at 38 ± 13 and 72 ± 22 Ma, respectively.

25 The freshest areas are characterized by sub-concordant ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U ratios,

26 identical chemical compositions and similar very low δ^{18} O values (-39.3 to -31.4 ‰). These

data indicate that the two uraninites both crystallized at ca. 1300 Ma, from the same fluid andunder identical physico-chemical conditions.

29 Alteration is characterized by i) the progressive incorporation of Ca, Si, and Fe, reaching 30 several wt. %, which substitute to the radiogenic Pb and cause a progressive decrease in the 31 Pb/U isotopic ratios. The radiogenic Pb is also substituted by water during the alteration, ii) 32 concomitant variations in trace element contents (As, Mn, V, LREEs, Sr, Th, B, Ba, Nb, for example) and iii) heavier δ^{18} O signatures (-22.5 to -8.91 ‰), typical of meteoric waters, in the 33 34 altered zones. This combined approach demonstrates that fluid-driven post-crystallization 35 exchanges affected each uraninite during recent fluid flow events (ca. 40 Ma and 70 Ma 36 respectively). The relatively high dispersion of the Pb/U ratios in relation to the Discordia for 37 both samples is considered as linked to a local (nm to µm-scale) differential mobility between 38 lead and uranium within the uranium oxides.

The chemical changes affecting elements previously considered as immobile in uraninite, such as REEs, indicate that these elements are not preserved during the post-crystallization alteration process studied here. Alteration processes may therefore have a major impact on the classical geochemical tracers, such as REE patterns or LREE/HREE ratios, currently used in nuclear forensic studies. The isotopic and chemical tracers currently used to track back the origin, age and history of natural uraninites should therefore be considered with a high degree of caution to avoid misleading and erroneous conclusions.

Moreover, the comparison of calculated U-Th-Pb chemical, ²⁰⁷Pb/²⁰⁶Pb, and Pb/U isotopic 46 47 ages shows that the use of age clustering for determining U-Th-Pb chemical ages and ²⁰⁶Pb/²⁰⁷Pb ages is not appropriate for constraining crystallization stage(s) of altered uraninites 48 49 and for deciphering the different fluid events that potentially altered or recrystallized the 50 uraninites over time. This study also indicates that estimation of the crystallization age of 51 uraninite from substitution trends of Pb to Ca is not applicable to unconformity-related U 52 deposits and results in overestimated ages because of an initial integration of calcium in the 53 uraninite lattice at the time of crystallization.

54

55 Keywords

uranium oxides, uraninite, forensic, rare earth elements, uranium deposits, chemical
substitution, alteration, U-Pb dating, geochronology

58

59 Highlights

60 - Post-crystallization interactions between uraninites and fluids can result in strong chemical

61 (major, minor, trace element) and isotopic (U-Pb-O) heterogeneities.

- U-Th-Pb chemical and ²⁰⁷Pb/²⁰⁶Pb clustering ages should be used with caution as they may
represent clusters of analyses of similar alteration intensity rather than distinct fluid flow
events.

Elements that have been considered immobile, like REEs, may in fact be significantly
affected by fluid-driven post-crystallization interactions.

67

68 **1. Introduction**

69 Uraninite (ideally UO_2) is the most common uranium oxide present in uranium deposits and 70 always contains, in varying proportions, "impurities" such as Pb, Ca, Si, Th, Zr, Fe, and Rare 71 Earth Elements (REEs), in such a way that its chemical formula should be written more realistically as $(U^{4_{+}}_{1-x-y-z-v}U^{6_{+}}_{x}REE^{3_{+}}_{y}M^{2_{+}}_{z}\Box^{4_{-}}_{v})O_{2+x-(0.5y)-z-2v}$ (Janeczek and Ewing, 1992b)). 72 73 This chemical variability, coupled with isotopic variations (U, O, Pb, Sr), has been used in a 74 increasing number of scientific studies to provide new constraints on different aspects of the 75 nuclear cycle, whether concerning the geological conditions at the origin of uranium deposits, 76 the classification of uranium deposits, or nuclear forensic issues for both uranium ore and 77 mill concentrates (Frondel, 1958; Leroy and Holliger, 1984; Fryer and Taylor, 1987; Pagel et 78 al., 1987; Fayek and Kyser, 1997; Keegan et al., 2008; Varga et al., 2009; Brennecka et al., 79 2010; Varga et al., 2010; Fayek et al., 2011; Mercadier et al., 2011; Keegan et al., 2012; 80 Depiné et al., 2013; Lach et al., 2013; Frimmel et al., 2014; Uvarova et al., 2014; Alexandre et 81 al., 2015; Balboni et al., 2016; Macmillan et al., 2016b; Varga et al., 2017; Spano et al., 82 2017). The dominant hypothesis of these studies is that the chemical and isotopic 83 compositions measured in natural uraninites today directly reflect their original compositions 84 as determined by the conditions of crystallization. It is on this basis, and on the quasi-85 systematic measurements of major, minor and trace elements and their possible isotopic 86 values in natural uraninities in recent years, that the current geological and forensic 87 classifications have been proposed. Such an assumption is particularly emphasized for minor 88 and trace elements like the REEs, providing confidence in their use as provenance indicators 89 or as tracers of the original geological conditions of formation (Fryer and Taylor, 1987; Pagel 90 et al., 1987; Keegan et al., 2008; Varga et al., 2010; Mercadier et al., 2011; Keegan et al., 91 2012; Depiné et al., 2013; Lach et al., 2013; Frimmel et al., 2014; Alexandre et al., 2015; 92 Balboni et al., 2016; Spano et al., 2017). The significant variations potentially measured in the 93 minor and trace elements at the scale of one crystal, one deposit or one deposit type 94 (Mercadier et al., 2011; Frimmel et al., 2014; Alexandre et al., 2015; Balboni et al., 2016; 95 Varga et al., 2017; Spano et al., 2017) have however not been discussed, except for recent 96 small-scale observations done for the Olympic Dam deposit (Australia; Macmillan et al., 97 2016a; 2016b) and are considered to be related to genetic processes even though the genetic 98 models for a vast majority of the uranium deposits have not been properly constrained (Cuney 99 and Kyser, 2015).

100 Uraninite is nevertheless known to be one of the mineral phases most likely to be affected by 101 post-crystallization processes (Isobe et al., 1992; Janeczek and Ewing, 1992a; Fayek and 102 Kyser, 1997; Finch and Murakami, 1999; Fayek et al., 2000a; Kempe, 2003; Alexandre and 103 Kyser, 2005; Deditius et al., 2007; Clauer et al., 2015; Macmillan et al., 2016b; Macmillan et 104 al., 2016a). These post-crystallization processes, which are mainly linked to late fluid 105 circulation events, are observed within individual uraninite crystals and induce for example 106 major changes in the major element contents, with the incorporation of Ca, Si, and Fe at up to 107 several wt. % through cationic substitution to radiogenic Pb (Kempe, 2003; Alexandre and 108 Kyser, 2005; Macmillan et al., 2016b; Ozha et al., 2017). Post-crystallization O isotopic 109 exchanges in uraninites have also been demonstrated (Kotzer and Kyser, 1993; Fayek et al.,

2002a; Fayek et al., 2011). Unlike for the major elements, the cation substitution processes for
minor and trace elements in uraninite have barely been studied with the exception of Deditius
et al. (2007) and Macmillan et al. (2016a).

113 The cationic substitutions of radiogenic Pb in uraninites affected by post-crystallization 114 alteration, coupled with the calculation of U-Th-Pb chemical ages by EMPA (Bowles, 1990), 115 have been proposed as a dating tool for i) the crystallization of the uraninite, and ii) the 116 different fluid events that may have affected the uraninites (Alexandre and Kyser, 2005; 117 Cloutier et al., 2009; Dieng et al., 2013; Pal and Rhede, 2013; Dieng et al., 2015; Ozha et al., 2017). On this basis, in situ measurements of the U-Pb and ²⁰⁷Pb/²⁰⁶Pb isotopic ages coupled 118 119 with U-Th-Pb chemical ages are currently considered to be the most suitable way to 120 determine the crystallization age of the uraninite and the timing of thermal and tectonic events 121 that generate fluid circulations and modification of the isotopic and chemical compositions of 122 uraninites. Such a methodology has been for example extensively applied to unconformity-123 related U deposits (Canada and Australia) and has led to the highly controversial proposal that 124 their exceptional grades and tonnages could be linked to a succession of several major fluid 125 episodes between ca 1.7 Ga and the present (Jefferson et al., 2007; Kyser and Cuney, 2015; 126 Skirrow et al., 2016).

127 The mechanisms that control and affect the incorporation and exchange of elements in natural 128 uraninite, and their impact on the applicability of chemical and isotopic tracers, remain poorly 129 understood. This knowledge is however essential in order to use, in a valuable way, the 130 chemical and isotopic compositions of uraninites to trace and date this mineral and subsequent 131 related products of the nuclear cycle. To address this same problematic, many new emerging 132 methodologies have been proposed for zircons such as atom probe tomography (Valley et al., 133 2014; Piazolo et al., 2017) or crystal-scale age mapping (Chew et al., 2017). The common 134 power of these new methodologies lies in the possibility to study and understand the small-135 scale chemical and structural variations of the studied mineral. Following this philosophy, the

136 present study aims at demonstrating the effect of post-crystallization alteration on the major 137 and trace element, Pb and O isotopic compositions of natural uraninite, and its impact on 138 elemental tracing and on the U-Th-Pb chemical and isotopic dating applications. Two samples 139 of massive uraninities from the Cigar Lake unconformity-related deposit (Saskatchewan, 140 Canada) have been selected for this objective. These two samples were carefully examined 141 using small-scale and *in situ* methods to provide a µm-scale cartography (scanning electron 142 microscopy, SEM), structural determinations (Raman spectroscopy), major (electron probe 143 micro- analyses, EPMA), minor and trace (laser ablation inductively-coupled plasma mass spectrometry, LA-ICP-MS) element quantifications, and δ^{18} O, U/Pb and Pb-Pb isotopic ratios 144 145 (secondary ion mass spectrometry, SIMS). Only primary uraninite grains and their alteration 146 counterparts were considered and examined, rejecting potentially newly-precipitated younger 147 uraninite grains (reprecipitated from dissolution of the primary mineralization) and alteration 148 products such as coffinite.

149

150 **2. Materials and methods**

151 Two samples (9672-131 and 9672-162; pictures in Supplementary Materials (ESM-1)) from 152 the high-grade U ore body of the Cigar Lake uranium deposit were selected. These two 153 samples were collected from two freezing holes (SF-910-10 and SF-910-09) drilled during the 154 2015 summer drilling campaign, focused on the East pod of the main U orebody (Phase 1). 155 These two samples display the usual optical and petrographic characteristics of the high-grade 156 U mineralizations known throughout unconformity-related U deposits of the Athabasca Basin 157 (Philippe et al., 1993; Reyx and Rulhmann, 1993; Alexandre and Kyser, 2005), with large 158 crystals of uraninite (>1 mm in diameter) that are favorable for a proper description and study 159 of alteration processes (ESM-1 and description in 3.1). The crystals occur as botryoidal 160 aggregates of UO₂ showing a slightly fibrous aspect in a matrix of intimately mixed illite and 161 sudoite. A suite of sulfide, arsenide and arsenic sulfide minerals, such as chalcopyrite, pyrite, 162 nickeline (NiAs), cobaltite (CoAsS) and gersdorffite (NiAsS) (among others), are commonly

disseminated in the clay matrix, either around the uraninite grains or in fractures that crosscut them. Aluminium phosphate sulphates (APS) can likewise be found in association with this illite-sudoite assemblage. The two samples were spatially separated by a few meters. The geological setting of the Cigar Lake U deposit is not described here but descriptions can be found in the numerous previous studies dedicated to this deposit (Bruneton, 1993; Fayek et al., 1997; Fayek et al., 2002a; Martz, 2017).

169 Polished thin sections were prepared from the two samples and were examined using 170 conventional transmitted and reflected light microscopies and a JEOL J7600F scanning 171 electron microscope (SEM) equipped with an energy dispersive spectrometer and a HITACHI 172 S-4800 SEM at the Service Commun de Microscopies Electroniques et de Microanalyses 173 (SCMEM) of the GeoRessources laboratory (Nancy, France). Major elements were 174 quantitatively measured using a CAMECA SX-100 electron microprobe analyzer (EMPA) at 175 SCMEM. The instrumental calibration was based on natural and synthetic oxides and/or 176 alloys (wollastonite, hematite, olivine, UO₂, ThO₂, PbCrO₄, YPO₄). The analytical conditions 177 were a 10 nA current, an accelerating voltage of 15 kV, counting times of 10 s for Ca, 20 s for 178 U, Si, Fe and Th, and 40 s for Pb, and the size of the spot analysis was about $1\mu m^2$. The 179 detection limits (in ppm) were on average 600 for Si, 850 for Ca, 2000 for Fe, 4500 for Pb, 180 2800 for U and 5000 for Th.

181 Structural determinations were done by Raman spectroscopy at GeoRessources laboratory. 182 The Raman spectra are recorded using a LabRAM HR spectrometer (Horiba Jobin Yvon) equipped with a 600 gr.mm⁻¹ grating and an Edge filter. The confocal hole aperture is of 183 184 1000 μ m, the slit aperture is of 200 μ m. The excitation beam is provided by a Stabilite 2017 185 Ar⁺ laser (Spectra Physics, Newport Corporation) at 514.53 at a power of 200 mW, 186 attenuated by a D1-10% neutral filter in order to avoid thermal degradation of oxide, and 187 focused on the sample using a \times 50 objective (Olympus). Each spectrum is acquired based on a laser focused on a 1 μ m² surface and corresponds to the average of 10 spectra of 30 s of 188 189 acquisition time.

Single-point U-Pb chemical ages for U-bearing minerals were calculated from EMPA data
using the iterative procedure of Bowles (1990). In this procedure, a first age approximation is
obtained from the following equation (1):

193
$$t = \lambda_{238}^{-1} \ln(\frac{{}^{206}Pb}{{}^{238}U} + 1)$$
 (1)

where *t* is the estimated age of mineral closure, and λ_{238} is the decay constant of ²³⁸U. The amounts of ²⁰⁶Pb and ²³⁸U were calculated from the total lead and uranium contents (atomic %).

197 The amount of Pb corresponding to this approximated age is then calculated using:

198
$$Pb = Th \times (e^{\lambda_{232}t} - 1) + U \times [0.99276 \times e^{\lambda_{238}t} - 1 + 0.007196 \times e^{\lambda_{235}t} - 1]$$
(2)

where t (output from equation 1) is the age of mineral closure, λ_{232} , λ_{235} , and λ_{238} are the 199 decay constants of ²³²Th, ²³⁵U, and ²³⁸U, respectively, and Pb, Th, and U are the contents in 200 201 atomic % of these elements. If the calculated lead content from equation 2 is greater than the 202 measured content, the age (t) is then iteratively modified by 10 Ma and then by 1 Ma until the 203 corresponding calculated lead content matches the measured one. The procedure assumes that 204 no U or Th has been reintroduced to or lost from the system, and that no common Pb was 205 present in the mineral during the initial crystallization. The SIMS analyses confirmed that 206 common Pb was not introduced at the time of crystallization or during post-crystallization alteration (extremely low ²⁰⁴Pb/²⁰⁶Pb ratios measured by SIMS, see below). This indicates that 207 208 the procedure proposed is suitable for obtaining chemical age dates from the two selected 209 uraninite samples. Pb, Si, Ca, and U X-ray elemental mapping was carried out on the two 210 samples using a 20 nA current, an accelerating voltage of 15 kV, and a counting time of 10 s 211 for each element. The step size was 3 μ m with a spot size of about 1 μ m².

212

The U/Pb and Pb/Pb isotopic compositions of the two samples were measured with a CAMECA IMS 1270 E7 ion microprobe at the Centre de Recherches Pétrographiques et Géochimiques (CRPG; Nancy, France) based on a method proposed by Deloule et al. (2002) 216 and adapted from the initial protocol developed by Compston et al. (1984) for the U/Pb and 217 Pb/Pb isotopic dating of zircons by SIMS. A 13-kV O⁻ primary ion beam of 3.5 to 10 nA 218 intensity was focussed on a spot of ca. 15 µm diameter. The primary beam was set in 219 Gaussian mode with a raster of 10 μ m. The field aperture was set to 2,000 μ m and the transfer 220 optic magnification was adjusted to 80. Rectangular lenses were activated in the secondary 221 ion optics to increase the transmission at high mass resolution. The energy window was 222 opened at 30 eV, and centred on the low energy side, 5 eV before the maximum value. The 223 activation volume for these conditions is ~ 260 μ m³. A mass resolving power of 5500 was 224 used to fully resolve potential isobaric interferences and an offset of 50 eV was applied during 225 the analyses in order to avoid matrix effects due to mixtures of uraninite and silicate in natural 226 samples. Ions were measured by peak jumping in monocollection mode using the axial Faraday cup (FC) for ²³⁸U and ²³⁸UO and the axial electron multiplier (EM) for ²⁰⁴Pb, ²⁰⁶Pb, 227 ²⁰⁷Pb, ²⁰⁸Pb, and ²⁴⁸ThO. Each analysis consisted of 8 successive cycles. Each cycle began 228 229 with measurement at masses 203.5 and 203.6 to obtain the background measurements for the 230 FC and EM respectively. The background value during our analytical sessions was 0.01 cps and 12,800 cps for the EM and FC respectively. A ²³⁸U/²³⁵U ratio of 137.88 was used to 231 calculate the ${}^{207}\text{Pb}/{}^{235}\text{U}$ ratios based on the measured ${}^{206}\text{Pb}/{}^{238}\text{U}$ and ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ ratios. In the 232 past decades, precise measurements of ²³⁸U/²³⁵U ratios in different minerals, including 233 234 uranium oxides, have shown that the use of the accepted reference value of 137.88 could be 235 incorrect since there are extensive evidences for natural U isotopic variations in those 236 minerals (Weyer et al., 2008; Bopp IV et al., 2009; Condon et al., 2010; Hiess et al., 2012; 237 Chernyshev et al., 2014; Murphy et al., 2014; Andersen et al., 2017). However, measurements 238 performed on different uranium oxides from 8 unconformity-related U deposits of the Athabasca Basin give ${}^{238}U/{}^{235}U$ ratios varying between 137.964 and 138.046, with a mean 239 value of 137.904 ± 0.038 (Uvarova et al., 2014). So, if the latter study shows that the 240 238 U/ 235 U ratio varies, the value of 137.88 remains nonetheless within the uncertainty range 241 242 measured by Uvarova et al. (2014) and can thus be used in the present study. Now, to get a higher reliability in future studies, direct *in-situ* measurement of the 238 U/ 235 U ratio should be performed for each SIMS analysis.

Counting times were 4 s for 203.5, 203.6, ²⁰⁸Pb and ²³⁸U; 3 s for ²⁴⁸ThO and ²³⁸UO; 6 s for ²⁰⁶Pb; 10 s for ²⁰⁴Pb; and 20 s for ²⁰⁷Pb (waiting time of 1 s). The standard used was a uraninite sample from Zambia (Holliger, 1988), which has a given concordant age at 540 \pm 4 Ma (Holliger, 1988; Cathelineau et al., 1990). Internal precisions obtained on the Zambia uraninite during the SIMS analytical sessions were 0.1% and 0.01% for ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb ratios respectively.

251 It is true that because only one reference material with a U/Pb ratio distinct from the analyzed 252 samples has been used, the correction for mass bias may be slightly erroneous and consequently 253 so might be the estimated age (Sharpe and Favek, 2016). However, such slight bias does not 254 change the aim of the present study. Initial data treatment, standardization against Zambia 255 uraninite, calculations of U/Pb and Pb/Pb ratios and related ages, and calculation of errors were done using an in-house Excel spreadsheet at the CRPG and previously used for all peer-reviewed 256 257 publications based on U-Pb SIMS analyses of uranium oxides and zircons carried out at the 258 CRPG for more than 25 years. Error calculation and error propagation assessment are based on 259 the same equations as indicated by Fayek et al. (2000b). Pb/U calibration for the two samples was done based on the linear relationship between ²³⁸U¹⁶O/²³⁸U and ²⁰⁶Pb/²³⁸U ratios on the Zambia 260 261 reference material (Compston et al., 1984). Uncertainties for Pb-U and Pb/Pb ratios and related 262 ages are reported at the 1σ level (ESM-2). Concordia ages and mean square-weighted deviation 263 (MSWD) were calculated using ISOPLOT (Ludwig, 2007). Common Pb corrections were based on the measured ²⁰⁴Pb content using the Pb isotope composition calculated from Stacev 264 265 and Kramers (1975), at the supposed age of the uranium oxide crystallization (value of 1300 Ma used for both samples). The high ²⁰⁶Pb/²⁰⁴Pb ratio (>10,000) obtained for all analytical 266 267 points in the two samples suggests however that common Pb is negligible (ESM-2).

268

269 Minor and trace element, including rare earth element (REE), concentrations were measured 270 with a laser-ablation inductively-coupled-plasma mass spectrometer (LA-ICP-MS) at the 271 GeoRessources laboratory (Nancy, France). The samples were ablated using a 193 nm Geolas 272 Q Plus system with an aperture-imaged Complex 103 ArF excimer laser (Microlas, Göttingen, 273 Germany) equipped with beam homogenization optics. The laser spot sizes were about 32 or 274 44 μ m in diameter and the fluence was ~ 7 J/cm². 200 laser shots were done per analysis, 275 leading to a penetration depth of ~ 20 μ m (considering a penetration depth of 0.1 μ m/laser 276 shot in uranium oxide (Lach et al., 2013)). Ablated particulate material was analyzed using an 277 Agilent 7500c Quadrupole ICP-MS. The transport gas was a mixture of He and Ar, at typical flow rates of 0.5 and 0.8 l.min⁻¹, respectively. All data were acquired as raw counts using 278 279 time resolved mode. Data reduction was performed using Iolite (Patton et al., 2011). Absolute 280 elemental concentrations were obtained using the equation developed by Longerich et al. 281 (1996). The calibration material (external standard) was a SRM NIST 610 glass standard with 282 certified concentrations published by Jochum et al. (2011). A uraninite in-house standard 283 from Mistamisk (Canada), developed for REE analysis by Secondary Ion Mass Spectroscopy 284 (SIMS; Bonhoure et al., 2007), was analyzed to monitor any matrix effect and SRM NIST 612 glass was analyzed to monitor the precision and accuracy of the measurements. The 285 286 matrix effects present when quantifying the REEs in a uraninite using SRM NIST 610 are 287 limited (<15%; Lach et al., 2013) and are considered to be in the same range as for the other 288 measured minor and trace elements in the present study, as previously proposed by Frimmel 289 et al. (2014) and Alexandre et al (2015). The internal standard was the U content, measured 290 by EMPA. The U concentration used was adjusted according to the type of zone analyzed (the 291 freshest or the altered ones), with values between 68.3 and 76.6 wt. % U as obtained by 292 EPMA data (ESM-2). The methodology used is modified from Lach et al. (2013). A series of 33 elements were analyzed for each experiment: ¹¹B, ⁴⁷Ti, ⁵¹V, ⁵²Cr, ⁵⁵Mn, ⁵⁹Co, ⁶⁰Ni, ⁶⁹Ga, 293 ⁷⁵As, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹³Nb, ⁹⁵Mo, ¹²¹Sb, ¹³⁷Ba, the 14 REEs, ¹⁸²W, ²⁰⁹Bi, ²³²Th, and ²³⁸U 294 295 (internal standard). The analytical precision was calculated for all elements analyzed using the

296 standard deviation of the recorded intensity and was better than \pm 20%. The accuracy was controlled based on the analyses of the two cross-calibration standards, i.e. SRM NIST 612 297 for all the elements and the Mistamisk uraninite for the REEs, following the methodology of 298 299 Lach et al. (2013), and was typically within 20% relative difference of the reference values. 300 The limit of detection (LOD) varies for each element and each analysis as a function of signal 301 intensity and was calculated for each ablation from signal intensities using the 3σ criterion 302 (Longerich et al., 1996). The LODs are given when the calculated values for a given element 303 are below these values (ESM-2).

304

 δ^{18} O measurements were performed on sample 9672-131 using a CAMECA ims 1270 ion 305 306 microprobe at CRPG (Vandoeuvre-lès-Nancy, France). Acquisition was performed in 307 multicollection mode with two Faraday Cups. A 2.5-3 nA Cs⁺ primary beam with an impact 308 energy of 20 keV was used. Each analysis spot was around 15 µm in diameter and with 309 penetration depth of ~ 1 μ m. The analysed volumes for U/Pb, Pb/Pb and O isotopic 310 measurements were similar. The mass resolving power m/ Δm was fixed at 7000 in order to resolve ¹⁷OH interference on ¹⁸O (contribution of up to 3% in hydrated uraninite). Each 311 312 analysis consisted of 30 cycles of 5 s, for a duration of 5 min per analysis. Isotopic 313 compositions are reported in ‰ relative to Vienna Standard Mean Ocean Water (V-SMOW) 314 and uncertainties are at the 2σ level. A synthetic UO_{2.1} standard was used for calibration 315 $(\delta^{18}O_{standard} = 8.1 \pm 0.3 \text{ }$; Fayek et al. 2002a). The internal precision obtained on synthetic 316 $UO_{2.1}$ standard was $\pm 0.3\%$ (2 σ) and the external precision on 9672-131 was $\pm 0.3\%$ (2 σ).

- 317
- 318 **3. Results**

319 **3.1.Optical and scanning electron microscopy**

Fig. 1. shows both reflected light optical microscopy photomicrographs and high-contrast
back-scattered electron (BSE) images of the uraninite grains from the two samples selected

322 (9672-131 and 9672-162). The uraninites occur as botryoidal millimeter-scale ribbons 323 (sample 9672-131, Fig. 1a, b, c, d) and nodular/radial aggregates of uraninite (sample 9672-324 162, Fig. 1e, f), and often show a fibrous aspect with serrated grain edges. The grains are 325 embedded in a mixed illite and sudoite (Mg-chlorite) clay mineral assemblage, along with 326 various disseminated sulfides and arsenides. The crystal habits of the uraninites and 327 mineralogical assemblages observed in these two samples are identical to those previously 328 described for primary uraninites at the Cigar Lake U deposit (Reyx and Rulhmann, 1993; 329 Fayek et al., 2002a). Under reflected light, these botryoids, nodules, and ribbons show varying 330 reflectivities, with areas of lower reflectivity located along fractures and grain margins (Fig. 331 1a and e). The low reflectivity areas present irregular shapes and vary in size from microns to 332 hundreds of microns (Fig. 1c and d) and correspond to low brightness regions in BSE images 333 linked to lower average atomic weight (Fig. 1b, c, d and f). The freshest zones considered 334 under reflected light are in fact of varying brightness in BSE pictures at the µm-scale. Sharp 335 contacts are observed between light and dark zones (Fig. 2a, b and c). The variations in BSE 336 brightness indicate variable chemical compositions, with areas of lower average atomic 337 weight reflecting changes in the chemical composition of the uraninite by substitution of 338 heavy elements (Pb) to lighter elements (Si and Ca; Fig. 2e). The structural determination 339 done by Raman spectroscopy at the sub-micron scale confirms that the freshest and altered 340 zones of the uraninities are uranium oxides, the alteration leading to a progressive shift of the second peak (543 to 585 cm⁻¹; Fig. 2d). These in situ elemental substitutions in the uraninite 341 342 are strong but progressive, and lead ultimately to a total conversion of uraninite to secondary 343 uranium minerals, such as coffinite USiO₄ $\cdot n$ H₂O and calciouranoite, CaU₂O_{7 \cdot}SH₂O (Fig. 1c; 344 Fayek et al. 2002a; Alexandre et al. 2005).

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346 3.2.Major element concentrations in freshest and altered zones

The brightest BSE domains of the two uraninite samples (i.e; the freshest zones) arecharacterized by the highest Pb contents and the lowest Ca, Si and Fe contents (Fig. 3). These

349 areas show U contents of around 70 wt. % and high Pb contents of up to 14.7 wt. % (Fig. 4). 350 They contain low Ca (about 0.5 wt. % Ca), and extremely low Si (<0.1 wt. % Si) and Fe (<0.1 351 wt. % Fe) contents, these contents being identical in the two samples. The alteration of the 352 uraninite grains, visible optically and by SEM (Fig. 1 and 2), is characterized by the removal 353 of radiogenic Pb that is compensated for by the incorporation of Ca, Si, and Fe, as observed 354 by X-ray EMPA elemental mapping of the uraninites (Fig. 3) and in situ spot electron 355 microprobe analyses (ESM-2 and Fig. 4). Lead loss can be also compensated by incorporation 356 of minor elements (Mn or As for example; see 3.4) and by water. The Pb concentrations 357 decrease strongly from the freshest (14.7 wt. % Pb) to the more altered regions (0 wt. % Pb 358 around fractures at the edges of the grains; Figs. 1, 2, 3 and 4). In the altered areas of the 359 uraninites, the total lead loss is compensated for by three dominant chemical substitutions of 360 Si, Ca, and Fe, with concentrations up to 2.3 wt. % Ca, 1.7 wt. % Si and 0.7 wt. % Fe (ESM-361 2). The dominantly progressive co-substitution of Pb by Ca and Si is visible in a Ca-Si-Pb 362 ternary diagram (Fig. 4b), the uraninite compositions plotting along a line representing an 363 increasing alteration from the freshest zones (80% Pb, 20% Ca, and 0% Si) to their altered 364 counterparts (0% Pb, 55% Ca and 45% Si). The slopes of the Pb-Ca and Pb-Si substitution 365 trends are different for samples 9672-131 and 9672-161, being -0.46 and -0.61 (Pb-Ca) and -366 0.8 and -0.7 (Pb-Si), respectively (Fig. 4). The coffinite conversion is characterized by a Si 367 increase (up to 5.69 wt. %) coupled with a Ca decrease (down to 0.8 wt. %). The U 368 concentration from the freshest to strongly altered zones range from 76.6 to 69.4 wt. %, 369 respectively (Fig. 4a). This moderate variation indicates that, while U is mobile during the 370 alteration, the overall U content remains conservative, as indicated by the X-ray U elemental 371 maps (Fig. 3). The ultimate conversion from uraninite to coffinite results in a significant drop 372 in the U content (to 61.9 wt. % U; Fig. 4a).

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374 **3.3.U-Pb** and ²⁰⁷Pb/²⁰⁶Pb isotopic compositions and related ages

The ${}^{206}\text{Pb}/{}^{238}\text{U}$ and ${}^{207}\text{Pb}/{}^{235}\text{U}$ isotopic ratios measured in the different zones of the uraninites 375 376 from 9672-131 and 9672-162 samples depict two quasi-identical Discordia lines (Fig. 5), with 377 upper intercept ages of 1299 \pm 4 Ma (102 analyses) and 1308 \pm 14 Ma (66 analyses) and 378 lower intercept ages of 38 ± 13 Ma and 72 ± 22 Ma, respectively. None outliers were removed 379 from the initial dataset. The calculated MSWD are 36 and 49 respectively. The two lower 380 intercept ages are very close considering the calculated errors. The freshest areas, marked by 381 the highest concentrations of Pb (EMPA data and map; Fig. 5), have relatively slightly 382 discordant Pb/U ratios (degree of concordance up to 94.78% for sample 9672-131 and 97.08% 383 for sample 9672-162, red circles on Fig. 5), indicating that these zones were affected by a 384 relatively limited but distinguishable lead loss. Systematic analysis of the different zones of the uraninites demonstrates a progressive decrease in both ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U values 385 386 (from red circles to black circles on Fig. 4) from the freshest to altered zones, in direct 387 correlation with the Pb contents (Fig. 5). The most altered areas (Pb contents ≈ 0 wt. % Pb) 388 have highly discordant values down to the lower intercept of the Concordia (black circles on 389 Fig. 5).

The ²⁰⁷Pb/²⁰⁶Pb ratios for sample 9672-131 lie between 0.060 and 0.085, regardless of the 390 391 alteration degree of the analyzed regions (ESM-2), with most of the values (the 4 lowest values excluded) within a restricted range (0.079 and 0.085). The related ${}^{207}Pb/{}^{206}Pb$ ages are 392 393 between 749 and 1325 Ma, or between 1162 and 1325 Ma (the 4 lowest values excluded), with mean ²⁰⁷Pb/²⁰⁶Pb ages of 1263 Ma (all data) and 1275 Ma (the 4 lowest values excluded). 394 The ²⁰⁷Pb/²⁰⁶Pb ratios for sample 9672-162 are less dispersed than for sample 9672-131, with 395 values of between 0.077 and 0.086 (ESM-2) leading to two populations of ²⁰⁷Pb/²⁰⁶Pb ages: a 396 first population with a mean ²⁰⁷Pb/²⁰⁶Pb age of 1207 Ma and a second population with a mean 397 ²⁰⁷Pb/²⁰⁶Pb age of 1312 Ma. Taking the two populations together we obtain a mean age of 398 1246 Ma for 9672-162. Finally, the mean ²⁰⁷Pb/²⁰⁶Pb age calculated from all data from both 399 400 samples is 1256 Ma.

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3.4. Minor and trace element contents in the freshest and altered regions 402 403 The minor and trace element compositions (measured by LA-ICP-MS) for 9672-131 and 404 9672-162 samples are given with the corresponding concentrations of the major elements 405 (measured by EPMA) in ESM-2 and 3. Minor and trace element concentrations are compared 406 to Pb contents in Fig. 6. The color scale is the same as that used in Figure 5 (red symbols = 407 the freshest zones, black symbols = the most altered zones). Nearly all of the 33 minor and 408 trace elements analyzed have concentrations above the limits of detection (LOD), whether in 409 the freshest or altered zones of the uraninites, with the exception of Cr. Ga, and Ni, whose 410 contents are systematically below the LOD (Cr: 89 ppm, Ga: 5 ppm, Ni: 279 ppm), and Bi 411 (98% above the LOD [4 ppm]), Sb (98% above the LOD [5 ppm]), La (96% above the LOD 412 [1 ppm]), As (85% above the LOD [46 ppm]), Mo (88% above the LOD [13 ppm]), Zr (79% 413 above the LOD [3 ppm]), Co (69% above the LOD [6 ppm]), Ba (58% above the LOD [14 414 ppm]) and B (54% of data above the LOD [127 ppm]). Thus, the minor and trace elements 415 have been incorporated into the uraninites in varying proportions. Excluding Cr, Ga and Ni, 416 all of the minor and trace elements (with the exception of B) have concentrations above the 417 LOD in the freshest zones (i.e. Pb-rich zones), suggesting that they were incorporated in the 418 uraninities at the time of their crystallization. The concentrations of Ti (3850 ± 1525 ppm), Sb 419 $(74 \pm 19 \text{ ppm})$, Zr (69 ± 99 ppm), W (188 ± 54 ppm), Y (942 ± 638 ppm), Lu (5.5 ± 5.5 ppm) 420 and Co (72 ± 94 ppm) are similar in the freshest and altered zones (Fig. 6). The concentrations 421 of the following elements increase from the freshest to the most altered areas: As (increase of 422 2501% in 9672-131 and 568% in 9672-162), Mn (431% in 9672-131 and 493% in 9672-162), 423 V (250% in 9672-131 and 698% in 9672-162), Ce (1007% in 9672-131 and 3713% in 9672-424 162) (the other LREEs behave similarly), Sr (762% in 9672-131 and 1315% in 9672-162), Th 425 (820% in 9672-131 and 257% in 9672-162), B (216% in 9672-131 and from 0 to 240 ppm in 426 9672-162), Ba (from 0 to 68 ppm in 9672-131 and from 0 to 309 ppm in 9672-162) and Nb 427 (425% in 9672-131 and 194% in 9672-162). The concentration increases indicate that these 428 elements substituted for Pb during the alteration of the uraninites, as observed for Ca, Si and

429 Fe. The concentrations of Mo (from about 1000 ppm down to 0 in 9672) and Bi (from about 430 200 ppm down to 0 in 9672-131 and from about 50ppm down to 0 in 9672-162) decrease 431 from the freshest to the altered regions. The concentrations of minor and trace elements in the 432 freshest zones are almost identical in the two samples (except Th, with about 50 ppm in 9672-433 131 against 200ppm in 9672-162, and Ti, with about 3000 ppm in 9672-131 against 5000 434 ppm in 9672-162). For a similar degree of lead loss, concentrations of several elements in the 435 altered areas differ between the two samples. The differences are particularly visible for Ba 436 (about 75 ppm in 9672-131 vs. 300 ppm in 9672-162), As (about 3500 ppm in sample 9672-437 131 vs. 1000 ppm in 9672-162) and V (about 1200 ppm in 9672-131 vs. 850 ppm in 9672-438 162). These differences result in different trends of element substitution between the two 439 samples, as observed for Si and Ca (Fig. 4).

440 As observed for the majority of the elements, REE concentrations in the freshest regions of 441 the two uraninites are identical, leading to identical REE patterns that are characterized by a 442 bell shape, with low contents of LREEs and HREEs compared to MREEs (Fig. 7). This shape 443 is characteristic of uraninities from unconformity-related U deposits (Mercadier et al., 2011; 444 Alexandre et al., 2015). The concentrations of the REEs in altered zones are different than in 445 the freshest zones, with a progressive increase in LREE concentrations observed for example, 446 Ce concentrations increase from around 20 ppm in the freshest regions to 417 and 990 ppm in 447 samples 9672-131 (+ 2085%) and 9672-162 (+ 4950%), respectively (ESM-2 and Fig. 7). 448 Overall, the MREEs show no variation between the two zones, whereas the HREEs are 449 slightly affected by the alteration showing a general decrease (Fig. 7). These changes in 450 concentration result in different LREE/HREE ratios (Fig. 7; LREE/HREE ratios increasing 451 from 0.15 to 0.7 and 1.4 for 9672-131 and 9672-162, respectively) and different total REE 452 contents (increasing from 1350 ppm to 2204 and 8280 ppm for altered regions of 9672-131 453 and 9672-162, respectively) in the freshest and altered regions. These changes in LREE 454 concentrations also induce modifications of the REE spectra and related factors such as 455 LREE/HREE in the freshest and altered zones. As observed for other minor and trace

elements, the concentrations of several LREEs in the altered regions differ between the twosamples (Figs 6 and 7).

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459 **3.5.** δ^{18} O compositions in the freshest and altered regions

The freshest regions of sample 9672-131 display a narrow range of low δ^{18} O values of between -39.35 and -31.42 ‰ (Fig. 8). In contrast, the most altered regions have higher and more dispersed δ^{18} O values (-22.12 to -8.91 ‰). Only one δ^{18} O value was measured for the intermediate degree of alteration (4 wt. % < Pb content < 10 wt. %; Fig. 8), however the available data nevertheless suggest that δ^{18} O increases as the degree of alteration increases.

466 **4. Discussion**

467 The objective of the present study was to characterize the effects of post-crystallization 468 alteration on the chemical and isotopic compositions of natural uraninites based on two 469 samples from the Cigar Lake U deposit. This work is not intended to provide new information 470 about the genetic processes at the origin of the formation of unconformity-related U deposits, 471 in particular the crystallization age of the first uranium mineralization, currently proposed to 472 be 1467 \pm 63 Ma at Cigar Lake (Fayek et al., 2000b). In this respect, the measured Discordia 473 isotopic ages of ca. 1300 Ma for both samples could indicate that 9672-131 and 9672-162 474 uraninites co-crystallized during a secondary U mineralization event. The geochemical 475 characteristics measured in the freshest zones of these uraninites (Ca, Si and Pb contents, 476 minor and trace elements contents, REE patterns and O isotopic values) are however 477 equivalent to those measured in what are considered to be older uraninites from the Cigar 478 Lake deposit (Fayek et al., 2002a; Martz, 2017). Such results suggest that the uraninites from 479 the present study i) probably formed at a different time but under the same physico-chemical 480 conditions as the presumed oldest uraninites at the Cigar Lake U deposit (as confirmed by the 481 identical illite-sudoite-uraninite mineralogical assemblage), and ii) do not correspond to

482 recrystallized and chemically modified older uraninites. If that were the case, the geochemical 483 characteristics would be different than those of the older uraninites (with Si, Ca and Fe 484 substitutions or possible modified REE patterns for example).

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4.1.Implications of post-crystallization alteration for Pb/U, ²⁰⁷Pb/²⁰⁶Pb 487 isotopic dating and U-Th-Pb chemical dating of uraninites

488 Lead loss is the most frequent chemical modification linked to post-crystallization processes 489 described for natural uraninites. This loss is mainly due to the significant differences in the ionic radii and charges of the two elements (respectively, 1.00 Å and 4^+ to 6^+ for uranium 490 (Janeczek and Ewing, 1995); 1.29 Å and 2^+ for lead), which favor i) non-incorporation of Pb 491 492 into the crystal lattice of uraninite during its crystallization (no common Pb), and ii) non-493 incorporation of the radiogenic Pb produced through time by radioactive decay into the crystal 494 lattice, and thus its easy removal from the mineral during interaction between the uraninite 495 and fluid (Alexandre and Kyser, 2005; Macmillan et al., 2016a; 2016b).

496 Uraninite can be thus considered one of the most difficult minerals to date with U-Pb and ²⁰⁷Pb/²⁰⁶Pb isotopic methods or U-Th-Pb chemical methods, even if this mineral is 497 498 theoretically one of the best targets for U-Pb dating due to its high U and Pb contents (wt. %). Uraninite should then be considered as an open system with ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U isotopic 499 ratios and related Pb/U and ²⁰⁷Pb/²⁰⁶Pb ages that are usually not concordant, and whose 500 501 degrees of discordancy are often much higher than 5% for both bulk analysis and *in situ* µm-502 scale measurements acquired by SIMS (Fayek et al., 2002a; Sharpe and Fayek, 2011; 503 Ballouard et al., 2017b) or LA-ICP-MS (Chipley et al., 2007; Alexandre et al., 2007; Cloutier 504 et al., 2009; Cloutier et al., 2011). These characteristics lead to uncertainty in the interpretation of ²⁰⁶Pb/²³⁸U, ²⁰⁷Pb/²³⁵U and ²⁰⁷Pb/²⁰⁶Pb values, even at the scale of a single 505 506 grain, and to debate about the use of these data for calculating ages and proposing geological 507 models for the formation and temporal evolution of uranium deposits. This is, for example, 508 the case for the unconformity-related U deposits in Paleo- to Mesoproterozoic sedimentary

basins in Canada and Australia, for which a very wide spread of Pb/U and ²⁰⁷Pb/²⁰⁶Pb
isotopic ages, of ca 1.7 Ga to the present time, have been calculated (Jefferson et al., 2017;
Kyser and Cuney, 2015; Skirrow et al., 2015). The same limitations affect the use of U-Th-Pb

512 chemical geochronometers for uraninites (Kempe, 2003; Alexandre and Kyser, 2005).

513 One way to overcome these limitations in the calculation of crystallization ages and alteration 514 stages of uraninite for a deposit or uranium province, might be to apply statistical clustering to the different types of measurements, such as ²⁰⁷Pb/²⁰⁶Pb ratios (Kotzer and Kyser, 1993; 515 516 Favek et al., 2002a; Alexandre et al., 2007; Polito et al., 2011) or chemical U-Th-Pb ages 517 (Alexandre and Kyser, 2005; Cloutier et al., 2009; Dieng et al., 2013; Pal and Rhede, 2013; 518 Dieng et al., 2015; Ozha et al., 2017). This type of clustering method has already been applied 519 to different types of U deposits, and especially to unconformity-related U deposits. For these deposits, the clustering approach has provided several ²⁰⁷Pb/²⁰⁶Pb and U-Th-Pb chemical age 520 521 peaks that have been considered representative of different successive fluid events that 522 occurred through time within the basin and affected the uranium budget of the deposits 523 (Fayek and Kyser, 1997; Fayek et al., 2002a; Alexandre and Kyser, 2005; Polito et al., 2011; 524 Sharpe et al., 2015; Sheahan et al., 2016). Based on this interpretation, several fluid 525 circulation events in both the Athabasca and Thelon Basins (Canada) have been proposed to 526 be associated with different near-field events (e.g. the emplacement of the McKenzie dyke 527 swarms at 1.27 Ga) and with different far-field, continent-wide tectonic events, such as the 528 Mazatzal Orogeny (1.6-1.5 Ga), the Berthoud Orogeny (ca. 1.4 Ga), the East Kootenay 529 orogeny (ca. 1.35 Ga), the Grenville Orogeny (1.1 Ga), and the assemblage and break-up of 530 the Rodinia (1-0.85 Ga) (Fayek et al., 2002a; Fayek et al., 2002b; Alexandre et al., 2007; 531 Cloutier et al., 2009; Cloutier et al., 2011; Kyser and Cuney, 2015; Sheahan et al., 2016). 532 The two samples analyzed in the present study are from the unconformity-related Cigar Lake 533 U deposit (Athabasca Basin, Canada). They can be considered as relatively simple cases 534 compared to published data on uraninites from unconformity-related U deposits because the

535 measurements demonstrate a two-stage evolution of the uraninites, with their crystallization at

536 1300 Ma and then their alteration by a meteoric fluid at around 40 Ma (9672-131) and 70 Ma (9672-162) (Fig. 5). This interpretation is considered both analytically and geologically 537 correct, in particular due to the large spread in the ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U ratios that 538 allowed the establishment of well-defined Discordia lines (Fig. 5). The high values of the 539 540 calculated MSWD (36 for 9672-131 and 49 for 9672-162) probably indicate a differential 541 µm-scale mobility of Pb and U within the two studied uraninites, which favor a dispersion of 542 the Pb/U ratios around the Discordia line. The process at the origin of this second-order 543 dispersion has not been defined and is not discussed in the present document, but the authors 544 do not consider it as related to a potential second event of alteration. Such event would have 545 indeed generated a much greater dispersion like what can be observed for the alteration at ca. 546 40 Ma (9672-131) or ca. 70 Ma (9672-162) described in this study. Specific studies based on 547 atomic to nm-scale works (atom probe or TEM for example) would help understanding such 548 distribution. Anyway, this second order dispersion of the Pb/U ratios does not obliterate the 549 first order distribution of the Pb/U ratios controlled by the two-stage scenario. In the 550 discussion that follows, we aim at confronting this robust interpretation of the evolution of these two uraninites with the results obtained from a statistical interpretation of the ²⁰⁷Pb/²⁰⁶Pb 551 552 and U-Th-Pb chemical ages.

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4.1.1. Are U-Th-Pb chemical ages and ages estimated on the basis of elemental substitutions a relevant strategy for uraninites?

The calculated U-Th-Pb chemical ages range from 1308 to 0 Ma for sample 9672-131 and from 1242 to 0 Ma for sample 9672-162, with main statistical peak ages calculated at ca. 1310, 1160, 990, 815, 570, 320, 200, and 60 Ma for sample 9672-131, and at ca. 1160, 980, 790, 650, 420, 320, 200, 120, and 55 Ma for sample 9672-162 (Fig. 9). When compared to calculated upper and lower Discordia intercepts (Fig. 9), these two series of statistical U-Th-Pb chemical age peaks do not present any mathematical or geological relevance; they are

562 related only to the variable degrees of lead loss that affected the different zones of the 563 uraninites during the ca. 40 and 70 Ma alteration events (Fig. 1, 2, 3, 4). The amplitudes and 564 positions of the age peaks are only dependent on the number of analyses performed within the 565 different zones and are thus only analytically-driven. The age peaks therefore correspond not 566 to the different fluid circulation events that could have affected the two samples through time, 567 but only to the variable degrees of lead mobility experienced by the different areas of the 568 uraninities during a single recent alteration event that took place < 51 Ma for 9672-131 569 (considering the error on the lower intercept) and < 94 Ma for 9672-162 (considering the error 570 on the lower intercept). The calculated peaks are similar to those proposed for uraninites from 571 the Athabasca Basin (Alexandre and Kyser, 2005; Cloutier et al., 2009; Cloutier et al., 2011). 572 The geological relevance proposed in these studies from the interpretations of the U-Th-Pb 573 chemical ages are therefore highly questionable. The present observations indicate that the use 574 of U-Th-Pb chemical ages for reconstructing the potential fluid interaction events that have 575 affected uranium deposits (Alexandre and Kyser, 2005; Cloutier et al., 2009; Cloutier et al., 576 2011; Pal and Rhede, 2013; Ozha et al., 2017) is biased and incorrect.

577 Substitution trends in uraninites between Pb and the major elements Ca, Fe, and Si have been 578 applied to calculate the crystallization ages of altered uraninites (Alexandre and Kyser, 2005). 579 This methodology relies on the assumption that the uraninite does not incorporate any 580 elements except U and O at the time of its crystallization, and that other cations (Ca, Si, and 581 Fe) are incorporated into the uraninite during post-crystallization alteration event(s) through 582 substitution with Pb. The method was initially proposed for use with unconformity-related U 583 deposits (Alexandre and Kyser, 2005) and has more and more frequently been used for these 584 deposits (Cloutier et al., 2009; Cloutier et al., 2010) as well as for other types of U deposits 585 (Dieng et al., 2013; Pal and Rhede, 2013; Dieng et al., 2015; Ozha et al., 2017). The 586 application of this method to samples 9672-131 and 9672-162 provided x-axis intercept ages 587 of 1592 and 1712 Ma respectively (using Ca only; Fig. 10), 1210 and 1216 Ma (using Si 588 only), 1430 and 1492 Ma (using Fe only), and 1388 and 1405 Ma (using Si+Ca+Fe). These

589 ages differ according to the substituting element selected and all are inconsistent with the 590 Discordia upper intercept ages and oldest U-Th-Pb chemical ages calculated for both samples 591 (Fig. 9). Moreover, the majority of the ages based on substitution trends are far older than the 592 crystallization age obtained using isotopic measurements (ca. 1300 Ma). The freshest regions 593 in the two uraninites provide U-Th-Pb chemical ages that are identical within error to the 594 Discordia upper intercept age, indicating that lead substitution was strongly limited in these 595 zones. Their current chemical compositions can thus be considered relevant as a marker of the 596 initial chemical composition of the uraninite at the time of crystallization. Ca (0.6 ± 0.2 wt. % 597 Ca) and Fe (0.2 \pm 0.1wt. % Fe) were consequently integrated into the uraninite lattice at the 598 time of crystallization. Such incorporation of up to several weight percent of Ca in uraninites 599 during crystallization is a common process in several types of U deposit (Förster, 1999; 600 Mercadier et al., 2013; Ballouard et al., 2017a; Bonnetti et al., 2018), with contents as high as 601 8 wt. % CaO recorded in fresh uraninites in granite-related hydrothermal deposits (Ballouard 602 et al., 2017a). Ca has a similar ionic radius to U (Shannon, 1976) and the majority of U 603 deposits are believed to have formed from Ca-rich mineralizing fluids or magmas. CaCl₂-rich brines with Ca contents of >2 mol.kg⁻¹ have for example been considered as the mineralizing 604 605 fluids for a number of unconformity-related U deposits (Pagel, 1975; Derome et al., 2005; 606 Richard et al., 2010; Richard et al., 2016). An initial incorporation of Ca in the crystal lattice 607 of the uraninities in unconformity-related U deposits is thus consistent with these findings. Si 608 is the only major element that does not enter the uraninite structure at the time of the initial 609 crystallization, suggesting that use of the U-Th-Pb chemical ages in Si-free areas could 610 provide the less-biased non-isotopic age estimate for the crystallization of uraninite. The use 611 of Ca, Fe or a combination of these elements, in a substitution trend plot results in the 612 calculation of ages older than the age of crystallization. Moreover, the slope of the 613 substitution trends for a given element might be different in contemporaneous samples and 614 could lead to the calculation of two different ages, as exemplified by samples 9672-162 and 615 9672-131. Such differences are thought to be related to local variations in the substitution mechanisms within the deposit and therefore to spatial variations in the alteration process.
The method of using substitution trends for calculating crystallization ages of uraninites can
be thus considered as invalid.

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4.1.2. ²⁰⁷Pb/²⁰⁶Pb ages and the clustering approach

621 The uncertainties that arise when interpreting the discordant isotopic U-Pb values of uranium 622 oxides have led some authors to propose distinct ages of uraninite crystallization based on 623 statistical clusters of ²⁰⁷Pb/²⁰⁶Pb ages obtained sometimes from spot analysis of a single 624 uraninite grain (e.g. in the Sue and McArthur deposit, Fayek et al., 2002b). When applied to 625 this study, sample 9672-131 provides a single age of 1275 Ma whereas sample 9672-162 626 provides two ages of 1207 Ma and 1312 Ma (1246 Ma if grouped together, Fig. 9 and 11a). 627 All three ages are different from the upper intercept age of ca. 1300 Ma. In fact, the definition of discordance implies that clusters of ²⁰⁷Pb/²⁰⁶Pb ages will give erroneous ages if obtained 628 629 from discordant analyses of uraninites that experienced at least one lead loss event ($\neq 0$ Ma). 630 It is true that in a system experiencing a fluid-related lead loss event, the leached Pb leaving the system will have a ²⁰⁷Pb/²⁰⁶Pb composition of the mineral at that time, a time that also 631 corresponds to its ²⁰⁷Pb/²⁰⁶Pb age. If the analyses were made at this exact same moment of 632 lead loss, by definition, the upper intercept age would be identical to the ²⁰⁷Pb/²⁰⁶Pb age. 633 634 However, when the system becomes closed after this event of lead loss, radiogenic Pb is again 635 accumulated, and the isotopic ratio evolves, and the Discordia line will then show a lower 636 intercept age that corresponds to the timing of lead loss (Fig. 11b). In this case, only the upper intercept age is correct and none of the U-Pb or ²⁰⁷Pb/²⁰⁶Pb dates will have any geological 637 638 meaning (Fig. 11). The two Discordia lines obtained for samples 9672-131 and 9672-162 give 639 lower intercept ages of 38 ± 13 Ma and 72 ± 22 Ma, respectively. Therefore, since the lead loss did not occur strictly at the present time, statistical clusters of ²⁰⁷Pb/²⁰⁶Pb dates will be 640 641 skewed by the number of analyses that show similar lead loss intensity (Fig. 11).

642 Consequently, it appears that the older the lower intercept age, the higher the risk of obtaining
 643 skewed ²⁰⁷Pb/²⁰⁶Pb distributions (Fig. 11b).

The work conducted on these two uraninites thus demonstrates that ²⁰⁷Pb/²⁰⁶Pb ages and U-644 645 Th-Pb chemical ages in uraninites, especially when derived from clustering, should not be 646 interpreted to have any geological significance. A misuse of the data, linked to the absence of 647 detailed preliminary petrographic and chemical studies, can directly lead to incorrect 648 geological interpretations that will affect any model proposed for the formation of the U 649 deposit and its evolution through time. In the case of unconformity-related U deposits, the 650 present study does not preclude the possibility that multiple mineralizing and/or remobilizing 651 events affected the uraninites following their crystallization. Investigating this hypothesis 652 further, however, is beyond the scope of the present study. Nevertheless, the study does 653 emphasize the strong effects of fluid-driven post-crystallization alteration on uraninites and 654 thus the need for careful analysis and description of the dated materials for proper 655 interpretation of the isotopic and chemical data.

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4.2.Implications of post-crystallization alteration for geochemical tracing

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of uraninites and related material from the nuclear cycle

659 The systematic measurements of i) the chemical compositions for major, minor and trace 660 elements, and ii) the isotopic compositions (U, O, Pb, Sr) in uraninites from different deposits 661 and different types of deposit revealed significant differences between the uraninites. These 662 differences are considered to be related to variabilities in the physico-chemical conditions that 663 led to the formation of each uraninite, deposit or type of deposit. From the observed 664 differences, several tools based on the specific variations of minor and trace elements (eg. $\Sigma LREE / \Sigma MREE$ or ΣREE) or isotopic compositions (eg. ${}^{87}Sr / {}^{86}Sr$, $\delta^{18}O$, ${}^{238}U / {}^{235}U$; 665 234 U/ 238 U, ...) have been proposed i) to understand and define the geological conditions at the 666 667 origin of uranium deposits (Fayek et al., 1997; Fayek et al., 2011; Mercadier et al., 2011;

Depiné et al., 2013; Lach et al., 2013; Uvarova et al., 2014; Macmillan et al., 2016b), and ii)
as forensic tools to trace back the source and origin of illegally traded nuclear materials
(Keegan et al., 2008; Varga et al., 2009; Brennecka et al., 2010; Varga et al., 2010; Keegan et
al., 2012; Depiné et al., 2013; Frimmel et al., 2014; Uvarova et al., 2014; Balboni et al., 2016;
Varga et al., 2017; Spano et al., 2017).

673 The prerequisite of these studies is that the composition of uraninites reflects only the 674 differences in the initial physico-chemical conditions at the time of their crystallization. 675 However, the present work demonstrates that post-crystallization alteration events can 676 generate significant changes not only in the major element contents and in the O isotopic 677 composition (Fig. 8), as previously demonstrated (Kotzer and Kyser, 1993; Fayek et al., 678 2002a; Alexandre and Kyser, 2005), but also in the concentrations of minor and trace 679 elements (Figs. 6 and 7). These differences can be quite significant, leading to major 680 variations in REE concentrations and therefore modification of the REE patterns, 681 $\Sigma LREE / \Sigma MREE$ or ΣREE between the freshest and altered zones (Fig. 7). The two samples 682 studied have identical initial chemical compositions in terms of major, minor, and trace 683 elements (except Th and Ti; Fig. 7) and identical ages of formation (ca. 1300 Ma), suggesting 684 that they formed under similar geological conditions. Moreover, the two samples experienced 685 only one alteration event, which can be considered rather contemporaneous for the two 686 samples (38 \pm 13 Ma and 72 \pm 22 Ma). The substitution trends and related chemical contents 687 in the altered regions for several elements, such as As (2500 % variation), V (250 % 688 variation), Th (820 % variation), or LREEs (527 % variation), are however different for the 689 two samples. Such differences are probably related to local variations in the physico-chemical 690 characteristics at the time of the alteration event. If the distinctions between the freshest and 691 altered regions are not made before measurement of the chemical and isotopic compositions 692 of uraninities, any direct comparison based on REE spectra or diagrams combining \sum REE and 693 LREE/HREE (Fig. 7) can lead to a biased distinction between the two samples and

694 consequently to the proposal of different geological and/or forensic fingerprint applications695 for these two samples.

696 Regarding unconformity-related U deposits, the contents of several minor and trace elements, 697 such as LREEs, in uraninite are affected by post-crystallization substitutions leading to 698 significant changes in the chemical composition of the uraninite. Minor and trace elements 699 therefore exhibit a behavior similar to major elements such as Si, Ca, and Fe. A similar 700 behavior can also be proposed for elements in other types of uranium deposits, as previously 701 observed for the REEs in the Jaduguda U deposit (Pal and Rhede, 2013) or in the Samarkiya 702 area (Ozha et al., 2017). The δ^{18} O signature varies strongly between the freshest and altered 703 zones within a single uraninite sample. Such behavior in uraninites from unconformity-related 704 U deposits has previously been described and has been inferred for other U deposit types (Kotzer and Kyser, 1993; Fayek and Kyser, 1997; Fayek et al., 2011). The use of ⁸⁷Sr/⁸⁶Sr 705 706 ratio in uraninite has been proposed as a pertinent tool to discriminate between basement-707 hosted and unconformity-hosted U deposits (Fayek et al., 1997) or to classify U ore material 708 (Balboni et al., 2016), however, this study shows that the strontium contents of uraninite are 709 also strongly affected by the alteration process, with an increase in Sr concentration from the 710 freshest to altered zones of 762 and 1315% in samples 9672-131 and 9672-162 respectively 711 (Fig. 5). The substitution trends are moreover different between the two samples. If the fluids 712 present at the initial crystallization of the uraninite and at the time of its alteration have different ⁸⁷Sr/⁸⁶Sr ratios, which is a likely situation, the ⁸⁷Sr/⁸⁶Sr ratios will change between 713 714 the freshest and altered zones, leading to mixed, variable, non-reproducible, and inconsistent bulk ⁸⁷Sr/⁸⁶Sr values between samples of a deposit and between deposits. 715

As explained earlier, the two uraninites studied here represent relatively simple examples for unconformity-related U deposits and probably for other types of uranium deposits, having been affected by only one alteration event. If uraninites experienced different and successive alteration events characterized by different physico-chemical conditions, as proposed for unconformity-related U deposits (Jefferson et al., 2007; Kyser and Cuney, 2015), and if the different fluids did not alter the same zones through time, then the uraninites will be characterized by numerous zones exhibiting small-scale variabilities in their chemical and isotopic compositions. It is clear that direct use of such mixed chemical signatures, without any deconvolution of the impact of the different alteration events, would add little to our overall understanding of uraninite geochemistry. Therefore, caution must be applied when using the geochemical compositions of uraninite to reveal the past geological conditions or as a provenance tool for a natural U-ore and related products of the nuclear cycle.

728

729 **5.** Conclusion

730 The present study demonstrates that the chemical and isotopic compositions of uraninites can 731 be significantly modified by post-crystallization interactions with fluids. These modifications 732 affect the U-Pb isotopic systems (lead loss), as well as the O isotopes, and the concentrations 733 of major (Pb, Ca, Si, and Fe), minor and trace elements. The variations in all these elements 734 and/or isotopic systems can be strong at a very small scale (micrometer to tens of 735 micrometers). Studies based on the geochemistry of natural uraninites must therefore take into 736 account these scales (spatial and chemical) of variability and use adequate descriptive, 737 analytical, and imaging techniques and methods to overcome the potential errors and bias 738 arising from the use of mixed data measured from regions of a sample that have been affected 739 by variable post-crystallization alteration. Such a detailed characterization work of uraninites 740 at the smallest possible scales is especially needed for geochronology applications, coupled to 741 the acquisition of a large amount of data (chemical and isotopic) to potentially discard suspicious data and calculate robust ages. The use of U-Th-Pb chemical ages and ²⁰⁷Pb/²⁰⁶Pb 742 743 clustering ages to reconstruct fluid events that have potentially affected the uraninites after 744 their crystallization should be not considered as a robust approach, even for the simple 745 example described in this study (uraninite affected by only one recent post-crystallization 746 alteration event). Similarly, estimation of the crystallization age from chemical substitution 747 trends leads to over-estimated ages due to the integration of these elements in uraninites

during their crystallization. Such a method cannot be considered as a robust approach unless it
is based on elements not initially incorporated into uraninite and substituted during alteration.
The present study demonstrates that such an element is not definable for unconformity-related
uranium deposits.

752 The geochemical tracing of uraninites and related products of the nuclear cycle based on 753 isotopic and chemical markers appears to be far less simple than thought up to now. Elements 754 that have been considered immobile, like REEs, may in fact be significantly affected by post-755 crystallization interaction between fluid and uraninite. However, in the specific case of 756 unconformity-related U deposits, the concentrations of several minor and trace elements, such 757 as Sb, HREEs, Co, W, and Ti, are constant in both the freshest and altered regions. These 758 elements could therefore only be used as conservative tracers for geological or forensic 759 purposes.

760

761 Acknowledgments

762 This work is part of a PhD thesis carried out at GeoRessources (CREGU, CNRS, Université 763 de Lorraine) and supported by Orano and Orano Canada Inc. We thank Cameco Corporation 764 for access to the samples. We are grateful to Dr. Mostafa Fayek of the University of Manitoba for providing the UO₂ standard needed for δ^{18} O measurements. We also thank the team from 765 766 the Service Commun de Microscopies Electroniques et de Microanalyses (SCMEM) and 767 particularly Olivier Rouer for the electron microprobe analyses. We thank Marie-Camille 768 Caumon (GeoRessources laboratory) for Raman spectroscopy analyses. The authors thank Y. 769 Amelin for editorial handling of the manuscript and two anonymous reviewers who have 770 significantly contributed to the improvement of this manuscript.

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772 **References**

Alexandre P., Kyser K., Layton-matthews Da. and Joy B. (2015) Chemical compositions of

- natural uraninites. *Can. Mineral.* **53**, 595–622.
- Alexandre P., Kyser K., Thomas D., Polito P. and Marlat J. (2007) Geochronology of
 unconformity-related uranium deposits in the Athabasca Basin, Saskatchewan, Canada
 and their integration in the evolution of the basin. *Miner. Depos.* 44, 41–59.
- 778 Alexandre P. and Kyser T. K. (2005) EFFECTS OF CATIONIC SUBSTITUTIONS AND
- ALTERATION IN URANINITE, AND IMPLICATIONS FOR THE DATING OF
 URANIUM DEPOSITS. *Can. Mineral.* 43, 1005–1017.
- Andersen M. B., Stirling C. H. and Weyer S. (2017) Uranium isotope fractionation. *Rev. Mineral. Geochemistry* 82, 799–850.
- Balboni E., Jones N., Spano T., Simonetti A. and Burns P. C. (2016) Chemical and Sr isotopic
 characterization of North America uranium ores: Nuclear forensic applications. *Appl. Geochemistry* 74, 24–32.
- 786 Ballouard C., Poujol M., Boulvais P., Mercadier J., Tartese R., Venneman T., Deloule E.,
- Jolivet M., Kéré I. and Cathelineau M. (2017a) Magmatic and hydrothermal behavior of uranium in syntectonic leucogranites: the uranium mineralization associated with the Hercynian Guérande granite (Armorican Massif, France). *Ore Geol. Rev.* **80**, 309–331.
- 790 Ballouard C., Poujol M., Mercadier J., Deloule E., Boulvais P., Baele J. M., Cuney M. and
- Cathelineau M. (2017b) Uranium metallogenesis of the peraluminous leucogranite from
 the Pontivy-Rostrenen magmatic complex (French Armorican Variscan belt): the result
 of long-term oxidized hydrothermal alteration during strike-slip deformation. *Miner*.
- 794 *Depos.*, 1–28.
- Bonhoure J., Kister P., Cuney M. and Deloule E. (2007) Methodology for Rare Earth Element
 Determinations of Uranium Oxides by Ion Microprobe. *Geostand. Geoanalytical Res.*31, 209–225.
- Bonnetti C., Liu X., Mercadier J., Cuney M., Deloule E., Villeneuve J. and Liu W. (2018) The
 genesis of granite-related hydrothermal uranium deposits in the Xiazhuang and
 Zhuguang ore fields, North Guangdong Province, SE China: Insights from mineralogical,

- trace elements and U-Pb isotopes signatures of the U mineralisation. *Ore Geol. Rev.* 92,
 588–612.
- Bopp IV C. J., Lundstrom C. C., Johnson T. M. and Glessner J. J. G. (2009) Variations in
 238U/235U in uranium ore deposits: Isotopic signatures of the U reduction process? *Geology* 37, 611–614.
- Bowles J. F. W. (1990) Age dating of individual grains of uraninite in rocks from electron
 microprobe analyses. *Chem. Geol.* 83, 47–53.
- Brennecka G. A., Borg L. E., Hutcheon I. D., Sharp M. A. and Anbar A. D. (2010) Natural
 variations in uranium isotope ratios of uranium ore concentrates: understanding the 238
- 810 U/235 U fractionation mechanism. *Earth Planet. Sci. Lett.* **291**, 228–233.
- Bruneton P. (1993) Geological environment of the Cigar Lake uranium deposit. *Can. J. Earth Sci.* **30**, 653–673.
- Cathelineau M., Boiron M. C., Holliger P. and Poty B. (1990) Metallogenesis of the French
 part of the Variscan orogen. Part II: Time-space relationships between U, Au and Sn-W
 ore deposition and geodynamic events mineralogical and U-Pb data. *Tectonophysics*177, 59–79.
- 817 Chernyshev I. V, Golubev V. N., Chugaev A. V and Baranova A. N. (2014) 238U/235U
- 818 isotope ratio variations in minerals from hydrothermal uranium deposits. *Geochemistry*819 *Int.* 52, 1013–1029.
- Chew D. M., Petrus J. A., Kenny G. G. and McEvoy N. (2017) Rapid high-resolution U–Pb
 LA-Q-ICPMS age mapping of zircon. *J. Anal. At. Spectrom.* 32, 262–276.
- Chipley D., Polito P. A. and Kyser T. K. (2007) Measurement of U-Pb ages of uraninite and
 davidite by laser ablation-HR-ICP-MS. *Am. Mineral.* 92, 1925–1935.
- Clauer N., Mercadier J., Patrier P., Laverret E. and Bruneton P. (2015) Relating
 unconformity-type uranium mineralization of the Alligator Rivers Uranium Field
 (Northern Territory, Australia) to the regional Proterozoic tectono-thermal activity: An
- 827 illite K-Ar dating approach. *Precambrian Res.* **269**, 107–121.

- 828 Clavier N., Szenknect S., Costin D. T., Mesbah A., Poinssot C. and Dacheux N. (2014) From
- thorite to coffinite: A spectroscopic study of Th1- xUxSiO4 solid solutions. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 118, 302–307.
- Cloutier J., Kyser K., Olivo G. R. and Alexandre P. (2010) Contrasting Patterns of Alteration
 at the Wheeler River Area, Athabasca Basin, Saskatchewan, Canada: Insights into the
 Apparently Uranium-Barren Zone K Alteration System. *Econ. Geol.* 105.
- 834 Cloutier J., Kyser K., Olivo G. R., Alexandre P. and Halaburda J. (2009) The Millennium
- 835 Uranium Deposit, Athabasca Basin, Saskatchewan, Canada: An Atypical Basement836 Hosted Unconformity-Related Uranium Deposit. *Econ. Geol.* 104, 815–840.
- Cloutier J., Kyser K., Olivo G. R. and Brisbin D. (2011) Geochemical, isotopic, and
 geochronlologic constraints on the formation of the Eagle Point basement-hosted
 uranium deposit, Athabasca Basin, Saskatchewan, Canada and recent remobilization of
 primary uraninite in secondary structures. *Miner. Depos.* 46, 35–56.
- 841 Compston W., Williams I. S. and Meyer C. (1984) U□Pb geochronology of zircons from
 842 lunar breccia 73217 using a sensitive high mass□resolution ion microprobe. *J. Geophys.*
- 843 *Res. Solid Earth* **89**, B525–B534.
- 844 Condon D. J., McLean N., Noble S. R. and Bowring S. A. (2010) Isotopic composition
- 845 (238U/235U) of some commonly used uranium reference materials. *Geochim.*846 *Cosmochim. Acta* 74, 7127–7143.
- Cumming G. L. and Krstic D. (1992) The age of unconformity-related uranium mineralization
 in the Athabasca Basin, northern Saskatchewan. *Can. J. Earth Sci.* 29, 1623–1639.
- 849 Cuney M. and Kyser T. K. (2015) *The geology and geochemistry of uranium and thorium*850 *deposits*. Mineralogi.,
- Deditius A. P., Utsunomiya S. and Ewing R. C. (2007) Fate of trace elements during
 alteration of uraninite in a hydrothermal vein-type U-deposit from Marshall Pass,
 Colorado, USA. *Geochim. Cosmochim. Acta* 71, 4954–4973.
- 854 Deloule E., Alexandrov P., Cheilletz A., Laumonier B. and Barbey P. (2002) In-situ U-Pb

- zircon ages for Early Ordovician magmatism in the eastern Pyrenees, France: the
 Canigou orthogneisses. *Int. J. Earth Sci.* **91**, 398–405.
- Depiné M., Frimmel H. E., Emsbo P., Koenig A. E. and Kern M. (2013) Trace element
 distribution in uraninite from Mesoarchaean Witwatersrand conglomerates (South
 Africa) supports placer model and magmatogenic source. *Miner. Depos.* 48, 423–435.
- 860 Derome D., Cathelineau M., Cuney M., Fabre C., Lhomme T. and Banks D. (2005) Mixing of
- 861 sodic and calcic brines and uranium deposition at McArthur River, Saskatchewan,
- 862 Canada: a Raman and laser-induced breakdown spectroscopic study of fluid inclusions.
- 863 *Econ. Geol.* **100**, 1529–1545.
- Dieng S., Kyser K. and Godin L. (2015) Genesis of multifarious uranium mineralization in
 the Beaverlodge area, northern Saskatchewan, Canada. *Econ. Geol.* 110, 209–240.
- 866 Dieng S., Kyser K. and Godin L. (2013) Tectonic history of the North American shield
- recorded in uranium deposits in the Beaverlodge area, northern Saskatchewan, Canada. *Precambrian Res.* 224, 316–340.
- Fayek M., Burns P., Guo Y.-X. and Ewing R. C. (2000a) Micro-structures associated with
 uraninite alteration. *J. Nucl. Mater.* 277, 204–210.
- 871 Fayek M., Harrison T. M., Ewing R. C., Grove M. and Coath C. D. (2002a) O and Pb isotopic
- analyses of uranium minerals by ion microprobe and U-Pb ages from the Cigar Lake
 deposit. *Chem. Geol.* 185, 205–225.
- Fayek M., Harrison T. M., Grove M. and Coath C. D. (2000b) A Rapid In Situ Method for
- Betermining the Ages of Uranium Oxide Minerals: Evolution of the Cigar Lake Deposit,
 Athabasca Basin. *Int. Geol. Rev.* 42, 163–171.
- Fayek M., Horita J. and Ripley E. M. (2011) The oxygen isotopic composition of uranium
 minerals: A review. *Ore Geol. Rev.* 41, 1–21.
- 879 Fayek M., Janeczek J. and Ewing R. C. (1997) Mineral chemistry and oxygen isotopic
- analyses of uraninite, pitchblende and uranium alteration minerals from the Cigar Lake
- deposit, Saskatchewan, Canada. *Appl. Geochemistry* **12**, 549–565.

- 882 Fayek M. and Kyser T. K. (1997) Characterization of multiple fluid-flow events and rare-
- earth-element mobility associated with formation of unconformity-type uranium deposits
 in the Athabasca Basin, Saskatchewan. *Can. Mineral.* 35, 627–658.
- Fayek M., Kyser T. K. and Riciputi L. R. (2002b) U and Pb isotope analysis of uranium
 minerals by ion microprobe and the geochronology of McArthur River and Sue Zone
 uranium deposits, Saskatchewan, Canada. *Can. Mineral.* 40, 1553–1570.
- Finch R. and Murakami T. (1999) Systematics and paragenesis of uranium minerals. *Rev. Mineral. Geochemistry* 38, 91–179.
- Förster H.-J. (1999) The chemical composition of uraninite in Variscan granites of the
 Erzgebirge, Germany. *Mineral. Mag.* 63, 239–252.
- Frimmel H. E., Schedel S. and Brätz H. (2014) Uraninite chemistry as forensic tool for
 provenance analysis. *Appl. Geochemistry* 48, 104–121.
- Frondel C. (1958) *Systematic mineralogy of uranium and thorium.*, US Government Printing
 Office.
- Fryer B. J. and Taylor R. P. (1987) Rare-earth element distributions in uraninites: implications
 for ore genesis. *Chem. Geol.* 63, 101–108.
- Hiess J., Condon D. J., McLean N. and Noble S. R. (2012) 238U/235U systematics in
- terrestrial uranium-bearing minerals. *Science* (80-.). **335**, 1610–1614.
- Holliger P. (1988) Ages U-Pb définis in situ sur pechblende à l'analyseur ionique. *Comptes Rendus Académie Sci. Paris, Série 2* 307, 367–373.
- Isobe H., Murakami T. and Ewing R. C. (1992) Alteration of uranium minerals in the
 Koongarra deposit, Australia: Unweathered zone. J. Nucl. Mater. 190, 174–187.
- Janeczek J. and Ewing R. C. (1992a) Dissolution and alteration of uraninite under reducing
 conditions. *J. Nucl. Mater.* 190, 157–173.
- 906 Janeczek J. and Ewing R. C. (1995) Mechanisms of lead release from uraninite in the natural
- 907 fission reactors in Gabon. *Geochim. Cosmochim. Acta* **59**, 1917–1931.
- 908 Janeczek J. and Ewing R. C. (1992b) Structural formula of uraninite. J. Nucl. Mater. 190,

909 128–132.

- 910 Jefferson C. W., Thomas D. J., Gandhi S. S., Ramaekers P., Delaney G., Brisbin D., Cutts C.,
- 911 Portella P. and Olson R. a. (2007) Unconformity-associated uranium deposits of the
 912 Athabasca basin, Saskatchewan and Alberta. *Bull. Geol. Surv. Canada*, 23–67.
- 913 Jochum K. P., Weis U., Stoll B., Kuzmin D., Yang Q., Raczek I., Jacob D. E., Stracke A.,
- 914 Birbaum K., Frick D. A., Günther D. and Enzweiler J. (2011) Determination of
- 915 Reference Values for NIST SRM 610-617 Glasses Following ISO Guidelines. *Geostand.*916 *Geoanalytical Res.* 35, 397–429.
- 917 Keegan E., Richter S., Kelly I., Wong H., Gadd P., Kuehn H. and Alonso-Munoz A. (2008)
- 918 The provenance of Australian uranium ore concentrates by elemental and isotopic 919 analysis. *Appl. Geochemistry* **23**, 765–777.
- Keegan E., Wallenius M., Mayer K., Varga Z. and Rasmussen G. (2012) Attribution of
 uranium ore concentrates using elemental and anionic data. *Appl. geochemistry* 27,
 1600–1609.
- Kempe U. (2003) Precise electron microprobe age determination in altered uraninite:
 consequences on the intrusion age and the metallogenic significance of the Kirchberg
 granite (Erzgebirge, Germany). *Contrib. to Mineral. Petrol.* 145, 107–118.
- Kotzer T. G. and Kyser T. K. (1993) O, U, and Pb isotopic and chemical variations in
 uraninite: implications for determining the temporal and fluid history of ancient terrains. *Am. Mineral.* 78, 1262–1274.
- 929 Kyser K. and Cuney M. (2015) Basins and uranium deposits, In: Geology and Geochemistry
- 930 of Uranium and Thorium Deposits, Short Course Series, Vol. 46. In pp. 224–250.
- 931 Lach P., Mercadier J., Dubessy J., Boiron M.-C. and Cuney M. (2013) In Situ Quantitative
- 932 Measurement of Rare Earth Elements in Uranium Oxides by Laser Ablation-Inductively
- 933 Coupled Plasma-Mass Spectrometry. *Geostandars Geoanalytical Res.* **37**, 277–296.
- 934 Leroy J. and Holliger P. (1984) Mineralogical, chemical and isotopic (U-Pb method) studies
- 935 of Hercynian uraniferous mineralizations (Margnac and Fanay mines, Limousin, France).

936 *Chem. Geol.* **45**, 121–134.

- 937 Longerich H. P., Jackson S. E., Günther D. and Fryer B. J. (1996) Inter-laboratory note. Laser
- ablation inductively coupled plasma mass spectrometric transient signal data acquisition
 and analyte concentration calculation. *J. Anal. At. Spectrom.* 11, 899–904.
- Ludwig K. (2007) Isoplot/Ex version 3.41b, a geochronological toolkit for Microsoft Excel.
 Berkeley Geochronol. Cent. Spec. Publ. No. 4.
- Lv J., Li G., Guo S. and Shi Y. (2016) Raman scattering from phonons and electronic
 excitations in UO2 with different oxygen isotopes. *J. Raman Spectrosc.* 47, 345–349.
- Macmillan E., Ciobanu C. L., Ehrig K., Cook N. J. and Pring A. (2016a) Chemical zoning and
 lattice distortion in uraninite from Olympic Dam, South Australia. *Am. Mineral.* 101,
 2351–2354.
- Macmillan E., Cook N. J., Ehrig K., Ciobanu C. L. and Pring A. (2016b) Uraninite from the
 Olympic Dam IOCG-U-Ag deposit: Linking textural and compositional variation to
 temporal evolution. *Am. Mineral.* 101, 1295–1320.
- Martz P. (2017) Caractéristiques, chronologie et rôles des circulations fluides dans le bassin
 d'Athabasca et de son socle: implications dans la formation et l'évolution du gisement
 d'uranium de Cigar Lake. Characteristics, chronology and roles of fluid circulations in t.
- Mercadier J., Annesley I. R., Mckechnie C. L., Bogdan T. S. and Creighton S. (2013)
 Magmatic and metamorphic uraninite mineralization in the western margin of the transhudson orogen (Saskatchewan, Canada): A uranium source for unconformity-related
 uranium deposits? *Econ. Geol.* 108, 1037–1065.
- Mercadier J., Cuney M., Lach P., Boiron M. C., Bonhoure J., Richard A., Leisen M. and
 Kister P. (2011) Origin of uranium deposits revealed by their rare earth element
 signature. *Terra Nov.* 23, 264–269.
- Murphy M. J., Stirling C. H., Kaltenbach A., Turner S. P. and Schaefer B. F. (2014)
 Fractionation of 238U/235U by reduction during low temperature uranium
 mineralisation processes. *Earth Planet. Sci. Lett.* 388, 306–317.

- Ozha M. K., Pal D. C., Mishra B., Desapati T. and Shaji T. S. (2017) Geochemistry and
 chemical dating of uraninite in the Samarkiya area, central Rajasthan, northwestern
 India–Implication for geochemical and temporal evolution of uranium mineralization. *Ore Geol. Rev.* 88, 23–42.
- 967 Pagel M. (1975) Détermination des conditions physico-chimiques de la silicification
 968 diagénétique des grès Athabasca (Canada) au moyen des inclusions fluides. *Comptes*969 *Rendus Académie Sci. Paris, Série D.* 280, 2301–2034.
- Pagel M., Pinte G. and Rotach-Toulhoat N. (1987) The rare earth elements in natural uranium
 oxides. In *Uranium mineralization-new aspects on geology, mineralogy, geochemistry,*and exploration methods
- Pal D. C. and Rhede D. (2013) Geochemistry and chemical dating of uraninite in the
 Jaduguda Uranium Deposit, Singhbhum Shear Zone, India—Implications for uranium
 mineralization and geochemical evolution of uraninite. *Econ. Geol.* 108, 1499–1515.
- Patton C., Hellstrom J., Paul B. and Woodhead J. H. (2011) Iolite: freeware for the
 visualization and processing of mass spectrometry data. *J. Anal. At. Spectrosc.* 26, 2508–
 2518.
- 979 Philippe S., Lancelot J. R., Clauer N. and Pacquet A. (1993) Formation and evolution of the
- 980 Cigar Lake uranium deposit based on. U- Pb and K- Ar isotope systematics. *Can. J.*981 *Earth Sci.* **30**, 720–730.
- Piazolo S., Belousova E., La Fontaine A., Corcoran C. and Cairney J. M. (2017) Trace
 element homogeneity from micron-to atomic scale: Implication for the suitability of the
 zircon GJ-1 as a trace element reference material. *Chem. Geol.* 456, 10–18.
- 985 Polito P. A., Kyser T. K., Alexandre P., Hiatt E. E. and Stanley C. R. (2011) Advances in

understanding the Kombolgie Subgroup and unconformity-related uranium deposits in

986

- the Alligator Rivers Uranium Field and how to explore for them using lithogeochemical
 principles. *Aust. J. Earth Sci.* 58, 453–474.
- 989 Reyx J. and Rulhmann F. (1993) Etude metallographique des differentes associations

- 990 minerales et caracterisation chimique des mineraux uraniferes du gisement de Cigar Lake
- 991 (Saskatchewan, Canada). *Can. J. Earth Sci.* **30**, 705–719.
- Richard A., Cathelineau M., Boiron M.-C., Mercadier J., Banks D. a. and Cuney M. (2016)
 Metal-rich fluid inclusions provide new insights into unconformity-related U deposits
 (Athabasca Basin and Basement, Canada). *Miner. Depos.* 51, 249–270.
- 995 Richard A., Pettke T., Cathelineau M., Boiron M. C., Mercadier J., Cuney M. and Derome D.
- 996 (2010) Brine-rock interaction in the Athabasca basement (McArthur River U deposit,
- 997 Canada): Consequences for fluid chemistry and uranium uptake. *Terra Nov.* 22, 303–
 998 308.
- Shannon R. D. (1976) Revised effective ionic radii and systematic studies of interatomic
 distances in halides and chalcogenides. *Acta Crystallogr.* 32, 751–767.
- Sharpe R. and Fayek M. (2016) Mass bias corrections for U□Pb isotopic analysis by
 secondary ion mass spectrometry: Implications for U□Pb dating of uraninite. *Rapid Commun. Mass Spectrom.* 30, 1601–1611.
- Sharpe R. and Fayek M. (2011) The world's oldest observed primary uraninite. *Can. Mineral.*49, 1199–1210.
- 1006 Sharpe R., Fayek M., Quirt D. and Jefferson C. W. (2015) Geochronology and genesis of the
- 1007 Bong uranium deposit, Thelon Basin, Nunavut, Canada. *Econ. Geol.* **110**, 1759–1777.
- Sheahan C., Fayek M., Quirt D. and Jefferson C. W. (2016) A combined ingress-egress model
 for the Kianna unconformity-related uranium deposit, Shea Creek Project, Athabasca
 Basin, Canada. *Econ. Geol.* 111, 225–257.
- 1011 Skirrow R. G., Mercadier J., Armstrong R., Kuske T. and Deloule E. (2016) The Ranger
- 1012 uranium deposit, northern Australia: Timing constraints, regional and ore-related
- alteration, and genetic implications for unconformity-related mineralisation. *Ore Geol.*
- 1014 *Rev.* **76**, 463–503.
- 1015 Spano T. L., Simonetti A., Wheeler T., Carpenter G., Freet D., Balboni E., Dorais C. and 1016 Burns P. C. (2017) A novel nuclear forensic tool involving deposit type normalized rare

- 1017 earth element signatures. *Terra Nov*.
- Stacey J. S. and Kramers J. D. (1975) Approximation of terrestrial lead isotope evolution by a
 two-stage model. *Earth Planet. Sci. Lett.* 26, 207–221.
- 1020 Uvarova Y. A., Kyser T. K., Geagea M. L. and Chipley D. (2014) Variations in the uranium
 1021 isotopic compositions of uranium ores from different types of uranium deposits.
 1022 *Geochim. Cosmochim. Acta* 146, 1–17.
- 1023 Valley J. W., Cavosie A. J., Ushikubo T., Reinhard D. A., Lawrence D. F., Larson D. J.,
- 1024 Clifton P. H., Kelly T. F., Wilde S. A. and Moser D. E. (2014) Hadean age for a post-
- 1025 magma-ocean zircon confirmed by atom-probe tomography. *Nat. Geosci.* **7**, 219–223.
- 1026 Varga Z., Krajkó J., Peńkin M., Novák M., Eke Z., Wallenius M. and Mayer K. (2017)
- 1027 Identification of uranium signatures relevant for nuclear safeguards and forensics. J.
 1028 *Radioanal. Nucl. Chem.* **312**, 639–654.
- 1029 Varga Z., Wallenius M. and Mayer K. (2010) Origin assessment of uranium ore concentrates
- based on their rare-earth elemental impurity pattern. *Radiochim. Acta Int. J. Chem. Asp. Nucl. Sci. Technol.* 98, 771–778.
- 1032 Varga Z., Wallenius M., Mayer K., Keegan E. and Millet S. (2009) Application of lead and
 1033 strontium isotope ratio measurements for the origin assessment of uranium ore
 1034 concentrates. *Anal. Chem.* 81, 8327–8334.
- Weyer S., Anbar A. D., Gerdes A., Gordon G. W., Algeo T. J. and Boyle E. A. (2008) Natural
 fractionation of 238U/235U. *Geochim. Cosmochim. Acta* 72, 345–359.
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1039 Figure captions

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- 1041 Figure 1: Photomicrograph under reflected light of the primary uranium oxide minerals (UO₂;
- a and e) from the two samples (9672-131 and 9672-162) of the high-grade U zone from
- 1043 the Cigar Lake U deposit (Saskatchewan, Canada), and SEM pictures in backscattered

1044 mode of the same crystals. Locations of the spot analyses for the different techniques 1045 used are indicated and areas mapped through X-ray elemental analysis are indicated by 1046 red rectangles with the reference to the concerned figures. UO₂: uranium oxide; coff: 1047 coffinite; Gers: gersdorffite

1048 Figure 2: a to c: SEM pictures in backscattered mode of the primary uranium oxide minerals 1049 (UO₂, see Fig. 1e) from sample 9672-162 of the high-grade U zone from the Cigar Lake 1050 U deposit (Saskatchewan, Canada), with freshest (light grey) and altered (dark grey) 1051 areas. Location of SIMS spots (white dashed ellipses), La-ICP-MS spots (black circles), 1052 Raman analyses (red stars) and WDS-EM measurements (yellow cross) are indicated. e) 1053 WDS-SEM spectra measured on the freshest (spectrum 1) and altered (spectrum 2) areas. 1054 d): Raman spectra for the freshest and altered areas. Spectra of UO2 and coffinite from 1055 other authors are given for comparison (Clavier et al., 2014; Lv et al., 2016).

1056 Figure 3: X-ray elemental maps of primary uraninite crystals from sample 9672-162 (Cigar 1057 Lake U deposit, Saskatchewan, Canada). Results of three quantitative EMPA analyses 1058 are displayed (EMPA spot ID n°28, 30 and 37 in ESM-2). On the top, Microphotograph 1059 under reflected light (left) and SEM picture (right) and elemental maps for U, Ca, Pb and Si below. Darker areas in SEM correspond to altered areas which express lead loss and a 1060 1061 concomitant Ca and Si gain. Ill: illite; sud: sudoite; coff: coffinite. The black holes on the 1062 uranium oxides for the microphotograph under reflected light are SIMS and LA-ICP-MS 1063 spots (see Fig. 1).

Figure 4: Major element composition of the primary uranium oxides from samples 9672-162 and 9672-131 (Cigar Lake U deposit, Saskatchewan, Canada). The express trends indicate an overall lead loss and Ca, Si gain during alteration. The trends for coffinitization are indicated and are different from the alteration. Note that calcium content is always non-null in contrast to the silica content (freshest zone with the highest Pb content).

1070 Figure 5: U-Pb Concordia diagram of the primary uranium oxides from samples 9672-162 and

1071 9672-131 (Cigar Lake U deposit, Saskatchewan, Canada). Pb X-ray elemental maps of
1072 the corresponding analyzed areas are indicated with the location of the distinct analyses.
1073 Colors of the spots on the maps and on the Concordia diagram indicate the ²⁰⁶Pb/²³⁸U
1074 ranges measured, which reflect the degree of lead loss.

1075 Figure 6: Minor and trace element content variations during alteration in primary uranium 1076 oxides from samples 9672-162 and 9672-131 (Cigar Lake U deposit, Saskatchewan, 1077 Canada). The degree of alteration is correlated to the lead loss. Colors indicate the corresponding ²⁰⁶Pb/²³⁸U ranges of associated SIMS analyses (see Fig. 4). The Blue 1078 1079 dashed lines correspond to the trend line for sample 9672-131 whereas the red ones 1080 correspond to sample 9672-162. The mean limit of detection (L.O.D.) value calculated 1081 from all the analyses for a considered element is represented by a dashed line. Data 1082 presented on the figure have individual calculated concentration above the individual 1083 calculated L.O.D and are therefore true concentration.

- 1084 Figure 7: Evolution of the REE patterns with increasing alteration and lead loss in primary 1085 uranium oxides from samples 9672-162 and 9672-131 (Cigar Lake U deposit, 1086 Saskatchewan, Canada). REE patterns are progressively enriched in LREE with the 1087 increase of the alteration degree whereas HREE are preserved. LREE include REE from 1088 La to Sm and HREE include elements from Eu to Lu. REE contents are plotted in a 1089 ΣREE vs. $\Sigma LREE / \Sigma HREE$ diagram, and the evolution of contents of Ce (LREE) compared to Lu (HREE) is given as a function of corresponding ²⁰⁶Pb/²³⁸U ages and thus 1090 1091 progressive lead loss.
- 1092 Figure 8: δ^{18} O composition of primary uranium oxides in primary uranium oxides from 1093 sample 9672-131 (Cigar Lake U deposit, Saskatchewan, Canada). δ^{18} O values increase 1094 with increasing alteration and lead loss. Corresponding ²⁰⁶Pb/²³⁸U ages given through the 1095 color scale (see Fig. 4)
- Figure 9: a) and b): U-Pb Concordia diagrams of two primary uranium oxides from samples
 9672-162 and 9672-131 (Cigar Lake U deposit, Saskatchewan, Canada) and

1098 corresponding histograms of 207 Pb/ 206 Pb (c and d) ages and U-Th-Pb chemical ages (e 1099 and f). The dashed lines on c), d), e) and f) are the calculated upper intercept Discordia 1100 age for each sample, and the thickness is representative of the error.

1101 Figure 10: Binary diagrams of SiO₂ (a), CaO (b), FeO (c) and SiO₂ + CaO + FeO (d) vs. U-1102 Th-Pb chemical age of two primary uranium oxides from samples 9672-162 and 9672-1103 131 (Cigar Lake U deposit, Saskatchewan, Canada). Extrapolation of the chemical ages 1104 to the age were Fe, Si and Ca were negligible (intercept of the X axis), following the 1105 methodology of Alexandre and Kyser (2005), give distinct and inconsistent ages 1106 compared to upper intercept Discordia ages (1299 \pm 4 Ma [blue dashed line] and 1308 \pm 1107 14 Ma [grey dashed line]) due to significant incorporation of Ca and Fe at the time of 1108 crystallization. The thickness of the dashed lines is representative of the error.

Figure 11: Effect of lead loss and post-crystallization alteration on ²⁰⁷Pb/²⁰⁶Pb age 1109 1110 distributions. U-Pb data from this study are plotted on a Concordia diagram (a). Colors correspond to ²⁰⁷Pb/²⁰⁶Pb age ranges. The data show a bimodal repartition of the 1111 ²⁰⁷Pb/²⁰⁶Pb dates even though they define a single well-defined Discordia line and thus a 1112 1113 single age of crystallization. b) Concordia diagram with a made-up dataset corresponding 1114 to a uranium crystal having crystallized at 1300 Ma and that suffered from a lead loss event at 500 Ma. The corresponding ²⁰⁷Pb/²⁰⁶Pb distribution reveals 3 meaningless 1115 1116 statistical clusters of ²⁰⁷Pb/²⁰⁶Pb dates that only correspond to groups of analyses with a 1117 similar lead loss intensity. Such "peak ages" cannot be accounted for distinct events of 1118 (re)crystallization.

ESM-1: Macroscopic pictures of the two studied samples from the high-grade uranium ore of
the Cigar Lake deposit (Saskatchewan, Canada). Above: Sample 9672-131, Below:
9672-162. Both samples consist of massive uraninites with minor coffinite and arsenides
embedded in a clay-rich matrix of intimately mixed illite and sudoite.

ESM-2: SIMS U, Pb, O isotopic data of the primary uraninites from samples 9672-131 and
9672-162 (Cigar Lake U deposit, Saskatchewan, Canada) and associated EMPA

- measurements for Si, P, Ca, Fe, Pb, Th and U (O: calculated from stoichiometry), plus
 corresponding calculated chemical ages following the iteration procedure of Bowles,
 (1990). a.p.: analytical problem. Errors are reported with 1σ.
- 1128 ESM-3: LA-ICP-MS minor and trace element data of primary uraninites from samples 9672-
- 1129 131 and 9672-162. Corresponding U-Pb, δ^{18} O SIMS and EMPA spots are indicated.
- 1130 Italic: Limit of detection, given when calculated values are below this limit. LREE
- 1131 include REE from La to Sm and HREE include elements from Eu to Lu.
- 1132

































