

# Partial retention of radiogenic Pb in galena nanocrystals explains discordance in monazite from Napier Complex (Antarctica)

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1	Partial retention of radiogenic Pb in galena nanocrystals explains discordance in
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## 13 ABSTRACT

14 The discordance of U-Th-Pb isotopic systems in geochronometers, and how such data are 15 interpreted, are still major issues in the geosciences. To better understand the disturbance of isotopic systems, and how this impacts the derivation of geologically-meaningful ages, 16 17 previously studied discordant monazite from the ultrahigh temperature paragneiss of the 18 Archean Napier Complex (Antarctica) have been investigated. Monazite grains were 19 characterized from the micro to the nanoscale using an analytical workflow comprising laser 20 ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), secondary-ion mass 21 spectrometry (SIMS), electron microprobe (EMP), transmission electron microscopy (TEM) 22 and atom probe tomography (APT). Results reveal that the least discordant monazite, hosted in

garnet and rutilated quartz, contain a large number of small Pb-bearing nanominerals ( $\emptyset \sim 50$ 23 24 nm) while the most discordant monazite, hosted in the quartzo-feldspathic matrix, contain a smaller number of Pb-bearing nanominerals bigger in size ( $\emptyset \sim 50$  to 500 nm). The degree of 25 the discordance, which was previously correlated with textural position is mechanistically 26 related to the partial retention of radiogenic Pb (Pb<sup>\*</sup>) in distinct Pb<sup>\*</sup>-bearing nanominerals (e.g. 27 PbS) within the monazite grains. *In-situ* dating (U–Pb systems with LA-ICP-MS and SIMS), 28 and isotopic information obtained by using APT (<sup>207</sup>Pb/<sup>206</sup>Pb isotopic signature of galena and 29  $^{208}$ Pb/ $^{232}$ Th ages of the monazite matrix) allow the timing of Pb-disturbance and mobility to be 30 constrained. Results show that monazite grains crystallized at ca. 2.44 Ga and were affected by 31 two episodes of Pb<sup>\*</sup> mobility. The first episode  $(t_1)$  at *ca*. 1.05 Ga, led to crystallization of a first 32 generation of Pb\*-bearing nanominerals and a complete resetting of the monazite matrix at the 33 nanoscale. The second episode  $(t_2)$  at *ca*. 0.55 Ga was associated with the crystallization of a 34 second generation of Pb\*-bearing nanominerals with a <sup>207</sup>Pb/<sup>206</sup>Pb signature indicating a mixing 35 of two Pb\* components: a component from the monazite matrix and remobilized Pb\* from the 36 first generation of Pb<sup>\*</sup>-bearing nanominerals. This second event is characterized by a more 37 localized resetting of the monazite matrix at the nanoscale compared to the t<sub>1</sub> event. These 38 results indicate the potential of nanoscale studies of Pb-rich nanominerals within monazite to 39 yield important details of the themal history of complex metamorphic terranes. 40

Keywords: U–Th–Pb discordance – monazite – Pb mobility – nanogeochronology- atom
probe tomography

43 **1. INTRODUCTION** 

Accessory mineral U–Th–Pb geochronology is widely used in Earth Sciences because the existence of two U–Pb and one Th–Pb decay chains, each with different half-lives, allows direct evaluation of isotopic disturbance and the accuracy of calculated dates. If the dates calculated 47 from the three decay chains differ, then the system under consideration is referred to as 48 discordant. Discordance is common in ancient and polymetamorphic rocks, where it typically indicates Pb mobility or loss, and if not recognized may lead to erroneous conclusions with 49 50 respect to the geological history (Corfu, 2013). In situations where only one event is responsible for Pb mobility, the time of Pb disturbance may be deduced by regression of discordant isotopic 51 data on graphs of  ${}^{206}$ Pb/ ${}^{238}$ U vs  ${}^{207}$ Pb/ ${}^{235}$ U or  ${}^{207}$ Pb/ ${}^{235}$ U vs  ${}^{208}$ Pb/ ${}^{232}$ Th (Allègre et al., 1974; Tera 52 53 and Wasserburg, 1972; Wetherill, 1963). However, multiple episodes of Pb disturbance result in more complex data distributions that may be difficult to identify and reliably interpret 54 (Gebauer and Grünenfelder, 1979). This is particularly the case when the scale or mechanism 55 56 of Pb mobility differs between events. However, assessing the scale of Pb mobility as well as the mechanisms by which Pb is disturbed, is typically difficult. The nanoscale quantification of 57 58 Pb distribution, coupled with isotopic analysis, has the potential to provide constraints on the 59 causes and scales of Pb mobility to yield a unique insight into the nature of discordance in the U-Th-Pb isotopic systems (Peterman et al., 2016; Valley et al., 2014). 60

61 Fine-scale characterization of the location and behaviour of the radiogenic daughter element (Pb<sup>\*</sup>) in host minerals relies on the correlation of structural observations with isotopic 62 measurements at the nanoscale. Transmission electron microscopy (TEM) has revealed Pb-rich 63 64 nanominerals in discordant zircon, either as native Pb (Kusiak et al., 2015) or Pb-oxide (Kusiak et al., 2019). Similar features have been reported in discordant monazite (Seydoux-Guillaume 65 et al., 2003) and phase separation of Pb-enriched domains in monazite have been identified 66 through the integration of TEM and atom probe tomography (APT) analyses (Seydoux-67 Guillaume et al., 2019). The isotopic compositions of such heterogeneities for U-Th-Pb 68 69 geochronometers such as zircon, monazite and rutile have been quantified using APT (Arcuri et al., 2020; Blum et al., 2018; Fougerouse et al., 2021a, 2021b, 2018; Peterman et al., 2016; 70 Seydoux-Guillaume et al., 2019; Valley et al., 2015, 2014; Verberne et al., 2020). These studies 71

typically use an advanced analytical workflow to constrain the scale of Pb mobility and the timing of isolation of Pb from parental U and Th (Peterman et al., 2016; Seydoux-Guillaume et al., 2019; Valley et al., 2015). This approach, which integrates textural, microstructural, compositional and isotopic analyses from the micro- to the nanoscale yields significant advances on the causes of isotopic discordance and ages variation at the microscale (Peterman et al., 2016; Seydoux-Guillaume et al., 2018a).

78 Studies on natural zircon have demonstrated that isotopic discordance may be caused by Pb<sup>\*</sup> mobility associated with the annealing of radiation damage during high temperature 79 metamorphic conditions, resulting in isolated Pb\* reservoirs (Kusiak et al., 2019, 2015; 80 81 Peterman et al., 2021, 2016; Whitehouse et al., 2017). In contrast, monazite is less sensitive to 82 the thermal history of the host rock since natural monazite remains crystalline thanks to a defect recovery mechanism operating event at moderate temperature (> 180 °C; Seydoux-Guillaume 83 et al. 2018b). Pb<sup>\*</sup> mobility in monazite from micro to nanoscale is promoted by fluid-assisted 84 mechanisms, such as a coupled dissolution-precipitation process (Grand'Homme et al., 2018; 85 86 Seydoux-Guillaume et al., 2002), and by deformation-assisted mechanisms both in fluidpresent (Wawrzenitz et al. 2012) and fluid-absent environments (Erickson et al., 2015; 87 Fougerouse et al., 2021b). As a result, the effects and interplay of such mechanisms, on the 88 formation and nature of nanoscale Pb<sup>\*</sup> heterogeneities as well as their impact on discordance in 89 monazite cannot simply be derived from our knowledge of zircon. 90

This study re-investigates discordant monazite grains reported by Black et al. (1984) from an Archean polymetamorphic granulite of the Napier Complex, East Antarctica. Multiple advanced micro- to nanoscale analytical techniques are used to provide unique constraints on the development and evolution of discrete Pb<sup>\*</sup> reservoirs within variably-discordant monazite. The integration of isotopic analyses over a range of scales is critically evaluated within the 96 context of a well-constrained metamorphic history to provide unique constraints on the
97 nanoscale mechanisms accommodating two stages of Pb-disturbance.

## 98 **2. METHODS**

Microscale imaging of monazite was conducted at 20 keV with field emission gun scanning
 electron microscopy FEG-SEM Zeiss supra 55vp. The instrument is also equipped with an
 energy dispersive X-ray (EDX) spectrometer.

Uranium-Th-Pb isotopic analyses by LA- ICP-MS were performed at the Laboratoire 102 Magmas et Volcans (Clermont-Ferrand, France). The laser ablation systems consist of a 103 Resonetics Resolution M-50E system equipped with an ultrashort pulse ATL excimer 193 nm 104 105 laser coupled to an Agilent 7500 cs ICP-MS. A Laser spot diameter of 9 µm was used with 1 Hz repetition rate and a fluence of 7.5 J/cm<sup>2</sup>. The <sup>204</sup>(Pb+Hg) signal was monitored but no 106 common-Pb correction was applied. Analytical procedures and reproducibility are reported in 107 108 detail in Appendix A. SIMS was undertaken on a CAMECA IMS 7f-Geo hosted at the NERC Ion Micro-Probe Facility, School of Geosciences, Edinburgh University (UK), under conditions 109 detailed in Appendix A. The technique was specifically employed to search for the presence of 110 any <sup>204</sup>Pb (common Pb; Pb<sub>c</sub>) because LA-ICP-MS cannot be employed due to the unresolvable 111 isobaric interference between <sup>204</sup>Pb (203.9730), and <sup>204</sup>Hg (203.9735). With the SIMS 112 technique there is a potential isobaric interference from the molecular species 113  $[^{232}\text{Th}^{144}\text{Nd}^{16}\text{O}_2]^{2+}$  (mass 407.9379, M/z = 203.9690). This interference can be resolved by 114 correlating  $[^{232}\text{Th}^{144}\text{Nd}^{16}\text{O}_2]^{2+}$  counts per second (cps) with  $^{143}\text{Nd}^{31}\text{P}^{16}\text{O}_2$  (205.87) in the 5037 115 monazite sample and comparing this to Moacyr reference material data, which shows that these 116 data follow a linear correlation (more details in Appendix A). SIMS analyses reported a 117 maximum of 0.06 cps associated with <sup>204</sup>Pb estimated in Moacyr reference material. As the 118 counts of mass 204 in sample 5037 monazite are less than, or overlap, those for Moacyr (2.8 119

cps and 3.7 cps respectively; Appendix C), the figure of 0.06 cps for <sup>204</sup>Pb is applied as a 120 maximum correction for common Pb on <sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb in sample 5037 monazite. Age 121 data from SIMS have higher uncertainties than those from LA-ICP-MS as the SIMS 122 methodology was optimized to assess Pbc and not to obtain high-precision dates. U-Th-Pb 123 EMP dating was conducted using a CAMECA SXFive at the Microcharacterization Center 124 125 Raimond Castaing, at Toulouse (France). The analytical conditions were 15 keV and 200-300 126 nA, following the protocol outlined in Laurent et al. (2016), and are detailed along with age reproducibility in Appendix A. 127

Nanoscale characterization by TEM and scanning transmission electron microscopy 128 129 (STEM) were performed with a Cs-corrected NeoARM200F Cold FEG TEM operated at 200 keV, owned by the Consortium Lyon Saint-Etienne de Microscopie (FED 4092) and hosted 130 within the Hubert Curien Laboratory, Saint-Etienne (France). APT data were collected using a 131 CAMECA Local Electrode Atom Probe LEAP 4000X HR hosted at the Geoscience Atom 132 Probe Facility at Curtin University, Perth (Australia). APT data were collected using a UV laser 133 134  $(\lambda = 355 \text{ nm})$  pulsed at 125 kHz and 30-300 pJ (details in Appendix A). In the APT mass spectra, peaks at least twice higher than the background level were identified and reconstructed in 3 135 dimensions. For monazite, voltage evolution reconstructions were utilized with an evaporation 136 field of 27.02 V/nm<sup>2</sup> and an atomic volume of 0.01245 nm<sup>3</sup> (Fougerouse et al., 2021c). TEM 137 samples were prepared using a with a Thermo Fisher Scientific FEI Helios Nanolab 600i 138 139 focused-ion beam scanning electron microscope (FIB/SEM) hosted by MANUTECH USD platform, at Hubert Curien laboratory, Saint-Etienne (France). A Tescan Lyra3 Ga<sup>+</sup> FIB-SEM 140 141 housed at Curtin University was used for preparation on needle-shaped APT specimens. More 142 details on instrument, analytical conditions and data processing are provided in Appendix A.

Isotopic dates from the APT data were calculated using  ${}^{208}$ Pb/ ${}^{232}$ Th ratios measured on 144  ${}^{208}$ Pb ${}^{2+}$  and  ${}^{232}$ ThO ${}^{2+}$  peaks, following the correction procedures of (Fougerouse et al., 2020; see Appendix A for details).  ${}^{207}$ Pb/ ${}^{206}$ Pb ratios were estimated from APT data on galena inclusions using  ${}^{207}$ Pb<sup>2+</sup> and  ${}^{206}$ Pb<sup>2+</sup> peaks and following the methodology of Blum et al., (2018) to correct the effect on the thermal peak of  ${}^{206}$ Pb<sup>2+</sup> on  ${}^{207}$ Pb<sup>2+</sup> peak (see Appendix A for details).

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## **3. GEOLOGICAL CONTEXT AND SAMPLE DESCRIPTION**

The studied monazite grains are from an Archean granulite (sample 5037; Black et al., 1984) 149 150 collected at Zircon Point in the Napier Complex, East Antarctica (Fig. 1A, B). The granulite is a garnet-rich migmatized paragneiss preserving a well-developed, high-grade, layer-parallel 151 fabric composed of rutilated quartz (Rt-quartz) ribbons, mesoperthitic feldspar, sillimanite and 152 elongated poikiloblastic garnet (Appendix B.1, S<sub>1</sub>, S<sub>2</sub>; Black et al., 1983, 1984). This mineral 153 paragenesis corresponds to a major late-Archaean ultrahigh temperature (UHT) event (1050 -154 1120°C, 7-11 kbar) at ca. 2.58 – 2.48 Ga (Harley and Motoyoshi, 2000; Hokada et al., 2004 155 Kelly and Harley, 2005). 156

157 The sample is affected by retrogression involving the development of secondary biotite 158 within fractures in garnet (Appendix B.1, S<sub>3</sub>; Black et al. 1983), exsolution of perthitic feldspar 159 and the recrystallization of the quartzo-feldspathic matrix as fine-grained granoblastic aggregates containing rutile-free quartz (Appendix B.1; Black et al., 1983). This retrogressive 160 161 episode in the southern Napier Complex area, including Zircon Point, corresponds to amphibolite-facies conditions and is associated with localized shearing and pegmatite 162 intrusions. This event overprints the Napier Complex, especially in Casey Bay and is temporally 163 constrained by ID-TIMS U-Pb zircon and monazite discordant fractions from paragneiss at 164 1073 Ma and  $1087 \pm 29$  Ma (zircon from McIntyre Island; Black et al., 1983, monazite from 165 Zircon Point; Black et al., 1984, Fig. 1B) as well as by a Pb-total age on monazite from a 166 pegmatite at  $1094 \pm 67$  Ma (Zircon Point; Asami et al., 2002). Hence, this lower-grade event 167 has been linked to the Rayner Structural Episode, which took place in the Rayner Complex at 168

amphibolite- to granulite-facies conditions around 1000 - 900 Ma ago (Black et al., 1987; Harley and Hensen, 1990; Harley, 2003; Sheraton et al., 1980). At *ca.* 500-550 Ma, hydrothermal activity is reported in the Napier Complex (Carson et al., 2002) and intrusion of pegmatites in the nearby Ayatollah Island (Fig. 1B) is recorded by a Rb–Sr age on a pegmatite at  $522 \pm 10$  ( $2\sigma$ ) Ma. These events reflect renewed magmatic and hydrothermal activity at Zircon Point (Black et al., 1983).

175 Monazite grains are hosted in garnet, sillimanite, Rt-quartz or along grain boundaries in the  $S_2$  or recrystallized  $S_3$  quartzo-feldspathic matrix. Previous petrographic and isotopic work 176 (isotope dilution thermal ionization mass spectrometry ID-TIMS on multigrain separates) on 177 178 monazite from sample 5037 identified three optically-distinct colour groups that were 179 correlated with the monazite host mineral and recorded three distinct, discordant isotopic compositions (Fig. 1C; Black et al., 1984). The three groups define a discordant line (mean 180 square weighted deviation - MSWD = 11), with upper and lower intercepts at  $2429 \pm 17 (2\sigma)$ 181 Ma and  $1087 \pm 29$  (2 $\sigma$ ) Ma respectively (Fig. 1C). Chemical compositions were reported to be 182 183 similar for the three monazite groups, and TEM investigations did not show differences in crystallinity (Black et al., 1984). Brown monazite, hosted either in garnet or Rt-quartz, were < 184 30% discordant whereas clear monazite (yellow and grey), hosted in the quartzo-feldspathic 185 186 matrix, were found to be at least 50% discordant (Fig. 1C). This unique pattern of discordance was tentatively explained in term of variable Pb loss with the three groups reflecting the 187 differing capacities of their host mineral to shield the monazite crystals from late, post-188 metamorphic fluids (Black et al., 1984). 189

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#### 4. MONAZITE CHARACTERIZATION

A microscale analytical survey of 35 *in-situ* monazite grains was complemented by
 nanoscale characterization of a subset of these monazite crystals (Mnz2, Mnz4, Mnz17, Mnz25;

Fig.2, Appendix B.2) according to their textural position (host mineral). A single TEM foil was
prepared from a monazite grain hosted in both Rt-quartz (Mnz17; Fig. 2A) and garnet (Mnz4;
Appendix B.2) and three TEM foils were prepared from a monazite grain located in the quartzofeldspathic matrix (Mnz25; Fig. 2B). Fourteen needle-shaped atom probe specimens were
prepared from Rt-quartz hosted monazite (Mnz17; Fig. 2A) and quartzo-feldspathic matrix
hosted monazite (Mnz25 and Mnz2; Fig. 2B, C). Specimen locations are shown in Fig. 2A, C,
F.

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#### 4.1. Microscale to nanoscale features

201 Monazite crystals display complex textural features in greyscale back-scattered electron (BSE) images (Fig. 2). These include a core-rim texture, highlighted generally by dark cores 202 (Fig. 2A-C), bright (Th-rich) linear features traversing the core (Fig. 2B, Appendix B.2), 203 204 zonation (Fig. 2A) or overgrowths (Appendix B.2). These different textures are present in monazite grains from different hosts but are not systematically present in all grains. Monazite 205 206 located in the quartzo-feldspathic matrix are range between 50-250 µm in size while monazite in garnet or Rt-quartz are range between 20-80  $\mu$ m in size. Sub-micrometer (Ø < 1 $\mu$ m) dark 207 (low-BSE coefficient) circular spots are present in all monazite grains, as are sub-micrometer 208 209  $(\emptyset < 1 \mu m)$ , bright (high-BSE coefficient) circular spots (Fig. 2D-F, Appendix B.2). Bright 210 spots are larger in monazite hosted in the quartzo-feldspathic matrix than those hosted in Rt-211 quartz or garnet (Fig. 2D-F). They are also more abundant and larger in the rim of Mnz25 than 212 in the core (Fig. 2E).

At the nanoscale the bright spots correspond to distinct crystalline Pb-bearing minerals (lightest nanoscale features on STEM images; Fig. 3) and are often spatially associated with a dark silicate and amorphous material (Fig. 3). Individual Pb-bearing minerals and amorphous silicate material also exist. The distribution and the size of these Pb-bearing minerals varies within the grain (e.g. core versus rim) and with the textural position of the monazite grain. Monazite grains in Rt-quartz and garnet have a large number of Pb-bearing minerals ( $\emptyset < 50$ nm; Fig. 3A, Appendix B.3) compared to grains within the quartzo-feldspathic matrix ( $\emptyset > 50$ nm; Fig. 3B, C). In monazite grains from the quartzo-feldspathic matrix, Pb-bearing minerals are also more abundant and smaller in the rim ( $\emptyset < 100$  nm; Fig. 3B), than in the core ( $\emptyset > 100$ nm; Fig. 3C).

Two of the largest Pb-bearing minerals ( $\emptyset \sim 1 \ \mu m$ ) have been analyzed by APT. These minerals comprise Pb and S, (Fig. 4) and are devoid of U or Th (Fig. 4B). Compositions estimated from the APT data (S = 47.76 ± 0.02 at % and Pb = 52.18 ± 0.02 at % and S = 48.79 ± 0.06 at % and Pb = 50.60 ± 0.06 at %; Appendix B.6) are consistent with the stoichiometry of galena. Electron diffraction patterns acquired by TEM on a similar Pb-bearing mineral ( $\emptyset \sim$ 500 nm) are compatible with these minerals being galena (Appendix B.4).

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#### 4.2. Isotopic data and geochronology

The corrected <sup>206</sup>Pb/<sup>204</sup>Pb ratios obtained with SIMS are on average, 44284 for sample 5037 monazite and 9225 for Moacyr reference material. In each case the amount of common <sup>206</sup>Pb ( $^{206}$ Pb<sub>c</sub>), is significantly less than 1% of total <sup>206</sup>Pb (0.038% for sample 5037 and 0.189% for Moacyr). Thus, monazite crystals contain negligible <sup>204</sup>Pb indicating that Pb<sub>c</sub> can be discounted as a contaminant in the LA-ICP-MS results and as a contributor to the Pb present in the galena grains.

The analytical volume of the different geochronological approaches applied to the monazite grains range over nine orders of magnitude. Dates from LA-ICP-MS (Appendix D), SIMS (Appendix C) and EMP (Appendix E) techniques range between  $2435 \pm 150$  Ma ( $2\sigma$ ) Ma and 874  $\pm$  28 Ma ( $2\sigma$ ) and are independent of the chosen chronometer ( $^{206}Pb/^{238}U$ ,  $^{208}Pb/^{232}Th$ ; Fig. 5, Appendix F).  $^{208}Pb/^{232}Th$  dates from APT data tend towards the lower end of this spectrum, whilst ID-TIMS on multiple grains (Black et al. 1984) tend towards the oldest dates (Fig. 5).
Moreover, at the scale of the population, the spread of monazite dates is systematically related
to where the monazite is hosted and not to its Th/U ratio nor to the analysis location with respect
to core and rim (Fig. 5, Appendix G.1-4).

245 U-Pb isotopic data gathered in-situ by LA-ICP-MS and SIMS are discordant and spread along a discordia line,  $D_{all}$ , defined by an upper intercept of 2383 ± 36 Ma (2 $\sigma$ ) and a lower 246 247 intercept of 931  $\pm$  45 Ma (2 $\sigma$ ) (MSWD = 4.7; Fig. 6A). U–Pb and Th–Pb systems are also 248 discordant (Appendix G.5). The data from monazite grains hosted in Rt-quartz and garnet plot close to the upper intercept of the discordia line and show less than 50% Pb-loss. These data 249 250 alone yield an upper and a lower intercept of 2440  $\pm$  39 Ma (2 $\sigma$ ) and 1045  $\pm$  132 Ma (2 $\sigma$ ) 251 respectively (MSWD = 0.84, discordia D<sub>IM</sub>; Fig. 6A, Appendix G.6). In contrast, the monazite grains hosted in the quartzo-feldspathic matrix record up to 90% Pb-loss (Fig. 6A). 252

253 LA-ICP-MS and SIMS U-Pb data from monazite grains hosted in the quartzo-feldspathic 254 matrix (Mnz2 and Mnz25; Fig. 3B, C) define two distinct discordia trends when ranged by 255 galena-rich rim or galena-poor core region (Fig. 6B) and also related locally to the Th/U ratio 256 of the analytical spots (Appendix G.7). The discordia D<sub>LI</sub> from the galena-rich rim region (yellow symbols, MSWD = 2), yields upper and lower intercepts at  $2434 \pm 181$  Ma ( $2\sigma$ ) and 257  $1049\pm248$  Ma (2  $\sigma)$  respectively, and intersect the  $^{207}Pb/^{206}Pb$  axis at ( $^{207}Pb/^{206}Pb)_{DLI}$  = 0.21  $\pm$ 258 259  $0.03 (2\sigma)$ . Data from the galena-poor core region (blue symbols) form a discordia D<sub>FI</sub> (MSWD = 2.6) which intersects the  ${}^{207}$ Pb/ ${}^{206}$ Pb axis at ( ${}^{207}$ Pb/ ${}^{206}$ Pb)<sub>DFI</sub> = 0.16 ± 0.03 (2 $\sigma$ ) and has upper 260 and lower intercepts with concordia at  $2120 \pm 207$  Ma ( $2\sigma$ ) and  $631 \pm 224$  Ma ( $2\sigma$ ) respectively. 261 By fixing the upper intercept at 2440 Ma for the sparse galena domain data, the lower intercept 262 is at 861  $\pm$  58 Ma (2 $\sigma$ ) (discordia D<sub>fix</sub>, MSWD = 4). 263

APT-derived <sup>208</sup>Pb/<sup>232</sup>Th dates from monazite grains hosted in the quartzo-feldspathic matrix (Mnz25 and Mnz2) and the Rt-quartz (Mnz17) are calculated from areas that do not

contain galena (Fig. 7, Appendix H, APT mass spectrum Appendix B.5). <sup>208</sup>Pb/<sup>232</sup>Th dates range 266 267 between 1188  $\pm$  202 Ma (2 $\sigma$ ) and 712  $\pm$  121 Ma (2 $\sigma$ ) (Fig. 5, Appendix G.8) and statistically correspond to a single date population (MSWD = 0.72; Appendix G.8-9). Using the complete 268 dataset, the mean  ${}^{208}\text{Pb}/{}^{232}\text{Th}$  ratio is 0.0518 ± 0.0137 (2 $\sigma$ ) corresponding to a date of 1021 ± 269 263 Ma (2 $\sigma$ ). The <sup>208</sup>Pb/<sup>232</sup>Th mean for specimens obtained from the rim of Mnz25 and Mnz2 270 is  $0.0540 \pm 0.0107$  (2 $\sigma$ ) yielding a date of  $1063 \pm 205$  Ma (2 $\sigma$ ) (MSWD = 0.34) while the mean 271  $^{208}$ Pb/ $^{232}$ Th for core specimens from the same grains is 0.0497  $\pm$  0.0156 (2 $\sigma$ ) corresponding to 272  $979 \pm 301$  Ma (2 $\sigma$ ) (MSWD = 1.04; Appendix G.8). 273

APT-derived <sup>207</sup>Pb/<sup>206</sup>Pb ratios from the two analysed galena (Gn 1 and Gn 2; Fig. 4) are 0.20  $\pm$  0.02 (1 $\sigma$ ) and 0.150  $\pm$  0.003 (1 $\sigma$ ) respectively. The APT data show no peaks associated with <sup>204</sup>Pb (Fig. 4C).

#### **5. DISCUSSION**

#### **5.1. Interpretation of microscale age pattern**

Isotopic analyses of Pb by SIMS in selected grains did not show any <sup>204</sup>Pb component in the time resolved signal, which is interpreted as the absence of significant "common"-Pb in the microscale analyses. Consequently, all the Pb present in monazite and galena is interpreted to be of radiogenic origin and is derived from within the monazite.

Considering the whole dataset (n = 89), the discordia  $D_{all}$  MSWD (4.7) indicates that the dispersion of the data cannot result from a single population (i.e. a single disturbing event) at 95% confidence level (Wendt and Carl, 1991). In contrast, the  $D_{IM}$  discordia derived from monazite hosted in Rt-quartz and garnet yields an acceptable MSWD of 0.84 compatible with a single disturbing event and is thus the most robust to derive monazite crystallization age (t<sub>0</sub>) at 2440 ± 39 Ma (Fig. 6A). This age is identical within errors to previous upper intercept ages calculated with ID-TIMS data on monazite and zircon grains from Casey Bay (Fig. 1C; Black

et al., 1984, 1983) and to  $2451 \pm 15$  Ma zircons in equilibrium with garnet from Crosby 290 Nunataks in Amundsen Bay (Fig. 1A; Taylor et al., 2017). Even if *in-situ* isotopic dating on 291 zircon may present slightly older ages than obtained in monazite (e.g. Hokada et al., 2004; Kelly 292 293 and Harley, 2005), monazite are truly and fully included in garnet implying garnet growth and/or recrystallization through to that age, extending the timescale of the UHT to HT 294 metamorphism even further. Thus, the monazite age of  $2440 \pm 39$  Ma provides a lower limit 295 296 for the UHT metamorphism in this part of the Napier Complex. The lower intercept t<sub>1</sub> of the 297  $D_{IM}$  discordia (1045 ± 132 Ma) is within error of the Rayner Complex event and reflects the time of U–Th–Pb chronometer disturbance. This is confirmed by the <sup>208</sup>Pb/<sup>232</sup>Th average age 298 299 of 1021  $\pm$  263 Ma (2 $\sigma$ ) derived by APT analysis of galena-free monazite that points to a complete resetting of the monazite matrix during the Rayner Complex tectonothermal event. 300

The monazite grains (Mnz25 and Mnz2) hosted in the quarzto-feldspathic matrix show two 301 discordia trends (yellow and blue symbols, Fig. 6B). DLI discordia is defined by the galena-rich 302 rim and is consistent with the D<sub>IM</sub> discordia. D<sub>FI</sub> is defined by the galena-poor core, 303 corresponding to areas which have undergone 70 - 90 % Pb<sup>\*</sup> loss at t<sub>1</sub>, and suggests a younger 304 disturbing event, defined by the lower intercept at  $t_2 = 631 \pm 224$  Ma (2 $\sigma$ ) (Fig. 6B). This age 305 lies within uncertainty of the timing of pegmatite intrusions within the Napier Complex at Casey 306 307 Bay at ca. 530 Ma (Carson et al., 2002; Black et al., 1983), so may correspond with this hydrothermal activity (t<sub>2</sub>). 308

309

## 5.2. Origin of discordance revealed at nanoscale

Black et al. (1984) highlighted that the least discordant monazite fraction was brown in color, whereas the most discordant was clear (grey and yellow). Our microscale data confirm a similar systematic relationship between monazite color and the percentage of Pb-loss. In addition, SEM and TEM investigations revealed that the color relates to the density of galena inclusions, with monazite showing the highest density of galena being brown in color, whilst
the clearest monazite grains contain a lower density of galena inclusions (Fig. 3, 5, 6).

316 Considering the microscale U-Th-Pb data, the dates of monazite hosted in the quartzo-317 feldspathic matrix, tend toward the lower intercept t<sub>1</sub> (80 % Pb-loss ; Fig. 5) whereas the dates from monazite hosted in Rt-quartz and garnet tend toward the upper intercept (t<sub>0</sub>) implying only 318 319 limited Pb<sup>\*</sup> loss (10-50 %) at the grain scale. This difference is again explained by the large 320 amount of galena, homogeneously distributed considering a micrometric analytical volume, in Rt-quartz hosted monazite compared to monazite hosted in the quartzo-feldspathic matrix (Fig. 321 322 3A) Thus, the discordia (D<sub>IM</sub>) is interpreted as a mixing pattern between galena and monazite host, representing two different reservoirs of Pb\* derived from the monazite itself. A similar 323 pattern is observed within individual grains (e.g. Mnz25), where core regions with a smaller 324 number of galena show a higher percentage of Pb-loss than the galena-rich rim (Fig. 6B). 325

The ability of monazite to retain galena crystals and thereby much of the Pb<sup>\*</sup> is partly related 326 to their textural position; monazite crystals hosted in Rt-quartz and garnet retain more Pb<sup>\*</sup> in 327 328 the form of galena than monazite crystals hosted in the quartzo-feldspathic matrix (Fig. 3, 5, 6A). High retention of  $Pb^*$  is associated with a small galena size (< 50 nm), and a more 329 homogenous distribution through the crystal (Fig. 3). This property could be related to fluids 330 331 access to monazite. Rt-quartz and garnet, which are anhydrous UHT phases, could limit the quantity of fluids which are thus rapidly saturated in Pb, inducing a short-range (re)precipitation 332 333 of Pb-bearing nanominerals within the grain. In contrast, a larger quantity of fluids might access monazite hosted in quartzo-feldspathic matrix implying a more efficient leaching of Pb<sup>\*</sup> which 334 is then lost from the grain. Shielding of monazite by its host-mineral, also observed at other 335 336 UHT localities (e.g. Paquette et al., 2004; Madagascar), does not act as the trigger for the development of the Pb-bearing minerals within monazite but is instrumental to their preferential 337

preservation and retention. Further studies will be undertaken to characterize the mineralogical
variety of the Pb-bearing nanominerals present in monazite grains.

340 To summarize, the difference in color is interpreted to relate to the amount and distribution 341 of galena crystals within the different monazite grains, which in turn is related to the percentage of Pb-loss. The inverse correlation between the percentage of Pb-loss and the amount of galena 342 (Fig. 3, 5, 6) reflects partial retention of radiogenic Pb<sup>\*</sup> at the grain scale through the 343 344 crystallization of galena. The volume analyzed with micro-scale dating methods (ID-TIMS, LA-ICP-MS, SIMS and EMP) therefore corresponds to a mixing between monazite and galena 345 preserving distinct isotopic composition. The retention of galena is promoted by monazite 346 347 shielding in (anhydrous) UHT phases like garnet and Rt-quartz.

348 The largest Pb-bearing nanominerals observed in this study have been identified as galena 349 (PbS). Crystallization of galena requires Pb but also S which may be derived either from an external source such as metamorphic fluids or from the monazite itself. Sulphur incorporation 350 in the monazite lattice occurs mostly through the clino-anhydrite substitution  $Ca^{2+} + S^{6+} =$ 351 REE<sup>3+</sup> + P<sup>5+</sup> (Chakhmouradian and Mitchell, 1999), although other studies suggest more 352 complex substitutions involving S<sup>2-</sup> and S<sup>4+</sup> (Broom-Fendley et al., 2020). The presence of S-353 354 rich monazite in metamorphic rocks is well-documented, including in UHT granulite (Laurent 355 et al., 2016). Under low-grade metamorphic conditions (greenschist facies), S incorporation in monazite is typically associated with high common Pb content and ore precipitation in the host 356 357 rock (Krenn et al., 2011; Pršek et al., 2010; Suzuki and Kato, 2008). Under high-grade conditions, S-rich monazite reflects Fe-sulphide breakdown under oxidizing conditions and 358 359 have been reported to contain negligible common Pb (Laurent et al., 2016). Since common Pb 360 is negligible in monazite and galena from the present study, sulfur could be derived from the monazite itself rather than from an external source. The presence of sulfur in high-grade 361 monazite could thus contribute heavily to the preservation of Pb<sup>\*</sup> as galena nanocrystals. 362

#### 363 **5.3. Galena Pb isotopic signatures**

Historically, discordance issues have been resolved by lowering the analytical volume until 364 homogenous Pb<sup>\*</sup> isotope reservoirs can be analyzed separately (i.e. galena and monazite 365 matrix). As there is no U or Th in the galena, their measured  $^{207}$ Pb/ $^{206}$ Pb ratios have not evolved 366 since their growth. As SIMS results support that common-Pb contamination of the monazite is 367 negligible, the <sup>207</sup>Pb/<sup>206</sup>Pb ratio of the galena records the Pb<sup>\*</sup> composition of the monazite when 368 the galena crystallised. Since the monazite crystallisation age is known, then the <sup>207</sup>Pb/<sup>206</sup>Pb of 369 galena can be used to estimate the time of Pb<sup>\*</sup> isolation from U and Th in the host monazite, 370 371 which corresponds to the time of galena growth. The evolution of the Pb isotopic ratio of the 372 monazite is constrained by the geological history highlighted in the previous sections and thus bounded by the *ca.* 2440 Ma ( $t_0$ ), 1045 Ma ( $t_1$ ), and 550 Ma ( $t_2$ ) geological events (Fig. 8C). 373 374 This assumption is confirmed by the scatter of microbeam analyses that fall in a triangle bounded by ca. 2.44 Ga, 1.05 Ga and 0.55 Ga in the Tera-Wasserburg plot (Fig. 6). 375

The <sup>207</sup>Pb/<sup>206</sup>Pb ratio measured in Gn 1 is best explained by Pb<sup>\*</sup> isolation at 1045 Ma from 376 a monazite that crystallized at 2440 Ma, which would correspond to a theoretical <sup>207</sup>Pb/<sup>206</sup>Pb of 377 0.2108 identical within uncertainty to the measured ratio of  $0.20 \pm 0.02$  (1 $\sigma$ ) in Gn 1 (Fig. 8A, 378 C). The isolation time of  $Pb_1^*$  (i.e.  $Pb^*$  formed by radioactive decay within monazite between 379 2440 and 1045 Ma) at *ca*. 1045 Ma is supported by the  ${}^{208}$ Pb/ ${}^{232}$ Th date of 1171 ± 170 Ma 380 381 (Appendix G.8) obtained by APT from the host monazite adjacent to Gn 1 in specimen M6 (Fig. 4A). Thus, we interpret that the isolation of  $Pb_1^*$  and the crystallization of galena Gn 1 382 occurred at  $t_1 = 1045$  Ma. 383

Galena Gn 2 has a significantly different  ${}^{207}$ Pb/ ${}^{206}$ Pb ratio of 0.150 ± 0.003 (1 $\sigma$ ) that cannot be explained by a single Pb\* isolation event since the present-day  ${}^{207}$ Pb/ ${}^{206}$ Pb ratio of a monazite that crystallized at 2440 Ma would be 0.1585 (Fig. 8A). The possibility for Gn 2 to result from

a mixing of two Pb<sup>\*</sup> components is thus explored using the well-known  $t_0$ ,  $t_1$  and  $t_2$  events. This 387 scenario involves a first Pb<sup>\*</sup> component (Pb<sub>1</sub><sup>\*</sup>) produced by U and Th decay between  $t_0$  and  $t_1$ 388 with a theoretical  ${}^{207}\text{Pb}/{}^{206}\text{Pb}$  isotopic signature of 0.2108, and a second Pb<sup>\*</sup> component (Pb<sub>2</sub><sup>\*</sup>) 389 produced by U and Th decay between  $t_1$  and  $t_2$  with a theoretical  ${}^{207}Pb/{}^{206}Pb$  isotopic signature 390 of 0.0901. At 550 Ma, the <sup>207</sup>Pb/<sup>206</sup>Pb ratio of 0.150 recorded by Gn 2 is then obtained by a 391 mixture of 53%  $Pb_2^*$  and 47%  $Pb_1^*$ , in a grain which underwent 70%  $Pb_1^*$  loss at  $t_1$  with 30% 392 remaining captured by the galena (Fig. 8B, C). This 70% Pb<sub>1</sub><sup>\*</sup> loss fits the microscale U–Th– 393 Pb data for monazite grain 25 domains with a low density of inclusions (Fig. 6B). The 394  $^{208}$ Pb/ $^{232}$ Th date of 712 ± 121 Ma (2 $\sigma$ ) (Appendix G.8) obtained by APT from the host monazite 395 396 adjacent to Gn 2 in specimen M17 (Fig. 4A) supports the formation of Gn 2 at t<sub>2</sub>, a younger event than t<sub>1</sub>. This preferred scenario is not unique since: (1) microscale data suggests variable 397  $Pb_1*$  loss at  $t_1$ , ranging from 10 to 90 % (Fig. 6) and (2) variable proportions of  $Pb_1*$  and  $Pb_2*$ 398 could be mobilized and mixed at  $t_2$ , corresponding to a theoretical range of  $^{207}$ Pb/ $^{206}$ Pb isotopic 399 compositions between 0.0901 - 0.1806 for the galena (Fig. 8C). This observation cautions about 400 the interpretation of <sup>207</sup>Pb/<sup>206</sup>Pb ratios in Pb-rich nanominerals in term of ages. 401

402

#### 5.4. Time-integrated model of monazite evolution

403 The theoretical evolution of U-Pb and Pb-Pb ratios in a monazite that crystalized at ca. 2440 Ma have been modelled and the results are displayed in Tera-Wasserburg diagrams along 404 405 with snapshots of Pb distribution in the monazite crystal over time (Fig. 8D). After monazite crystallization at t<sub>0</sub>, U and Th decay in monazite produce  $Pb_1^*$  (red spots, Fig. 8D). The APT 406 average  ${}^{208}\text{Pb}/{}^{232}\text{Th}$  age of  $1021 \pm 263$  Ma  $(2\sigma)$  indicates that the monazite matrix becomes 407 completely reset at the nanoscale. This resetting event corresponds to the amphibolite-facies 408 409 Rayner event at *ca*. 1045 Ma. This metamorphic event is recorded in our rock sample 5037 by garnet retrogression into biotite and by recrystallization of (UHT) Rt-quartz in rutile-free, low-410 Ti quartz ribbons. Clear evidence of fluid-rock interaction and plastic deformation thus exists 411

in the rock sample 5037 at *ca.* 1045 Ma. Lead mobility in monazite has been shown to be
enhanced both by fluid present conditions (Seydoux-Guillaume et al., 2002) and deformation
(Erickson et al., 2015; Fougerouse et al., 2021b) or a combination of both (Wawrzenitz et al.,
2012).

416 In presence of reactive metamorphic fluids, experimental studies demonstrate that the resetting of monazite U-Pb and Th-Pb chronometers at the nanoscale could arise through 417 pseudomorphic replacement with the formation of a new monazite free of Pb<sup>\*</sup> only recognizable 418 at the nanoscale (Grand'Homme et al., 2018, 2016). Whilst the APT age of  $1021 \pm 263$  Ma ( $2\sigma$ ) 419 suggests that the monazite matrix is completely reset at  $t_1$ , we cannot completely exclude that 420 421 subordinate nanodomains of monazite crystallized at 2440 Ma may still be present after t<sub>1</sub>, accounting for the dispersion and large uncertainties of the monazite matrix dates measured by 422 APT (Appendix G.9). Compared to these experimental studies, the replacement process in this 423 natural example is coupled with Pb-bearing nanominerals (galena) crystallization. This contrast 424 could reflect differences in experimental versus natural rock reaction kinetics or fluid/mineral 425 426 ratios, or fluid compositions. Indeed, nanopores filled with SiO<sub>2</sub> are frequently observed in experimental studies because a NaOH fluid saturated in Si is used. In natural monazite, the local 427 fluid saturation in Pb might be achieved by relatively low fluid/monazite ratio typical of dry 428 rocks like UHT granulite and a high Pb\* concentration typical of old Th-rich monazite. 429

Following the  $t_1$  event, Pb<sub>2</sub><sup>\*</sup> forms from the further decay of U and Th in the monazite (green spots, Fig. 8D). At *ca.* 550 Ma (t<sub>2</sub>), a hydrothermal event associated with pegmatite formation triggers the crystallization of a second generation of galena (Gn 2) composed by the mixing of Pb<sub>1</sub><sup>\*</sup> + Pb<sub>2</sub><sup>\*</sup>. The Pb<sub>2</sub><sup>\*</sup> component is derived from the monazite matrix at t<sub>2</sub> and correspond to Pb<sup>\*</sup> growth between t<sub>1</sub> and t<sub>2</sub>. Mobilization of Pb<sub>2</sub><sup>\*</sup> to form Gn 2 is more cryptic as it is not related to an extensive resetting of the Th–Pb chronometer in the monazite matrix compared to the first generation of galena. The monazite matrix adjacent to Gn 2 yields the youngest Th–Pb date of  $712 \pm 121$  Ma  $(2\sigma)$ , which sits between  $t_1$  and  $t_2$ . Consequently, Pb migration at  $t_2$ occurred at a smaller scale than at  $t_1$  and might not be completely resolved at the current scale of investigation. This is confirmed by the microscale observation that in contrast to  $t_1$  event, the effect of the  $t_2$  event is insufficient to cause significant Pb<sup>\*</sup> loss at the grain scale (Fig. 6). The galena 2 therefore rather witnesses intra-grain and short-range redistribution of Pb, involving a Pb<sub>2</sub><sup>\*</sup> and a Pb<sub>1</sub><sup>\*</sup> component that could be derived from either the first galena (Gn 1) or from monazite matrix in case of old nanodomains have been preserved in the matrix at  $t_1$ .

444

### 6. CONCLUSION and PERSPECTIVES

This study explores the isotopic disturbance of the U-Th-Pb systems in monazite from a 445 UHT Archean granulite using multiple methods for characterization and dating from the micro-446 (LA-ICP-MS, SIMS, EMP) to the nanoscale (TEM, APT). At the microscale the dates are 447 448 discordant and spread along a discordia between ca. 2440 and ca. 1045 Ma. Our observations reveal that the least discordant monazite grains are brown in color because they contain a high 449 density of small (~ 50 nm) Pb-bearing nanominerals homogeneously distributed in the grain 450 whereas the most discordant and optically clear monazite grains contain larger (50- 500 nm) 451 but sparser Pb-bearing nanominerals, some of them being identified as galena (PbS) on the basis 452 453 of TEM and APT observations. The discordia observed with conventional in-situ methods at 454 the microscale thus reflects a mixing within the analytical volume of matrix monazite and galena. The percentage of Pb-loss is in turn linked to monazite textural position as initially 455 456 observed by Black et al. (1984). Monazite shielded in UHT phases like garnet or Rt-quartz show a low percentage of Pb-loss and a high density of galena inclusions. In contrast monazite 457 hosted in the re-equilibrated quartzo-feldspathic matrix show a high percentage of Pb-loss and 458 459 lower density of galena inclusions. The retention of Pb\* in galena is promoted by monazite shielding in (anhydrous) UHT phases like garnet and Rt-quartz. 460

The Pb isotopic compositions of the galena grains are variable but imply an *in-situ* 461 radiogenic origin with no participation of common Pb. The <sup>207</sup>Pb/<sup>206</sup>Pb ratios of the galena, 462 when considered in combination with the <sup>208</sup>Pb/<sup>232</sup>Th ages of the monazite matrix (excluding 463 galena) measured with APT, and the constrains given by regional geology, indicate two 464 episodes of Pb<sup>\*</sup> mobility. This study suggests that monazite crystallized at *ca*. 2440 Ma and was 465 affected at *ca*. 1045 Ma by variable Pb<sup>\*</sup>-loss at the grain scale, characterized at the nanoscale 466 by a resetting of the monazite matrix through pseudomorphic replacement associated with Pb<sup>\*</sup> 467 retention as galena Gn 1 in variable proportions. A second episode of Pb<sup>\*</sup> mobility is recorded 468 by the crystallization of a second generation of galena Gn 2 and is likely related to a younger 469 event at *ca*. 550 Ma. Pb<sup>\*</sup> in Gn 2 galena corresponds to a mixing of Pb<sub>1</sub><sup>\*</sup> and Pb<sub>2</sub><sup>\*</sup> likely 470 reworked from the pre-existing Gn 1  $(Pb_1^*)$  and monazite matrix  $(Pb_2^*)$  with much more 471 localized effect on the resetting of the monazite matrix as no date of 550 Ma was found by APT. 472

Combining a multi-scale characterization, this study demonstrates the importance of 473 nanoscale structural, chemical and isotopic observations to understand microscale age 474 475 disturbances by providing a new perspective on the origin of the discordance in monazite. Indeed, the retention of Pb<sup>\*</sup> in the form of Pb-bearing nanominerals within monazite grain could 476 be a phenomenon that is, if not prevalent, at least shared by monazite crystals when certain 477 478 conditions are met. These conditions may include an ancient and long-lived geological history (Archean – Proterozoic) resulting in high Pb\* content, a monazite composition having a 479 sufficient S content to form galena and the presence of reactive fluids. However other Pb-480 481 bearing nanominerals might crystallize if S is unavailable. For example, Pb-bearing nanominerals have been found in discordant Archean UHT monazite from Madagascar 482 483 (Paquette et al., 2004; Seydoux-Guillaume et al., 2003). Hence, discordance in monazite is explained by the partial loss of Pb<sup>\*</sup> through a coupled dissolution-precipitation process and the 484 retention of the remaining Pb<sup>\*</sup> within monazite as Pb<sup>\*</sup>-bearing nanominerals (e.g. galena). In 485

combination with a good understanding of the regional framework and the thermal events in an
area, the identification of Pb\*-bearing nanominerals can be used to understand the complexities
of Pb\* migration processes in minerals. The presence of numerous Pb\*-bearing nanominerals
within monazite grains therefore presents new opportunities for geochronologists to decipher
the thermal history of complex metamorphic terrains.

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## 498 Appendices

- 499 Appendix A. Details on the methods, including sample preparation, analytical conditions,
- 500 calibration and data processing
- 501 Appendix B. Complementary observations of microscale to nanoscale features including
- 502 optical microscopy, scanning electron imaging, transmission electron microscopy and atom
- 503 probe mass spectrum of monazite
- 504 Appendix C. U-Th-Pb SIMS dataset
- 505 Appendix D. U-Th-Pb LA-ICP-MS dataset
- 506 Appendix E. U-Th-Pb EMP dataset
- 507 Appendix F. U-Th-Pb data plotted on figure 5

- 508 Appendix G. Complementary figures of U–Th–Pb geochronology
- 509 Appendix H. Th-Pb APT dataset

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#### 694 **Figures and captions**

1.5-column fitting image Figure 1. Location map of the sampling area (~  $67^{\circ}22'30"$  S and 49°03'45"E) and previous geochronological results. A, B: map location of Zircon Point in the Napier Complex, showing the UHT zone (green dotted line) and the assumed limit between the Napier and the Rayner complex (black dotted line) from Harley et al. (2019). C: Previous U–Pb geochronological result on monazite measured by ID-TIMS (multi grain) from Black et al. (1984). White diamonds along the discordia represent the percentage of Pb loss. Analytical uncertainties are lower than the size of the symbols.



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2-column fitting image Figure 2. Microscale characterization of monazite. A, B, C: High-705 contrast BSE SEM imaging of grains Mnz17 (A) hosted in Rt-quartz, Mnz25 (B) and Mnz2 706 707 (C) hosted in the quartzo-feldspathic matrix showing a core - rim texture along with NE-SW oriented bright (high-BSE contrast) linear features traversing the core of Mnz25 (B). The 708 location of SIMS (white-dashed ellipses), LA-ICP-MS (full white circle) and EMP (white 709 710 square) analytical spots are shown (A-C). D-F: High-contrast BSE SEM imaging of selected region of interest (red rectangles in A and B) displaying bright (high-BSE contrast) and dark 711 712 (low-BSE contrast) circular inclusions. Note the smaller size of inclusions in Rt-quartz hosted 713 monazite (D) compared to quartzo-feldspathic matrix hosted monazite (E-F) as well as the 714 core-rim feature in (E) with inclusion-poor core and inclusion-rich rim. The location of TEM-715 FIB foils (A, B) and APT tips (A, C, F) are also shown with an inset showing the real size of 716 APT site of interest (F).



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720 2-column fitting image Figure 3. Scanning transmission electron microscopy annular dark 721 field images (STEM-ADF) with the same field of view for garnet hosted monazite (A) and 722 quartzo-feldspathic matrix hosted monazite (B, C). Light grey inclusions correspond to distinct crystalline Pb-bearing minerals often polyphased and spatially associated with a dark 723 amorphous Si-rich part. Quartzo-feldspathic matrix hosted monazite display a lower density 724 725 and larger ( $\emptyset > 50$  nm) light Pb-bearing minerals compared to garnet hosted monazite. Note that within quartzo-feldspathic matrix hosted monazite Mnz25, the rim (B) display a higher 726 727 density of Pb-bearing minerals than the core (C). Vertical dark bands in B correspond to 728 artefacts from FIB polishing (curtaining effects).



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1.5-column fitting image Figure 4. APT reconstructions of M6 (from Mnz2) and M17 (from 732 Mnz25) specimens showing S, Pb, Ce and Th atomic distribution (A). Pb and S are 733 concentrated at the top of the tips and define galena while Pb, Ce and Th are concentrated at 734 the bottom, highlighting the interface with monazite. <sup>207</sup>Pb/<sup>206</sup>Pb ratios were calculated for 735 each of the galena (errors are  $1\sigma$  uncertainty) and <sup>208</sup>Pb/<sup>232</sup>Th dates for the monazite (errors 736 are 2 $\sigma$  uncertainty). B: Representative mass spectrum of galena acquired from Gn 1. Peaks are 737 colored by molecular ions and element species. The main peaks are in good agreement with 738 739 galena peaks from Cappelli and Pérez-Huerta (2020). C: Mass spectrum showing mass peaks and overlaps for  $Pb^{2+}$ . Scale bar = 100 nm. Tips locations are shown on Fig. 2C, F. 740



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1.5-column fitting image Figure 5. Range of dates depending on the analytical volume. Boxplots of dates discriminated by the analytical volume referring to the technique used (ID-TIMS on multi grain from Black et al., 1984, *in-situ* LA-ICP-MS ~ 950  $\mu$ m<sup>3</sup>, SIMS ~ 600  $\mu$ m<sup>3</sup>, EMP ~ 5  $\mu$ m<sup>3</sup> and APT < 0.008 nm<sup>3</sup> – this study), the analyzed domain (entire grain, core or rim), and the textural position of the analyzed grain (quartzo-feldspathic matrix = matrix, Rt-quartz, garnet or sillimanite).



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1-column fitting image Figure 6. Tera-Wasserburg diagram from LA-ICP-MS (ellipses) and 753 754 SIMS (crosses) U–Pb data denoting  $2\sigma$  uncertainties. White diamonds along the discordia lines represent the percentage of Pb loss. A: U-Pb data with the full dataset color-coded by 755 756 host mineral. The discordia line D<sub>all</sub> (solid) constructed with all data defines an upper intercept of  $2383 \pm 36$  Ma and a lower intercept of  $931 \pm 45$  Ma (MSWD = 4.7). Discordia 757 constructed with data from included monazite in Rt-quartz and garnet, D<sub>IM</sub> (dashed) lead to an 758 upper intercept of  $2440 \pm 39$  Ma and a lower intercept of  $1045 \pm 132$  Ma (MSWD = 0.84). B: 759 U-Pb data for selected quartzo-feldspathic matrix hosted monazite grains discriminated by the 760 content of galena in the analyzed area. Discordia DLI (solid) is constructed from the galena-761 762 rich rim domain analyses and indicate a MSWD = 2, an upper intercept of  $2434 \pm 181$  Ma and a lower intercept of  $1049 \pm 248$  Ma. The isotopic composition of Pb produced in the 2434– 763 1049 Ma time interval is given by the intercept of the  ${}^{207}$ Pb/ ${}^{206}$ Pb axis at 0.21 ± 0.03 (2 $\sigma$ ). 764 765 Discordia D<sub>FI</sub> (large dashed) constructed from the galena-poor core domain analyses indicates a MSWD = 2.6, an upper intercept of  $2120 \pm 207$  Ma, a lower intercept of  $631 \pm 224$  Ma and 766 intercepts the  ${}^{207}$ Pb/ ${}^{206}$ Pb axe at 0.16 ± 0.03 (2 $\sigma$ ). By fixing the upper intercept (discordia D<sub>fix</sub>, 767 small dashed) at 2440 Ma, the lower intercept yields a date of  $861 \pm 58$  Ma (MSWD = 4). The 768 purple boxes are the  ${}^{207}$ Pb/ ${}^{206}$ Pb ratios, including the 1 $\sigma$  error, calculated for Gn 1 in M6 and 769 Gn 2 in M17. 770



1-column fitting image Figure 7. APT reconstructions of quartzo-feldspathic matrix hosted
monazite Mnz25 and Mnz2 in core (M16, M15, M5) and rim (M19) showing Ce and Th
atomic distribution. One dot represents one atom. Scale bar = 100 nm. Tips locations are
shown on Fig. 2C, F.



1.5-column fitting image Figure 8. A: Theoretical <sup>207</sup>Pb/<sup>206</sup>Pb evolution in a monazite 782 crystallized at 2440 Ma and showing the theoretical value of an isolated reservoir (i.e. galena) 783 formed at 1045 Ma correlating with <sup>207</sup>Pb/<sup>206</sup>Pb of Gn 1 within error limits (purple box). B: 784 Theoretical Pb<sub>1</sub><sup>\*</sup> component proportion required to form a <sup>207</sup>Pb/<sup>206</sup>Pb signature of 0.150 785 considering a  $Pb_1^* + Pb_2^*$  mixing over time in the studied monazite. C: Theoretical evolution 786 of <sup>238</sup>U/<sup>206</sup>Pb and <sup>207</sup>Pb/<sup>206</sup>Pb ratio in a Tera-Wasserburg diagram for a monazite which 787 crystallizes at 2440 Ma (t<sub>0</sub>) and undergoes two events of Pb<sup>\*</sup> mobility at 1045 Ma (t<sub>1</sub>) and 550 788 789 Ma (t<sub>2</sub>). D: Schematic Pb<sup>\*</sup> mobility in monazite; t<sub>0</sub> monazite crystallization free of Pb<sup>\*</sup>, t<sub>0</sub> to t<sub>1</sub>  $Pb_1^*$  growth (red spots), at  $t_1 x\%$  of  $Pb_1^*$  loss at the grain scale along with resetting of 790 monazite matrix and 1-x% of  $Pb_1^*$  isolation as galena. Then  $t_1$  to  $t_2 Pb_2^*$  growth in monazite 791 matrix (green spots). At t<sub>2</sub> Pb<sup>\*</sup> mixing and isolation as galena in variable proportion of Pb<sub>1</sub><sup>\*</sup> 792 and Pb<sub>2</sub><sup>\*</sup> and t<sub>actual</sub> theoretical state of the monazite grain. 793

