⁴⁰Ar/³⁹Ar age constraints on the formation of fluid-rich quartz veins from the NW Rhenohercynian zone (Rursee area, Germany)

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Abstract. A substantial part of the subsurface geology in northwestern and central Europe is defined by the late Palaeozoic Variscan Orogeny (~350 Ma). Our focus is mainly on veining in anchi-metamorphic sedimentary rocks affected by this orogeny. Mineral veins serve as repositories for documenting the origin of subsurface fluid flows, dynamics and dating them may provide crucial insight into the timing of orogenic and possible reactivation events. The Rursee area (Rhenish Massif, Germany), part of the Variscan foreland zone on the Avalonia microcontinent, represents a key locality for studying Variscan quartz vein formation. Based on structural grounds, two groups/types of Rursee quartz veins have been linked with the early stages of Variscan, but their absolute ages are still unknown.

The aim of this study is to date these quartz veins using the 40 Ar/ 39 Ar stepwise crushing method based on the radioactive decay of 40 K dissolved in high-salinity fluid inclusions. We obtained Jurassic to Cretaceous ages, and isotopic analysis of the argon gases revealed that the fluid-rich quartz fractions release 39 Ar in two distinct phases. Regardless of the salinity of fluid inclusions in quartz veins, stepwise crushing provides apparent K/Cl > 1. Electron Probe Micro Analyser data confirm the presence of K (39 Ar) in the K-bearing mineral inclusions (e.g., sericite, white mica, and chlorite) and microcracks and possibly in the crystal lattice of quartz.

Secondary fluid inclusions or K-bearing mineral inclusions and/or the crystal lattice of quartz, which formed subsequently in the Variscan vein fractures, provide a plausible explanation for the young apparent isotopic ages. Deformation-induced quartz sub-grains may suggest that obtained maximum apparent ages are likely to reflect post-Variscan fluid-assisted reactivationrecrystallization due to tectonic activity, or its cooling moment during the Jurassic-Cretaceous period rather than the original Variscan vein formation.

24 1 Introduction

Quartz veins are abundant in metamorphosed terranes and sedimentary basins filled with siliciclastic sediments, witnessing significant fluid movement during diagenesis and metamorphism (Yardley, 1983; Mullis et al., 1994; Cartwright and Buick, Oliver and Bons, 2001). An increase in both temperature and pressure during burial diagenesis, orogenesis, and deformation causes sedimentary and volcanic rocks to lose their volatile components and to release warm fluids, which cumulate minerals in fractures and faults (Baumgartner and Ferry, 1991; Yardley and Bottrell, 1993; Oliver and Bons, 2001;

30 Cox, 2007). These often saline fluids contain, among others, KCl $_{(aq)}$ or K₂CO_{3 (aq)} (Rauchenstein-Martinek et al., 2014), which</sub>31 are partly precipitated during the crystallization of minerals in veins or as inclusions in these minerals (Sterner et al., 1988). 32 One of the isotopes of potassium, ⁴⁰K, is radioactive and can be used for K-Ar or its derivative, ⁴⁰Ar/³⁹Ar dating. Progressive 33 crushing techniques enable the liberation of gases from fluid inclusions, mineral inclusions, and/or crystal lattice for the age 34 determination of geological events provided that K-concentrations are high enough (Oiu and Dai, 1989; Turner and Bannon, 35 1992; Turner and Wang, 1992; Qiu, 1996; Kendrick et al., 2001; Qiu and Wijbrans, 2006; Kendrick et al., 2006; Qiu and 36 Wijbrans, 2008; Oiu and Jiang, 2007; Jiang et al., 2012; Bai et al., 2013; Liu et al., 2015). This method not only defines an age but also quantifies the ratio of noble gases (e.g., ³⁹Ar_K/³⁷Ar_{Ca}, ³⁹Ar_K/³⁸Ar_{Cl}) derived from Ca, K, and Cl, respectively, that have 37 38 been formed during neutron radiation before analysis. The ${}^{39}Ar_{K}/{}^{38}Ar_{C1}$ provides crucial information on the composition of 39 parental fluids and their sources (Sumino et al., 2011; Cartwright et al., 2013). Beyond studies on fluid composition and 40 provenance (Kelley et al., 1986; Turner and Bannon, 1992; Kendrick et al., 2001, 2006), the initial ⁴⁰Ar/³⁶Ar values of fluid 41 inclusions in quartz can considerably vary and may be used to differentiate between meteoric-sourced water (~ 298.6) 42 (Ballentine et al., 2002; Ozima and Podosek, 2002) and deeper crustal or mantle-derived fluids (>10,000; MORB >40,000) (Burnard et al., 1997). Additionally, hydrothermal waters can present sub-atmospheric ⁴⁰Ar/³⁹Ar ratios, as can be deduced from 43 44 inverse isochrons of fluid-altered rocks (e.g., 280-290; Baksi, 2007).

45 To accurately determine the age of fluid inclusions in quartz veins using the ⁴⁰Ar/³⁹Ar stepwise crushing method or the source of the fluid based on ${}^{40}\text{Ar}_{\text{A}}$ ratios, it is necessary to consider three distinct components of ${}^{40}\text{Ar}_{\text{A}}$, namely (1) radiogenic ${}^{40}\text{Ar}_{\text{B}}$ 46 or 40 Ar*, which is produced in the sample itself through the radioactive decay of 40 K, and (2) 40 Ar that was initially trapped in 47 the fluid inclusion, either as (2a) atmospheric ⁴⁰Ar_A or (2b) excess ⁴⁰Ar_E. The presence of ⁴⁰Ar_E in fluid inclusions could be a 48 49 challenge in determining accurate vein formation ages using the K-Ar dating technique (Rama et al., 1965). More recently, isochron diagrams using ⁴⁰Ar/³⁹Ar geochronology helped to overcome this issue (McKee et al., 1993; Qiu, 1996; Qiu et al., 50 51 2002). In addition to 40 Ar_E, the origin of 39 Ar_K (or K content) has been a topic of debate, with the possibility that the 39 Ar_K (and 52 thus K) may come from the dissolved salts in fluid inclusions, leaking from the crystal lattice during crushing (Kendrick et al., 53 2011), and/or from any K-bearing mineral inclusions trapped inside the crystals (Qiu and Wijbrans, 2006; Kendrick, 2007; 54 Oiu and Wijbrans, 2009; Kendrick and Phillips, 2009).

This study aims i) to determine the absolute age of quartz vein formation by analyzing fluid inclusions using the stepwise crushing ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ dating method, ii) to elucidate the location of K in the vein minerals (e.g., fluid inclusions, mineral inclusions, and/or crystal lattice), and iii) to identify when different K sources release their ${}^{39}\text{Ar}_{\text{K}}$ through the examination of released argon gases during the crushing process and geochemical analysis of quartz mineral samples using an Electron Probe Micro Analyser (EPMA).

60 Quartz samples were obtained from an outcrop near the Rursee in the upper reaches of the Rur River in the North Eifel region

61 of Western Germany. Detailed structural investigations of this area have been previously conducted by Van Noten et al. (2007),

62 who differentiated quartz veins into two groups. The older generation of quartz veins, the so-called bedding normal veins

63 (BNVs), is assigned to the early stages of the Variscan Orogeny, and the second group, comprising bedding parallel veins

- 64 (BPVs), is linked to the main stage of the Variscan Orogeny. Absolute ⁴⁰Ar/³⁹Ar ages of fluid inclusions representing the age
- 65 of quartz vein formation would allow us to better constrain the structural evolution and subsurface fluid flow during the
- 66 Variscan Orogeny in northwestern Europe. Reliable ⁴⁰Ar/³⁹Ar age constraints of quartz vein formation would provide the
- 67 opportunity to understand the timing and evolution of mountain building in analogue fold-and-thrust belts.

68 1.1 Geological Setting

The Rhenohercynian fold-and-thrust belt, part of the Variscan, is primarily located in the Rhenish Massif in Germany and extends westward into the Ardennes, southwest England, and eastward to the Harz Mountains (Kołtonik et al., 2018). The Ardennes Allochthone (Fig. 1a), the western part of the Rhenish Massif, structurally comprises three main components: the Dinant fold-and-thrust belt, the Lower Palaeozoic Inliers, and the High-Ardennes Slate Belt (HASB). The HASB primarily consists of Lower Devonian metasediments, including the Rurberg (upper Pragian) and Heimbach (upper Pragian to lower Emsian) units.

For this study, quartz vein samples were collected near the Schwammenauel dam in the Rursee area of the North Eifel region, Germany (Fig. 1b). The Rurberg and Heimbach units feature alternating layers of siltstones and fine- to coarse-grained sandstones (Goemaere and Dejonghe, 2005), deposited in shallow marine to deltaic environments in the northern Rhenohercynian Ocean (Oncken et al., 1999). The Early Devonian strata have accumulated to a total thickness of up to 7 km due to rapid subsidence and deposition (Winterfeld, 1994), forming the Eifel syncline (Fig. 1b). These strata are overlain by a ~3 km thick sequence of Lower Lochkovian to Pragian deposits.

The late Carboniferous deformation of the Variscan foreland led to initial burial metamorphism (Mansy et al., 1999), with prehnite-pumpelleyite facies similar to the anchizone conditions in the North Eifel area (Fielitz 1995), where temperatures reached up to 220 °C (Littke et al., 2012). There is also evidence of the upward migration of warm fluids into the northern Variscan front in Ardennes, driven by Variscan thrusting (Muchez et al., 2000; Schroyen and Muchez, 2000; Lünenschloss et al., 2008).

86 Following the Variscan period, the Rhenish Massif has been affected by transpressional and transtensional deformation that

- 87 resulted in the formation of complex fault networks that host vein mineralization (Franzke and Anderle, 1995; Ziegler and
- 88 Dèzes, 2005). During the Jurassic-Cretaceous period, the southern Rhenish Massif was periodically affected by hydrothermal
- 89 activities (Kirnbauer et al., 2012), as indicated by geochronological data for post-Variscan vein mineralization (Bonhomme et
- 90 al., 1983; Mertz et al., 1986; Bähr, 1987; Jakobus, 1992; Hein and Behr, 1994; Klügel, 1997; Schneider and Haack, 1997;
- 91 Glasmacher et al., 1998; Schneider et al., 1999; Chatziliadou and Kramm, 2009).



92 Figure 1: (a) Geological map with the Variscan frontal zone in the Ardenne-Eiffel region (study area marked with a red star). (b)

- 93 Geological map of the North Eifel region (modified after Ribbert, 1992; Van Noten et al., 2011). The Lower Devonian layers overlay 94 metamorphic deposits of the Lower Palaeozoic Stavelot-Venn Inlier. These layers have been locally distorted in the Monschau Shear
- 254 Inclain of pric deposits of the Lower Falaeozoic Stavelot-venn finner. These layers have been locally distorted in the Monschau Shear 255 Zone (MSZ), as documented by Fielitz (1992). Triassic sediments overlay the Lower Devonian layers in the eastern region. The
- sample location, indicated by a green star, is situated next to the Rursee reservoir, which is near the Schwammenauel dam. Below,
- 97 the cross-section illustrates the continuous northwest-southeast trending overturned folds that characterize the North Eifel zone.

- 98 The ⁴⁰Ar/³⁹Ar study targets the BNVs and BPVs (Fig. 2), which formed in low-grade metamorphosed (prehnite-pumpelleyite
- 99 facies) conditions as a result of the precipitates from warm fluids in fractures (Van Noten et al., 2008). The structural cross-
- 100 cutting relationships between these quartz vein generations suggest that they originated from different geological events (Van
- Noten et al., 2008), revealing that BPVs are younger than BNVs. BNVs are mostly found within the competent psammite and 101
- 102 hardly occur in incompetent pelitic layers. This positioning suggests that BNVs formed during the early stages of the Variscan
- 103 orogeny, associated with the final burial phases of the Ardennes-Eifel basin (Sintubin et al., 2000; Urai et al., 2001; Van Noten
- 104 et al., 2008, 2009).
- 105 In contrast, BPVs follow the strata between the psammatic and pelitic layers due to bedding-parallel slip caused by flexural
- 106 folding during the Variscan Orogeny (Van Noten et al., 2008).



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Figure 2: Images of studied outcrops from the Rursee area. The image (a) presents the bedding normal veins (red lines), while (b) 108 shows the bedding parallel veins (red lines). Yellow lines indicate the bedding in both images.

109 2 Material and methods

110 2.1 Quartz and inclusions in quartz minerals

In total, seven samples of different veins (3 BNVs and 4 BPVs) were collected from the Rursee outcrop for 40 Ar/ 39 Ar analysis (Table 1). Both vein types mainly consist of elongated-fibrous milky quartz grains that exhibit syntaxial growth, whereby the growth starts from the wall of the veins towards the central part of the veins (Ramsay, 1986). The pelitic host rock consists of sericite, illite, white mica, and chlorite. Chlorite is abundant within the vein fractures and between the host rock and the vein wall.

- Both quartz vein generations lack primary fluid inclusions in the crystal growth zones and contain pseudo-secondary and secondary fluid inclusion assemblages (FIAs) (<10 μ m) (Van Noten et al., 2011) in the sealed microcracks being perpendicular to crystal elongation (Fig. 3). The Rursee quartz vein samples yield average fluid inclusions homogenization temperatures (minimum trapping temperature, T_h) of ~135 ±25 °C and ~160 ±20 °C for BPV and BNV, respectively, with salinities of 3.5-8 eq. wt.% NaCl. The T_h of pseudo-secondary and secondary fluid inclusions cover an equally broad range of 110-180 °C
- 121 (Van Noten et al., 2011).

122 2.2 Mineral separation

- Before ⁴⁰Ar/³⁹Ar analysis, mineral separation was conducted at Vrije Universiteit Amsterdam (VU; The Netherlands). The bulk vein samples were crushed, washed, and cleaned in an ultrasonic bath for at least one hour to remove the adhering host
- 125 rock contaminants from quartz grains. The samples were sieved into 250 and 500 µm fractions and dried in an oven at 60 °C.
- 126 The samples were further separated by a custom-made system using an overflow centrifuge with conventional heavy liquids
- 127 based on IJlst (1973) and Frantz magnetic separation (Porat, 2006). We used heavy liquids with a density of 2.62 g cm⁻³ and
- 128 2.64 g cm⁻³ to obtain a fluid inclusion-rich fraction of quartz grains ($\rho = 2.62 2.64$ g cm⁻³). The fraction was rinsed with acetone,
- 129 dried, and further sieved to separate the 400-500 µm grain size range. From this fraction, only the purest quartz grains were
- 130 handpicked under a binocular microscope for ⁴⁰Ar/³⁹Ar dating.



131 Figure 3: Fluid inclusions in quartz veins under optical microscopy. (a) Image of BNVs under crossed polarizer light microscopy.

132 Both (a.1.1) and (a.2.1) are the zoom of (a.1) and (a.2) images, respectively, indicating pseudo-secondary fluid inclusion assemblages

133 (FIAs) (white arrow). (b) Crossed polarizer images of the BPV sample under microscopy. (b.1.1) and (b.2.1) images are secondary

134 and pseudo-secondary fluid inclusion (respectively) focused areas, which are zooms of the (b.1) and (b.2) images, respectively. The

135 white arrows represent the FIAs. Both generations of quartz veins bear FIAs in sealed microcracks rather than in crystal growth

136 zones.

137 2.3⁴⁰Ar/³⁹Ar stepwise crushing

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138 Fluid-rich quartz grains (400-500 μm; 2.62-2.64 g cm⁻³) were carefully selected under a binocular zoom microscope, and a

140 Drachenfels (DRA-2) sanidine standard was loaded after each three samples to monitor the neutron flux. The samples were

quantity of 200-270 mg of material was packed in aluminium foil and placed in 20 mm ID - 22 mm OD aluminium cups.

141 irradiated at Oregon State University (USA) using the CLICIT (Cadmium-Lined In-Core Irradiation Tube) facility for 12 hours

142 (batch VU123). After irradiation, standards were placed in 2 mm copper planchet holes for single grain fusion analysis and

143 vacuum pre-baked at 250 °C. The samples were then placed in an ultra-high vacuum system, baked at 120 °C, and connected

144 with hot NP10 and ST172 getters, Ti getter sponge at 400 °C, and a cold trap at -70 °C. The standards were fused with a Synrad

145 48–5 CO₂ continuous-wave laser fusion system.

146 The samples were crushed in an in-house developed and built crusher consisting of a stainless-steel tube (height: 18 cm, outer 147 diameter: 1.8 cm) that has a spherical curve on its interior base and a magnetic stainless-steel pestle (height: 5 cm, diameter:

148 1.6 cm, weight: ~69.5 g) with rounded tips with a slightly narrower outer radius. These geometries allow optimization of the

1.6 cm, weight. -09.5 g) with founded ups with a signify harfower outer radius. These geometries anow optimization of the

impact on the sample while crushing. Once a split of the sample (~30 mg of quartz grains) was loaded into the crusher tube, the pestle was carefully relocated to the bottom of the tube to avoid crushing the sample. The crush tube, the pestle, and the

151 sample were baked overnight at 250 °C. The pestle was dropped into a free-fall state using an external electromagnet with a

152 frequency of 1 Hz controlled by an adjustable power supply and pulse generator to crush the sample. The pestle was dropped

153 from a height of ~3, ~4, or ~5 cm *in vacuo*. Subsequently, the gases emitted from fluid inclusions in the fragmented quartz

155 extraction step and drop height were systematically increased during the experiment, with a maximum of 999 drops per analysis

sample were analyzed. To obtain a sufficient amount of argon in the mass spectrometer, the number of pestle drops per

156 (in total, ~40000 cumulated pestle drops per experiment).

The gas released from the samples and standards was analyzed isotopically using a ThermoFisher Scientific Helix MC+ mass spectrometer. The Helix MC+ mass spectrometer is a 5 collector channel instrument, equipped with a total of 10 collectors, a Faraday collector optionally fitted with a 10¹² Ohm or 10¹³ Ohm resistor amplifier, and a compact discrete dynode secondary electron multiplier (CDD-SEM) collector on each collector channel. Five collectors can be used at the same time to simultaneously collect the beam intensity signals of the 5 isotopes of argon. The H2-Faraday collector is employed to detect ⁴⁰Ar using a 10¹³ Ohm amplifier. Similarly, the H1- CDD collector is used for the measurement of ³⁹Ar (H1 Faraday was used for the runs on the DRA-2 sanidine standard because of the higher ³⁹Ar signal), the AX-CDD collector for ³⁸Ar, the L1-CDD

164 collector for 37 Ar, and the L2-CDD collector for 36 Ar.

Line blanks were measured after every three to four unknowns and subtracted from the succeeding sample data. Gain calibration is done by correcting for gain relative to the beam intensity measured on the AX-CDD, using measurements of \sim 50 fA (⁴⁰Ar measured beam intensities) pipettes of air on each cup, and mass discrimination corrections are made by measuring a series of ~400 fA (⁴⁰Ar measured beam intensities) air pipettes roughly every 12 hours. Raw data were processed using the

169 ArArCalc software (Koppers, 2002). Ages are calculated relative to Drachenfels (DRA-2) sanidine of 25.552 ± 0.078 Ma

- 170 (Wijbrans et al., 1995) which was recalibrated against Fish Canyon Tuff sanidine of 28.201 ± 0.023 Ma (Kuiper et al., 2008). 171 The decay constants of Min et al. (2000) are used. The atmospheric 40 Ar/ 36 Ar ratio of 298.56 ± 0.31 is based on Lee et al. (2006). The correction factors for neutron interference reactions are $(2.64 \pm 0.02) \times 10^{-4}$ for $({}^{36}\text{Ar}/{}^{37}\text{Ar})_{Ca}$, $(6.73 \pm 0.04) \times 10^{-4}$ 172 173 for $({}^{39}\text{Ar}/{}^{37}\text{Ar})_{Ca}$, $(1.21 \pm 0.003) \times 10^{-2}$ for $({}^{38}\text{Ar}/{}^{39}\text{Ar})_{K}$, and $(8.6 \pm 0.7) \times 10^{-4}$ for $({}^{40}\text{Ar}/{}^{39}\text{Ar})_{K}$. Gain correction factors and their standard errors (± 1 SE) are 1.00162 ± 0.00028 for H2-Far, 0.97963 ± 0.00021 for H1-CDD, 0.99921 ± 0.00027 for L1-CDD 174 175 and 0.96163 ± 0.00064 for L2-CDD for data measured in 2022 (R2.1) and 1.00465 ± 0.00031 for H2-Far, 0.97033 ± 0.00027 176 for H1-CDD, 0.99824 ± 0.00033 for L1-CDD, and 0.96309 ± 0.00070 for L2-CDD for data measured in 2023 (R1-R6). The K/Cl ratios are calculated by K/Cl = $\beta \times {}^{39}\text{Ar}/{}^{38}\text{Ar}$ with $\beta = 0.06$ derived from K/Cl = ~ 18.7 in GA1550 and ${}^{39}\text{Ar}_{K}/{}^{38}\text{Ar}_{Cl} =$ 177 \sim 316 for a 12-hour irradiation at the OSU Triga CLICIT facility. All errors are quoted at the 2 σ level and include all analytical 178 179 uncertainties (Table 1). 180 Please note that it is impossible to directly correct the crushing blank because we cannot perform the exact experiment without 181 crushing sample material. We tested the blanks for each tube without sample material, following the identical procedures as 182 for real experiments. With this approach, we have direct metal-to-metal contact during pestle drops, which might not be representative for a real sample. We did observe a substantial increase in background, with a higher number of drops and a 183
- higher drop level. Notably, the composition of this blank is similar to that of atmospheric argon. Therefore, we follow the approach that the 40 Ar signal derived from the line blank (measured every 3-4 unknowns where we mimic the sample experiment, but without the crushing/pestle drops) is subtracted from the measured 40 Ar intensity. The real blank has an atmospheric 40 Ar/ 36 Ar ratio and is incorporated in the air corrections, leading to a lower radiogenic 40 Ar^{*} if the real blanks are relatively high.

189 2.4 Electron Probe Microanalysis (EPMA)

Quartz grains of sub-samples that were analyzed for 40 Ar/ 39 Ar were mounted in epoxy resin and carbon coated for the JEOL JXA-8530F hyperprobe field emission electron probe microanalyzer (EPMA) at Utrecht Universiteit (UU; The Netherlands) to define the elemental compositions of 1) the host quartz, 2) minerals that are present in fluid inclusions, filled cavities, or fractures, and 3) mineral inclusions in the quartz. For this analysis, an accelerating voltage of 15 kV and a beam current of 8 nA for host rock (quartz) and 7 nA for mineral inclusions are used with beam sizes of 10 µm and 1 µm, respectively. The elements analyzed are Si, Ti, Al, Fe, Mn, Ca, Na, K, P, Cl, F, Ba, and Zr. The data are calibrated using Icelandic rhyolite glass (ATHO-G) and basalt glass (KL2-G) standards that were both measured with a beam size of 10 µm multiple times before and

197 after measurements of the samples.

198 3 Results

The age spectra of the *in vacuo* stepwise crushing of the quartz samples are plotted in Figure 4. All samples show typical release patterns with unrealistically old apparent ages (>6 Ga) in the initial 10 % of 39 Ar_K released. Note that samples Rursee 1a BNV and Rursee 1b BNV are measured in two different experiments on subsets from the same irradiated sample, yielding different results. A lighter pestle (68 g) has been used for the sample Rursee 1a BNV than for sample Rursee 1b BNV (69.5 g) and all other samples.

204 The apparent ages of the spectra in samples Rursee 1b BNV, Rursee 2 BPV, Rursee 2.1 BNV, and Rursee 4 BPV exhibit a 205 gradual decrease in age over the next 10 - 40 % of 39 Ar_K released, eventually stabilizing at a more or less consistent maximum apparent age from ~80 to ~100 % ³⁹Ar_K. Rursee 3 BPV, Rursee 5 BNV, and Rursee 6 BPV show comparable behaviour with, 206 after the initial old apparent ages, a decrease in a maximum apparent age to an "early converging section" from ~15 % to ~40 207 208 % ³⁹Ar_K released, followed by a gradual decrease in apparent age and a more or less uniform apparent age in the >80 % released 39 Ar_k part of the spectrum. For these early converging sections, we arrive at averaged maximum apparent ages of ~84 Ma for 209 210 Rursee 1b BNV, ~97 Ma for Rursee 2 BPV, ~117 Ma for Rursee 4 BPV, ~216 Ma for Rursee 2.1 BNV, ~190-200 Ma for 211 Rursee 5 BNV, and Rursee 6 BPV, and ~560 Ma for Rursee 3 BPV. The maximum apparent ages of Rursee 2.1 BNV and 212 Rursee 4 BPV correspond to the inverse isochron maximum apparent ages; however, due to significant uncertainty, the 213 maximum apparent ages of other samples were obtained from the average late converging section age (Table 1).

The inverse isochrons (Fig. 5) confirm that the first part of all experiments is heavily affected by excess argon (36 Ar/ 40 Ar ratios are much lower than atmospheric composition), followed by an increase in 36 Ar/ 40 Ar and 39 Ar/ 40 Ar ratios and clustering of data points on the reference line. We derived maximum apparent ages from the data points that cluster along the reference line in the isochrons in the final part of the age spectra. There is no systematic maximum apparent age difference between BNV and BPV.

219 All quartz samples release argon during in vacuo stepwise crushing with different isotopes of argon contributing to the gas 220 release at different stages of the experiment. Figure 6 shows, for each step, the percentage (relative to the total amount) of a 221 specific isotope released through the experiment. All quartz samples are characterized by a release of most of the ${}^{36}Ar_{air}$ in the first 20 steps. 40 Ar^{*} and 38 Ar_{Cl} follow the pattern of 36 Ar_{air}. The 39 Ar_K generally increases after the first 20 analyzing steps (~790 222 223 pestle drops from 3 cm height). At steps 30-35, we observe fluctuations in the data. These shifts are artefacts caused by 224 increasing the drop height (from 3 to 4 cm at ~step 30 and from 4 to 5 cm at ~step 35) and adjusting the number of pestle 225 drops. To prevent high signals, we started with a relatively low number of pestle drops at a higher drop height, yielding low signals, as observed as two troughs at ~step 30 and ~step 35 in all experiments. All quartz samples are low in ³⁶Ar_{air}, ³⁸Ar_{Cl}, 226 and ⁴⁰Ar* at the end of analysis compared to their total release. For ⁴⁰Ar*, we still measure a small, reliable signal, but this is 227 228 obscured in Figure 6 due to the high signals in the first steps since we plot percentages of the total released ⁴⁰Ar per experiment. Note that huge amounts of excess ⁴⁰Ar (as part of the ⁴⁰Ar^{*} signal) are released in the initial steps of the experiment and 229 230 dominate the total percentage.



Cumulative ³⁹Ar Released [%]

Figure 4: The apparent "late converging section" age of all quartz vein experiments. The red boxes focus on the last part of the age spectra, where apparent ages are more or less stable.



233 Figure 5: Inverse isochrons of all quartz vein samples. The black line corresponds to a regression where the ⁴⁰Ar/³⁶Ar intercept with

the vertical is fixed at the ratio of atmospheric argon, and hence its radiogenic intercept corresponds to the age obtained from a regression of the corresponding steps in the age spectrum, whereas the pink line represents a regression without this restriction, providing us with information on the actual ⁴⁰Ar/³⁶Ar ratio of non-radiogenic components in the fluid mixture.

Cumulative pestle drop



237 Figure 6: Released argon isotopes per analyzing step relative to their total release. Note that the data are expressed against the

analyzing steps instead of the crushing steps, and that the upper x-axis scaling (cumulative pestle drops) is neither linear nor

239 logarithmic (non-continuous scaling).

- Table 1 Summary of ⁴⁰Ar/³⁹Ar age spectra, including inverse isochron data of all analysed quartz samples. The maximum apparent 240
- 241 ages of the late converging section and inverse isochron selected, as discussed in the text, are highlighted in bold, with an asterisk 242
- marking those used for geological interpretation.

Locality			Rur	see, outcrop near Sch	wammenauel dam (G	ermany)		
Rock type				Qua	rtz veins			
Mineral				Q	uartz			
Sample ID	Rursee 1a BNV	Rursee 1b BNV	Rursee 2 BPV	Rursee 2.1 BNV	Rursee 3 BPV	Rursee 4 BPV	Rursee 5 BNV	Rursee 6 BPV
Sample ID Ar	R01a	R01b	R02	R021	R03	R04	R05	R06
GPS coordinate	Lat.: 50.63378406	Long.: 6.44191402	Lat.: 50.63377933 Long.: 6.44190753	Lat.: 50.63388498 Long.: 6.44184657	Lat.: 50.63418108 Long.:6.44176707	Lat.: 50.6344143 Long.: 6.4418217	Lat.: 50.63367794 Long.: 6.44201891	Lat.: 50.63392217 Long.: 6.44181953
Grain Size (µm)				400	0 - 500			
Density (g.cm ⁻³)				2.6	2 - 2.64			
Max. apparent age (Ma)	2844	84*	97*	145	560	129	193	201
±2σ analytical error + J error	\pm 88	± 1	± 2	± 7	± 45	± 5	± 14	± 6
±2σ full external error	± 96	± 2	± 3	± 8	± 47	± 6	± 15	± 7
MSWD (app.age)	42.8	1.6	3.3	4.3	6.1	5.4	2	0.4
K/Ca	0.32	1.54	14.28	5.33	0.285	3.21	0.75	3.48
⁴⁰ Ar/ ³⁶ Ar inverse isochrone intercept	3874	326	858	258	329	311	289	243
±2σ analytical error + J error	\pm 7285	± 51	± 860	± 38	± 183	± 6	± 29	± 181
Inverse isochrone age	-	74	81	216	399	117*	259	26
±2σ analytical error + J error	± 5770	± 16	± 225	± 51	± 425	± 7	± 129	± 177
±2σ full external error	± 5770	± 16	± 225	± 51	± 425	± 8	± 129	± 177
n/n _{tot} (n: number of analyses included weighted mean, n _{tot} : total number of analysis)	22 / 67	11 / 83	4 / 67	19 / 73	4 / 62	4 / 75	9 / 64	3 / 75
MSWD (iso. age)	14.5	1.6	0.2	3.8	8.8	0.9	2.2	0.5

243 4 Discussion

During *in vacuo* stepwise crushing, the release of argon isotopes from the samples follows systematic patterns. The challenge is to link this release of argon from the samples to the different potential reservoirs of K and, as a next step, the geological meaning of the age and elemental ratios of K/Cl and Ca/Cl. Here, we first discuss potential issues related to the analytical quality of the data. Next, we discuss potential reservoirs of K and subsequently 40 Ar^{*} that need to be considered evaluating the maximum apparent ages and their wider implications.

249 4.1 Data quality

256

250 4.1.1 Rursee 1a/1b BNV

We speculate that for the experiment Rursee 1a BNV, we sampled a smaller part of the argon reservoirs in the quartz minerals comparable to the first 10 % of the spectrum of Rursee 1b BNV. This is corroborated by the fact that for Rursee 1a BNV, 46 mg of quartz released 12.7 fA ³⁹Ar_K (0.3 fA/mg quartz), while for Rursee 1b BNV, 89.1 fA was released from 25 mg of quartz (3.6 fA/mg of quartz). We therefore do not further discuss the results of Rursee 1a BNV but note that sample heterogeneity might also have contributed to this difference.

4.1.2 Impact of blank correction

257 The blank correction procedure likely does not impact the weighted mean age computation; however, it does influence the 258 40 Ar/ 36 Ar intercept of the inverse isochron. This is only the case when the regression line has a non-radiogenic intercept that 259 differs from the atmospheric ³⁶Ar/⁴⁰Ar. When the intercept is within the error overlapping with the atmospheric ratio, the blank 260 correction only causes the point to move along the regression line, as comes out of the discussion below. We described our blank correction procedure in methods (supplementary file 1). The fact that we cannot mimic the dropping of the pestle when 261 262 a sample is present in the tube limits on how well we can determine the blank during the experiments. The blank tends to increase with a higher number of pestle drops, but the composition of this blank is atmospheric. For the test of the blank, we 263 used quartz glass fragments to mimic zero-age minerals, as a blank determination using metal-on-metal impacts was considered 264 265 to be an unrealistic scenario. As a next test, we artificially increase the ⁴⁰Ar blank (and thus the ³⁶Ar blank) assuming atmospheric composition. If the data are located on the mixing line between radiogenic and atmospheric argon, this should not 266 267 affect the isochron apparent age (pink part - final stage in Figs. 5 or 11). We tested this for sample Rursee 1b BNV with an apparent age of ~ 88 Ma. The 40 Ar/ 36 Ar intercepts increase with increasing blank values, and the weighted mean late converging 268 section ages change with a maximum of 2.5 Ma in the chosen example. We therefore conclude that the isotopic ages remain 269 270 largely unaffected by varying the amounts of atmospheric argon of the blanks. Note that if the isochron is not a mixing line 271 between radiogenic and atmospheric argon (e.g., blue and green parts in Figs. 5 or 11), this assumption is incorrect. The ⁴⁰Ar/³⁶Ar intercept is then pulled away from the real ⁴⁰Ar/³⁶Ar composition in the direction of the atmospheric ⁴⁰Ar/³⁶Ar 272 273 intercept. Consequently, the intercept with the inverse isochrons' X-axis (and thus age) will also be affected.

274 4.1.3 Recoil artefacts

Recoil artefacts occur when ³⁷Ar and ³⁹Ar, which are formed from K and Ca isotopes, form with kinetic energy. As a result,
they can travel from their original sites to other sites, potentially even into the adjacent phase (Turner and Cadogan, 1974;
Foland, 1983; Lo and Onstott, 1989; Féraud and Courtillot, 1994; Baksi, 1994; Onstott et al., 1995; Villa, 1997). However,
this phenomenon is assumed to have a smaller impact than the blank correction.

279 4.2 Potential reservoirs of K

To date, three main hypotheses are being debated about the origin of the released argon in a stepwise crushing experiment. 280 281 The first group (Qiu and Wijbrans, 2006, 2008; Bai et al., 2019) suggests that progressive crushing releases gases mainly from 282 fluid inclusions and therefore represents fluid inclusions maximum apparent ages. Additionally, the possibility of argon 283 releasing within K-mineral by prolonged crushing when the grain sizes were reduced to tens of nanometres (Bai et al., 2019). 284 The second group (e.g., Kendrick and Philips (2007)) discusses the possibility of K-bearing mineral inclusions within the 285 inclusion cavity and/or in microcracks serving as argon reservoirs in the later crushing stages. Obtained maximum apparent ages therefore represent mineral closure ages or a mixture of fluid inclusions and mineral inclusion ages. Accordingly, the gas 286 287 release sequence under sufficient crushing progresses from microcracks to secondary fluid inclusions, followed by primary fluid inclusions, and finally to micro- to nanometre-sized minerals (Bai et al., 2022). 288

289 In addition, the third potential source of potassium in the minerals might be the presence of K^+ in the crystal lattice, which 290 was postulated for zeolites (Kendrick et al., 2011), but could also work for feldspars, but may be less of an issue in nominally 291 potassium-free minerals such as quartz (or garnet), which is representative of the formation age of veins. Hydrothermal quartz 292 veins, characterized by their substitution in the crystal structure, have been studied by Weil (1984) and Götze et al. (2021). These studies indicate that Si^{4+} derived from hydrothermal quartz veins can be substituted by other ions such as Al^{3+} , Ga^{3+} , 293 Fe³⁺, B³⁺, Ge⁴⁺, Ti⁴⁺, and P⁴⁺, Al³⁺ is usually replacing Si⁴⁺ since it is found in significant numbers (~300-700 ppm) in quartz, 294 295 based on EPMA data. Additionally, small numbers of monovalent ions such as K⁺ may fill empty spaces in the crystal structure, serving as charge balancers for trivalent substitutional ions such as Al³⁺ (Bambauer, 1961; Kats, 1962; Perny et al., 1992; 296 297 Stalder et al., 2017; Potrafke et al., 2019). However, Jourdan et al. (2009) postulated that substitutions of these components 298 may be so minor that it is even undetectable using a Secondary Ion Mass Spectrometer (SIMS). Furthermore, it is important 299 to note that not all hydrothermal sources or quartz minerals have this particular form of substitution (Jourdan et al., 2009).

- 300 Apart from these potential 39 Ar_K reservoirs above, detrital minerals (e.g., mica present in the surrounding pelitic rock) that
- 301 might be trapped by the quartz veins during the growth may also contribute to the obtained maximum apparent ages.

302 4.2.1 Identification of different K reservoirs in the Rursee quartz samples

303 During in vacuo stepwise crushing, the release of argon isotopes from the samples follows systematic patterns. In this study,

304 we aim to connect this release to the sequential contributions of different reservoirs of K and, consequently, argon from the

- Rursee samples. The release patterns of ${}^{36}Ar_{air}$, ${}^{38}Ar_{Cl}$, ${}^{39}Ar_{K}$, and ${}^{40}Ar^*$ (Fig. 6) for all quartz vein samples may originate from multiple existing argon reservoirs.
- 307 Depending on the size (<10 μ m), location, and generation of fluid inclusions, they may contribute successively to the argon 308 release patterns in the early or middle stage of stepwise crushing. Figure 6 reveals that the concentration of ³⁹Ar_K increases 309 throughout the process of *in vacuo* stepwise crushing, while the concentration of other argon isotopes decreases. This suggests 310 that K-containing reservoirs were not opened in the first part of the experiment. The release patterns of ³⁹Ar_K can be categorized
- 311 into two distinct groups during stepwise crushing:
- a) The *first group* of samples shows a small initial release in the early stages. This is followed by a drop around the 10^{th} step, then an increase from the $\sim 10^{th}$ to $\sim 35^{th}$ step, and finally a gradual decrease (Rursee 3 BPV, Rursee 5 BNV, and Rursee 6 BPV).
- b) The *second group* does no not have the ${}^{39}Ar_K$ release in the steps 1-10 but after that it shows a similar pattern to the first group, gradually increasing until about the 35^{th} step and then gradually decreasing (Rursee 1b BNV, Rursee 2 BPV, Rursee 2.1 BNV, and Rursee 4 BPV).
- The continuous rise in ³⁹Ar_K levels after ~10 steps in both sample groups suggests that the gas release process can be divided into at least two phases. Initially, during the first ~10 steps, ³⁹Ar_K is emitted from fluid inclusions in microcracks (secondary fluid inclusions). From steps ~10th to ~70th, the release happens as a result of the mixing of potential pseudo-secondary fluid inclusions (~10-~15th steps), mineral inclusions, and/or the crystal lattice of quartz veins. This interpretation is supported by the K/Cl correlation plots (Fig. 7), which show a consistently lower K/Cl ratio until the ~10th step.
- From the 10th to the 15th K/Cl ratio, it reaches ~1 with a steep rise for all quartz samples, and later (from the ~20th step) this ratio continues to increase steeply for *the second group* of samples, while it shows a less pronounced increase for *the first group* of samples.
- The lower K/Cl ratio may be attributed to the presence of Cl and a lack of or limited amounts of K in combination with relatively constant low salinity levels (3.5-8 eq. wt.% NaCl) inside the fluid inclusions, which are likely to be opened in the early phase. After most fluid inclusions have been mechanically opened, the subsequent rapid increase in K (reflected by the ³⁹Ar_K) and the steady decline in Cl (reflected by the ³⁸Ar_{Cl}) occur throughout successive crushing steps and are reflected in the K/Cl ratio. Therefore, this increase is likely due to the exhaustion of the Cl-rich fluid inclusions along with the presence of minerals containing potassium and/or potassium from the crystal lattice of quartz that release their argon in the later crushing steps.
- This approach to distinguish between fluid inclusions and other K reservoirs was first suggested by Kendrick et al. (2006, 2011): K/Cl ratios \leq 1 are representative of fluid inclusions, and K/Cl ratios > 1 for other sources. If K/Cl \leq 1, the apparent age we measure is the oldest possible age for the fluid inclusions. In case K/Cl > 1, the obtained apparent age corresponds to the maximum apparent age of the trapped K-bearing mineral and/or K from the crystal lattice (Kendrick et al., 2006, 2011). In our samples, the K/Cl is greater than 1 after the first ~15±3 steps in all quartz vein samples, indicating the presence of major
- 338 K-related reservoir(s) other than fluid inclusions. It is worth noting that this is based on the assumption that there are no other

- 339 K-bearing phases, such as KNO₃, K₂SO₄, or K₂CO₃, rather than KCl dissolved in aqueous fluid inclusions. This assumption
- 340 may be verified by Raman analysis (see Figure A1), which does not show significant peaks for these alternative K-bearing
- 341 phases. However, the low peaks in ~ 1080 cm⁻¹ may be related to either K₂CO₃ or interferences related to the epoxy background.
- 342 Therefore, K/Cl > 1 suggests that K is related to the salinity of the fluid inclusions along with different K-components (i.e.,
- 343 KCl and K₂CO₃). Alternatively, if there is interference from the epoxy background, it suggests that there should be at least one
- 344 significant additional source present, which could include the crystal lattice of quartz and/or mineral inclusions within the
- 345 quartz crystals and/or even microcracks.



346 Figure 7: K/Cl ratios plotted against analysis steps for all quartz veins.

347 4.2.2 K-bearing mineral inclusions

EPMA data (Table 2) from cleaned hand-picked fluid-rich separated quartz grains indicate the presence of sericite, chlorite-348 349 sericite, and illite-sericite in the microfractures and cavities of fluid inclusion. The presence of such minerals (or mixtures) in 350 the inclusion cavity and microfractures is also invisible under a binocular or petrographic microscope during the mineral 351 separation and was confirmed captured using electron-backscattered imaging (Fig. 8). In thin sections of quartz veins with the 352 associated host rock, illite-sericite, and white mica are abundant in the surrounding pelitic layer of the Rursee formation (Fig. 353 9). These minerals that contain a significant amount of K_2O are also detected by EPMA, in the separated quartz samples, 354 especially in Rursee 2 BPV (see EPMA data, Table 2). High K concentrations (~8.8 wt. % K₂O) are likely related to intergrowth 355 with sericite or a closely related mineral.

- 356 Petrographic analysis of thin sections of whole rock samples representing both vein generations (BPV and BNV) reveals a
- 357 significant presence of chlorite located between the vein wall and host rock, as well as in fractures (Fig. 10). Although chlorite
- 358 typically lacks K in its crystal structure, previous studies have reported trace amounts of K in chlorites (Pacey et al., 2020; Li
- 359 et al., 2022).



Figure 8: Backscattered electron images of mineral inclusions obtained by SEM. Secondary minerals (e.g. chlorite, sericite and white mica as determined using EPMA) occur in cavities and microfractures (white arrow) in fluid-rich quartz.



Figure 9: Microscopic image of the quartz vein host rock matrix from the Rursee formation. (a) Crossed polarizer (b) plane polarizer images of the pelitic host rock (Rursee 2 BPV). White arrows (image a) indicate the presence of the white mica and sericite in the host pelitic rock. (c) Crossed polarizer (d) plane polarizer images of the quartz veins matrix (Rursee 1 BNV). The white arrow (image c) shows the presence of the quartz sub-grains. Quartz sub-grains in the vein are due to the local tectonic activity, indicating that this period corresponds to tectonic activity.



367 Figure 10: Chloritization distribution in the vein wall and fractures for both generations of quartz veins. (a) Plane (a.1) and crossed 368 (a.2) polarizer of bedding parallel veins: chloritization mainly between vein wall and host rock and fractures. (b) Plane (b.1) and

369 cross (b.2) polarizer of bedding normal veins: chloritization in fractures.

370 4.2.3 K from crystal lattice and detrital minerals

EPMA analyses of the quartz matrix indicate that K concentrations in the crystal lattice are below the detection limit of ~100 ppm. A maximum K concentration of ~100 ppm K (for example, 100 ppm K in Rursee 2.1 BNV) and a maximum apparent age of 144 Ma would result in ~16000 fA 40 Ar^{*} when measured on our Helix-MC mass spectrometer, which is a comparable amount of total 40 Ar^{*} released from K-bearing mineral inclusion. Given the large sample amount (~30 mg), this would translate into a significant contribution of K from the crystal lattice of quartz. We therefore suggest that K in the crystal lattice may contribute to the observed 40 Ar^{*} signals (see calculation on supplementary file 2).

- In this study, argon molecules might also be derived from secondary minerals in cracks and embedded detrital minerals (e.g., mica from host rock). This interpretation aligns with the observation that the homogenization temperatures of fluid inclusions within the quartz veins are below the closure temperature for argon in detrital minerals. Under such conditions, the expected maximum apparent ages from K-bearing detrital minerals would correspond to pre-Variscan periods, reflecting the maximum apparent age of the deposits hosting the quartz veins, although the obtained maximum apparent ages are significantly younger in this study. Therefore, we infer that detrital minerals do not significantly contribute to the ⁴⁰Ar^{*} signals.
- To summarise, during the first stages (until the ~20th analysis steps) of the stepwise *vacuo* crushing, gases are likely released only from fluid inclusions (secondary and pseudo-secondary, as is also observed for fluid inclusion in garnets (Qiu and Wijbrans, 2006, 2008)). Huseynov et al. (2024) demonstrated that a significant amount of fluid inclusion water can be extracted from these samples by a single crushing step using a spindle crusher. In this study, throughout the crushing process, the total amount of argon released steadily increases (Fig. 6). In the latter stages of the experiment (from the 20th analyzing steps), the substantial release of ³⁹Ar_K isotopes may originate as follows:
- a) The gas release only from the small-sized fluid inclusions (i.e., $<5 \mu m$ pseudo-secondary) until the last stage of the experiment (~40-50th analyzing step) and then in the last stage (after the 50th step) from solid-phase K-bearing minerals and/or crystal lattice, which corresponds to the end of the "early converging section" in some samples. As K/Cl > 1 after (the 20th analyzing step), the low peak (~1080 cm⁻¹) in Raman spectroscopy may correspond to a K-related component (e.g., K₂CO₃) from fluid inclusions.
- b) The significant release of ³⁹Ar_K isotopes in the mid-to later stages of the experiment may be related to the presence of noncrushed, small-sized fluid inclusions ($<5 \mu$ m) together with K-bearing mineral inclusions in the samples and/or ⁴⁰Ar^{*} from the crystal lattice under the condition that low peak in ~1080 cm⁻¹ from Raman spectroscopy belongs to the epoxy background of the quartz grain. The contribution of crushing-induced degassing K-bearing mineral inclusions is also corroborated by EPMA data, and the presence of K in the lattice cannot be ruled out for the Rursee samples.

399 4.3 Age spectra and isochrons

400 As aforementioned, the distribution of argon isotopes (Fig. 6) indicates that ${}^{39}Ar_K$ is derived from distinct sources, likely 401 mineral inclusions and/or eventually crystal lattice rather than fluid inclusions in particular in the later phase of the experiment, 402 which was used for the age determinations. These potential sources of K, including fluid and mineral inclusions and/or crystal 403 lattice, may all contribute to the variability observed in the age spectra derived from the different samples. Due to the presence of 40 Ar_E from the fluid inclusions, the initial analytical stages of the analyses yield anomalously high apparent ages in the first 404 part of their age spectra (Fig. 4). Some samples (Rursee 3 BPV, Rursee 5 BNV, and Rursee 6 BPV) show an "early converging 405 section" in the first part of the experiment. The "early converging section" effect occurs between the 20th and 30th analyzing 406 407 steps, which may be associated with sudden changes in K/Cl ratios (Fig. 7). These sudden changes may be due to the sharp 408 transition from fluid state reservoirs (e.g., small-sized fluid inclusions) to solid-state reservoirs (e.g., K-bearing mineral inclusions). However, it does not occur in the second group of quartz samples (Rursee 1b BNV, Rursee 2 BPV, Rursee 4 409 BPV), revealing smooth transitions from fluid to solid states of ${}^{39}Ar_{K}$ reservoirs. The transition for the Rursee 2.1 BNV is 410 neither abrupt like for the first group samples nor smooth as for the second group samples; hence, the impact of the "early 411 412 converging section" is minimal.

The transition from fluid-state reservoirs to solid-state reservoirs can be supported by grain size distribution (see supplementary file 4), indicating that fluid-state reservoirs may remain unreleased beyond around 800 crushes (around the 20th analysis step). However, the presence of small particles at the bottom of the crusher (non-recoverable size) after 800 crushes may result in the measured results not accurately representing the whole grain size distribution. As the grain size distribution depends on many factors (i.e., crushing efficiency, presence of microcracks), there may even be a factor of difference for two groups.

418 The impact of ${}^{40}\text{Ar}_{\text{E}}$ results in inverse isochrons (Fig. 5) during the initial stage. The relationship between the ${}^{36}\text{Ar}/{}^{40}\text{Ar}$ and

419 ³⁹Ar/⁴⁰Ar for all samples resulted in a decrease in the ³⁶Ar/⁴⁰Ar ratio and an increase in the ³⁹Ar/⁴⁰Ar ratio (initial stage in Fig.

420 11). The presence of an elevated concentration of 36 Ar at the beginning of the experiment could be either due to the atmospheric

421 argon gas that is trapped in the stainless steel crusher and/or the original fragment surfaces and perhaps released during the

422 initial stage of crushing. Following the opening of fluid inclusions, the ratio of ³⁶Ar/⁴⁰Ar increases linearly with the ratio of

423 ${}^{39}\text{Ar}/{}^{40}\text{Ar}$. This is probably due to a decrease in excess argon throughout the crushing and an increase in ${}^{39}\text{Ar}_{K}$ associated with

424 K-bearing minerals and/or crystal lattice (intermediate stage in Fig. 11). In the last phase of 40 Ar/ 39 Ar analysis, the 425 concentration of 39 Ar_K decreases (final stage in Fig. 11). This last part is particularly important for determining the age of 426 quartz vein samples.

427 Inverse isochrons may assist in determining the maximum apparent age of fluid inclusions by linear regression of the data 428 related to fluid inclusions. However, the high amounts of excess argon in the system obscure geologically meaningful ages.



429 Figure 11: Inverse isochron representation of quartz veins (ex: Rursee 2.1 BNV): 3 stages: (1) initial stage with the opening of fluid 430 inclusions; (2) intermediate stage where argon is released from mineral inclusions or microfractures and/or crystal lattice; (3) Final

431 stage of argon release from mineral inclusions and neglectable excess argon in samples.

432 4.4 Implications

433 Unlike studies that obtained consistent maximum apparent ages from high salinity (>20 eq. wt.% NaCl) primary fluid 434 inclusions of garnet (in eclogite) and wolframite (Qiu and Wijbrans, 2006; Qiu et al., 2011; Bai et al., 2013, 2019), we were 435 unable to date pseudo-secondary and secondary fluid inclusions in recrystallized Rursee quartz samples, likely due to high 436 ⁴⁰Ar_E concentrations and/or low salinity (3.5-8 eq. wt.% NaCl). The reduced K concentration in the pseudo-secondary and 437 secondary fluid inclusions, due to the loss of the primary brine and its replacement by a lower salinity, lower K fluid, likely 438 led to inaccurate maximum apparent age determination. While no precise age was determined for the fluid inclusions, ⁴⁰Ar/³⁶Ar 439 ratios (above atmospheric but below 4000) indicate a mixed metamorphic-meteoric fluid source (Ballentine et al., 2002; Ozima 440 and Podosek, 2002). Later, during the crushing experiment, the K-bearing mineral inclusions may provide geologically 441 meaningful ages, although the argon closure temperatures in quartz remain uncertain. For reference, the closure temperature 442 of smaller-size sericite grains (~20 um) corresponds to temperatures (~300-350 °C) (Glasmacher et al., 2001; Watson and 443 Cherniak, 2003), while the vitrinite reflectance from psammatic and pelitic layers indicates maximum burial temperatures (220 444 °C) near the Carboniferous-Permian boundary, with gradual cooling thereafter (Littke et al., 2012).

Three ⁴⁰Ar/³⁹Ar maximum apparent ages ranging from 117 to 84 Ma differ from the interpretation based on structural analyses, which posit that veining occurred during the early Variscan Orogeny (Van Noten et al., 2007), possibly due to argon loss during cooling and/or recrystallization. The obtained maximum apparent ages may be influenced to some extent by the presence of neo-crystallized quartz sub-grains, although their volume appears relatively small (Fig. 9c). However, since the maximum apparent ages primarily reflect solid-phase reservoirs (i.e., K-bearing mineral inclusions) rather than fluid-phase components, likely, K-bearing solid-phase reservoirs intergrow simultaneously with the recrystallization process.

451 Post-Variscan tectonic activity is known for southern Rhenish Massif due to late- and post-orogenic fault movements and 452 coeval reactivation of Variscan structures leading to the fluids (re)activity (Herbst and Muller, 1969; Schwab, 1987; Korsch 453 and Schäfer, 1991; Hein and Behr, 1994; Moe, 2000; Kirnbauer et al., 2012).

454 Given that reactivation of existing veins could have occurred without forming new fractures (Virgo et al., 2013), this 455 reactivation is usually associated with the infiltration of high saline (>20 eq. wt.% NaCl) fluids in Central Europe and the 456 Rhenish Massif (Behr et al., 1987; Redecke, 1992; Hein and Behr, 1994; Germann and Friedrich, 1999; Heijlen et al., 2001; 457 Kučera et al., 2010).

This saline fluid activity is at odds with the low-salinity fluid inclusions (3.5-8 eq. wt.% NaCl) in the Rursee quartz veins (Van

459 Noten et al., 2011). However, they agree with low-saline fluid inclusions in quartz veins of the Rhenish Massif, which are 460 attributed to upward migration of Variscan fluid remnants during Jurassic-Cretaceous reactivation (Kirnbauer et al., 2012).

461 Near Rursee (Stavelot Inlier), low saline (0.2-7.2 eq. wt.% NaCl) and high-temperature fluid activity (~250 °C) along the

462 Variscan front reflect warm meteoric fluid circulation (Schroyen and Muchez, 2000). Such warm, low-saline fluids may have

463 also contributed to the chloritization of veins in the Rursee outcrops. We propose that tectonic activity and quartz vein

464 reactivation-recrystallization could explain the observed ⁴⁰Ar/³⁹Ar maximum apparent ages, as low saline Variscan fluids

- 465 perhaps moved along the reactivated fractures, forming new quartz minerals within the Variscan-related veins during Jurassic-
- 466 Cretaceous tectonic activity (i.e. opening of North Atlantic).

	Sample ID	Grain ID	SiO ₂	TiO ₂	AI_2O_3	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	CI	F	BaO	ZrO ₂	0	H ₂ O	TOTAL
Internal	KL2-1		51.90	2.56	13.50	10.74	0.17	7.47	10.74	2.39	0.48	0.23	bdl	bdl	bdl	bdl	0.00	0.00	100.01
standard			51.20	2.51	13.36	10.79	0.17	7.46	10.83	2.38	0.47	0.27	0.00	bdl	bdl	bdl	0.00	0.00	99.28
0000			50.80	2.55	13.41	10.98	0.16	7.31	10.96	2.34	0.51	0.26	0.00	bdl	bdl	0.00	0.00	0.00	99.13
Internal	ATHO-1		75.73	0.21	12.23	3.28	0.11	0.11	1.67	3.85	2.73	0.02	0.05	0.06	0.09	bdl	0.00	0.00	100.10
standard			75.61	0.24	12.44	3.47	0.12	0.13	1.63	3.73	2.78	0.05	0.05	0.03	0.00	0.02	0.00	0.00	100.29
01.00			75.69	0.28	12.30	3.43	0.12	0.11	1.60	3.78	2.81	0.02	0.03	0.04	0.04	0.10	0.00	0.00	100.35
Rursee	Rursee 1	B_1.01a	99.75	0.02	0.00	0.00	0.00	bdl	0.01	0.02	1.00	0.01	0.59	bdl	bdl	bdl	0.00	0.00	101.21
quartz	BNV	B_1.02a	55.07	bdl	0.31	0.29	0.01	0.61	0.88	0.39	0.51	0.13	0.40	bdl	0.03	0.01	0.00	0.00	58.57
veins		B_1.03a	71.35	0.02	0.69	2.83	0.07	14.04	0.15	0.38	0.51	0.05	0.12	bdl	bdl	0.00	0.00	0.00	90.05
		B_1.03b	38.76	0.04	2.80	1.85	0.02	6.30	0.74	1.53	0.95	0.13	0.30	bdl	0.04	bdl	0.00	0.00	53.29
		B_1.06a	47.68	0.01	37.73	0.04	bdl	0.04	0.19	5.61	0.86	0.05	0.06	0.04	bdl	bdl	0.00	0.00	92.27
		B_1.06b	99.52	bdl	0.67	0.01	0.01	0.00	0.05	0.04	0.04	0.05	0.00	0.00	0.02	0.05	0.00	0.00	100.45
		B_1.06c	92.43	0.02	5.79	bdl	bdl	0.04	0.05	1.01	0.28	0.01	0.03	bdl	0.05	bdl	0.00	0.00	99.60
		B_1.06d	50.05	0.03	25.07	0.01	0.02	0.10	0.08	2.44	3.24	0.05	0.03	0.02	0.00	bdl	0.00	0.00	81.10
		B_1.10a	50.90	0.03	33.68	0.13	bdl	0.13	0.05	1.66	6.22	0.00	0.12	0.04	0.04	bdl	0.00	0.00	92.98
		B_1.11a	52.33	bdl	31.93	0.09	0.00	0.08	0.07	0.29	8.08	0.07	0.03	0.02	0.15	bdl	0.00	0.00	93.00
		B_1.15a	68.06	0.02	24.01	0.00	0.00	0.10	0.39	3.14	0.93	bdl	0.13	bdl	0.03	0.03	0.00	0.00	96.82
	Rursee 2	B_2.02a	78.24	bdl	0.25	0.32	0.00	0.04	0.37	0.22	0.03	0.19	0.05	bdl	0.05	0.03	0.00	0.00	79.76
	BPV	B_2.02b	13.65	0.03	1.51	59.78	bdl	0.31	0.37	1.52	0.95	0.16	0.61	0.02	bdl	0.04	0.00	0.00	78.90
		B_2.03a	47.72	0.07	6.23	5.85	0.15	5.35	3.09	1.64	0.40	0.05	0.20	0.04	bdl	0.01	0.00	0.00	70.79
		B_2.03b	55.38	0.58	2.11	12.35	0.34	9.12	12.46	0.64	0.24	0.02	0.07	bdl	0.04	bdl	0.00	0.00	93.29
		B_2.03c	35.63	bdl	0.79	37.24	0.15	0.22	1.06	1.02	0.56	0.12	0.25	0.00	bdl	0.01	0.00	0.00	77.02
		B_2.04a	24.10	0.01	22.59	30.81	0.18	7.20	0.03	0.04	0.03	0.05	0.01	0.00	0.03	0.01	0.00	0.00	85.09
		B_2.05a	24.15	0.04	22.79	31.10	0.15	8.04	bdl	0.01	bdl	0.00	0.00	bdl	bdl	bdl	0.00	0.00	86.14
		B_2.09a	23.19	0.04	23.09	33.29	0.20	7.22	0.03	0.01	0.03	0.00	0.02	0.02	0.00	0.01	0.00	11.05	98.18
		B_2.09b	47.70	0.05	35.29	0.83	0.02	0.88	0.01	0.28	8.78	0.00	0.02	0.13	0.13	bdl	0.00	4.59	98.70
		B_2.12a	100.15	bdl	0.06	1.62	0.00	0.01	0.02	0.01	0.00	0.06	0.02	bdl	bdl	bdl	0.00	0.00	101.78
		B_2.12b	56.62	bdl	1.83	26.39	0.02	0.04	0.05	0.13	0.33	0.55	0.32	0.07	0.00	0.00	0.00	0.00	86.34

EPMA analysis of mineral inclusions and microfractures of clean fraction of quartz veins grain of Rursee samples (wt.%).

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	Sample ID	Grain ID	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	CI	F	BaO	ZrO ₂	0	H ₂ O	TOTAL
Rursee quartz veins	Rursee 2.1 BNV	B_2.1-03	97.91	0.02	0.04	1.69	0.00	0.01	0.00	0.01	0.00	0.00	0.02	bdl	0.00	bdl	0.00	0.00	99.58
		B_2.1- 05a	100.31	bdl	0.32	0.19	0.02	0.02	0.00	0.02	0.01	0.00	bdl	bdl	bdl	bdl	0.00	0.00	100.80
		B_2.1- 07a	45.73	bdl	0.36	0.11	29.58	0.22	1.79	0.38	1.25	0.02	0.29	bdl	bdl	bdl	0.00	0.00	77.74
		B_2.1- 07b	52.22	0.02	0.24	0.05	24.09	0.21	1.52	0.29	0.89	0.00	0.22	bdl	0.03	bdl	0.00	0.00	78.46
		B_2.1- 07c	61.70	0.01	0.23	0.10	21.09	0.20	1.21	0.18	0.72	0.01	0.25	bdl	0.02	bdl	0.00	0.00	84.39
		B_2.1- 11a	40.79	0.07	26.15	19.64	0.10	3.03	0.01	0.28	3.65	0.03	0.03	0.05	0.12	0.05	0.00	0.00	94.03
		B_2.1- 11b	67.46	0.01	15.25	4.91	0.01	0.84	0.07	0.14	3.41	2.12	0.03	0.13	bdl	bdl	0.00	0.00	94.24
	Rursee 3	B_3.02a	42.77	0.01	15.84	22.60	0.17	4.89	0.07	0.02	0.67	0.07	0.15	bdl	bdl	bdl	0.00	0.00	87.12
	BPV	B_3.02b	66.75	0.02	9.82	13.59	0.08	3.14	bdl	0.05	0.17	0.02	0.03	0.00	0.04	0.02	0.00	0.00	93.70
		B_3.02c	90.77	0.02	3.20	3.97	0.03	1.03	bdl	bdl	0.04	0.01	0.00	0.00	0.00	0.05	0.00	0.00	99.08
		B_3.02d	24.66	0.01	21.55	27.73	0.16	6.22	0.06	0.04	0.79	0.53	0.21	0.07	bdl	0.00	0.00	0.00	81.96
		B_3.05a	30.48	0.03	23.88	25.27	0.16	7.25	0.03	0.03	0.29	0.04	0.06	bdl	bdl	bdl	0.00	0.00	87.44
		B_3.05b	39.46	0.00	30.20	13.10	0.06	2.88	0.05	0.16	2.88	0.18	0.10	0.08	bdl	0.09	0.00	0.00	89.24
		B_3.05c	64.23	0.03	16.31	2.75	0.00	1.11	0.01	0.11	4.01	0.01	0.06	bdl	bdl	bdl	0.00	0.00	88.58
		B_3.08a	56.03	0.26	21.87	6.45	0.01	2.10	0.02	0.15	4.74	0.03	0.00	0.09	0.05	bdl	0.00	0.00	91.79
		B_3.08b	70.37	0.01	10.47	12.40	0.05	2.86	0.03	0.00	0.62	0.01	0.02	0.00	0.03	bdl	0.00	0.00	96.82
		B_3.08c	71.23	bdl	15.55	3.49	0.03	0.74	0.04	7.15	0.08	bdl	0.01	0.01	bdl	bdl	0.00	0.00	98.29
		B_3.08d	32.87	0.73	19.01	25.07	0.13	8.40	0.01	0.07	0.09	0.01	0.01	bdl	bdl	0.01	0.00	0.00	86.40
		B_3.11a	64.26	0.01	1.66	9.68	0.06	0.00	0.23	0.33	0.13	0.17	0.16	0.02	0.03	bdl	0.00	0.00	76.76
		B_3.11b	51.24	bdl	12.87	20.70	0.11	4.48	0.01	bdl	0.01	bdl	0.01	0.02	0.03	0.05	0.00	0.00	89.48
	Rursee 4	B_4.02a	47.91	0.07	3.98	1.07	0.01	0.22	0.58	2.30	2.47	0.15	0.34	0.10	0.06	bdl	0.00	0.00	59.23
	BPV	B_4.03	100.84	0.00	bdl	0.02	0.00	0.00	0.02	0.00	0.02	bdl	0.02	bdl	0.08	bdl	0.00	0.00	100.78
		B_4.04	32.13	0.05	3.95	22.69	0.00	0.15	6.00	0.63	0.64	0.17	0.27	0.13	bdl	0.01	0.00	0.00	66.80
		B_4.05	85.80	0.00	0.03	0.01	0.02	0.02	0.32	0.02	0.03	0.24	0.03	bdl	0.71	bdl	0.00	0.00	87.15
		B_4.08	78.34	0.01	0.73	0.04	10.49	0.22	0.96	0.07	0.09	0.00	0.06	bdl	bdl	bdl	0.00	0.00	90.27
	Rursee 5	B_5-03	60.18	0.12	1.28	1.08	0.05	1.33	3.01	0.98	0.97	0.11	0.37	0.00	bdl	bdl	0.00	0.00	69.38
	BNV	B_5-05	96.03	0.12	0.42	0.22	0.03	0.02	0.08	0.07	0.11	0.04	0.01	bdl	0.00	0.00	0.00	0.00	97.09
		B_5-06a	39.40	0.03	5.43	49.86	0.21	0.23	0.17	0.27	0.51	0.93	0.19	0.00	bdl	0.07	0.00	0.00	97.27
		B_5-06b	48.32	0.09	36.38	0.65	0.00	0.66	0.03	0.45	9.16	0.01	0.01	0.10	0.15	bdl	0.00	0.00	95.97
		B_5-06c	47.07	0.05	34.95	0.69	bdl	0.67	0.06	0.35	9.02	0.00	0.02	0.14	0.06	0.06	0.00	0.00	93.12
		B_5-07	83.67	0.01	8.19	0.07	bdl	0.03	0.13	0.09	2.24	0.07	0.03	bdl	bdl	0.00	0.00	0.00	94.48

	Sample ID	Grain ID	SiO ₂	TiO ₂	AI_2O_3	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	CI	F	BaO	ZrO_2	0	H_2O	TOTAL
Rursee	Rursee 6 BPV	B_6-07b	85.19	0.02	8.13	0.00	bdl	bdl	0.12	1.28	0.71	0.07	0.03	bdl	bdl	0.02	0.00	0.00	95.52
quartz		B_6-07a	79.39	0.00	3.32	0.00	0.01	0.03	0.31	0.06	0.94	0.24	0.09	bdl	bdl	bdl	0.00	0.00	84.32
veins		B_6-16a	49.44	bdl	37.34	0.06	bdl	0.10	0.08	5.13	1.63	0.01	0.02	0.05	0.04	bdl	0.00	0.00	93.85
		B_6-16b	57.16	0.01	19.71	0.03	bdl	0.06	0.16	2.85	1.57	0.03	0.03	bdl	0.05	bdl	0.00	0.00	81.61
		B_6-17	30.47	0.03	21.91	31.64	0.17	6.42	0.01	0.02	bdl	0.02	0.02	bdl	bdl	bdl	0.00	0.00	90.55
		B_6-19	69.23	0.04	17.80	0.12	bdl	0.04	0.04	0.46	4.81	0.00	0.03	0.00	0.01	bdl	0.00	0.00	92.51
Internal	KL2-2		50.09	2.55	13.10	10.78	0.17	6.99	10.80	2.33	0.47	0.25	0.00	0.00	0.01	bdl	0.00	0.00	97.49
standard			50.37	2.59	13.11	10.79	0.14	6.93	10.94	2.42	0.51	0.25	0.00	bdl	0.04	bdl	0.00	0.00	98.00
0100			50.27	2.65	13.13	10.83	0.16	6.97	10.93	2.30	0.46	0.27	0.01	bdl	bdl	0.01	0.00	0.00	97.95
Internal	ATHO-2		74.10	0.23	12.11	3.37	0.10	0.11	1.63	3.60	2.80	0.03	0.05	0.04	0.04	0.02	0.00	0.00	98.23
standard			74.00	0.24	12.22	3.38	0.10	0.09	1.59	3.60	2.68	0.03	0.04	0.10	0.06	0.01	0.00	0.00	98.13
0100			74.39	0.21	12.11	3.41	0.10	0.09	1.63	3.55	2.70	0.06	0.04	0.02	0.08	0.08	0.00	0.00	98.48
Internal	KL2-3		51.64	2.60	13.46	10.89	0.19	7.46	10.98	2.33	0.47	0.30	0.00	bdl	0.00	0.02	0.00	0.00	100.29
standard			50.51	2.62	13.24	10.82	0.13	7.29	10.81	2.28	0.48	0.29	0.00	bdl	bdl	0.04	0.00	0.00	98.43
0100			50.83	2.61	13.13	10.97	0.15	7.29	11.01	2.30	0.48	0.29	0.01	bdl	bdl	0.02	0.00	0.00	99.00
Internal standard of UU	ATHO-3		76.25	0.24	12.22	3.29	0.10	0.09	1.62	3.65	2.77	0.04	0.05	0.06	0.03	0.11	0.00	0.00	100.53
			75.81	0.24	12.01	3.32	0.10	0.10	1.62	3.55	2.76	0.02	0.03	0.04	0.08	bdl	0.00	0.00	99.63
			75.50	0.26	12.08	3.39	0.10	0.11	1.63	3.69	2.68	0.00	0.03	0.08	0.05	0.07	0.00	0.00	99.67

EPMA analysis of crystal lattice of clean fraction of quartz veins grain of Rursee samples (wt.%).

	Veins generation	Grain ID	SiO ₂	TiO ₂	AI_2O_3	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	CI	F	BaO	ZrO ₂	0	H ₂ O	TOTAL
Rursee	Bedding Normal Veins	AH2.1_04	101.97	bdl	0.03	0.00	bdl	0.00	bdl	0.00	0.00	bdl	0.00	0.01	0.00	bdl	0.00		101.91
quartz		AH2.1_05	101.47	0.00	bdl	bdl	0.00	bdl	0.00	0.01	bdl	0.00	0.00	bdl	0.01	0.02	0.00		101.38
veins		AH2.1_07	101.68	0.00	0.03	bdl	0.00	0.01	bdl	0.01	0.01	0.00	0.01	bdl	0.02	bdl	0.00		101.68
		AH2.1_09	102.02	bdl	bdl	bdl	0.01	0.01	bdl	bdl	0.01	0.00	bdl	bdl	0.00	bdl	0.00		101.89
	Bedding Parallel Veins	AH2_05	102.67	bdl	0.01	bdl	bdl	0.00	0.01	bdl	0.00	bdl	0.00	bdl	0.01	bdl	0.00		102.61
		AH2_06	102.41	0.02	0.08	bdl	bdl	bdl	0.00	0.02	0.01	0.00	0.00	bdl	0.06	bdl	0.00		102.48
		AH2_07	101.69	bdl	0.05	0.00	bdl	0.01	bdl	bdl	bdl	0.01	0.00	bdl	0.00	0.02	0.00		101.61
		AH2_08	101.42	0.01	0.03	0.01	0.00	bdl	0.00	0.00	bdl	0.01	0.01	bdl	bdl	0.07	0.00		101.47
		AH2_09	102.34	0.01	0.04	bdl	0.00	bdl	bdl	bdl	bdl	bdl	0.00	bdl	0.03	bdl	0.00		102.22

* bdl - below detection limit

472 5 Conclusions

- The analysis of argon isotope patterns and their interpretations (including K/Cl and inverse isochrons) indicate that
 the main reservoir ³⁹Ar_K for geologically meaningful ages originated from the K-bearing minerals (illite-sericite and
 possibly chlorite) in quartz vein microcracks and/or cavities of fluid inclusions and/or crystal lattice of quartz.
- The determination of a primary crystallization age, i.e., Variscan age, for the quartz veins, is not feasible owing to the
 low amount of K in fluid inclusions and the high amount of excess argon within the FIAs, resulting in anomalously
 old apparent ages in the first ~20 crushing steps.
- The reduced K concentration, due to the loss of primary fluid from inclusions and replacement by a lower salinity,
 lower K fluid, led to bias in the age determination of fluid inclusions. The obtained ages potentially correspond either
 to the presences of a secondary generation of low-salinity fluids or to the contribution of radiogenic argon reservoirs
 hosted in solid phases related to intergrowth mineral inclusions during the recrystallization of guartz veins.
- The maximum apparent ages obtained from the quartz samples span the Jurassic-Cretaceous period. The presence of
 neo-crystallized quartz sub-grains in the veins is due to the local tectonic activity, indicating that this period
 corresponds to the tectonic activity of the Rhenish massif.

486 Data availability

487 All data are included in the text and/or supplementary files.

488 Author contributions

489 The manuscript was primarily authored by Akbar Aydin Oglu Huseynov, who is the corresponding author. Co-authors Prof. 490 Dr. Klaudia F. Kuiper, Em. Prof. Dr. Jan R. Wijbrans, and Dr. Jeroen van der Lubbe made substantial contributions to data 491 interpretation and refinement of the manuscript, enhancing its clarity and depth.

492 Competing interest

493 The authors declare that they have no conflict of interest.

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505 Review statement

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507

508 Supplementary file 1 Impact of blank correction on age.

- 509 Supplementary file 2 K (and thus ⁴⁰Ar^{*}) contribution from chlorite is estimated from 2D electron backscattered images.
- 510 Supplementary file 3 Analytical data used for ⁴⁰Ar/³⁹Ar dating.
- 511 Supplementary file 4 Grain size distribution analysis of separated fluid-rich quartz fraction after crushing.
- 512

513 Figure A1: Raman spectroscopy of fluid inclusion from Rursee quartz veins. (a) Microscopic image of an epoxied and polished

514 fluid-rich quartz fraction. The fluid inclusion that underwent Raman analysis is represented by the red box. (b) The Raman

515 plot is presented with the wavelength on the x-axis and intensity on the y-axis. The Raman spectra show a stretching band in

516 the wavelength range of 3000 to 3700 cm⁻¹, which indicates the presence of an aqueous system.

517 Figure B1: Normal isochron plots of all quartz vein samples.

518 Table C1: Rursee quartz vein samples J values and MDF with analytical error.



520 Figure A1: Raman spectroscopy of fluid inclusion from Rursee quartz veins. (a) Microscopic image of an epoxied and polished fluid-

521 rich quartz fraction. The fluid inclusion that underwent Raman analysis is represented by the red box. (b) The Raman plot is 522 presented with the wavelength on the x-axis and intensity on the y-axis. The Raman spectra show a stretching band in the wavelength

523 range of 3000 to 3700 cm⁻¹, which indicates the presence of an aqueous system.



525 Figure B1: Normal isochron plots of all quartz vein samples.

526 Table C1: Rursee quartz vein samples J values and MDF with analytical error.

Sample ID	Sample ID Ar	MDF	1σ %	J - value	1σ %
Rursee 1a BNV	R01a	0.99635	± 0.04	0.0034347	± 0.06
Rursee 1b BNV	R01b	0.99519	± 0.04	0.0034737	± 0.06
Rursee 2 BPV	R02	0.99469	± 0.03	0.0035113	± 0.03
Rursee 2.1 BNV	R021	0.99492	± 0.03	0.0034868	± 0.04
Rursee 3 BPV	R03	0.99868	± 0.03	0.0035113	± 0.03
Rursee 4 BPV	R04	0.99749	± 0.03	0.0035113	± 0.03
Rursee 5 BNV	R05	0.99494	± 0.04	0.0034868	± 0.04
Rursee 6 BPV	R06	0.99709	± 0.04	0.0034868	± 0.04

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