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

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Abstract. The late Palaeozoic Variscan orogeny (~350 Ma) dictates a significant part of the subsurface geology in north-western and central Europe. Our focus is particularly on veining that occurred in metamorphosed sedimentary rocks that are affected by this orogeny. Vein minerals serve as repositories for documenting the origin of subsurface fluid flows and dynamics, and dating them provides crucial insight into the timing of orogenic and possible reactivation events. The Rursee area (Rhenish Massif, Germany) that is part of the Variscan foreland zone on the Avalonia micro-continent represents a key locality for studying Variscan quartz vein formation. Based on structural grounds, the two different 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 (FIs). We obtained Jurassic to Cretaceous ages, and the isotopic analysis of argon gases revealed that the fluid-rich quartz fractions release ^{39}Ar in two distinct phases. Regardless of quartz veins FIs salinity, stepwise crushing provides apparent K/Cl >1. Electron Probe Micro Analyser data confirm the presence of the K (^{39}Ar) in the K-bearing mineral inclusions (e.g., sericite, mica, and chlorite) and in microcracks and possibly in the crystal lattice of quartz.

K-bearing mineral inclusions and/or crystal lattice of quartz, which form in the Variscan-origin vein fractures, provide a plausible explanation for the young apparent isotopic ages. The presence of the quartz sub-grains may suggest that obtained ages are likely to reflect post-Variscan reactivation-recrystallisation due to tectonic activity or its cooling moment during the Jurassic-Cretaceous period rather than the original Variscan vein formation.

This study emphasizes the complexities of isotopic dating of FIs, as well as the importance of careful interpretation of such data, especially in cases where different K-bearing mineral inclusions and/or radiogenic argon from crystal lattice obscure the initial FIs signal.

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 & Buick, 2000; Oliver & Bons, 2001). Increase in both temperature and pressure during burial diagenesis, orogenesis and deformation

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cause sedimentary and volcanic rocks to lose their volatile components and to release warm fluids, which cumulate minerals in fractures and faults (Baumgartner & Ferry, 1991; Yardley & Bottrell, 1993; Oliver & Bons, 2001; Cox, 2007). These often saline fluids contain, among others, $KCl_{(aq)}$ or $K_2CO_{3\,(aq)}$ (Rauchenstein-Martinek et al., 2014), which are partly precipitated during crystallisation of minerals in veins or as inclusions in these minerals (Sterner et al., 1988). One of the isotopes of potassium, ^{40}K, is radioactive and can be used for K-Ar or its derivative $^{40}Ar/^{39}Ar$ dating. Progressive crushing techniques enable to liberate gasses from fluid inclusions (FIs), mineral inclusions and/or crystal lattice for the age determination of geological events provided that K-concentrations are high enough (Qiu & Dai, 1989; Turner & Bannon, 1992; Turner & Wang, 1992; Qiu, 1996; Kendrick et al., 2001; Qiu & Wijbrans, 2006; Kendrick et al., 2006; Qiu & Wijbrans, 2008; Qiu & Jiang, 2007; Jiang et al., 2012; Bai et al., 2013; Liu et al., 2015). This method does not only define an age, but also quantifies the ratio of noble gases (e.g. $^{39}Ar_K/^{37}Ar_{Ca}$, $^{39}Ar_K/^{38}Ar_{Cl}$) derived from Ca, K and Cl, respectively, that have been formed during neutron radiation prior to analysis. The $^{39}Ar_K/^{38}Ar_{Cl}$ provides important information on the composition of parental fluids and their sources (Sumino et al., 2011; Cartwright et al., 2013). In addition to fluid composition and provenance studies (Kelley et al.,1986; Turner & Bannon, 1992: Kendrick et al., 2001, 2006), the initial $^{40}Ar/^{36}Ar$ values of FIs in quartz can considerably vary and may be used to differentiate between meteoric-sourced water (~298.6) (Ballentine et al., 2002; Ozima & Podosek, 2002) and deeper crustal or mantle-derived fluids (>10,000; MORB >40,000) (Burnard et al., 1997).

In order to accurately determine the age of FIs in quartz veins using the $^{40}Ar/^{39}Ar$ stepwise crushing method or the source of the fluid based on $^{40}Ar/^{36}Ar$ ratios, it is necessary to consider three distinct components of ^{40}Ar, namely (1) radiogenic $^{40}Ar_R$ 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 the fluid inclusion, either as (2a) atmospheric $^{40}Ar_A$ or (2b) excess $^{40}Ar_E$. The presence of $^{40}Ar_E$ in FIs creates a significant challenge to determining accurate vein formation ages using the $^{40}Ar/^{39}Ar$ technique (Rama et al., 1965), although isochron diagrams might help to overcome this issue (McKee et al., 1993; Qiu, 1996; Qiu et al., 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 thus K) may come from the dissolved salts in FIs, leaking from the crystals lattice during crushing (Kendrick et al., 2011), and/or from any K-bearing mineral inclusions trapped inside the crystals (Qiu & Wijbrans, 2006; Kendrick, 2007; Qiu & Wijbrans, 2009; Kendrick & Phillips, 2009).

This study aims i) to determine the absolute age of quartz vein formation by analysing FIs using the stepwise crushing $^{40}Ar/^{39}Ar$ dating method, ii) to elucidate the location of K in the vein minerals (e.g., FIs, mineral inclusions, and/or crystal lattice) and iii) to identify when different K sources release their $^{39}Ar_K$ 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).

Quartz samples were obtained from an outcrop near the Rursee in the upper reaches of the Rur river in the North Eifel region of Western Germany. Detailed structural investigations of this area have been previously conducted by Van Noten et al. (2007), who differentiated quartz veins into two groups. The older generation of quartz veins, the so-called bedding normal veins (BNVs) is assigned to the early stages of the Variscan orogeny, whereas the second group, comprising bedding parallel veins (BPVs), is linked to the main stage of the Variscan orogeny. Absolute $^{40}Ar/^{39}Ar$ ages of FIs representing the age of quartz vein

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formation would allow us to better constrain the structural evolution and subsurface fluid flow during the Variscan orogeny in north-western Europe. Reliable $^{40}Ar/^{39}Ar$ age constraints of quartz vein formation would provide the opportunity to understand the timing and evolution of mountain building in analogue fold-and-thrust belts.

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), western part of 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 veins 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 & 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 & Muchez, 2000; Lünenschloss et al., 2008).

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

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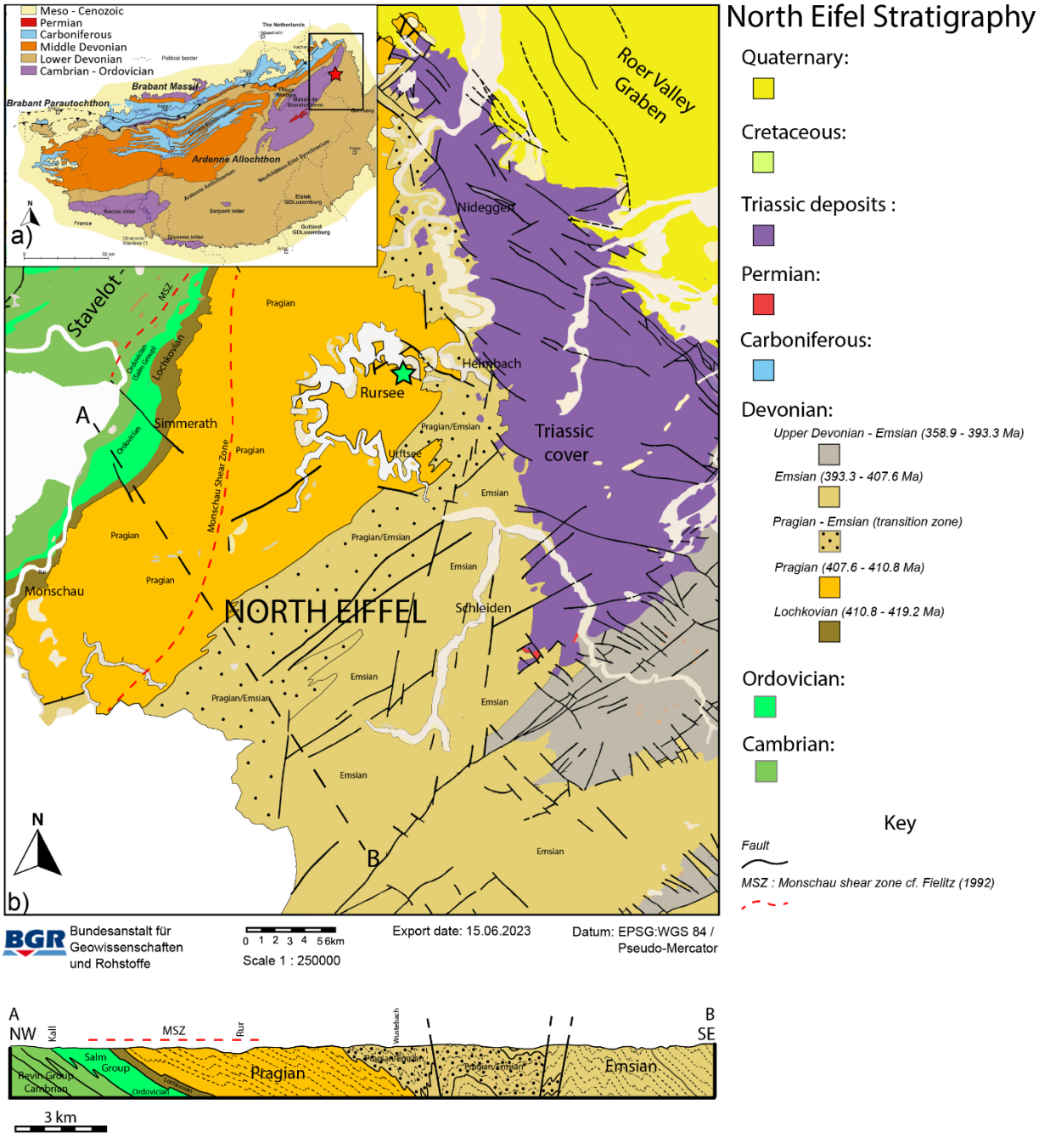

Figure 1: (a) Geological map with the Variscan frontal zone in the Ardenne-Eiffel region (study area marked with a red star). (b) Geological map of the North Eifel region (modified after Ribbert, 1992; Van Noten et al., 2011). The Lower Devonian layers overlay metamorphic deposits of the Lower Palaeozoic Stavelot-Venn Inlier. These layers have been locally distorted in the Monschau Shear 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, cross-section illustrates the continuous northwest-southeast trending overturned folds that are characteristic of the North Eifel zone.

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The $^{40}Ar/^{39}Ar$ study targets the BNVs and BPVs (Fig. 2), which formed in low-grade metamorphosed (prehnite-pumpelleyite facies) conditions as a result of the precipitates from warm fluids in fractures (Van Noten et al., 2008). The structural cross-cutting relationships between these quartz vein generations suggest that they originated during different geological events (Van Noten et al., 2008) revealing that BPVs are younger than BNVs. BNVs are found mostly within the competent psammite and hardly occur in incompetent pelitic layers. This positioning suggests that BNVs formed during the early stages of the Variscan orogeny, associated with the final burial phases of the Ardennes-Eifel basin (Sintubin et al., 2000; Urai et al., 2001; Van Noten et al., 2008, 2009).

In contrast, BPVs follow the strata between the psammatic and pelitic layers as a result of the bedding-parallel slip caused by flexural folding during the Variscan orogeny (Van Noten et al., 2008).

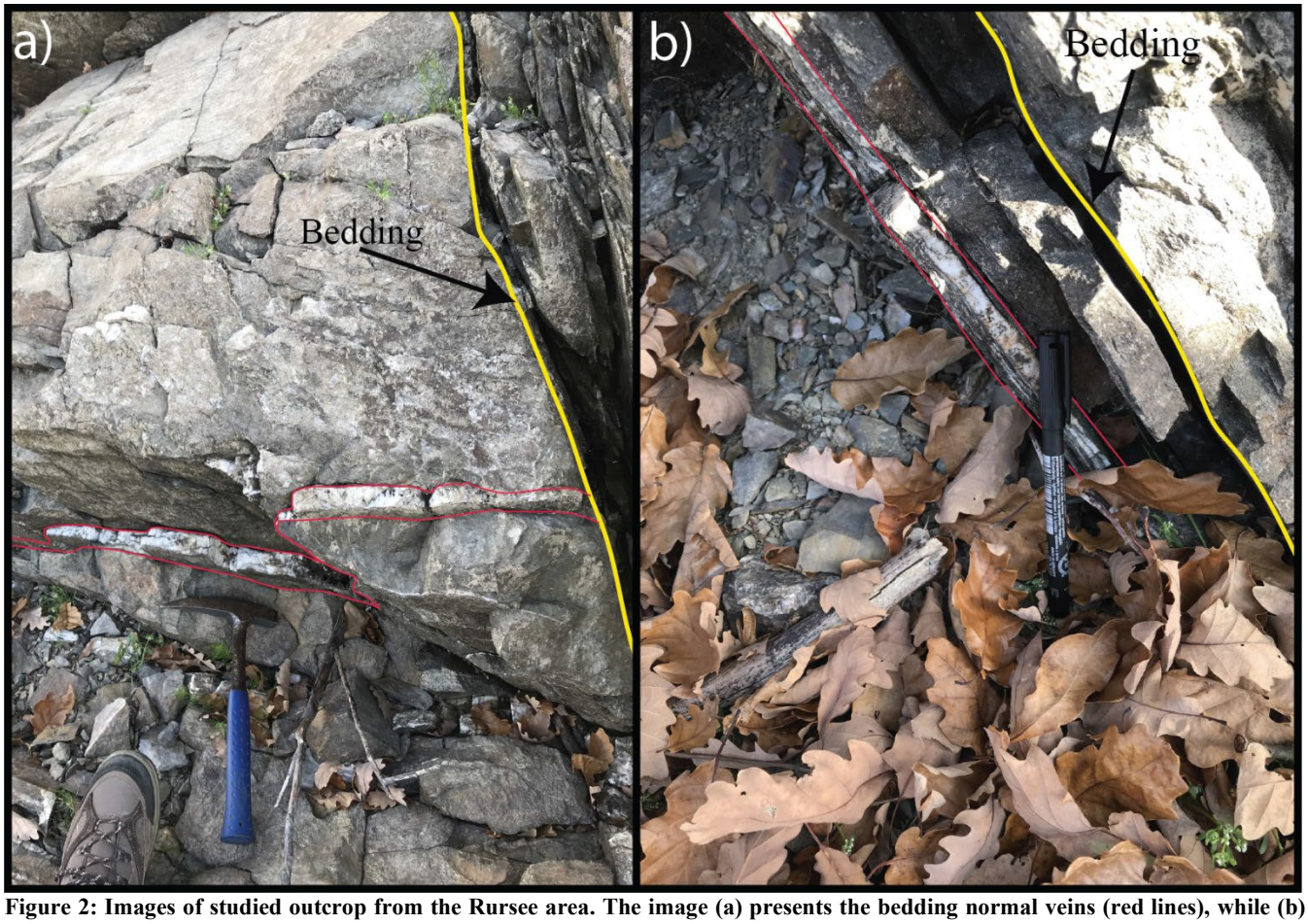

Figure 2: Images of studied outcrop from the Rursee area. The image (a) presents the bedding normal veins (red lines), while (b) shows the bedding parallel veins (red lines). Yellow lines indicate the bedding in both images.

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2 Material and methods

2.1 Quartz and inclusions in quartz minerals

A total of 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 are characterised by syntaxial growth, whereby the growth starts from the wall of the veins towards the central part of the veins (Ramsay, 1986). The pelitic host rocks consist of sericite, illite, mica and chlorite. Chlorite is also abundant within the vein fractures and between the host rock and the vein wall.

Both quartz vein generations lack of primary FIs in the crystal growth zones and contain pseudo-secondary and secondary fluid inclusion assemblages (FIAs) (<10 µm) (Van Noten et al., 2011) in the sealed microcracks being perpendicular to crystal elongation (Fig 3.). The Rursee quartz vein samples yield average FIs 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 In general, T_h of pseudo-secondary and secondary FIs span an equally broad range of 110-180 °C (Van Noten et al., 2011).

2.2 Mineral separation

Prior to $^{40}Ar/^{39}Ar$ 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 rock contaminants from quartz grains. The samples were sieved into 250 and 500 µm fraction and dried in an oven at 60 °C. The samples were further separated by a custom-made system using an overflow centrifuge with conventional heavy liquids based on IJlst (1973) and Frantz magnetic separation (Porat, 2006). We used heavy liquids with a density of 2.62 g/cm^3 and 2.64 g/cm^3 to obtain fluid inclusion-rich fraction of quartz grains (ρ= 2.62-2.64 g/cm^3). The fraction was rinsed with acetone, dried, and further sieved to separate the 400-500 µm grain size range. From this fraction, only the purest quartz grains were hand-picked under binocular microscope for $^{40}Ar/^{39}Ar$ dating.

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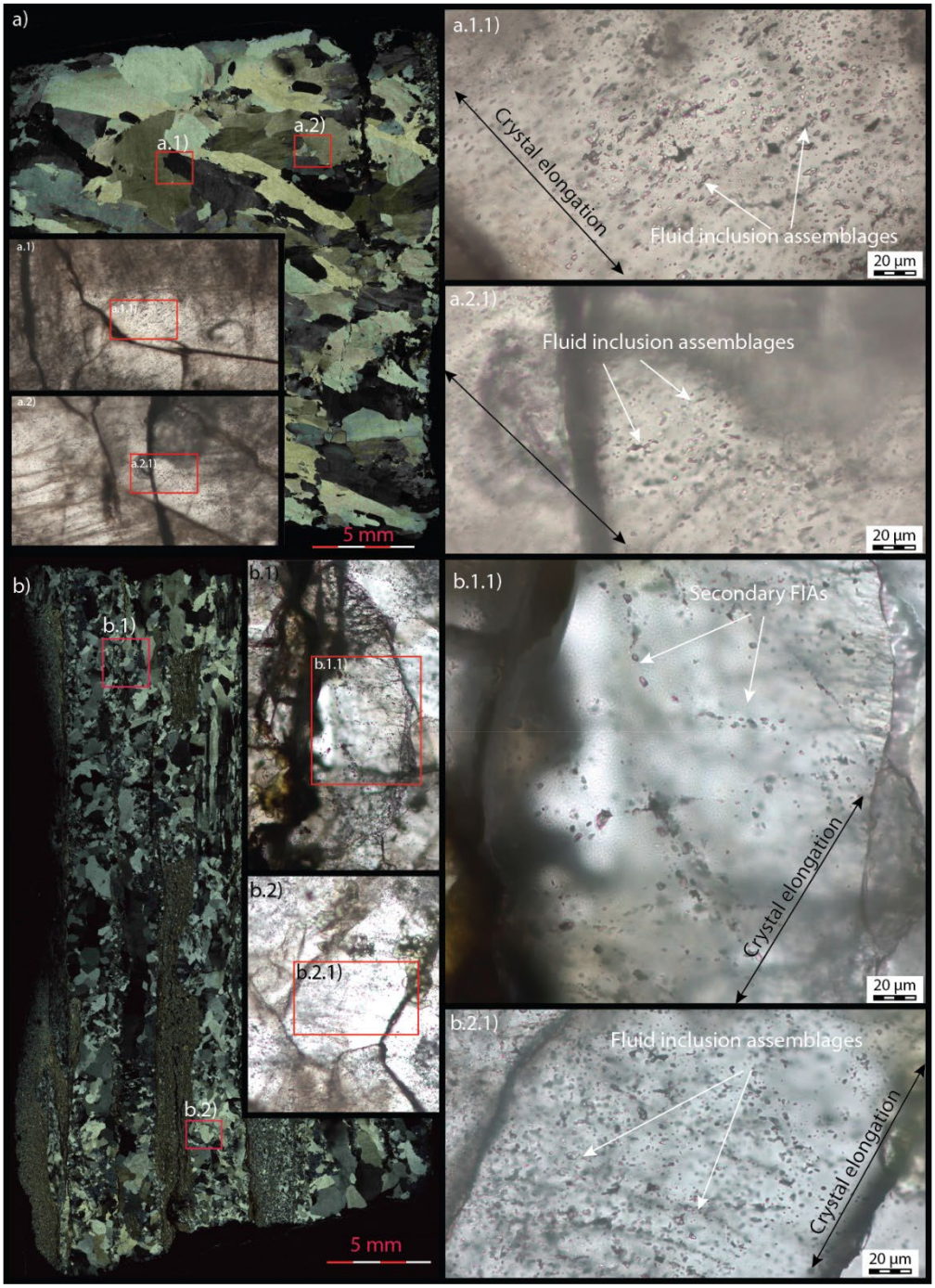

Figure 3: Fluid inclusions in quartz veins under optical microscopy. (a) Image of BNVs under cross-polarizer light microscopy. Both (a.1.1) and (a.2.1) are the zoom of (a.1) and (a.2) images, respectively, indicating pseudo-secondary fluid inclusion assemblages (FIAs) (white arrow). (b) Cross polarizer images of the BPV sample under microscopy. (b.1.1) and (b.2.1) images are secondary and pseudo-secondary fluid inclusion (respectively) -focused areas, which are zooms of the (b.1) and (b.2) images, respectively. The white arrows represent the FIAs. Both generations of quartz veins have FIAs that are present in sealed microcracks rather than in crystal growth zones.

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2.3 $^{40}Ar/^{39}Ar$ stepwise crushing

Fluid-rich quartz grains (400-500 µm; 2.62-2.64 g/cm^3) were carefully selected under a binocular zoom microscope, and a quantity of 200-270 mg of material was packed in aluminium foil and placed in 20 mm ID - 22mm OD aluminium cups. Drachenfels (DRA-2) sanidine standard was loaded between each set of three samples to monitor the neutron flux. The samples were irradiated at Oregon State University (USA) using the CLICIT (Cadmium-Lined In-Core Irradiation Tube) facility for 12 hours (batch VU123). After irradiation, standards were placed in 2 mm copper planchet holes for single grain fusion analysis and vacuum pre-baked at 250 °C. The samples were then placed in an ultra-high vacuum system, baked at 120 °C, and connected 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 48–5 CO_2 continuous-wave laser fusion system.

The samples were crushed in an in-house developed and built crusher consisting of a stainless-steel tube (height: 18 cm, outer diameter: 1.8 cm) that has a spherical curve on its interior base and a magnetic stainless-steel pestle (height: 5 cm, diameter: 1.6 cm, weight: ~69.5 g) with rounded tips with a slightly narrower outer radius. These geometries allow optimisation 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 sample were baked overnight at 250 °C. The pestle was dropped into a free-fall state using an external electromagnet with a frequency of 1 Hz controlled by an adjustable power supply and pulse generator to crush the sample. The pestle was dropped from a height of ~3, ~4 or ~5 cm *in vacuo*. Subsequently, the gases emitted from FIs in the fragmented quartz sample were analysed. To obtain a sufficient amount of argon in the mass spectrometer, the number of pestle drops per extraction step and drop height were systematically increased during the experiment, with a maximum of 999 drops per analysis (in total, ~40000 cumulated pestle drops per experiment).

The gas released from the samples and standards was analysed 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 10^{12} Ohm or 10^{13} 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 for the detection of ^{40}Ar using a 10^{13} Ohm amplifier. Similarly, the H1- CDD collector is used for the measurement of ^{39}Ar (H1 Faraday was used for the runs on DRA-2 sanidine standard because of the higher ^{39}Ar signal), the AX-CDD collector for ^{38}Ar, the L1-CDD 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. A Gain calibration is done by correcting for gain relative to the beam intensity measured on the AX-CDD, using measurements of ~50 fA (^{40}Ar measured beam intensities) pipettes of air on each cup, and mass discrimination corrections are made by measuring a series of ~400 fA (^{40}Ar measured beam intensities) air pipettes roughly every 12 hours. Raw data were processed using the ArArCalc software (Koppers, 2002). Ages are calculated relative to Drachenfels (DRA-2) sanidine of 25.552 ± 0.078 Ma

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(Wijbrans et al., 1995) which was recalibrated against Fish Canyon Tuff sanidine of 28.201 ± 0.023 Ma (Kuiper et al., 2008). 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 ± 0.02) x10^{-4} for $(^{36}Ar/^{37}Ar)_{Ca}$, (6.73 ± 0.04) x10^{-4} for $(^{39}Ar/^{37}Ar)_{Ca}$, (1.21 ± 0.003) x10^{-2} for $(^{38}Ar/^{39}Ar)_{K}$, and (8.6 ± 0.7) x10^{-4} for $(^{40}Ar/^{39}Ar)_{K}$. Gain correction factors and their standard errors (±1SE) are 1.00162 ± 0.00028 for H2-Far, 0.97963 ± 0.00021 for H1-CDD, 0.99921 ± 0.00027 for L1-CDD 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 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 = β × $^{39}Ar/^{38}Ar$ with β = 0.06 derived from K/Cl = ~18.7 in GA1550 and $^{39}Ar_K/^{38}Ar_{Cl}$ = ~316 for a 12-hour irradiation at the OSU Triga CLICIT facility. All errors are quoted at the 2σ level and include all analytical uncertainties (Table 1).

Note that it is not possible to directly correct the crushing blank because we cannot perform the exact experiment without crushing sample material. We tested the blanks for each tube without sample material, following the identical procedures used for real experiments. With this approach, we have direct metal-to-metal contact during pestle drops, which might not be fully representative of a real sample. We did observe a substantial increase in background, with a higher number of drops and a higher drop level. Importantly, 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 unknows 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.

2.4 Electron Probe Microanalysis (EPMA)

Quartz grains of sub-samples that were analysed 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 FIs, 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 analysed 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, and multiple times before and after measurements of the samples.

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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 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. For sample Rursee 1a BNV, a lighter pestle (68 g) has been used than for sample Rursee 1b BNV (69.5 g) and for all other samples.

The apparent ages of the spectra in samples Rursee 1b BNV, Rursee 2 BPV, Rursee 2.1 BNV, and Rursee 4 BPV exhibit a gradual decrease in age over the next 10 - 40 % of $^{39}Ar_K$ released, eventually stabilising at a more or less consistent age from ~80 to ~100 % $^{39}Ar_K$. Rursee 3 BPV, Rursee 5 BNV, and Rursee 6 BPV show comparable behaviour with, after the initial old ages, a decrease in age to a "pseudo-plateau" from ~15 % to ~40 % $^{39}Ar_K$ released, followed by a gradual decrease in age and a more or less uniform age in the >80 % released $^{39}Ar_K$ part of the spectrum. For these pseudo-plateaus, we arrive at averaged ages of ~84 Ma for 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 Rursee 5 BNV, and Rursee 6 BPV, and ~560 Ma for Rursee 3 BPV. The ages of Rursee 2.1 BNV and Rursee 4 BPV correspond to the inverse isochron ages; however, due to significant uncertainty, the ages of other samples obtained from the average plateau 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. The ages that we derive are based on the data points that cluster along the reference line in the isochrons in the final part of the age spectra. There is no systematic age difference between BNV and BPV.

All quartz samples release argon during *in vacuo* stepwise crushing with different isotopes of argon contributing to the gas release at different stages of the experiment. Figure 6 shows, for each step, the percentage (relative to total amount) of a specific isotope that is released through the experiment. All quartz samples are characterised 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 starts to increase after the first 20 analysing steps (~790 pestle drops from 3 cm height). At steps 30-35, we observe fluctuations in the data. These shifts are artefacts caused by 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 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 $^{36}Ar_{air}$, $^{38}Ar_{Cl}$, and ^{40}Ar* at the end of analysis compared to their total release. For $^{40}Ar^*$, we still measure a small, reliable signal, but this is obscured in Figure 6 due to the high signals in the first steps since we plot percentages of the total released ^{40}Ar per experiment. Note that huge amounts of excess ^{40}Ar (which is part of the $^{40}Ar^*$ signal) are released in the initial steps of the experiment and dominate the total percentage.

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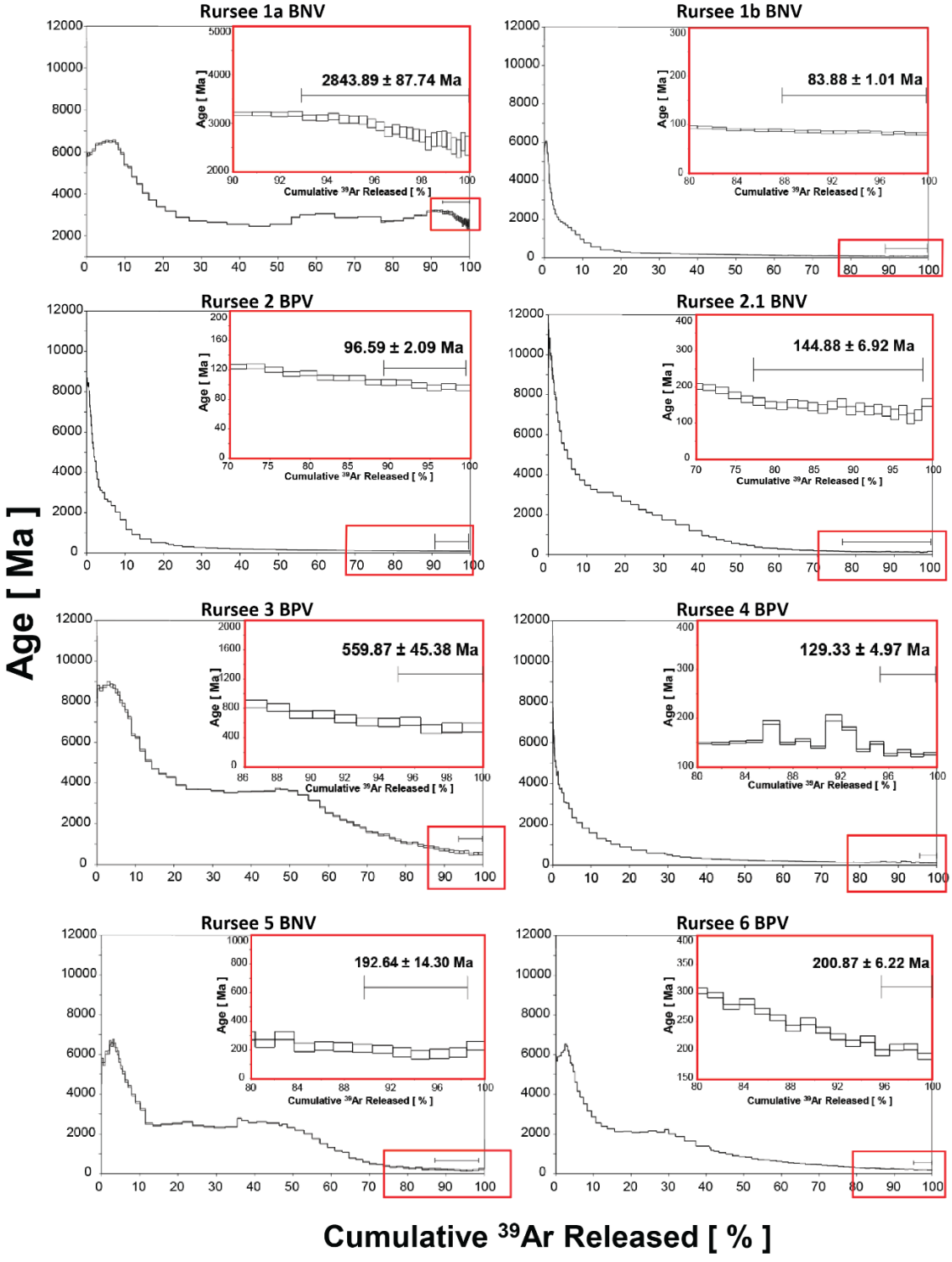

227 **Figure 4: The apparent plateau age of all quartz vein experiments. The red boxes focus on the last part of the age spectra, where**
228 **apparent ages are more or less stable.**

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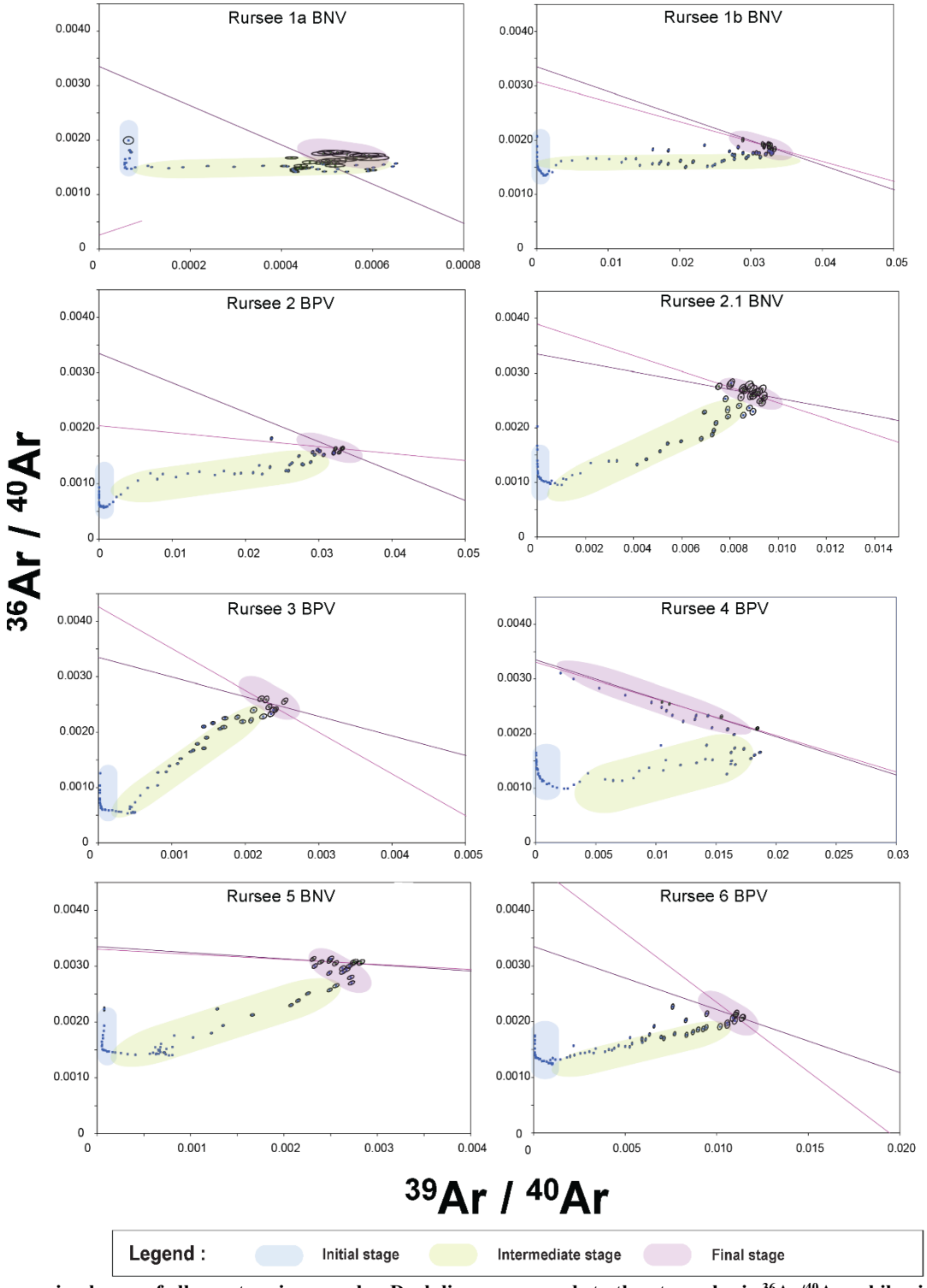

229 **Figure 5: Inverse isochrons of all quartz veins samples. Dark line corresponds to the atmospheric $^{36}Ar/^{40}Ar$, while pink line shows**
230 **mean weighted.**

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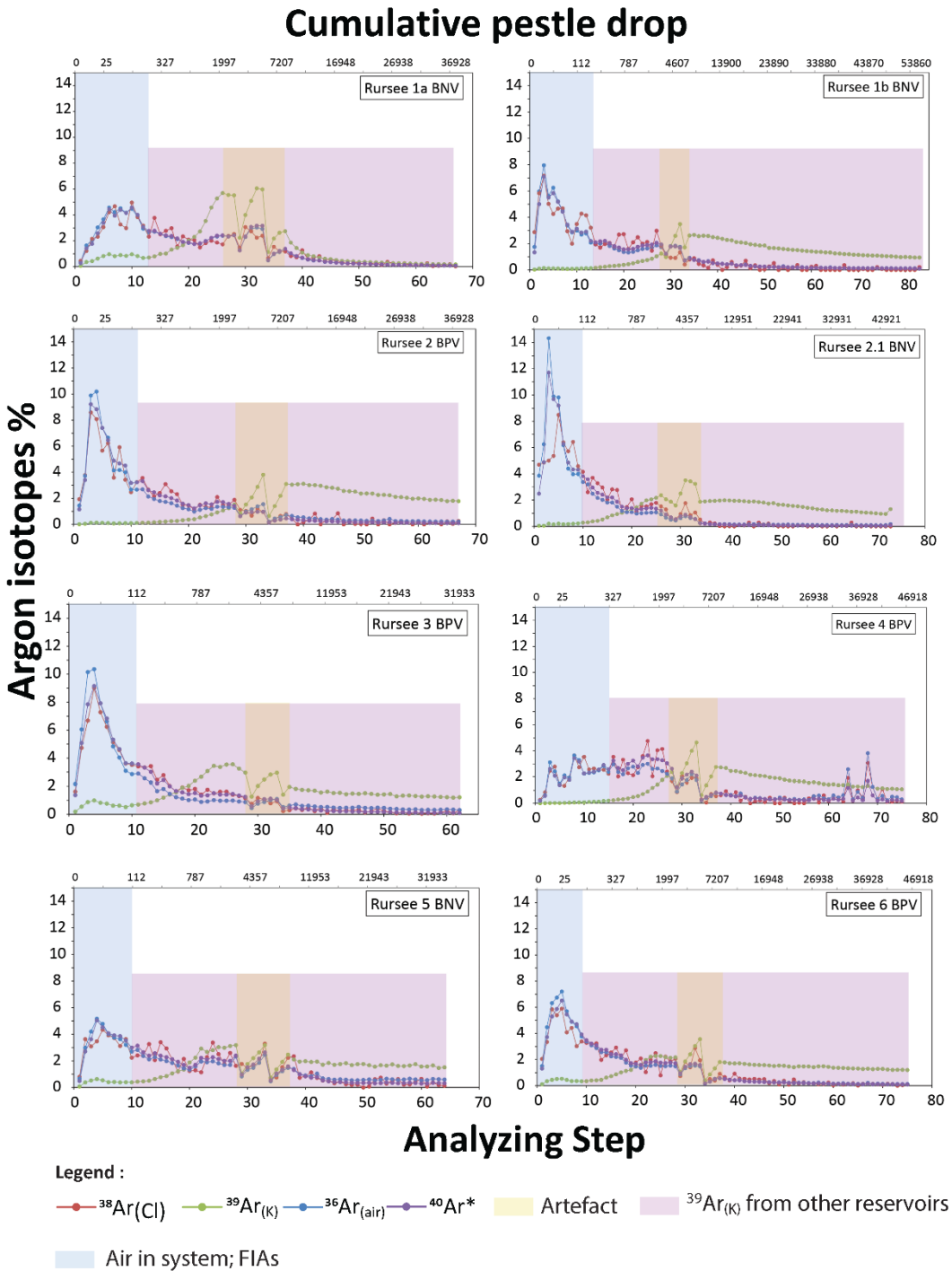

231 **Figure 6: Released argon isotopes per analysing step relative to its total release. Note that the data are expressed against analysing**
232 **step instead of the crushing step, and that the upper x-axis scaling (cumulative pestle drops) are neither linear, nor logarithmic (non-**
233 **continuous scaling).**

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234 **Table 1 Summary of $^{40}Ar/^{39}Ar$ age spectra, including invers isochron data of all analysed quartz samples.**

Locality	Rursee, outcrop near Schwammenauel dam (Germany)							
Rock type	Quartz veins							
Mineral	Quartz							
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 – 500							
Density (g.cm^{-3})	2.62 - 2.64							
Age (Ma)	2843.9	83.9	96.6	144.9	559.9	129.3	192.6	200.9
±2σ analytical error + J error	± 87.7	± 1.0	± 2.1	± 6.9	± 45.3	± 5.0	± 14.3	± 6.2
±2σ full external error	± 95.9	± 2.0	± 2.9	±7.5	± 46.5	± 5.6	± 14.8	± 7.4
MSWD	42.8	1.6	3.34	4.34	6.05	5.39	2.01	0.37
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	± 7284.5	± 51.1	± 860.2	± 38.4	± 183.4	± 6.4	± 29.0	± 180.8
Inverse isochrone age	-	74.1	80.7	215.5	399.2	116.7	258.6	26.2
±2σ analytical error + J error	± 5769.6	± 16.0	± 224.8	± 50.6	± 425.1	± 7.1	± 129.0	± 176.5
±2σ full external error	± 5769.7	± 16.0	± 224.8	± 50.8	± 425.2	± 7.5	± 129.1	± 176.6
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	14.48	1.56	0.19	3.82	8.83	0.87	2.21	0.46

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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 $^{40}Ar^{*}$ to link these options to our results, and to finally assess the ages and their broader implications.

4.1 Data quality

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 $^{39}Ar_K$ (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

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

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4.1.3 Recoil artefacts

These artefacts occur when ^{37}Ar and ^{39}Ar, 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 & Cadogan, 1974; Foland, 1983; Lo & Onstott, 1989; Féraud & Courtillot, 1994; Baksi, 1994; Onstott et al., 1995; Villa, 1997). However, this phenomenon is assumed to have a smaller impact than that of the blank correction.

4.2 Potential reservoirs of K

To date, three main hypotheses are being debated as to the origin of the released argon in a stepwise crushing experiment. The first group (Qiu & Wijbrans, 2006, 2008; Bai et al., 2019) suggests that progressive crushing releases gases mainly from FIs and therefore represents FIs ages. The second group (e.g., Kendrick and Philips (2007)) discusses the possibility of K-bearing mineral inclusions within the inclusion cavity and/or in microcracks serving as argon reservoirs in the later stages of crushing. Obtained ages therefore represent mineral closure ages or a mixture of FIs and mineral ages.
In addition, the third potential source of potassium in the quartz minerals might be the presence of minor amounts of K^+ in the crystal lattice (Kendrick et al., 2011) of quartz minerals, which is representative of the formation age of veins. Hydrothermal quartz veins, characterised by their substitution in crystal structure, have been studied by Weil (1984) and Götze et al. (2021). These studies indicate that Si^{4+} derived from hydrothermal quartz veins has the ability to be substituted by other ions such as Al^{3+}, Ga^{3+}, Fe^{3+}, B^{3+}, Ge^{4+}, Ti^{4+}, and P^{4+}. Al^{3+} is most commonly replacing Si^{4+} since it is found in significant quantities (~300-700 ppm) in quartz, based on EPMA data. Additionally, small quantities of monovalent ions such as K^+ may fill empty spaces in the crystal structure, serving as charge balancers for trivalent substitutional ions such as Al^{3+} (Bambauer, 1961; Kats, 1962; Perny et al., 1992; Stalder et al., 2017; Potrafke et al., 2019). However, Jourdan et al. (2009) postulated that the substitution of these components may be so minor that it is even undetectable using a Secondary Ion Mass Spectrometer (SIMS). Furthermore, it is important to note that not all hydrothermal sources or quartz minerals have this particular form of substitution (Jourdan et al., 2009).
Apart from these potential $^{39}Ar_K$ reservoirs above, detrital minerals (e.g., mica present in the surrounding pelitic rock) that might be trapped by the quartz veins during the growth may also contribute to the obtained ages.

4.2.1 Identification of different K reservoirs in the Rursee quartz samples

During *in vacuo* stepwise crushing, the release of argon isotopes from the samples follows systematic patterns. Here, we attempt to link this release to the sequential contributions of different reservoirs of K and, thus, 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.
Depending on the size (<10 µm), location, and generation of FIs, they may contribute successively to the argon release patterns in the early or middle stage of stepwise crushing. Figure 6 reveals that the concentration of $^{39}Ar_K$ increases throughout the

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process of *in vacuo* stepwise crushing, while the concentration of other argon isotopes decreases. This suggests that K-containing reservoirs were not opened in the first part of the experiment. The release patterns of $^{39}Ar_K$ can be categorised into two distinct groups during stepwise crushing:

a) The *first group* of samples exhibits a small initial release during the early stages, followed by a decrease in the ~10th step and an increase from the ~10th to ~35th step followed by a gradual decrease (Rursee 3 BPV, Rursee 5 BNV, and Rursee 6 BPV).

b) The *second group*, on the other hand, lacks the initial release of $^{39}Ar_K$ steps 1-10, but behaves the same for step 10 onwards with a gradual increase to the ~35th step followed by a gradual decrease (Rursee 1b BNV, Rursee 2 BPV, Rursee 2.1 BNV, and Rursee 4 BPV).

The continuous rise in $^{39}Ar_K$ 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, $^{39}Ar_K$ is emitted from FIs in microcracks (secondary FIs). From steps ~10th to ~70th, the release occurs as a result of mixing of potential pseudo-secondary FIs (~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 consistent 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 ~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 FIs, which are likely to be opened in the early phase. After most FIs have been mechanically opened, the subsequent rapid increase in K (reflected by the $^{39}Ar_K$) and the steady decline in Cl (reflected by the $^{38}Ar_{Cl}$) occur throughout successive crushing steps and is reflected in the K/Cl ratio. Therefore, this increase is most likely caused by the exhaustion of the Cl-rich FIs in combination 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 FIs and other K reservoirs was first suggested by (Kendrick et al., 2006, 2011): K/Cl ratios ≤1 are representative for FIs and K/Cl ratios >1 for other sources. Therefore, if K/Cl ≤1, the obtained age corresponds to the age of the FIs. If the K/Cl >1 the obtained age corresponds to the 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 K-related reservoir(s) other than FIs. It is worth noting that this is based on the assumption that there are no other K-bearing phases, such as KNO_3, K_2SO_4 or K_2CO_3, rather than KCl dissolved in aqueous FIs. This assumption seems to be verified by Raman analysis (see Figure A1), which does not show detectable peaks for these alternative K-bearing phases. Therefore, K/Cl >1 suggests that K does not only relate to the salinity of the FIs, and at least one major other source should be present, e.g., the crystal lattice of quartz and/or mineral inclusions in the quartz crystals and/or in microcracks.

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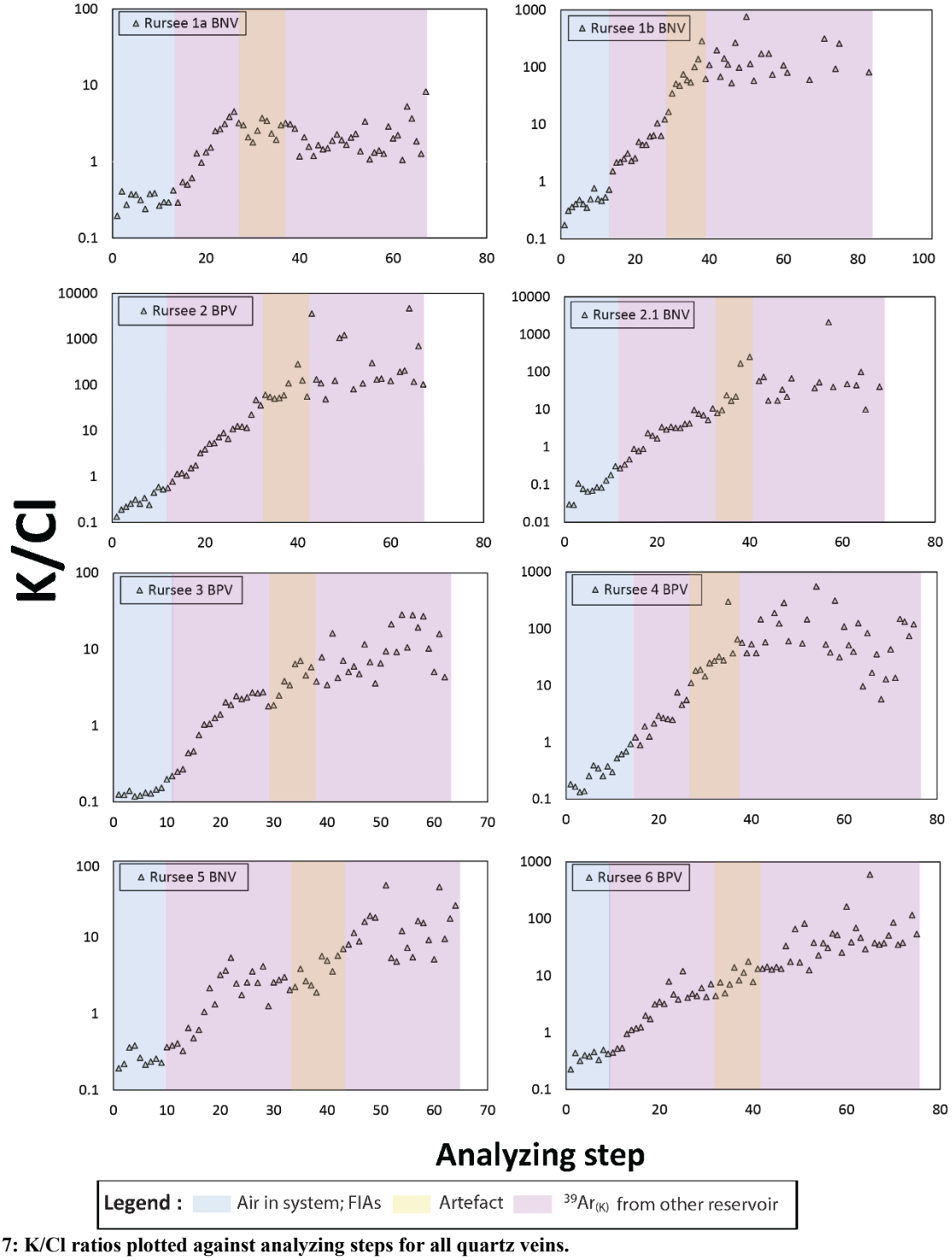

330 **Figure 7: K/Cl ratios plotted against analyzing steps for all quartz veins.**

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331 **4.2.2 K-bearing mineral inclusions**

332 EPMA data (Table 2) from cleaned hand-picked fluid-rich separated quartz grains indicate the presence of sericite, chlorite-
333 sericite and illite-sericite in the microfractures and in the cavities of fluid inclusion, which might explain the subsequent
334 increase of $^{39}Ar_K$ from the ~10th analysing step onwards. The presence of these minerals (or mixtures) in the inclusion cavity
335 and microfractures is also invisible under a binocular or petrographic microscope during the mineral separation, but it was also
336 captured using electron-backscattered imaging (Fig. 8). In thin sections of quartz veins with associated host rock, illite-sericite
337 and white mica are abundant in the surrounding pelitic layer of the Rursee formation (Fig. 9). These minerals that contain a
338 significant amount of K_2O are also detected by EPMA, in the separated quartz samples, especially in Rursee 2 BPV (see EPMA
339 data, Table 2). High K concentrations (~8.8 wt. % K_2O) are likely related to intergrowth with sericite or a closely-related
340 mineral.
341 Additionally, petrographic analysis of thin sections of whole rock samples representing both vein generations (BPV and BNV)
342 show an abundance of chlorite in between the vein wall and host rock, as well as in fractures (Fig. 10). Despite the absence of
343 K in the crystal structure of chlorite, traces of K were reported for chlorites in previous studies (Pacey et al., 2020; Li et al.,
344 2022).

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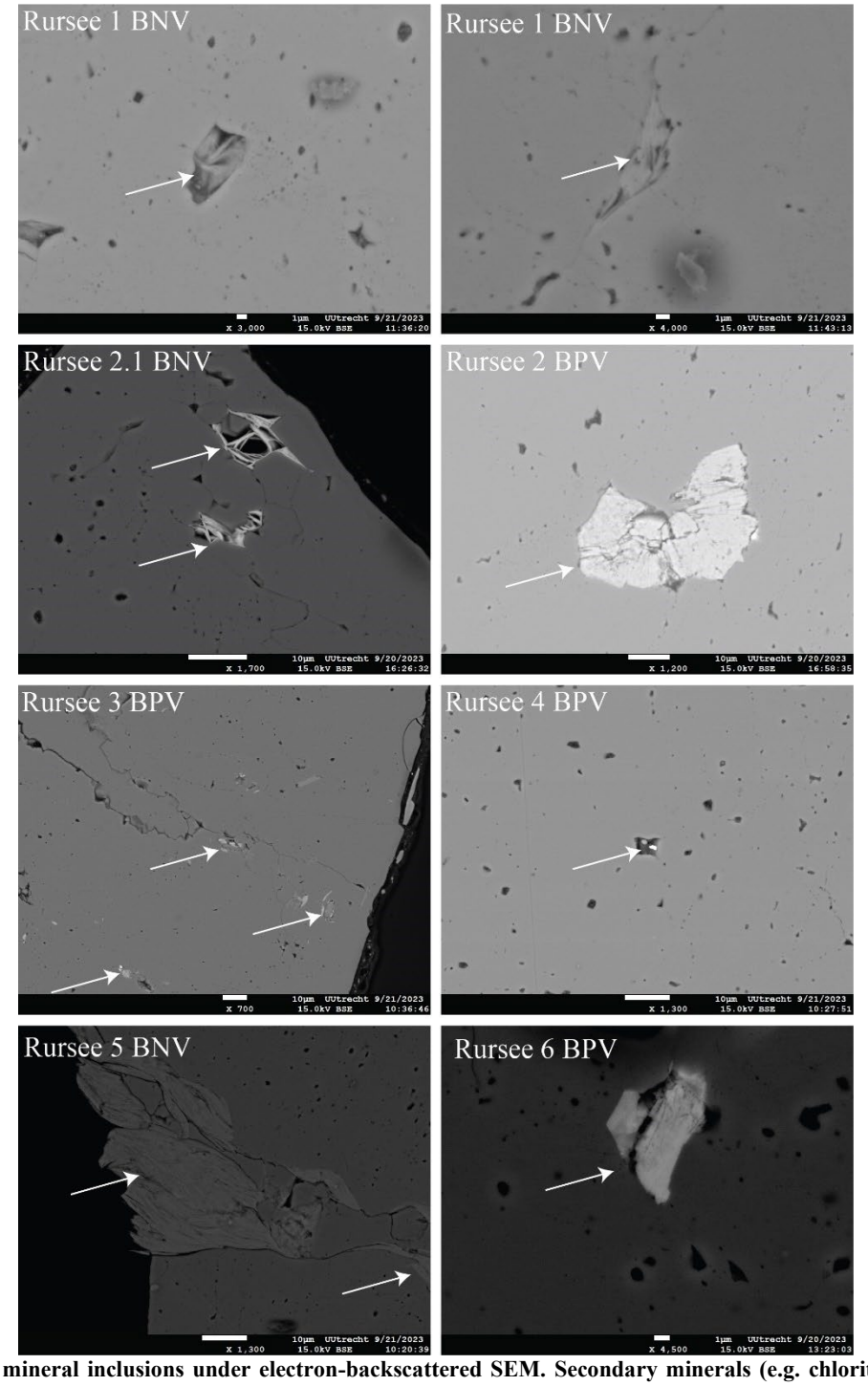

345 **Figure 8: Images of mineral inclusions under electron-backscattered SEM. Secondary minerals (e.g. chlorite, sericite and mica)**
346 **occur in cavities and microfractures (pointed by white arrow) in separated fluid-rich quartz fraction as determined using EPMA.**

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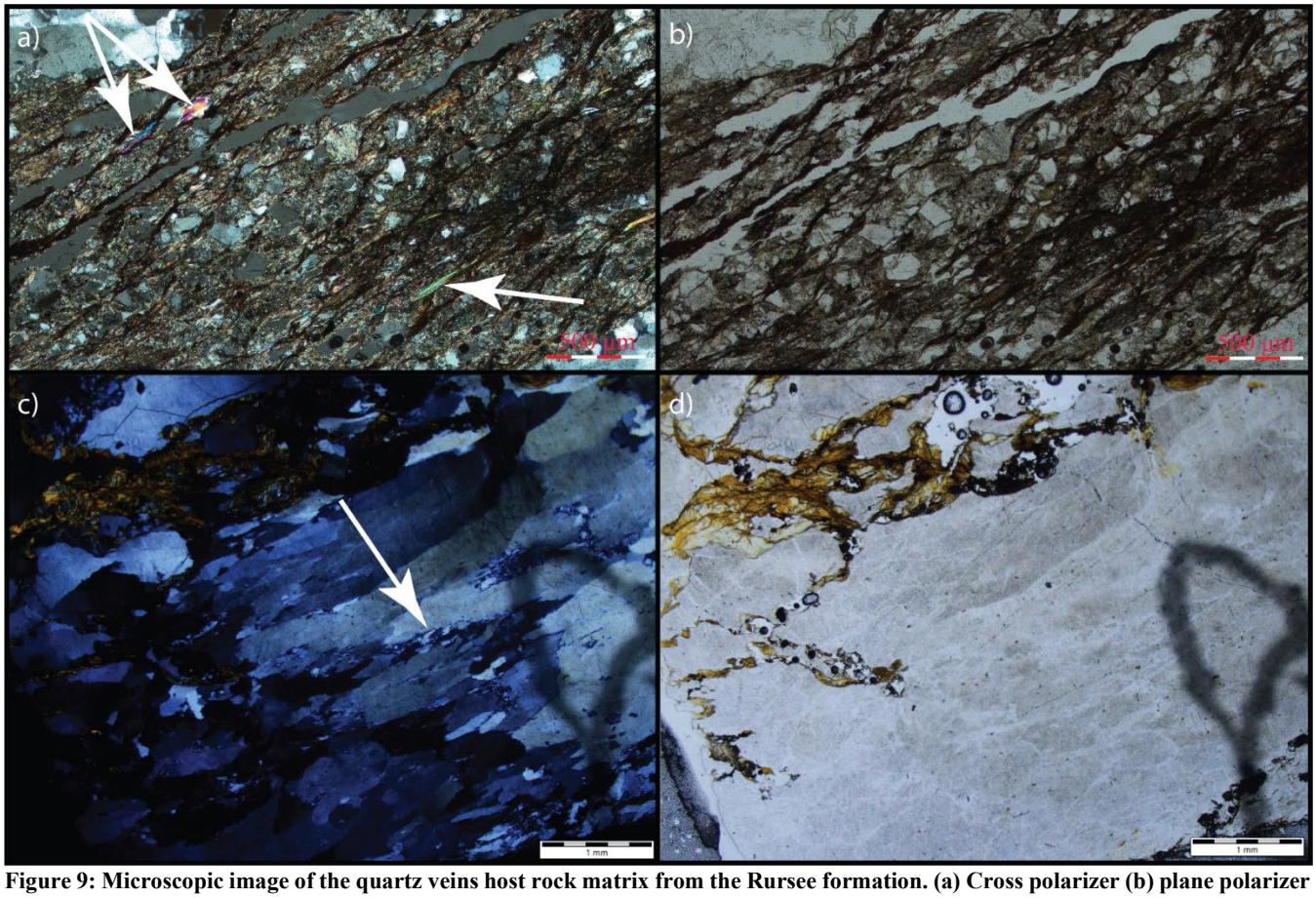

Figure 9: Microscopic image of the quartz veins host rock matrix from the Rursee formation. (a) Cross polarizer (b) plane polarizer images of the pelitic host rock (Rursee 2 BPV). White arrows (image a) indicate the presence of the mica and sericite in the host pelitic rock. (c) Cross polarizer (d) plane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

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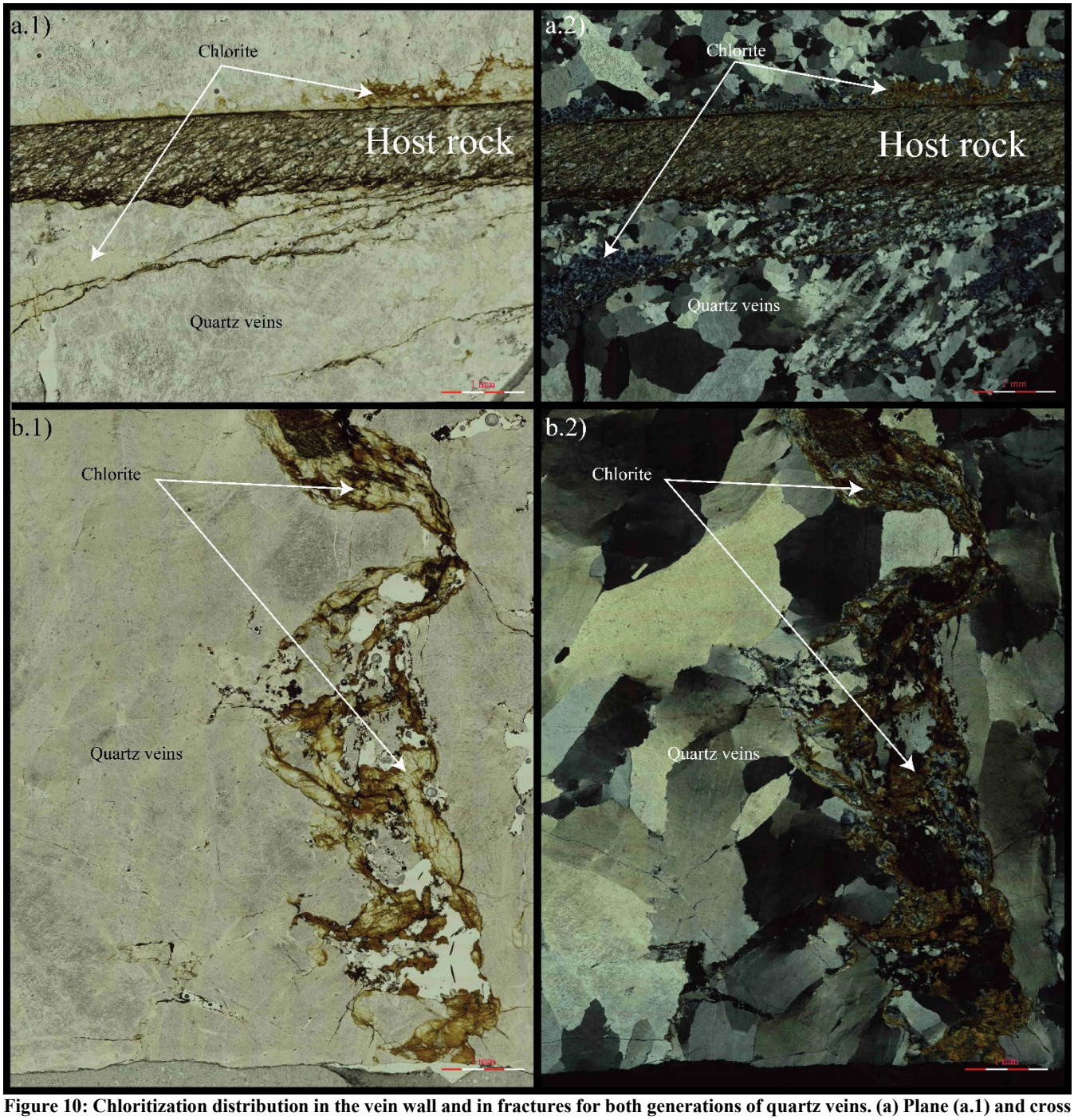

352 **Figure 10: Chloritization distribution in the vein wall and in fractures for both generations of quartz veins. (a) Plane (a.1) and cross**
353 **(a.2) polarizer of bedding parallel veins: chloritization mainly between vein wall and host rock, and fractures. (b) Plane (b.1) and**
354 **cross (b.2) polarizer of bedding normal veins: chloritization in fractures.**

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4.2.3 K from crystal lattice and detrital minerals

EPMA analyses of 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 an 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 amount of sample (~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 as well as embedded detrital minerals (e.g., mica from host rock). This interpretation aligns with the observation that the homogenization temperatures of FIs within the quartz veins are below the closure temperature for argon in detrital minerals. Under such conditions, the expected ages from K-bearing detrital minerals would correspond to pre-Variscan periods, reflecting the age of the deposits hosting the quartz veins, while the obtained ages are significantly younger in this study. Therefore, we infer that detrital minerals do not significantly contribute to the $^{40}Ar^{*}$ signals.

To summarise, during the first stages (until the ~20th analysis steps) of the stepwise *vacuo* crushing, gases are likely released only from FIs (secondary and pseudo-secondary, as is also observed for FI in garnets (Qiu & 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 analysing steps), the substantial release of $^{39}Ar_K$ isotopes may support the hypothesis proposed by Kendrick and Philips (2007) and Kendrick et al., (2011), suggesting the presence of K-bearing mineral inclusions in the samples and/or $^{40}Ar^{*}$ from the crystal lattice and also non-crushed small-sized FIs (<5 µm). The presence of 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.

4.3 Age spectra and isochrons

As aforementioned, the distribution of argon isotopes (Fig. 6) indicates that $^{39}Ar_K$ is derived from distinct sources, likely mineral inclusions and/or eventually crystal lattice rather than FIs in particular in the later phase of the experiment, which was used for the age determinations. These various sources of K, including fluid and mineral inclusions and/or crystal 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 FIs, the initial analytical stages of the analyses yield anomalously high ages in the first part of their age spectra (Fig. 4). Some samples (Rursee 3 BPV, Rursee 5 BNV, and Rursee 6 BPV) show a "pseudo-plateau" in the first part of the experiment. The “pseudo-plateau” effect occurs between the 20-30th analysing steps, which may be associated with sudden changes in K/Cl ratios (Fig. 7). These sudden changes may be due to sharp transition from fluids states reservoirs (e.g. small sized FIs) to solid states reservoirs (e.g. K-bearing mineral inclusions). However, it does not occur in *the second group* quartz

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samples (Rursee 1b BNV, Rursee 2 BPV, Rursee 4 BPV) revealing smooth transitions from fluids to solid states $^{39}Ar_K$ reservoirs. The transition for the Rursee 2.1 BNV is neither abrupt like for the *first group* samples nor smooth as for the *second group* samples; hence, the impact of the "pseudo-plateau" 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 accumulation 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), even for separated clean quartz grains, that may be a factor of difference for two groups.

The impact of $^{40}Ar_E$ results in inverse isochrons (Fig. 5) during the initial stage. The relationship between the $^{36}Ar/^{40}Ar$ and $^{39}Ar/^{40}Ar$ for all samples resulted in a decrease in the $^{36}Ar/^{40}Ar$ ratio and an increase in the $^{39}Ar/^{40}Ar$ ratio (initial stage in Fig. 11). The presence of an elevated concentration of ^{36}Ar at the beginning of the experiment could be either due to the atmospheric argon gas that is trapped in the stainless steel crusher and/or the original fragment surfaces and perhaps released during the initial stage of crushing. Following the opening of FIs, the ratio of $^{36}Ar/^{40}Ar$ increases linearly with the ratio of $^{39}Ar/^{40}Ar$. This is probably due to a decrease in excess argon throughout the crushing and an increase in $^{39}Ar_K$ associated with K-bearing minerals and/or crystal lattice (intermediate stage in Fig. 11). In the last phase of $^{40}Ar/^{39}Ar$ analysis, the concentration of $^{39}Ar_K$ decreases (final stage in Fig. 11). This last part is particularly important for determining the age of quartz vein samples.

Inverse isochrons may assist in determining the age of FIs by linear regression of the data related to FIs. However, the high amounts of excess argon in the system obscure geologically meaningful ages.

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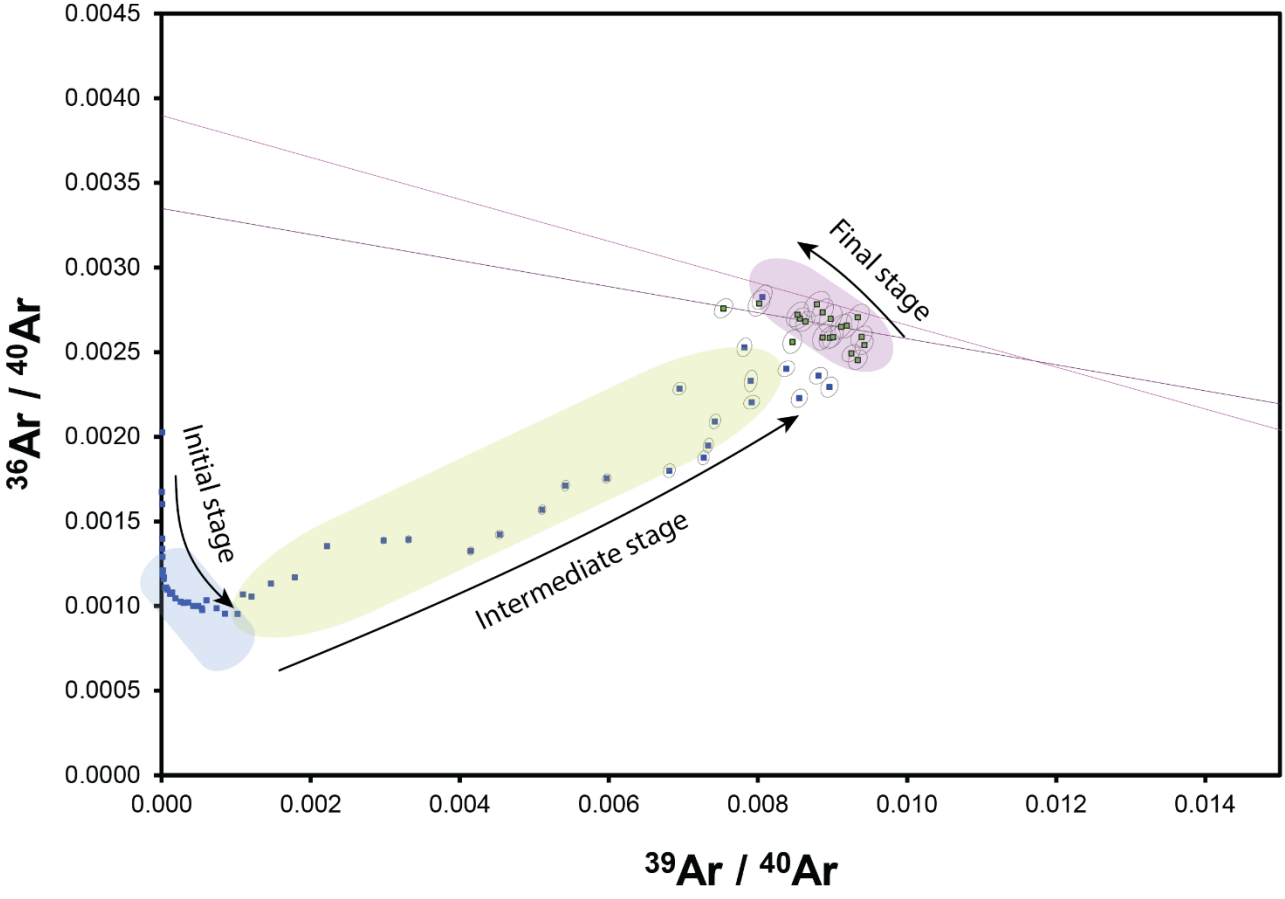

406 **Figure 11: Inverse isochron representation of quartz veins (ex: Rursee 2.1 BNV): 3 stages: (1) initial stage with opening of fluid**
407 **inclusions; (2) intermediate stage where argon is released from mineral inclusions or microfractures and/or crystal lattice; (3) Final**
408 **stage of argon release from mineral inclusions and neglectable excess argon in samples.**

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4.4 Implications

Unlike studies that obtained consistent ages from FIs (Qiu & Wijbrans, 2006; Qiu et al., 2011; Bai et al., 2013, 2019), we were unable to date FIs in Rursee quartz samples, likely due to high $^{40}Ar_E$ concentrations and/or low salinity. While no age was determined for the FIs, $^{40}Ar/^{36}Ar$ ratios (above atmospheric but below 4000) indicate a mixed metamorphic-meteoric fluid source (Ballentine et al., 2002; Ozima & Podosek, 2002). Later, during the crushing experiment, the K-bearing mineral inclusions may provide geologically meaningful ages although the argon closure temperatures in quartz remain uncertain. For reference, the closure temperature of smaller size sericite grains (~20 μm) correspond to temperatures (~300-350 °C) (Glasmacher et al., 2001; Watson & Cherniak, 2003), while the vitrinite reflectance from psammatic and pelitic layers indicate maximum burial temperatures (220 ºC) near the Carboniferous-Permian boundary, with gradual cooling thereafter (Littke et al., 2012).

The obtained $^{40}Ar/^{39}Ar$ ages (117-84 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 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 ages primarily reflect solid-phase reservoirs (i.e., K-bearing mineral inclusions) rather than fluid-phase components, it is likely that K-bearing solid-phase reservoirs intergrowth simultaneously with the recrystallization process.

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

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

This saline fluid activity is at odds with the low-salinity FIs (3.5-8 eq. wt.% NaCl) in the Rursee quartz veins (Van Noten et al., 2011). However they agree with low saline FIs in quartz veins of the Rhenish Massif, which are attributed to upward migration of Variscan fluid remnants during Jurassic-Cretaceous reactivation (Kirnbauer et al., 2012).

Near Rursee (Stavelot Inlier), low saline (0.2-7.2 eq. wt.% NaCl) and high-temperature fluid activity (~250 °C) along the Variscan front reflect warm meteoric fluid circulation (Schroyen & Muchez, 2000). Such warm, low saline fluids may have also contributed to chloritization of veins in the in Rursee outcrops. We propose that tectonic activity and quartz vein reactivation could possibly explain the observed $^{40}Ar/^{39}Ar$ ages, as low saline Variscan fluids perhaps moved along the reactivated fractures, forming new quartz minerals within the Variscan-related veins during Jurassic-Cretaceous tectonic activity (i.e. opening of North Atlantic).

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Table 2 Elemental analysis of quartz grain, microcracks, and mineral inclusions in quartz vein samples under EPMA.

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

	Sample ID	Grain ID	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	BaO	ZrO_2	O	H2O	TOTAL
Internal standard of UU	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
			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
			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 standard of UU	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
			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
			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 quartz veins	Rursee 1 BNV	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
		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
		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 BPV	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
		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

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443 **Table 2 (continue).**

	Sample ID	Grain ID	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	BaO	ZrO_2	O	H2O	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 BPV	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
		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 BPV	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
		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 BNV	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
		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

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445 **Table 2 (continue).**

	Sample ID	Grain ID	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	BaO	ZrO_2	O	H2O	TOTAL
Rursee quartz veins	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
		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
		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 standard of UU	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
			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
			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 standard of UU	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
			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
			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 standard of UU	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
			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
			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	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	BaO	ZrO_2	O	H_2O	TOTAL
Rursee quartz veins	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
		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
		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

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5 Conclusions

- The analysis of argon isotope patterns and their interpretations (including K/Cl and inverse isochrons) indicate that the main reservoir $^{39}Ar_K$ for geologically meaningful ages originated from the K-bearing minerals (illite-sericite and some possible chlorite) in quartz vein microcracks and/or inclusions cavities and/or crystal lattice of quartz.
- The determination of a primary crystallization age of the quartz veins is not feasible owing to the low amount of K in FIs and the high amount of excess argon within the FIAs resulting in anomalously old apparent ages in the first ~20th crushing steps.
- Estimates for a closure temperature for argon in K-bearing minerals inclusions is higher than the homogenization temperature of FIs of quartz. However, the activity of argon diffusion within the crystal lattice of quartz is high at this temperature. This may reveal that the apparent ages obtained belong to the moment of reactivation-recrystallisation of veins or its cooling moment.
- The 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 is corresponds to tectonic activity of the Rhenish massif.

Data availability

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

Author contributions

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

Competing interest

The authors declare that they have no conflict of interest.

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Supplementary file 1 Impact of blank correction on age.

Supplementary file 2 K (and thus $^{40}Ar^{*}$) contribution from chlorite is estimated from 2D electron backscattered images.

Supplementary file 3 Analytical data that have been used for $^{40}Ar/^{39}Ar$ dating.

Supplementary file 4 Grain size distribution analysis of separated fluid-rich quartz fraction after crushing.

Figure A1: Raman spectroscopy of fluid inclusion from Rursee quartz veins. **(a)** Microscopic image of an epoxied and polished fluid-rich quartz fraction. The fluid inclusion that underwent Raman analysis is represented by the red box. **(b)** The Raman plot is presented with the wavelength on the x-axis and intensity on the y-axis. The Raman spectra shows a stretching band in the wavelength range of 3000 to 3700 cm^{-1}, which indicates the presence of an aqueous system.

Figure B1: Normal isochron plots of all quartz veins samples.

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

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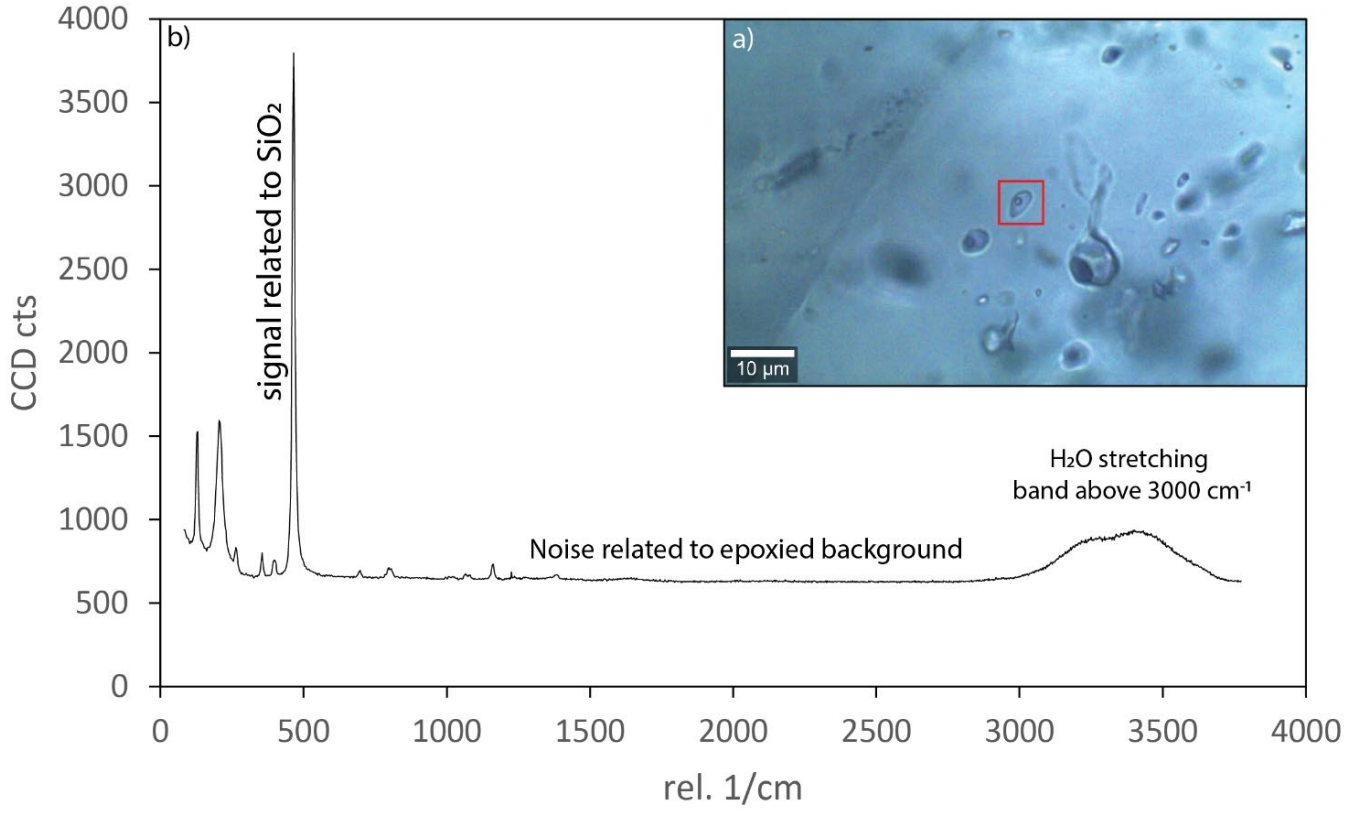

488 **Figure A1: Raman spectroscopy of fluid inclusion from Rursee quartz veins. (a) Microscopic image of an epoxied and polished fluid-**
489 **rich quartz fraction. The fluid inclusion that underwent Raman analysis is represented by the red box. (b) The Raman plot is**
490 **presented with the wavelength on the x-axis and intensity on the y-axis. The Raman spectra shows a stretching band in the**
491 **wavelength range of 3000 to 3700 cm^{-1}, which indicates the presence of an aqueous system.**

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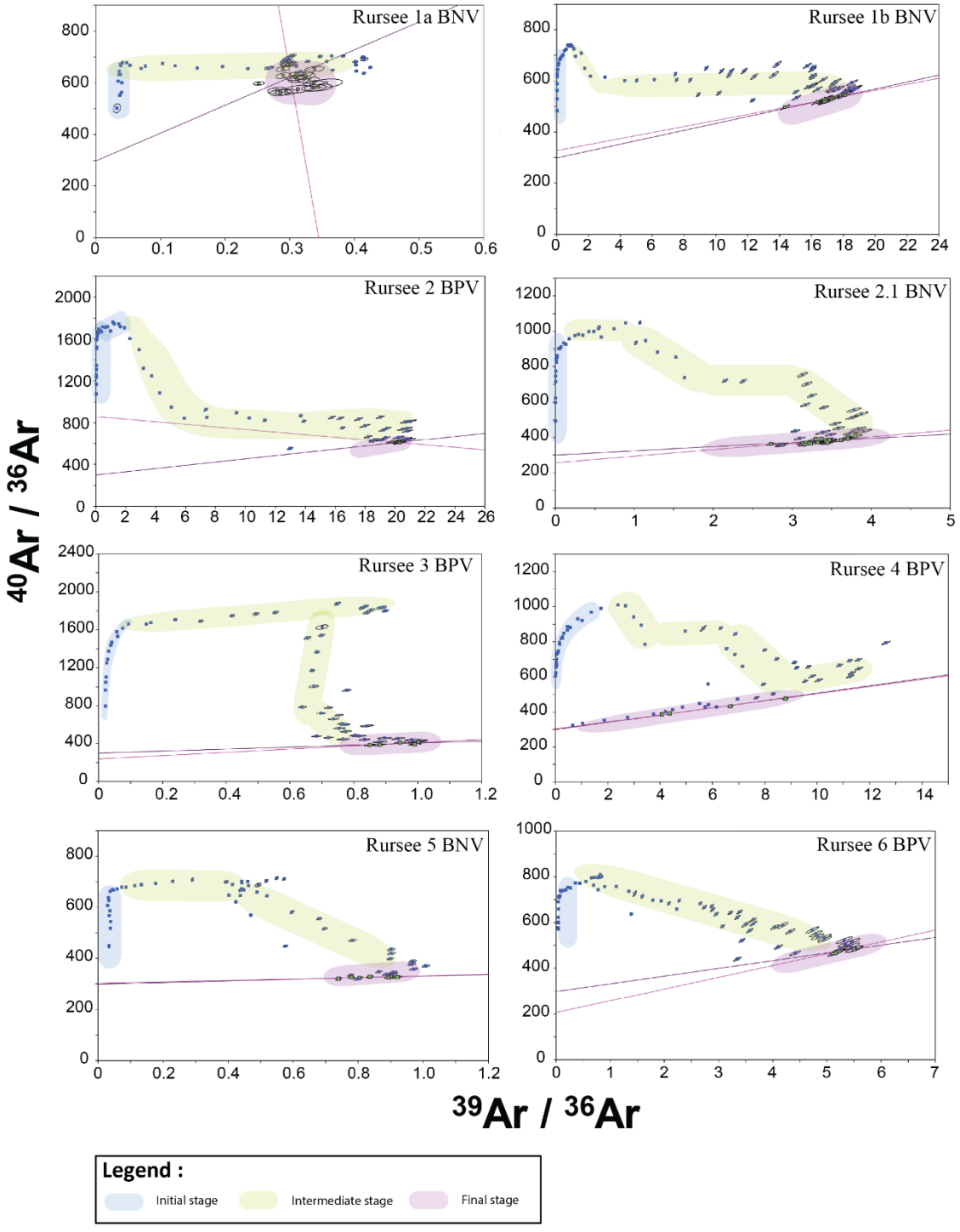

493 **Figure B1: Normal isochron plots of all quartz veins samples.**

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494 **Table C1: Rursee quartz veins 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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