6 Fluid inclusions study and direct $^{40}\text{Ar}/^{39}\text{Ar}$ dating by in vacuo crushing of quartz veins in HP/UHP rocks from Yuka terrane, North Qaidam

6.1 Introduction

Within eclogite-facies HP/UHP metamorphic rocks found in continental collision zones there are commonly abundant quartz-veins that were formed due to water-rock interaction caused by localized (Selverstone et al., 1992; Yardley and Bottrell, 1992; Rubatto et al., 1999; Zheng et al., 2003; Zheng et al., 2007; Wu et al., 2009b) or large-scale fluid transport (Nelson, 1991; John et al., 2008). Based upon field occurrences, mineral assemblages and formation stages, three groups of HP/UHP quartz veins can generally be distinguished: syn-metamorphic veins, early retrograde veins and late retrograde veins (Becker et al., 1999; Rubatto et al., 1999; Franz et al., 2001; Li et al., 2001a; Rubatto and Hermann, 2003; Wu et al., 2009b; Sheng et al., 2012). As a significant indicator of fluid flow and thus, a potential source of important information for fluid processes in subduction/exhumation zones, quartz veins within HP/UHP rocks have attracted extensive scientific interest. However, most previous geochemical studies have concentrated on fluid inclusion composition, hydrogen/oxygen stable isotopes and quartz micro-structure studies (Becker et al., 1999; Franz et al., 2001; Li et al., 2001b; Xiao et al., 2002; Zheng et al., 2003; Nuhter and Stokhert, 2007; Birtel and Stokhert, 2008; Zhang et al., 2008b; Zheng et al., 2011b). In previous geochronological studies, only a few Rb-Sr isochron studies of fluid-inclusions within quartz from the eclogites have been reported (Wang et al., 2000a; Wang et al., 2003). Currently, most studies focus on the selection of accessory minerals like zircon and rutile for U-Pb dating, or coexisting minerals such as muscovite for $^{40}\text{Ar}/^{39}\text{Ar}$ dating (Franz et al., 2001; Gao et al., 2006; Zheng et al., 2007; Wu et al., 2009b; Zong et al., 2010; Chen et al., 2012; Sheng et al., 2012) to constrain the time of quartz vein formation. In the case of $^{40}\text{Ar}/^{39}\text{Ar}$ dating of micas, the occurrence of excess $^{40}\text{Ar}$ within HP/UHP muscovite in many cases may obscure the geological information contained within these mica crystals (Li et al., 1994). Meanwhile, accessory minerals in quartz veins are often too scarce and too small to be used for isotopic dating, and when present, they may have formed after crystallization of the quartz vein. Consequently, the results of isotopic dating studies may not always precisely represent the formation ages of the veins.

The formation age of quartz veins may alternatively be constrained directly by applying $^{40}\text{Ar}/^{39}\text{Ar}$ dating by in vacuo crushing, as the dating is based on the age information obtained from K and Ar dissolved in the fluid-inclusions (Kelley et al., 1986; Turner, 1988; Qiu et al., 2002; Kendrick et al., 2006). Quartz is a good mineral for such an approach as it is nominally

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* This chapter was part of the Chinese version of the thesis.
free of K, is relatively free from impurities in the crystal lattice and commonly has a high abundance of fluid inclusions. Also, the slow rate of lattice diffusion of argon in quartz indicates that quartz may have a relatively high closure temperature for argon diffusion (Clay et al., 2010). An additional benefit of $^{40}$Ar/$^{39}$Ar dating is the neutron induced production of $^{39}$Ar$_K$, $^{38}$Ar$_{Cl}$ and $^{37}$Ar$_{Ca}$, which are formed during neutron irradiation for $^{40}$Ar/$^{39}$Ar dating and can be used as proxies for the K, Cl and Ca concentrations in the fluid. As such, they can be used to obtain additional information on the chemistry of the postulated reservoirs (Kelley et al., 1986; Turner and Bannon, 1992).

Fluid inclusions are commonly encapsulated by quartz crystals during first growth and in later stages by crack-seal mechanisms (Roedder, 1984). The primary fluid inclusion (PFI) composition reflects the composition of the fluids trapped during diagenesis or the early stages of metamorphism, and is commonly an aqueous fluid with variable levels of salinity. Secondary fluid inclusions (SFI s) are introduced when cracks develop that are subsequently sealed by precipitation of minerals.

Over the past 10 years, considerable progress has been made in the study of the petrology, mineralogy, geochemistry and geochronology of the HP/UHP metamorphic rocks and granites of the Yuka terrane, north Qaidam orogen, Qinghai province, western China (Chen et al., 2005; Zhang et al., 2005a; Yin et al., 2007; Chen et al., 2009a; Menold et al., 2009; Zhang et al., 2009a; Xiong et al., 2012; Wang et al., 2013; Song et al., 2014, and chapter 3, 4 and 5 of this thesis). As yet, there are no studies that have focused on fluid inclusions, separately, or in combination with direct isotopic dating of the quartz veins. Here we present a study using a combined approach of petrographic observation, micro-thermometric measurement and $^{40}$Ar/$^{39}$Ar in vacuo crushing and dating, that is the first of its kind of the Yuka HP-terrane quartz veins. The objective of our study is to decipher the origin of fluid flow and to further constrain the timing of quartz vein formation using a direct approach.

### 6.2 Geological setting and samples

The Yuka terrane is located in the westernmost segment of the North Qaidam orogenic belt in Qinghai province, western China, and is composed of pelitic and granitic gneisses/schists intercalated with some minor eclogites. Eclogites are commonly overprinted by amphibolite-facies retrogression and contain variably sized quartz veins/lenses. The quartz veins filling in the fractures of host rocks occur as thin tubes, or as thin sheets on the surface of the metasites (see Figure 6.1).

Quartz sample 09NQ05Qz formed in a fracture of a garnet-amphibolite block and is ca. 50 cm in length and 2-5 cm wide. It contains 95% of quartz, with minor paragenetic minerals including amphibole, feldspar and chlorite (Figure 6.1a). Sample 09NQ06Qz was taken from an outcrop 3 meters away from 09NQ05Qz, and is characterized by a similar field occurrence, mineral assemblage and textural features. Sample 09NQ14Qz occurs as thin layer on the
surface of a tectonically elongated retrogressed eclogite block (Figure 6.1b and d). It has a size of ca. 6 × 8 cm, a medium to fine grained texture and a smoky gray color. Its quartz content is around 85% and coexisting minerals include white mica and amphibole (Figure 6.1d). Sample 09NQ30Qz is from a 150 cm long and 10 cm wide milky quartz vein, with a quartz content of ca. 95%. It cuts through a phengite-bearing garnet-amphibolite lens and quartz in the vein is coexisting with amphibole, chlorite and feldspar (Figure 6.1c).

Figure 6.1 Field photographs of quartz veins and host garnet-amphibolites in the Yuka terrane, North Qaidam. Open circles denote the sample locality for quartz veins. The diameter of the hand lens and coin used in (a) and (d) is 2.5 cm; the length of the pen and notebook in (b) and (c) is 14 and 16 cm respectively.

6.3 Results

Fluid inclusions heating and freezing measurements were performed on doubly polished thick sections of four high pressure quartz vein samples using a Linkam MDS 600 freezing/heating stage coupled to a BX51 Olympus polarizing microscope, with nitrogen as the cooling medium, at State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, China.

6.3.1 Fluid inclusion analyses

First, petrographic observation and micro-thermometric measurements have been
applied to the vein quartz samples from the Yuka terrane. Three principal types of fluid inclusions have been distinguished by textural criteria (Roedder, 1984), including hypersaline inclusions, intermediate to high-salinity fluid inclusions, and low-salinity aqueous inclusions. Analytical methods are given in detail in Appendix A – Methods.

Primary fluid inclusions (PFIs) occur as isolated, randomly and clustered distributed inclusions. Pseudo-secondary fluid inclusions were identified as those that formed in healed fractures terminating at grain boundaries and growth zones. Secondary fluid inclusions (SFIs) were identified in healed fractures cross-cutting grain boundaries and growth zones. Examples of textural setting and typical occurrences of fluid inclusions are shown in Figure 6.2. The different textural types correspond with different fluid compositions and densities. The total salinities (W) were calculated with the reduction formula based on the final ice-melting temperatures (|Tm|) (Hall et al., 1988): 

\[ W = 1.78 |T_m| - 0.0442 |T_m|^2 + 0.000557 |T_m|^3 \]

Two or three single fluid inclusions in each cluster were selected for measurement. In total, about 88 fluid inclusions in quartz were investigated. Final melting and homogenization temperatures were measured on the same inclusions where possible. Table 6.1 shows the analytical data.

Table 6.1 Characteristics and microthermometric data of fluid inclusions in Yuka quartz veins

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Type of inclusions</th>
<th>Distributions of inclusions</th>
<th>Final melting temperature °C</th>
<th>Homogenization temperature °C</th>
<th>Salinity wt.% NaCl eq.</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>09NQ14Qz</td>
<td>Type-a</td>
<td>Isolated</td>
<td>−39 to −30.5</td>
<td>242-200</td>
<td>35.2-29</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Type-b</td>
<td>Isolated, clustered or</td>
<td>−24 to −10.5</td>
<td>237-208</td>
<td>25-14.5</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>along fractures</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>09NQ05Qz</td>
<td>Type-c</td>
<td>Along fractures</td>
<td>−6 to −2.1</td>
<td>245-227</td>
<td>9.2-3.5</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Type-b</td>
<td>Isolated or along</td>
<td>−24 to −13</td>
<td>250-174</td>
<td>25-16.9</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>fractures</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>09NQ06Qz</td>
<td>Type-c</td>
<td>Along fractures</td>
<td>−7 to −3.1</td>
<td>238-154</td>
<td>10.5-5.1</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Type-b</td>
<td>Along fractures</td>
<td>−23 to −15</td>
<td>223-187</td>
<td>24.3-18.6</td>
<td>10</td>
</tr>
<tr>
<td>09NQ30Qz</td>
<td>Type-c</td>
<td>Along fractures</td>
<td>−1.2 to −1.1</td>
<td>225-190</td>
<td>2.1-1.9</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Type-b</td>
<td>Isolated or along</td>
<td>−14.5 to −7.3</td>
<td>240-180</td>
<td>18.5-10.9</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>fractures</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Type-c</td>
<td>Along fractures</td>
<td>−5.9 to −3.9</td>
<td>230-186</td>
<td>9.1-6.3</td>
<td>13</td>
</tr>
</tbody>
</table>

Note: Type-a = Hypersaline primary inclusions; Type-b = Intermediate to high-salinity primary and pseudo-secondary fluid inclusions; Type-c = Low-salinity secondary aqueous inclusions; No. : Total numbers of measured fluid inclusions.

Hypersaline inclusions (type-a) are extremely rare and were only observed in sample 09NQ14Qz. The size of these inclusions is in the range of 10-15μm; they display isolated distributions and regular morphologies, suggesting a primary origin. These inclusions may represent the oldest recognizable generation of fluid inclusions found in this study. Most of these inclusions are two-phase (liquid-vapor) inclusions with an extremely small CO₂ bubble at room temperature (Figure 6.2a). These inclusions usually froze at around −80 to −160 °C, and showed a granular texture between −55 and −42 °C on subsequent heating, that was
interpreted as a transition from a meta-stable non-crystalline to a crystalline state. The brines have final ice melting temperatures ($T_m$) between –39 and –30.5 °C, corresponding to extremely high salinities of 35.2-29 wt.% NaCl equivalent. Homogenization temperatures (homogenization to the liquid phase; $T_h$) are between 242 to 200 °C.

Figure 6.2 Photomicrographs of fluid inclusions in quartz from Yuka. (a)-a isolated hypersaline salinity inclusion (type-a, primary, 09NQ14Qz); (b)-isolated medium-high salinity inclusions (type-bl, primary, 09NQ14Qz); (c)-along fractures but terminating at grain boundaries medium-high salinity fluid inclusions (type-bl, pseudo-secondary, 09NQ14Qz); (d)-isolated and clustered medium-high salinity inclusions (type-bl, primary, 09NQ05Qz); (e)-isolated medium-high salinity inclusions with solid-phase (S) occasionally (type-bl, primary, 09NQ06Qz); (f)-along fractures and cross-cutting grain boundary low brine aqueous fluid inclusions (type-c, secondary, 09NQ30Qz).

Intermediate to high-salinity fluid inclusions (type-b) have been observed in all the quartz samples. They are the predominant type and very abundant in all measured samples. Based on textural criteria, the type-b inclusions are subdivided into type-bl and type-bII
types. The type-b1 inclusions are 5–20 μm in size, displaying negative crystal morphologies and observed as isolated, random or clustered distributions (Figure 6.2b to e), suggesting a primary origin. They are commonly two-phase inclusions (liquid-vapor, CO₂ + H₂O) at room temperature, occasionally containing solid-phases (Figure 6.2e). In contrast, the type-b1 inclusions mostly occur in micro-fractures that never crosscut the crystal boundaries between individual quartz grains (Figure 6.2c), indicating they are pseudo-secondary rather than secondary inclusions (Roedder, 1984). Heating-freezing stage analysis shows that the type-b inclusions have Tₘ between −24 and −7.3 °C, corresponding to salinities of 25-10.9 wt.% NaCl equivalent. The homogenization temperature is between 250 and 174 °C.

Low-salinity aqueous inclusions (type-c) have also been distinguished in all quartz samples, and occur along mutually cross-cutting healed fractures, indicating their secondary origin (Figure 6.2e and f). They are 0.5-20μm in size, commonly showing compositions with two-phases (CO₂ + H₂O), but pure aqueous inclusions have been observed occasionally. The measured results gave Tₘ – values between −7 and −1.1 °C, corresponding to salinities of 10.5-1.9 wt.% NaCl equivalent. Values for Tᵣ were measured between 245 and 154 °C.

6.3.2 ⁴⁰Ar/³⁹Ar plateau and isochron ages

In vacuo crushing experiments were carried out in an in-house designed crushing apparatus which was connected to a three stage extraction line and a quadrupole mass spectrometer in the argon isotope laboratory in VU University Amsterdam (Schneider et al., 2009). Samples were loaded into a 40 cm long, 4 cm diameter Inconel® tube and crushed by an iron pestle that is lifted and dropped with a frequency of one time per second (1 Hz) using external electromagnet-control. Before analyses, the crushers were baked overnight at 250 °C. The extracted gases were first passed through the cryotrap to adsorb the moisture from the fluid inclusions, and then purified at 250 °C by a Fe/V/Zr getter pump and 450 °C by a Zr/Al getter pump. Experiments began and ended with cold blank analyses to correct for system blanks with the procedure described above but without moving the pestle.

The ⁴⁰Ar/³⁹Ar data were calculated and plotted using the ArArCALC software package of Koppers (2002). Age spectra and inverse isochrons for each of the samples are illustrated in Figure 6.3 through Figure 6.7. Both the plateau and inverse isochron age uncertainties are given at the 2σ level.

The apparent age spectrum for sample 09NQ05Qz consists of 24 steps, with in total more than 9000 times pestle drops during progressive crushing. This quartz sample exhibits a monotonically declining release spectrum: the first segment yielded anomalously old apparent ages that decrease from the initial crushing steps and the final steps form a flat plateau with concordant apparent ages (Figure 6.3a). Apparent ages decrease from 4865 to 508 Ma with steps 1 to 15. On the inverse isochron diagram of ³⁶Ar/⁴⁰Ar vs. ³⁹Ar/⁴⁰Ar, the data points gradually move from near the origin of the diagram to the atmospheric argon component end member along the Y axis (⁳⁶Ar/⁴⁰Ar) (Figure 6.3b). A reliable plateau age of 418.5 ± 4.7 Ma (MSWD = 0.3, ³⁹Arᵣ = 46%) is obtained from steps 16-24. The data points
constituting the plateau form a well-defined isochron with an intercept age of 421.7 ± 5.1 Ma (MSWD = 0.3) on the inverse isochron diagram, corresponding to an initial $^{40}$Ar/$^{36}$Ar ratio of 295 ± 1 (Figure 6.3b).

In vacuo crushing $^{40}$Ar/$^{39}$Ar analyses of the other three quartz samples yielded similarly shaped age spectra. All spectra begin with abnormally old apparent ages during the first several steps, then a significant decrease during following steps and finally the occurrence of flat plateaux with Silurian-Devonian plateau ages of 410.6 ± 40 Ma (MSWD = 0.03, $^{39}$Ar$_K$ = 34%), 429.2 ± 6.6 Ma (MSWD = 0.3, $^{39}$Ar$_K$ = 35%) and 419.7 ± 14.5 Ma (MSWD = 0.09, $^{39}$Ar$_K$ = 37%), for samples 09NQ06Qz, 09NQ14Qz and 09NQ30Qz, respectively (Figure 6.3c, e and g).
The data points of the plateaux form well-defined isochrons on inverse isochron plots of 36Ar/40Ar vs. 39Ar/40Ar, with ages of 420.6 ± 46.5 Ma, 437.7 ± 18.4 Ma and 412 ± 24.6 Ma, respectively (Figure 6.3d, f and h). The initial 40Ar/36Ar ratios of all isochrons are indistinguishable from the modern atmospheric ratio of 295.5.

6.3.3 Correlations between Cl and K derived Ar isotopes

To search for elemental correlations, we performed multiple regressions on the amount of 40Ar*, K-derived 39ArK, Cl-derived 38ArCl and air-derived 36Ar with the aim of identifying the different sources of argon in the fluid inclusions (Kelley et al., 1986; Turner, 1988; Turner and Bannon, 1992; Kendrick et al., 2001; Qiu and Wijbrans, 2006; 2008; Jiang et al., 2012; Bai et al., 2013). Here, 40Ar* denotes total 40Ar minus atmospheric 40Ar (40ArA) and 40Ar produced by neutron irradiation, including both K in situ decay-derived radiogenic 40Ar (40ArR) and parentless excess 40Ar (40ArE). The neutron-induced argon isotopes of 38ArCl and 39ArK are used as proxies for Cl and K, respectively.

Three axes diagrams for 40Ar*/36Ar vs. 39ArK/36Ar vs. 38ArCl/36Ar based on isotopic analyses of Yuka quartz samples by crushing are shown in Figure 6.4. In the plot, two 40Ar end-member components air (40ArA and 36Ar) and fluid can be seen. The fluid is rich in 40ArE and Cl, and probably rich in K if K-bearing daughter minerals exist. On the 40Ar*/39ArK/38ArCl plane as shown in Figure 6.4, the crushing data points of the first several steps have relatively high 38ArCl/36Ar and 40Ar*/36Ar combined with low 39ArK/36Ar ratios. Moreover, the data show...
that there is a good correlation between the $^{40}\text{Ar}^*$ and $^{38}\text{Ar}_{\text{Cl}}$, which define a plane with high correlation coefficient of 0.92-0.99 (Figure 6.4). Detailed correlations and the significance of these K and Cl derived Ar isotopes will be shown and discussed in the following sections.

6.3.3.1 $^{40}\text{Ar}^*/^{38}\text{Ar}_{\text{Cl}}$ vs. $^{39}\text{Ar}_K/^{38}\text{Ar}_{\text{Cl}}$

The plots of $^{40}\text{Ar}^*/^{38}\text{Ar}_{\text{Cl}}$ vs. $^{39}\text{Ar}_K/^{38}\text{Ar}_{\text{Cl}}$ based on isotopic analyses of Yuka quartz samples by in vacuo crushing are shown in Figure 6.5. Similar to the features of many crushing experiments on UHP metamorphic garnet (Qiu and Wijbrans, 2006; 2008), the data points of the first several steps are too scattered to form correlation lines (Figure 6.5, gray points). As expected, the data points that contribute to the age plateaus define correlation lines with slopes corresponding to Silurian ages of 412, 418, 440 and 420 Ma, for samples 09NQ05Qz, 09NQ06Qz, 09NQ14Qz and 09NQ30Qz, respectively (Figure 6.5, dark points, note that the slope of the line represents the $^{40}\text{Ar}^*/^{39}\text{Ar}_K$ ratio of the sample). These ages are in good agreement with the corresponding weighted mean ages and interpreted as the ages of the primary fluid inclusions.

6.3.3.2 $^{40}\text{Ar}^*/^{39}\text{Ar}_K$ vs. $^{38}\text{Ar}_{\text{Cl}}/^{39}\text{Ar}_K$

On the plots of $^{40}\text{Ar}^*/^{39}\text{Ar}_K$ vs. $^{38}\text{Ar}_{\text{Cl}}/^{39}\text{Ar}_K$ shown in Figure 6.6, the data points of the first steps show good linear correlations with $^{40}\text{Ar}^*/^{39}\text{Ar}_K$ intercepts of 35.8-51.1,
corresponding to Devonian-Carboniferous ages of 392-341 Ma (Figure 6.6a-d, gray points). By contrast, the data points defining the age plateaux with lower \(^{38}\text{Ar}_{\text{Cl}}\) values and without any apparent correlation between \(^{40}\text{Ar}^{*}/^{39}\text{Ar}_{\text{K}}\) and \(^{38}\text{Ar}_{\text{Cl}}/^{39}\text{Ar}_{\text{K}}\) (Figure 6.6a-d, dark points), indicate a distinctly different origin for the gas of the plateau age steps. The data points show relatively constant \(^{40}\text{Ar}^{*}/^{39}\text{Ar}_{\text{K}}\) ratios of 59-44, corresponding to individual ages from 440 to 399 Ma and average ages from 430 to 407 Ma, respectively. These results are interpreted to represent the ages of PFIs.

6.3.3.3 \(^{38}\text{Ar}_{\text{Cl}}/^{40}\text{Ar}^{*}\) vs. \(^{39}\text{Ar}_{\text{K}}/^{40}\text{Ar}^{*}\)

As noted previously, unlike the \(^{40}\text{Ar}^{*}\) component, the \(^{39}\text{Ar}_{\text{K}}\) does not yield any apparent correlation with the \(^{38}\text{Ar}_{\text{Cl}}\) based on the data of the early crushing steps (Figure 6.7). As shown in the plots of \(^{38}\text{Ar}_{\text{Cl}}/^{40}\text{Ar}^{*}\) vs. \(^{39}\text{Ar}_{\text{K}}/^{40}\text{Ar}^{*}\), the data points that have been selected as defining the age plateaus and isochrons are showing relatively constant values of \(^{38}\text{Ar}_{\text{Cl}}/^{40}\text{Ar}^{*}\) but wide range of \(^{39}\text{Ar}_{\text{K}}/^{40}\text{Ar}^{*}\) ratios (Figure 6.7, gray points). In contrast, the late crushing steps show concordant \(^{39}\text{Ar}_{\text{K}}/^{40}\text{Ar}^{*}\) ratios but variable \(^{38}\text{Ar}_{\text{Cl}}/^{40}\text{Ar}^{*}\) ratios (Figure 6.7, dark points). The \(^{39}\text{Ar}_{\text{K}}/^{40}\text{Ar}^{*}\) ratios are ranging from 0.017 to 0.023 with average ages from 430 to 407 Ma.

Figure 6.6 Plots of \(^{40}\text{Ar}^{*}/^{39}\text{Ar}_{\text{K}}\) vs. \(^{38}\text{Ar}_{\text{Cl}}/^{39}\text{Ar}_{\text{K}}\) for in vacuo crushing data of the quartz samples. \(^{40}\text{Ar}^{*}\) yield strong correlation with \(^{38}\text{Ar}_{\text{Cl}}\) in the initial crushing steps. Crushing steps were numbered to show the sequence of crushing. Only the steps that defining the age plateaux (white points) and the \(^{40}\text{Ar}^{*}/^{38}\text{Ar}_{\text{Cl}}\) line (dark points) are shown.
6.4 Discussion

6.4.1 Veining stage

Quartz samples in this study are almost pure quartz veins (95%) and cross-cut retrogressed eclogite blocks in random directions. An exception is the sample 09NQ14Qz, whose quartz contents are clearly lower (85%) and that occurs as sheet on the surface of a retrogressed eclogite block (Figure 6.1a). The mineral paragenesis indicates retrograde assemblages including amphibole and white mica. Therefore, from the petrological relationships between quartz vein and host rocks, as well as the mineral assemblage characteristics, all quartz veins analyzed in this study belong to the group of retrograde veins that formed near the end of retrograde metamorphism (Li et al., 2001a; Zheng, 2004). In contrast, quartz in eclogite or granulite lithologies that were formed during UHP metamorphism commonly contains gaseous fluids (i.e. N₂–CH₄, etc.). These are interpreted as syn-metamorphic fluids that could be the remnants of pre-metamorphic or prograde pore fluids (Andersen et al., 1993; Fu et al., 2003). In this study, no such fluids were detected in any of the Yuka quartz veins, which was taken as indirect evidence that the Yuka veins have not experienced UHP metamorphism but formed during exhumation.

6.4.2 Gas release pattern and argon reservoirs

An experimental crushing test has been proposed by Bai et al. (2013), that states that after more than 10,000 pestle drops, the crushed quartz residue ranges in grain size from...
4-1μm (82%), and the powder contains fragments as small as 50 nm. The primary fluid inclusions in Yuka quartz are mostly in the range 15-5 μm in size (Figure 6.2). This indicates that the fluid inclusions in the size range that can be observed by optical microscope have effectively been extracted using the crushing method.

Anomalously old apparent ages are obtained from the early crushing steps, ages often even older than the age of the Earth, indicating that significant amounts of excess argon (\(^{40}\text{Ar}_{\text{ex}}\)) were incorporated in the fluid inclusions. Following the reasoning of Qiu and co-workers (Qiu and Wijbrans, 2006; Qiu and Jiang, 2007; Qiu and Wijbrans, 2008; Jiang et al., 2012; Bai et al., 2013), we suggest that the extremely old initial apparent ages are derived from the largest, most easily crushed SFIs and that these were most likely incorporated in the quartz by a crack-seal mechanism during greenschist-facies retrogression, or later. As illustrated on Figure 6.6, this component shows significant correlation between \(^{40}\text{Ar}^*\) (\(^{40}\text{Ar}_{\text{R}} + ^{40}\text{Ar}_{\text{E}}\)) and \(^{38}\text{Ar}_{\text{Cl}}\). Because the entrapment of Cl in aqueous fluids generally leads to the correlation between neutron-induced \(^{38}\text{Ar}_{\text{Cl}}\) and naturally occurring argon dissolved in the fluids, the correlation between \(^{40}\text{Ar}^*\) and \(^{38}\text{Ar}_{\text{Cl}}\) has been regarded as an effective indicator to monitor the degassing of fluid inclusions (Turner, 1988; Turner and Bannon, 1992; Harrison et al., 1993). Thus, the strong correlation between \(^{40}\text{Ar}^*\) and \(^{38}\text{Ar}_{\text{Cl}}\) not only confirms a fluid-related origin for the measured ages obtained in the step-wise crushing experiments, but also indicates that the excess \(^{40}\text{Ar}^*\) (\(^{40}\text{Ar}_{\text{ex}}\)) and Cl in the SFIs are derived from the same source. The apparent ages that decrease gradually in the subsequent steps probably reflect mixtures between SFIs with excess \(^{40}\text{Ar}\) and PFIs. In the final stages of the experiments, gas components are predominately derived from smaller PFIs. Mixtures of radiogenic argon from the PFIs and atmospheric argon from the crusher form a well-defined isochron and flat age plateau over the last several steps (see Figure 6.3).

### 6.4.3 Origin of quartz vein hosted fluids

The Ar-isotopic compositions of fluid inclusions can be used to constrain the origin of fluids (Kelley et al., 1986; Turner and Bannon, 1992; Villa, 2001; Jiang et al., 2012). In this study, the gases that were released in the early and late crushing steps have quite different argon compositions. Early liberated gases are rich in \(^{40}\text{Ar}_{\text{E}}\) and \(^{38}\text{Ar}_{\text{Cl}}\), whereas the late ones are poor in \(^{40}\text{Ar}_{\text{E}}\) and \(^{38}\text{Ar}_{\text{Cl}}\) but rich in \(^{37}\text{Ar}_{\text{Ca}}\). We interpret the gases in the early steps to be derived from SFIs and those in the late steps from PFIs. The PFIs show higher \(^{37}\text{Ar}_{\text{Ca}}\) but lower \(^{38}\text{Ar}_{\text{Cl}}\), which suggests that lower chlorine and higher calcium contents are dissolved in the PFI fluid in comparison with the SFI fluid. In other words, the calcium and potassium in the PFIs are probably correlated with \(\text{CO}_3^{2-}\) and \(\text{HCO}_3^-\) rather than Cl” (Jiang et al., 2012). This can also be used to explain the seemingly contradictory phenomenon that the higher salinity PFIs have lower \(^{38}\text{Ar}_{\text{Cl}}\) than the lower salinity SFIs.

There are several possible origins of the PFIs (type-a and type-b). Previous studies have argued that partial melting of both UHP rocks (eclogite) and host rocks (gneiss) during the stage of exhumation can induce a significant high salinity fluid flow that results in the
precipitation of the quartz veins. Geochemical analyses show that the felsic veins in the Xitieshan terrane, north Qaidam, are tonalitic with high Na/K ratios, high Sr contents paired with low Y and Yb contents, and LREE-enriched patterns, consistent with partial melting of omphacite in eclogite at elevated pressures (Chen et al., 2012). In Sulu ultrahigh-pressure terrane, zircon Lu–Hf isotope investigation shows that the initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of zircon rims from the quartz vein are lower than in zircons from an eclogite lens, but overlap with the coeval zircon domains from the nearby granite dikes produced by partial melting of orthogneiss, which suggests that the fluid flow responsible for quartz vein formation could be derived from the host gneiss during exhumation (Zong et al., 2010). Thus, high salinity hydrothermal fluids produced during partial melting of eclogite and host gneiss could be the main origin of type-a fluids and one possible origin of type-b fluids, which were trapped during the amphibolite/greenschist-facies retrogression at the onset of quartz veining.

Aqueous fluids derived from the decomposition of hydrous minerals (e.g. lawsonite and zoisite) also form an important source of retrograde fluids (Li et al., 2001a; Zheng, 2004; 2007). Therefore, it is possible that the intermediately saline PFIs (type-b) were derived from two mechanisms: partial melt of UHP rocks and dehydration of hydrous minerals. Moreover, the atmospheric initial $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of the PFIs (see inverse isochron plot in Figure 6.3) suggest that the meteoric water is an additional important source for the PFIs (Turner, 1988).

Dating by in vacuo crushing of vein quartz has demonstrated that the SFIs (type-c) contain a significant amount of excess $^{40}\text{Ar}$ ($^{40}\text{Ar}_e$). Deep metamorphic hydrothermal aqueous fluids commonly with high partial pressure of $^{40}\text{Ar}_e$ probably resulted from outgassing of crustal rocks during regional metamorphism (Kelley et al., 1986; Turner, 1988; Turner and Bannon, 1992). Consequently, the possible origin of the SFIs could be these deep metamorphic fluids.

6.4.4 Implication of $^{40}\text{Ar}/^{39}\text{Ar}$ dating by in vacuo crushing

Previous studies have shown that crushing has little effect on the gas trapped within the crystal lattice but predominately extracts the gas that was trapped in fluid inclusions and along cracks and cavities in crystals (Dunlap and Kronenberg, 2001; Qiu and Wijbrans, 2006; Qiu and Jiang, 2007; Qiu and Wijbrans, 2008; Jiang et al., 2012; Bai et al., 2013). Therefore, the dating of fluid inclusions by the in vacuo crushing method in HP/UHP quartz minerals promises to be an effective means of dating the fluid, as well as the age of veining if the two are related and nearly synchronous.

In the case of Yuka quartz samples, low salinity aqueous SFIs generally occur along or cross-cutting healed fractures and are variable in size (see Figure 6.2). Therefore, during gas-extraction by in vacuo crushing, SFIs are easily crushed and their gases are liberated in the initial steps. The fluids from part of the bigger PFIs and pseudo-secondary fluid inclusions that occur along healed micro-cracks are probably also extracted during the same time. Consequently, due to mixing of gases originating from SFIs and PFIs, SFIs on the isotope correlation diagram rarely show an isochron, although successful analyses have been
reported (Qiu and Jiang, 2007; Jiang et al., 2012). On the other hand, the $^{38}$Ar$_{Cr}$-based correlation diagram provides a potential approach for correlating the effect of excess $^{40}$Ar within SFIs and further obtaining meaningful ages (Turner and Bannon, 1992; Jiang et al., 2012; Bai et al., 2013). As illustrated in the plots of $^{40}$Ar$^*$/39Ar$^*$ vs. $^{38}$Ar$_{C}$/$^{39}$Ar$^*$ (see Figure 6.6), the isochron ages of 392 ± 9 Ma and ~344 Ma of the SFIs reveal episodes of post-collisional fluid flow activities during Middle Devonian and Early Carboniferous, respectively.

As crushing continues, the SFIs and excess $^{40}$Ar were gradually exhausted whereas primary and pseudo-secondary inclusions (type-b) dominate the gas contribution and yield concordant late Silurian plateau ages of 429-411 Ma for this stage (see age spectra in Figure 6.3, left). The inclusions of type-b were trapped during the crystallization or recrystallization of quartz within the HP veins, and the gases liberated from these inclusions in the final stages of the experiments yielded geologically interpretable age results. Therefore, the plateau ages of 429-411 Ma can be taken as a good estimate for the time of quartz vein formation. That is, the $^{40}$Ar/$^{39}$Ar dating by in vacuo crushing of HP quartz veins document a protracted Silurian fluid flow event during the exhumation of HP/UHP rocks.

Similar ages of about 428 Ma were also obtained from the Xitieshan felsic vein via zircon U-Pb dating (Chen et al., 2012), indicating there is a synchronous fluid activity during the exhumation of UHP rocks in different parts of the North Qaidam UHP terrane. There are two cryptic tectono-thermal events during the late Silurian, which may have generated the post-collisional vein-forming fluid activity: (1) magmatic activity that was identified by zircon U-Pb dating of ca. 428 Ma in the north Qaidam orogen (Meng et al., 2005; Meng and Zhang, 2008); (2) regional ductile strike-slip shearing in the North Qaidam orogen that occurred between 426-401 Ma and was constrained by $^{40}$Ar/$^{39}$Ar dating of foliated white mica (Qi, 2003; Menold, 2006; Xu et al., 2006).

### 6.5 Conclusions

Quartz veins are abundant in the Yuka eclogite-gneiss terrane, North Qaidam, where they provide vital information of the characteristics, origin and timing of fluid flow during the subduction/exhumation of the UHP metamorphic rocks.

1. Three categories of fluid inclusions have been recognized based on petrographic observation in Yuka quartz veins: hypersaline brine inclusions (type-a, primary), intermediate to high-salinity fluid inclusions (type-b, primary and pseudo-secondary) and low salinity aqueous fluid inclusions (type-c, secondary).

2. Due to the differences in distribution and size between SFIs and PFIs, when they are crushed, the gases are liberated in the early and later steps during crushing, respectively, and thus PFIs and SFIs can potentially be separated by stepwise crushing.

3. Type-a and type-b inclusions originate from mixed sources: dehydration of hydrous minerals, partial melting of eclogite and felsic host rock, and meteoric water transported
by fault or shear zones. Type-c fluid inclusions may have resulted from deep metamorphic hydrothermal aqueous fluids.

4. There is an obvious correlation between excess $^{40}$Ar and Cl in the secondary fluid inclusions. On the isotope correlation diagram of $^{40}$Ar*/$^{39}$Ar$_K$ vs. $^{38}$ArCl/$^{39}$Ar$_K$, the early data points form well-defined isochrons with two group intercept ages of 392 Ma and $\sim$344 Ma.

5. The data points from the later of crushing *in vacuo* $^{40}$Ar/$^{39}$Ar dating yield plateau ages of 429–411 Ma, indicating a protracted fluid flow during the exhumation of the Yuka HP/UHP rocks in the Silurian. A Silurian magmatic pulse in the area or regional ductile shearing may have caused this post-collisional fluid flow.