The varying composition of metamorphic fluids affects their hydration/dehydration reactions. Generally, high-salinity fluids exhibit low H₂O activities, and therefore, shift dehydration reactions to lower-temperature conditions and significantly change the solubility of minerals (e.g., Newton and Manning, 2010). Previous studies mainly focused on NaCl-rich aqueous fluids due to their ubiquitous occurrence in metamorphic rocks, although numerous works have also reported the existence of other salts such as CaCl₂ and KCl, especially in continental collision zones (e.g., Gao and Klemd, 2001; Okudaira et al., 2017).

Phase diagrams and microthermometry are commonly employed in the determination of the chemical compositions of fluid inclusions (e.g., Bodnar, 1993). However, the application of microthermometry to small inclusions measuring as little as a few microns is hampered by the difficulty of optical observation of the phase transition.
(e.g., Raimburg et al., 2014). Furthermore, if there are more than four types of electrolytes, estimation of chemical compositions of the inclusion based on the phase diagram would be almost impossible (e.g., Spencer et al., 1990). Researchers of fluid inclusions have therefore developed several techniques for directly analyzing the chemical composition of individual inclusions over the past quarter century. For example, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), in which a laser beam is used as a boring and vaporizing tool, has been developed for application to inclusions of diameter 15–20 μm (e.g., Heinrich et al., 2003). Another method that employs a scanning electron microprobe (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) is used for frozen fluid inclusions at cryo-temperatures (e.g., Ayora and Fontarnau, 1990). This method enables direct quantitative measurement based on comparison of the X-ray intensities for the sample and standard ice. The mineral chip sample containing the frozen fluid inclusions is broken in an evacuated chamber using a manipulator. However, samples prepared by this procedure should ideally contain many inclusions because of the uncertainty of the mechanical breaking. The application of this method has thus been mainly limited to halite-hosted fluid inclusions.

Recent developments and the proliferation of the focused ion beam (FIB) system have enabled the sample processing of an area of interest with very good submicron precision (Reyntjens and Puers, 2001; Wirth, 2004), which can be combined with other high-resolution analysis technique such as SEM, TEM, and micro-X-ray tomography (e.g., Liu et al., 2016; Yoshida et al., 2016). FIB-based micro-excavation of buried fluid inclusions has been employed for the SEM-EDS analysis of daughter minerals and precipitated salts such as Fe-K(-Mn) chlorides (Assadzadeh et al., 2016). However, this novel tool can be combined with a cold stage for application to the direct analysis of liquid materials (i.e., using cryo-FIB; e.g., Desbois et al., 2008, 2012), resulting in high-resolution observation of the wet boundaries of minerals. A combination of cryo-FIB-SEM-EDS would significantly enhance the possibility of analyzing the chemical compositions of liquid materials sporadically enclosed in the solid phase, such as fluid inclusions in metamorphic rocks, the sizes and numbers of which commonly limit the application of existing methods.

In the present study, we performed conventional fluid inclusion petrography on Tlc-Grt-Cld schist collected from the Makbal metamorphic complex in Kyrgyz. In addition to textual observation under an optical microscope, Raman analysis at room temperature, and microthermometry, we performed low-temperature Raman (cryo-Raman) analysis of the sample. Finally we attempted cryo-FIB-SEM-EDS analysis of the inclusion to

Fig. 1. (a) Geological overview of the tectonic units of central Asia after Bakirov et al. (1998). NTS - Northern Tien-Shan; MTS - Middle Tien-Shan; STS - Southern Tien-Shan. (b) Geologic map of the Makbal UHP metamorphic complex composed of the Akdjon and Sharkyrak Groups. Sample locality of the studied sample is also shown.
determine the solute species, although there were challenges to using the same for a quantitative analysis. The determined chemical composition was complex and could not have been established by conventional microthermometry and the cryo-Raman technique. Based on our findings, we propose an importance of a sequential investigation for a single fluid inclusion with respect to the petrographic description. The mineral abbreviations used in this paper follow Whitney and Evans (2010).

GEOLOGICAL BACKGROUND AND INVESTIGATED SAMPLE

The Makbal metamorphic complex is located in the western part of Northern Kyrgyz Tian-Shan (Fig. 1) and consists of two main units, namely, upper Sh Decode and lower Akdjon Group that exhibits higher-grade metamorphism (HP-UHP conditions) (Bakirov, 1978; Bakirov et al., 1998; Tagiri et al., 2010). The Akdjon Group is subdivided into the Neldy and Makbal Formations. The Neldy Formation is mainly composed of mica-quartz (tzgarnet) schists with mafic lenses, some of which (eclogites) show peak P-T metamorphic conditions of 550–610°C and 2.2–2.5 GPa (Togonbaeva et al., 2010). The Makbal Formation consists mainly of quartzites, garnet-mica schists, and marbles (e.g., Bakirov, 1978). Talc-garnet-chloritoid schists are found in the quartzites as layers measuring hundreds of meters to a few kilometers long. UHP metamorphism has been confirmed by the finding of coesite inclusions within garnet from both Tlc-Grt-Cld schists and surrounding quartzites (Tagiri et al., 2015). The peak P-T conditions of Tlc-Grt-Cld schists have been variously estimated by different methods; Pb SHRIMP age of 502 ± 10 Ma for metamorphic zircon (Meyer et al., 2014). Paleozoic metamorphic ages of the Tlc-Grt-Cld schists are reported by different methods; U-Pb SHRIMP age of 502 ± 10 Ma for metamorphic zircon (Konoepolko et al., 2012), phenite K-Ar age of 509 ± 13 Ma (Tagiri et al., 2010), and Th-Pb CHIME monazite ages of 481 ± 26 Ma and 480 ± 56 Ma (Togonbaeva et al., 2009).

The studied fluid inclusions investigated in the present study existed in a Tlc-Grt-Cld schist collected from the Makbal Formation. The hand-specimen was collected from the outcrop which is investigated in detail by Orozbaev et al. (2015). Orozbaev et al. (2015) reported that the large garnet porphyroblast and quartz pressure shadows were embedded in the matrix mainly composed of talc and chloritoid. The petrographic description of the studied sample (KG1223) exhibited similar mineral textures and assemblages described by Orozbaev et al. (2015). In this previous study, three stages of mineral assemblages were distinguished, namely, the prograde stage: Grt + Tlc + Ctd + Qz + Chl + Lws + Ap + Rt ± Tur; the peak UHP stage: Grt + Tlc + Ctd + Gln + Coe + Ph + Ap + Rt ± Lws ± Tur ± Ky; and the retrograde stage: Qz + Pg + Mrg + Bt + Chl + Cz + Ky + Ap ± fIm. In the garnet porphyroblast, they reported polyphase mineral aggregates mainly composed of clinozoisite, kyanite, and quartz, the combined bulk composition of which resembles that of lawsonite. Based on a petrogenetic grid, Orozbaev et al. (2015) concluded that breakdown of lawsonite had occurred during a nearly-isothermal-decompression of the rock (510–580°C and 1.6–2 GPa). In the following sections, we present a detailed description of the fluid inclusions in quartz pressure shadows newly described in the present study.

ANALYTICAL METHODS

The fundamental fluid inclusion petrography was performed by using optical microscope, a laser Raman spectrophotometer (JASCO, NRS-3100), and a heating and cooling stage (LINKAM, LW-600) at the Department of Geology and Mineralogy, Kyoto University. The Raman spectroscopic analysis was conducted using a 532-nm line of diode-pumped solid-state laser (Cobolt, Samba) at 3–15 mW on the sample surface. Calibration of the wave number was performed using a 520.7-cm–1 Si-wafer band and a neon spectrum. To determine the salinity and solute species of the aqueous phase of the fluid inclusions, microthermometric measurements were performed following the procedure of Yoshida et al. (2015). Raman spectroscopy under low-temperature conditions (~190°C) was also performed using a combination of the above instruments to obtain the spectra of the ice and chloride hydrates.

In addition, the solute composition of the aqueous fluid was investigated by energy-dispersive X-ray spectrometry (EDS) using a focused ion beam (FIB) system (Helios NanoLab G3 CX, FEI) at the Department of Geology and Mineralogy, Kyoto University. A gallium ion source installed at an angle of 52° was used to bore and polish the sample. The cryo-preparation of the sample was performed using a cold stage (C1001, Gatan), and the X-ray spectra were obtained by an EDS system (Octane Elite 25, EDAX). The quartz chip containing the fluid inclusions was carbon coated and placed on the cold stage in the FIB evacuated chamber. The cold stage was then cooled and maintained at approximately –130°C by the circulation of cold nitrogen gas. After determining the position of the target fluid inclusion, micro-excavation was performed using the gallium ion beam at 30 kV and 2.5–9.5 nA until the cross section of the frozen inclusion was exposed. EDS analysis was then performed on the...
exposed cross section of the inclusion at an acceleration voltage of 15 kV and beam current of 0.34 nA. The X-ray spectra of the exposed cross section, tilted at 38° from the horizontal plane, were obtained, with the tilt causing the EDS detector to be partly blindfolded by the excavated wall of the host phase (quartz). This geometric arrangement precluded quantitative analysis of the peak intensity by ordinary quantification calculation. The EDS result was used only for checking the existence of the detected elements.

RESULTS OF THE FLUID INCLUSION PETROGRAPHY AND CHEMISTRY

Large pressure shadows were found to have developed along the garnet porphyroblasts of up to 10–20 mm in

Fig. 2. (a) Scan of the garnet porphyroblast and corresponding quartz pressure shadows. Red rectangle shows the location of the studied fluid inclusion trail. Scale bar is 5 mm. Matrix is mainly composed of chloritoid, talc, and Na-amphibole. (b) Studied fluid inclusions arranged at a certain plane observed under transmitted light. The white arrow indicates the inclusion investigated by cryo-FIB-SEM-EDS. (c) Typical Raman spectra of the studied fluid inclusion measured at room temperature and –190°C. Liquid H₂O peaks measured at room temperature show a single strong peak with weak shoulder indicating high salinity. For a comparison, Raman spectra of synthetic fluid inclusions (pure water and 10 mass% NaCl aqueous solution) are also shown.
Cryo-FIB-SEM-EDS analysis of individual fluid inclusion diameter (Fig. 2a). The pressure shadows could be divided into two domains, namely, a dusty part developed in the direction of the main foliation, and a clear part developed along the roof of the host garnet. In the dusty part, several trails of tiny fluid inclusions were observed in the direction perpendicular to the main foliation, having possibly originated from a later stage deformation taken place after the development of the pressure shadows. The clear part appeared to occur as the embayment of the garnet. It contained high-salinity fluid inclusions arranged on the intracrystalline planes, which did not cut across the grain boundaries (Fig. 2b). These observations suggest that the fluid inclusions were trapped simultaneously with the formation of the pressure shadows. The inclusions were weakly faceted, but did not have clear negative crystal shapes, with their maximum size being <10 μm along the longer axis.

The Raman spectra of a sample fluid inclusion obtained at room temperature showed liquid H₂O peaks showing a single strong peak at around 3450 cm⁻¹ with a weak shoulder at lower wavenumber, indicating high salinity compared to the pure water and 10 mass% NaCl aqueous solution (Fig. 2c). No gas species were detected. Conversely, the Raman spectra obtained under low temperature (−190°C) yielded an intense ice peak at 3093 cm⁻¹. Other peaks were observed within 3200–3500 cm⁻¹.

Fig. 3. (a) Schematic image of geometric relationship between the sample surface, fluid inclusion (FI), and (b). (b) SEM image of the frozen fluid inclusion exposed on the excavated wall. (c) Another cross-section of the same fluid inclusion. A large cavity that has been originally a bubble is observed. (d) A representative EDS spectrum of the frozen fluid. Na, K, Ca, and Cl are observed as the solute elements. Ga peak from the plugged gallium ion and Si peak from the host quartz are also observed.
sive excavation, with a cavity of about 1–2 m appearing. After exposure of the edge of the fluid inclusion, the size of the fluid inclusion appeared weakly faceted, although the solid phases disappeared at –45.5°C, which corresponds to the melting point of hydrohalite. Finally, the ice disappeared at –23.1°C, suggesting that all the observed melting events were explained by the phase relationship of the CaCl₂-NaCl-H₂O system. The salinity was roughly calculated using a software package (Bakker, 2003), assuming CaCl₂-NaCl-H₂O ternary system. The results indicated 20.5 mass% CaCl₂ and 1.7 mass% NaCl as the dissolved salts. However, the chemical system used for the calculation was incorrect as described below.

The chemical composition of the dissolved salts was further investigated by cryo-FIB-SEM-EDS. The frozen fluid inclusion was clearly exposed on the excavated surface of the host quartz (Figs. 3a and b). The cross section of the fluid inclusion appeared weakly faceted, although no clear negative crystal shape of the quartz was observed. After exposure of the edge of the fluid inclusion, the size of the inclusion was observed to increase with progressive excavation, with a cavity of about 1–2 μm appearing at a certain cross-sectional surface (Fig. 3c). The EDS spectra of a smooth part of the exposed surface of the inclusion was obtained, and revealed Na, K, Ca, and Cl as solute elements. Considerable levels of Ga plugged by the ion beam, and Si from the host quartz were also observed (Fig. 3d). O from both ice (H₂O) and the host SiO₂ were detected. The non-detection of C (0.277 keV) and F (0.677 keV) can be attributed to the negligible abundance as solute elements. Considerable levels of Ga plugged by the ion beam, and Si from the host quartz were also observed (Fig. 3d). O from both ice (H₂O) and the host SiO₂ were detected. The non-detection of C (0.277 keV) and F (0.677 keV) can be attributed to the negligible abundance in the EDS analysis (generally considered to be about 0.1 mass%, which is equivalent to 0.7 mass% of dissolved NaHCO₃), or 2) that a small C peak might have been hidden due to absorbance by the host quartz. The present analytical geometry set obstacle host phase in the X-ray path because of the inclined excavated wall (Fig. 3a). This geometric problem precludes quantitative analysis. However, the EDS results show a considerable amount K which is hardly recognized from the microthermometry experiment and under assumption of simple chemical system (Fig. 3d).

**Discussion and Implications**

Although there are few previous reports on metamorphic fluid containing NaCl-KCl-CaCl₂, either Ca or K in addition to Na has been observed in several metamorphic terranes. High-salinity CaCl₂-bearing brine has been found in some high-P metamorphic rocks in eastern Asia, UHP metamorphic rocks in the Dabie Shan and Sulu region (Rolfo and Ferrando, 2004; Zhang et al., 2005), and HP eclogite in the Dabie Shan (Fu et al., 2002). Rolfo and Ferrando (2004) reported CaCl₂-rich (15 mass% CaCl₂–2.5 mass% NaCl) aqueous fluid as the primary fluid inclusion in OH-rich topaz in UHP quartzite. The aqueous fluid exhibited an isochore crossing at 2.8 GPa and 800°C, and there were indication of the existence of high-density brines under the conditions of the quartz-coesite transition. These observations indicate that the presence of a high-density and high-saline fluid is a possible characteristic of HP-to-UHP metamorphic conditions. Conversely, reports of KCl-bearing fluid inclusions in metamorphic rocks are rare; some have nevertheless being observed as KCl crystals in crustal rocks (e.g., Markl and Bucher, 1998; Okudaira et al., 2017). As far as the use of microthermometry and phase diagrams is concerned, it is difficult to determine the chemical compositions of multi component aqueous solutions (e.g. Spencer et al., 1990). However, the present observation of NaCl-KCl-CaCl₂-bearing fluid inclusions qualitatively indicates the common existence of a KCl component in the metamorphic fluids.

The investigated CaCl₂-bearing fluid inclusions were found as intra-crystalline fluid inclusion trails in the less-deformed part of the quartz pressure shadows of the investigated Tlc-Grt-Cld schist. This indicates that the fluid inclusions were trapped during the formation stage of the pressure shadows. If the fluids were to have an external origin, perhaps from the fluid infiltration during the exhumation of the rocks, their high salinity would affect the hydrous minerals in the matrix. However, such hydration and increased Cl content of the matrix hydrous minerals were not observed in the investigated sample. This suggests that the observed NaCl-KCl-CaCl₂-bearing fluid may have an in situ origin. During the formation stage of the quartz pressure shadows, CaCl₂-bearing fluids may have been generated from the dehydration reaction that occurred in the garnet. One possible reactant of the dehydration reaction is lawsonite, which is one of the most important water carriers in a cold subduction system (e.g., Pawley, 1994; Kuwatani et al., 2011; Vitale Brovarone et al., 2011; Sato et al., 2016). Orozbaev et al. (2015) found polymineralic aggregates mainly composed of clinzoisite, kyanite, and quartz, which had been produced by the decomposition of lawsonite during the exhumation stage. They distinguished the polycrystalline pseudomorphs of lawsonite based on the following observations: 1) the reconstructed composition of the aggregates determined from the modal amounts of clinzoisite, kyanite, and quartz was the same as that of
fluids are capable of dissolving considerable amounts of processes. At elevated temperatures and pressures, such moderate temperature conditions, the dissolved salts in the aqueous fluids act as electrolytes and are also capable of dissolving metal complexes.

CONCLUSION

Previous studies on fluid inclusions in ore deposits and granitic rocks have commonly observed complex chemical systems of the trapped fluids (e.g., Assadzadeh et al., 2016). However, fluid inclusions in metamorphic rocks are assumed to have a rather simple composition. This is because of the difficulty of conducting a detailed analysis, mainly owing to their small sizes and populations.

We conducted conventional fluid inclusion petrography on a Tlc-Grt-Cld schist collected from the Makbal metamorphic complex in Kyrgyz. In addition to textual observation under an optical microscope, Raman analysis, and microthermometry, we attempted cryo-FIB-SEM-EDS analysis of the inclusions to determine the solute species. Although the present observations are only qualitative, they indicate that even fluid inclusions trapped under moderate temperature conditions may contain complex chemical systems that are hardly detectable by microthermometry and other conventional analytical techniques. Misidentification of the solute species introduces errors into salinity estimates, and this may cause propagated inaccuracy in quantitative analytical methods such as LA-ICP-MS. A detailed fluid inclusion petrography would require an accurate quantitative analysis that combines FIB-based sample preparation and cryo-SEM-EDS quantitative analysis. Although this would pose several new questions, they are worth pursuing in a future study.

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