

Possibility of Scanning Electron Microscope Observation and Energy Dispersive X-Ray Analysis in Microscale Region of Insulating Samples Using Diluted Ionic Liquid

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Abstract: The possibility of scanning electron microscope (SEM) observation and energy dispersive X-ray (EDX) spectrometry analysis in microscale regions of insulating samples using diluted ionic liquid was investigated. It is possible to obtain clear secondary electron images of insulating samples such as a rock and mineral at 5,000 times magnification by dropping 10 μL of 1 wt% of 1-ethyl-3-methylimidazolium acetate (EMI- CH_3COO) diluted with ethanol onto the samples. We also obtained EDX spectra of the samples in microscale regions ($\sim 5 \mu\text{m}^2$) without overlapping EDX spectra of other minerals with different composition. It might be possible to perform quantitative analysis of the samples if a method that does not need standard samples is applied or an X-ray detector sensitive for light elements was attached. The method of dropping 1 wt% EMI- CH_3COO diluted with ethanol onto insulating samples is useful for SEM observation, EDX analysis in microscale regions, and the preservation of scarce rock and mineral samples because ionic liquid can be easily removed with acetone.

Key words: ionic liquid, SEM, EDX, insulating sample, electrical charging, microscale region

INTRODUCTION

Ionic liquid consists solely of ions and has been attracting a lot of attention since the discovery of a moisture stable ionic liquid. Igarashi and Yotsuyanagi (1989) first reported a moisture stable ionic liquid that consists of perfluorooctanoate anion and quaternary ammonium cation, but this report did not attract much attention at that time (Yamaguchi, 2007). Then, Wilkes and Zaworotko (1992) reported 1-ethyl-3-methylimidazolium tetrafluoroborate, and many researchers began to investigate ionic liquids. Due to their remarkable physical and chemical properties, such as quite low vapor pressure, nonflammability, and high ionic conductivity, ionic liquids are expected to act as new electrochemical media, e.g., for batteries (Carlin et al., 1994; Tobishima, 2002), capacitors (McEwen et al., 1997; Nanjundiah et al., 1997; Ue et al., 2002), and electrochemical solar cells (Papageorgiou et al., 1996; Matsumoto & Matsuda, 2002). Kuwabata et al. focused on the property of low vapor pressure in ionic liquids and tried to use them for scanning electron microscope (SEM) observation in order to prevent electrical charging. They successfully obtained SEM images of insulating samples without electrical charging (Kuwabata et al., 2006; Arimoto et al., 2008; Kuwabata & Torimoto, 2008). Generally, when insulating samples, except for very fine particles, are observed with an SEM whose pressure of the sample chamber are less than 10^{-3} Pa, a thin layer of metal or carbon has to be coated on the insulating samples by vacuum deposition or ion sputtering to prevent electrical charging. However, it is possible to observe insulating sam-

ples without a thin coating layer of metal or carbon with low vacuum or environmental SEM whose pressure in the sample chamber is more than 10 Pa. Especially if the insulating samples have complicated shape such as rocks, fossils, and minerals, it takes more than 1 h to complete this coating process because the process has to be repeated several times to form a uniform thin layer on the insulating samples. On the other hand, the method using ionic liquid for preventing electrical charging during SEM observation is quite easy because insulating samples are dipped into ionic liquid or diluted ionic liquid. However, the highest magnification of SEM images using this method is about $1,000\times$ (Inoue et al., 2010; Ishigaki et al., 2011a, 2011b; Okuyama et al., 2011). This is because a thick ionic liquid layer is formed when dipping insulating samples into an ionic liquid, and the thick ionic liquid layer prevents the electron beam from reaching the surface of insulating samples. Thus, we tried to form a thin ionic liquid layer by dropping a very small amount of ionic liquid onto insulating samples. We obtained clear SEM images at $5,000\times$ magnification at 10^{-3} Pa by dropping a few microliters of 10^{-2} wt% ionic liquid diluted with ethanol or acetone onto a fossil (*Baculogypsina* sp.) as shown in Figure 1 (Ze et al., 2011). In addition, we verified that it is possible to perform qualitative elemental analysis of the fossil with energy dispersive X-ray (EDX) spectroscopy using 10^{-2} wt% of 1-ethyl-3-methylimidazolium acetate (EMI- CH_3COO). These results show that it is possible to perform EDX analysis in the microscale region of insulating samples without coating a thin layer of a metal or carbon. In the present study, we tried to examine the possibility of microanalysis of insulating samples whose compositions are different in the microscale region using diluted ionic liquid.

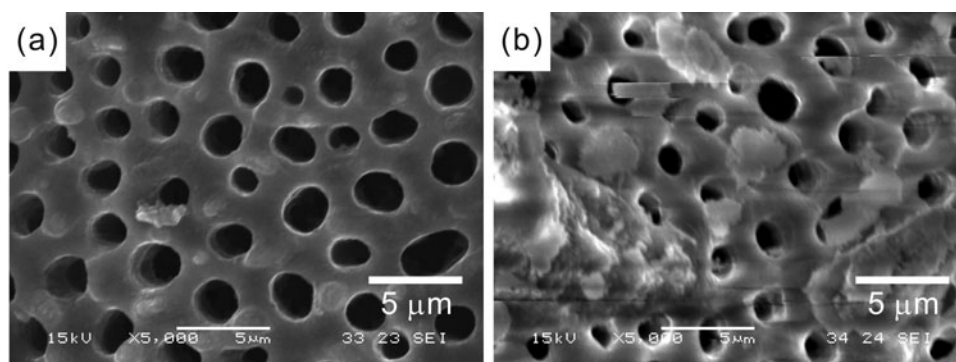


Figure 1. Secondary electron images of *Baculogypsina* sp. (a) ionic liquid diluted with ethanol (10^{-2} wt% EMI-Tf₂N) was dropped onto and (b) without ionic liquid.

MATERIALS AND METHODS

Samples observed in the present study were garnet-biotite gneiss and orthoclase with albite lamella. The garnet-biotite gneiss was collected from Akarui Point, Lützow-Holm Complex, East Antarctica (sample TK2002122204B). This sample was prepared as a thin section whose surface was polished using diamond paste. Using a polarized light microscope, we observed the existence of minerals of garnet, biotite, plagioclase, orthoclase, and quartz with subordinate amounts of rutile-ilmenite intergrowth, zircon, apatite, pyrite, and retrograde muscovite in the garnet-biotite gneiss. The chemical formulas of these minerals are summarized in Table 1 (Deer et al., 1992). The orthoclase with albite lamella was collected from the Sør Rondane Mountains, East Antarctica and consists of orthoclase and albite, whose chemical formulas are written in Table 1. This sample was prepared as a fragment and observed with a JEOL JSM-5610LVS SEM (JEOL Ltd., Tokyo, Japan). Before SEM observation, carbon tape was used to attach the sample stage to the surface of the samples and about 10 μ L of EMI-CH₃COO diluted with ethanol to 1 wt% was dropped around the carbon tape. The accelerating voltage and probe current of the SEM were set to 15 kV and 85 pA, respectively, during SEM observation. The pressure of the SEM chamber was about

10^{-3} Pa during the observation. Compositional analysis was carried out using an EDX silicon drift detector (OURSTEX Corporation, Osaka, Japan, SDD System) (Ishii & Kawai, 2006) at the probe current of 1 nA. Measurement duration of EDX collection was set to 300 s. Energy of the EDX spectra was calibrated by the K α -lines of aluminum and copper using metals of aluminum and copper.

RESULTS AND DISCUSSION

Garnet-biotite gneiss was first observed with SEM at an accelerating voltage of 15 kV, and a lamellar intergrowth structure of biotite and plagioclase with a distance of several micrometers was found as shown in Figures 2a and 2c. At 500 $\times$ magnification on the microscope screen, the lamellar structure can be observed in the garnet-biotite gneiss even without dropping diluted EMI-CH₃COO onto the sample. However, flickering was found at the top of Figure 2a because of electrical charging on the surface of the sample. It was difficult to obtain a clear secondary electron image in a microscale region such as 5,000 $\times$ magnification without dropping diluted EMI-CH₃COO because of electrical charging (Fig. 2b). Electrical charging was prevented by dropping diluted EMI-CH₃COO onto the sample, and clear secondary electron images were obtained at 500 $\times$ (Fig. 2c) and 5,000 $\times$ (Fig. 2d) magnification. The fact that dropping diluted EMI-CH₃COO onto the garnet-biotite gneiss prevented electrical charging was also verified by EDX analysis. Figures 3a and 3b show EDX spectra of the garnet-biotite gneiss without and with diluted EMI-CH₃COO at an accelerating voltage of 15 kV. The analyzed area was approximately 0.3 mm². The Duane-Hunt limit of the garnet-biotite gneiss without and with the diluted EMI-CH₃COO was 11 and 14 keV, respectively. The Duane-Hunt limit was extended from 11 to 14 keV, which was near the primary beam energy (15 keV) by dropping diluted EMI-CH₃COO onto the sample. Thus, it was verified that dropping diluted EMI-CH₃COO onto the garnet-biotite gneiss prevented electrical charging. Then, we performed EDX analysis at points 1 and 2 in Figure 2d by focusing the electron beam. Figure 3c shows the EDX spectra of points 1 and 2 at an accelerating voltage of 15 kV. K-lines of sodium,

Table 1. Chemical Formulas of Minerals Contained in the Garnet-Biotite Gneiss and Orthoclase with Albite Lamella We Observed.

Minerals	Chemical Formula
Garnet	(Mg,Fe ²⁺ ,Mn,Ca) ₃ (Al,Fe ³⁺ ,Cr) ₂ (Si,Al) ₃ O ₁₂
Biotite	K ₂ (Mg,Fe ²⁺) ₆₋₄ (Fe ³⁺ ,Al,Ti) ₀₋₂ [Si ₆₋₅ Al ₂₋₃ O ₂₀](OH,F) ₄
Plagioclase	Na[AlSi ₃ O ₈] – Ca[Al ₂ Si ₂ O ₈]
Orthoclase	K[AlSi ₃ O ₈]
Quartz	SiO ₂
Rutile	TiO ₂
Ilmenite	FeTiO ₃
Zircon	Zr[SiO ₄]
Apatite	Ca ₅ (PO ₄) ₃ (OH,F,Cl)
Pyrite	FeS ₂
Muscovite	K ₂ Al ₄ [Si ₆ Al ₂ O ₂₀](OH,F) ₄
Albite	Na[AlSi ₃ O ₈]

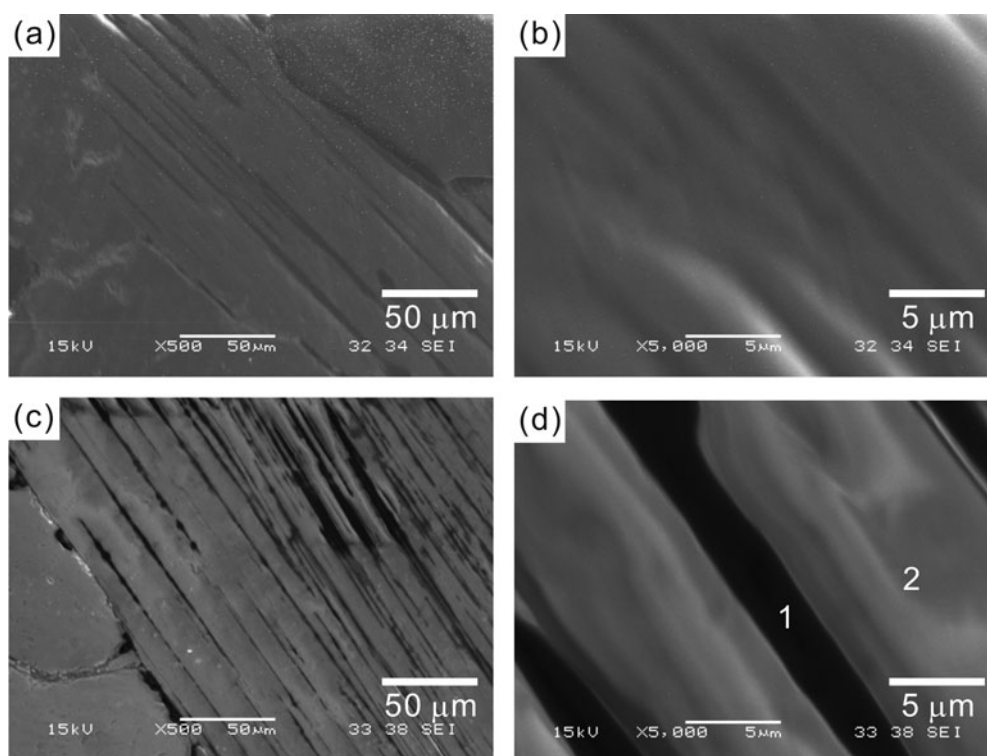


Figure 2. Secondary electron images of garnet-biotite gneiss onto which no ionic liquid was dropped (a,b) and EMI-CH₃COO diluted with ethanol (1 wt%) was dropped (c,d). Panels a and c are 500× magnification on the microscope screen, and panels b and d are 5,000× magnification on the microscope screen, respectively.

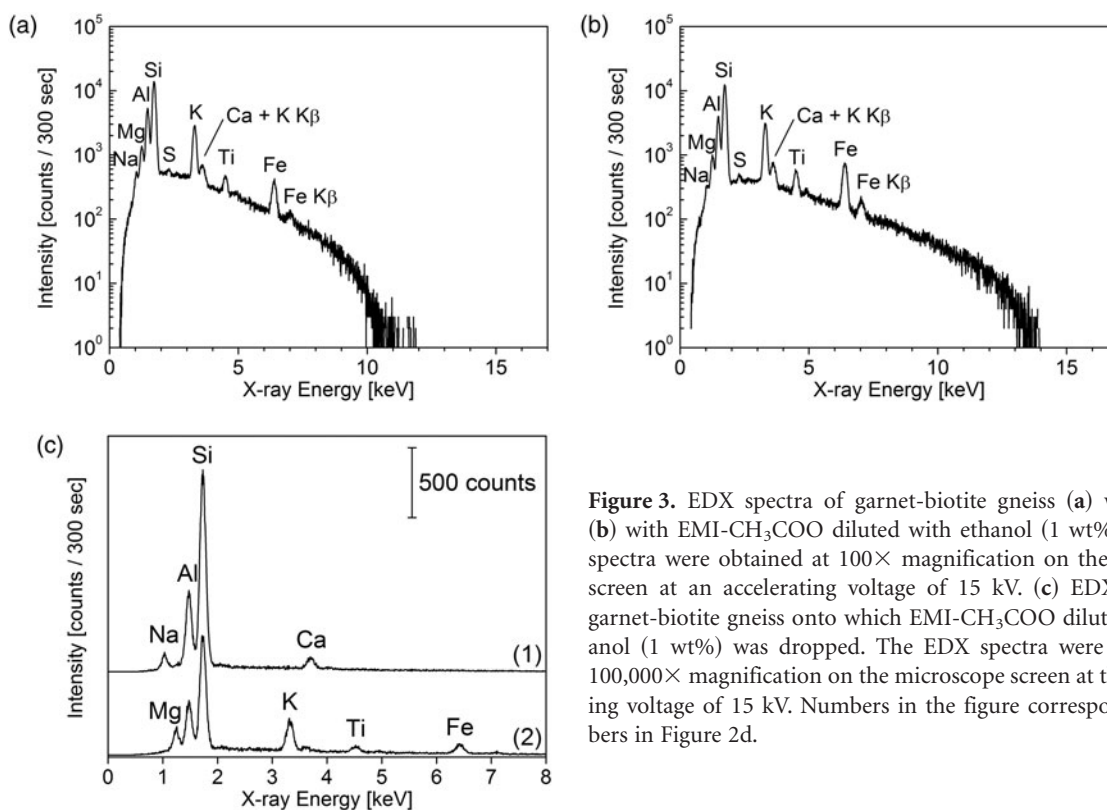


Figure 3. EDX spectra of garnet-biotite gneiss (a) without and (b) with EMI-CH₃COO diluted with ethanol (1 wt%). The EDX spectra were obtained at 100× magnification on the microscope screen at an accelerating voltage of 15 kV. (c) EDX spectra of garnet-biotite gneiss onto which EMI-CH₃COO diluted with ethanol (1 wt%) was dropped. The EDX spectra were obtained at 100,000× magnification on the microscope screen at the accelerating voltage of 15 kV. Numbers in the figure correspond to numbers in Figure 2d.

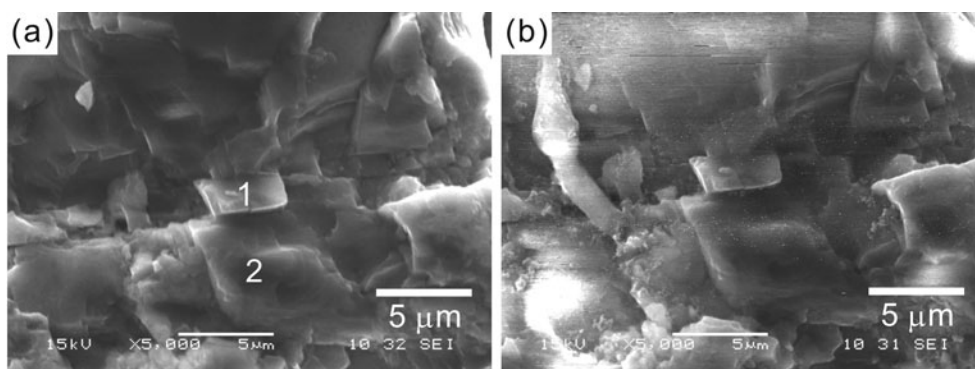


Figure 4. Secondary electron images of orthoclase with albite lamella onto which (a) EMI-CH₃COO diluted with ethanol (1 wt%) was dropped and (b) no ionic liquid dropped.

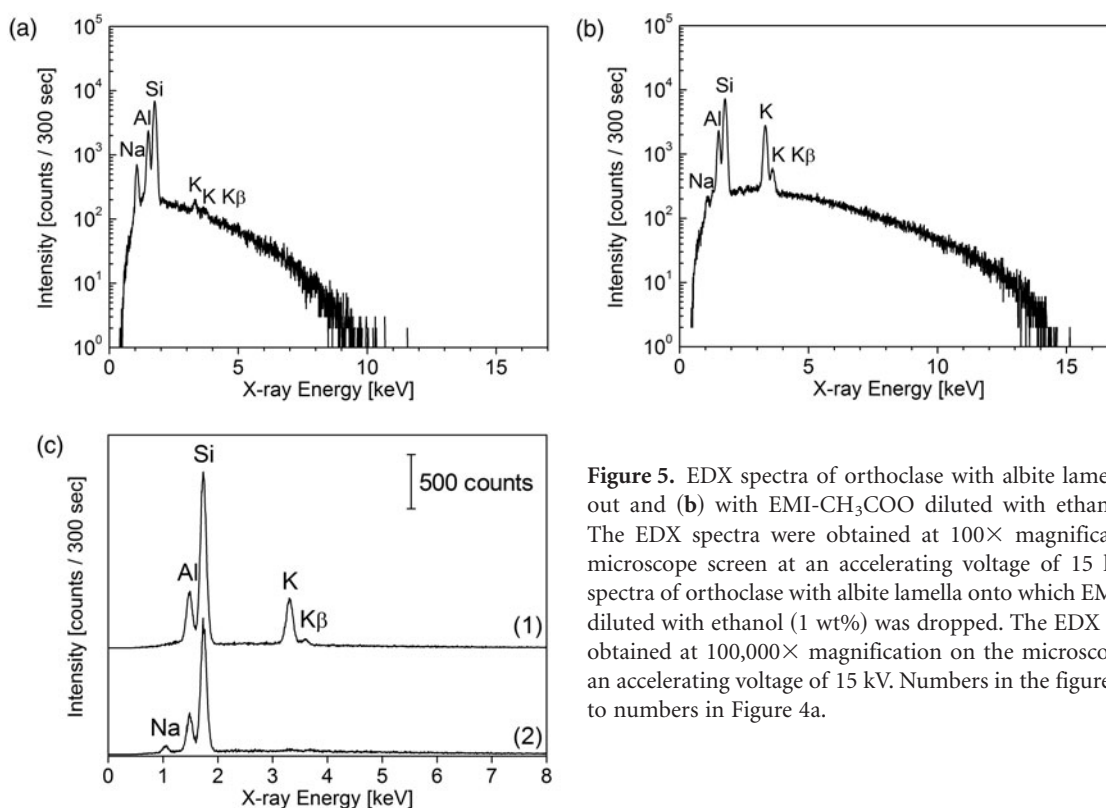


Figure 5. EDX spectra of orthoclase with albite lamella (a) without and (b) with EMI-CH₃COO diluted with ethanol (1 wt%). The EDX spectra were obtained at 100 $\times$ magnification on the microscope screen at an accelerating voltage of 15 kV. (c) EDX spectra of orthoclase with albite lamella onto which EMI-CH₃COO diluted with ethanol (1 wt%) was dropped. The EDX spectra were obtained at 100,000 $\times$ magnification on the microscope screen at an accelerating voltage of 15 kV. Numbers in the figure correspond to numbers in Figure 4a.

aluminum, silicon, and calcium were detected in point 1. From Table 1, the dark area in Figure 2d is plagioclase. K-lines of magnesium, aluminum, silicon, potassium, titanium, and iron were detected in the point 2, which means that the bright area in Figure 2d is biotite (Table 1). As seen in Figure 3, there was no overlap of EDX spectra in minerals of points 1 and 2 in Figure 2d. Thus, we can say that it is possible to carry out compositional analysis in a microscale region with the SEM and EDX that we used.

Next, orthoclase with albite lamella was observed with the SEM at an accelerating voltage of 15 kV. In this sample, it was difficult to find minerals, which have different compositions, from a secondary electron image because there is not a significant difference in atomic number between orthoclase and albite. Thus, we first tried to find a region with a micro-

size mineral with a composition different from other minerals by backscattered electron imaging, and then we obtained a secondary electron image of the region. Figure 4 shows the region we tried to find. Point 1 in Figure 4a was darker than areas around point 1 in the backscattered electron image. As shown in Figure 4b, the secondary electron image of the orthoclase with albite lamella was clearer than that of the garnet-biotite gneiss at 5,000 $\times$ magnification without diluted EMI-CH₃COO. However, there was still flickering at the top and middle of the image because of electrical charging. In the same manner of the garnet-biotite gneiss, a clear secondary electron image was obtained using diluted EMI-CH₃COO. We also performed EDX analysis of the orthoclase with albite lamella without and with the diluted EMI-CH₃COO at an accelerating voltage of 15 kV in the same way as the garnet-

biotite gneiss (Figs. 5a, 5b). The Duane-Hunt limit of the orthoclase with albite lamella without and with the diluted EMI-CH₃COO was 10 and 15 keV, respectively. As with the garnet-biotite gneiss, we verified that it is possible to prevent electric charging by dropping diluted EMI-CH₃COO onto the orthoclase with albite lamella. Figure 5c shows the EDX spectra of points 1 and 2 shown in Figure 4a. K-lines of aluminum, silicon, and potassium were detected in point 1. From Table 1, the mineral at point 1 in Figure 4a consists of orthoclase. K α -lines of sodium, aluminum, and silicon were detected in point 2 in Figure 4a, which means that the mineral at point 2 in Figure 4a is albite (Table 1). There was also no overlap of EDX spectra in minerals of points 1 and 2 in Figure 4a.

We tried to perform simple quantitative analysis of the samples using EDX spectra shown in Figures 3 and 5. However, we could not obtain reasonable results for light elements such as sodium, magnesium, and aluminum. The relative errors were above 40%. Also, as for orthoclase with albite lamella, surface roughness might be another reason for the difficulties of quantitative analysis. If we apply a method that does not need standard samples to our samples, use an X-ray detector sensitive for light elements, or make the surface of samples flat, it might be possible to perform quantitative analysis.

CONCLUSIONS

We successfully obtained clear secondary electron images of insulating samples (garnet-biotite gneiss and orthoclase with albite lamella) in a microscale region such as 5,000 $\times$ magnification on the microscope screen by dropping 10 μ L of EMI-CH₃COO diluted to 1 wt% with ethanol onto the insulating samples. It was also verified that it is possible to perform qualitative analysis in a microscale region ($\sim 5 \mu\text{m}^2$) of the insulating samples by focusing the electron beam of the SEM. If a method that does not need standard samples is applied or an X-ray detector sensitive for light elements was attached, it might be possible to carry out quantitative analysis.

Generally, when elemental analysis is carried out for samples of rocks and minerals using SEM-EDX, a thin layer of carbon has to be coated on the samples by vacuum deposition before the analysis. However, if rocks and minerals are scarce or processing is prohibited for some reason (e.g., relics from the monument), it is not possible to use this deposition process for preservation of the scarce samples. Thus, it is difficult to perform EDX analysis of the samples. On the other hand, it is possible to apply the method of dropping diluted ionic liquid onto the scarce samples because ionic liquid is easily removed by ultrasonic cleaning of the samples with acetone. Therefore, the method of dropping 1 wt% EMI-CH₃COO diluted with ethanol onto insulating samples is useful not only from the viewpoint of SEM observation and EDX analysis in a microscale region but also from the viewpoint of the preservation of scarce rock and mineral samples.

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REFERENCES

- ARIMOTO, S., SUGIMURA, M., KAGEYAMA, H., TORIMOTO, T. & KUWABATA, S. (2008). Development of new techniques for scanning electron microscope observation using ionic liquid. *Electrochim Acta* **53**, 6228–6234.
- CARLIN, R.T., DE LONG, H.C., FULLER, J. & TRULOVE, P.C. (1994). Dual intercalating molten electrolyte batteries. *J Electrochem Soc* **141**, L73–L76.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. (1992). *An Introduction to the Rock-Forming Minerals*. Essex, UK: Longman Scientific & Technical.
- IGARASHI, S. & YOTSUYANAGI, T. (1989). Temperature dependent phase transformation in the homogeneous liquid-liquid extraction with fluorocarbon surfactant. In *Symposium on Solvent Extraction*, Japanese Association of Solvent Extraction & Nihon Kagakkai (Eds.), pp. 51–54. Sendai, Japan: Japanese Association of Solvent Extraction.
- INOUE, M., SUGANAMI, M., HASHIMOTO, Y., IYASU, T., SAITO, H., MORIGUCHI, K. & TANAKA, T. (2010). Application of ionic liquid coating method to observation of non-conductive samples by a mobile scanning electron microscope for elementary science education. In *5th International Symposium on Practical Surface Analysis*, p. 138. Gyeongju, Japan: The Surface Analysis Society of Japan and The Korean Vacuum Society.
- ISHIGAKI, Y., NAKAMURA, Y., TAKEHARA, T., NEMOTO, N., KURIHARA, T., KOGA, H., NAKAGAWA, H., TAKEGAMI, T., TOMOSUGI, N., MIYAZAWA, S. & KUWABATA, S. (2011a). Ionic liquid enables simple and rapid sample preparation of human culturing cells for scanning electron microscope analysis *Microsc Res Tech* **74**, 415–420.
- ISHIGAKI, Y., NAKAMURA, Y., TAKEHARA, T., SHIMASAKI, T., TATSUNO, T., TAKANO, F., UEDA, Y., MOTOO, Y., TAKEGAMI, T., NAKAGAWA, H., KUWABATA, S., NEMOTO, N., TOMOSUGI, N. & MIYAZAWA, S. (2011b). Scanning electron microscopy with an ionic liquid reveals the loss of mitotic protrusions of cells during the epithelial–mesenchymal transition. *Microsc Res Tech* **74**(11), 1024–1031.
- ISHII, H. & KAWAI, J. (2006). SEM-EDX with an SDD X-ray detector installed onto the scanning electron microscope. *Adv X-Ray Chem Anal Jpn* **37**, 281–288 (in Japanese).
- KUWABATA, S., KONGKANAND, A., OYAMATSU, D. & TORIMOTO, T. (2006). Observation of ionic liquid by scanning electron microscope. *Chem Lett* **35**, 600–601.
- KUWABATA, S. & TORIMOTO, T. (2008). Observation of ionic liquid by electron microscopy. *J Surf Sci Soc Jpn* **28**, 322–326 (in Japanese).
- MATSUMOTO, H. & MATSUDA, T. (2002). Photoelectrochemical solar cells using ionic liquid as an involatile electrolyte. *Electrochemistry* **70**, 190–193.
- MC EWEN, A.B., MCDEVITT, S.F. & KOCH, V.R. (1997). Nonaqueous electrolytes for electrochemical capacitors: Imidazolium cations and inorganic fluorides with organic carbonates. *J Electrochem Soc* **144**, L84–L86.
- NANJUNDIAH, C., MCDEVITT, S.F. & KOCH, V.R. (1997). Differential capacitance measurements in solvent-free ionic liquids at Hg and C interfaces. *J Electrochem Soc* **144**, 3392–3397.

- OKUYAMA, M., SATO, M. & AKADA, M. (2011). Studies on the excavated archaeological textile fibers using room temperature ionic liquid (1)—The utility of ionic liquid for the SEM observation of natural fibers. *Sen'i Gakkaishi* **67**, 47–52 (in Japanese).
- PAPAGEORGIOU, N., ATHANASSOV, Y., ARMAND, M., BONHÔTE, P., PETTERSSON, H., AZAM, A. & GRÄTZEL, M. (1996). The performance and stability of ambient temperature molten salts for solar cell applications. *J Electrochem Soc* **143**, 3099–3108.
- TOBISHIMA, S. (2002). Application of ionic liquids as electrolytes in rechargeable cells. *Electrochemistry* **70**, 198–202.
- UE, M., TAKEDA, M., TAKAHASHI, T. & TAKEHARA, M. (2002). Ionic liquids with low melting points and their application to double-layer capacitor electrolytes. *Electrochem Solid-State Lett* **5**, A119–A121.
- WILKES, J.S. & ZAWOROTKO, M.J. (1992). Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. *J Chem Soc Chem Commun* **13**, 965–967.
- YAMAGUCHI, H. (2007). Does research on ionic liquid begin from analytical chemistry? *Bunseki* 608–609 (in Japanese).
- ZE, L., IMASHUKU, S., ICHIDA, M. & KAWAI, J. (2011). SEM observation at high magnification and EDX analysis of insulating sample by diluted ionic liquid. *J Surf Sci Soc Jpn* **32**, 659–663 (in Japanese).