Abstract

To gain an insight into geological environment, open nanospaces in natural minerals and rocks were investigated by positron annihilation spectroscopy. Positronium (Ps) formation occurs with ortho-positronium (o-Ps) intensities ranging from a few % to 20 %. Size distributions of sub-nanoscale pores are evaluated from o-Ps lifetimes. In addition to that, hydration and dehydration processes in clay minerals are clearly indentified through the local structural changes in interlayer spaces.

Keywords: Geological environment, Nanospace, Interlayer space, Positronium, Hydration

1. INTRODUCTION

In geological environment, open spaces offer the evolutionary pathway of elemental migration together with underground fluid [1]. A series of long-term physicochemical reactions take place between pore wall and flowing fluid, influencing the precipitation, transformation, and dissolution of rock-forming minerals. It is thus of great significance to investigate open nanospaces in natural minerals and rocks with respect to geological environment.

For estimating the size of pores, mercury porosimetry has been employed in the geology field. This technique is however unsuitable for pores with radius smaller than a few tens of nanometer, because quite large molecules of mercury have to be penetrated into the pores. In the present study, we employed the positron (e+), antiparticle of electron (e-), to investigate open nanospaces in natural minerals and rocks [2-4]. Open nanospaces associated with geological environment are discussed. Furthermore, nano-scale interlayer spaces in synthetic clay minerals are investigated for the purpose of detecting hydration and dehydration processes [5].

2. EXPERIMENTAL

The following specimens were examined in the present study: 1. SiO₂ quartz crystal, 2. SiO₂ fused quartz, 3. chert, 4. silicified wood, 5. chalcedony, 6. volcanic glass 1 taken at Tokachi, Japan, 7. volcanic glass 2 taken at Wadatoge, Japan, 8. borosilicate glass, 9. soda-lime glass, and 10. sedimentary rock.
In natural materials and rocks, Ps formation occurs. Singlet para-Ps (p-Ps) with the spins of the positron and electron antiparallel and triplet ortho-Ps (o-Ps) with parallel spins are formed at a ratio of 1 : 3 [6]. In vacuum, p-Ps annihilates into two $\gamma$ rays with a lifetime of 125 ps, whereas o-Ps decays into three $\gamma$ rays with a longer lifetime of 142 ns. The o-Ps lifetime is shortened to a few ns, because the positron in o-Ps undergoes two-photon pick off annihilation with one of the bound electrons with opposite spin. Since the pick-off annihilation rate is proportional to the probability of Ps being in contact with the pore wall, the lifetime is correlated with pore size. The size of open pore can be thus deduced from the positron lifetime of o-Ps [7-8].

For the lifetime measurements, the positron source ($^{22}$Na), sealed in a thin foil of Kapton, was mounted in a sample-source-sample sandwich. The positron annihilation lifetime spectra (~ $1 \times 10^6$ coincidence counts) with a time resolution of 230 ps full-width at half-maximum (FWHM) were recorded at room temperature. The present positron lifetime spectrometer was characterized by the standard samples of synthetic fused silica (NMIJ CRM 5601-a) and polycarbonate (NMIJ CRM 5602-a) provided by National Institute of Advanced Industrial Science and Technology (AIST) [9-10]. Typical three-component analysis was performed using the POSITRONFIT code [11]. Pore-size distributions are evaluated by using the MELT code [12].

3. RESULTS AND DISCUSSION

Positron lifetime spectra obtained were analyzed in terms of three components of positron lifetimes. The longest-lived component $\tau_3$ was attributed to pick-off annihilation of o-Ps localized in the open nanospaces in natural minerals and rocks. The positron lifetimes $\tau_3$ and their relative intensities $I_3$ are plotted together with the data of glass specimens of borosilicate glass, soda-lime glass, and $\text{SiO}_2$ fused quartz in Fig. 1 [13]. The lifetime $\tau_3$ ranges from 1.0 ns to 2.2 ns, indicating the presence of sub-nanoscale pores in natural minerals and rocks. The relative intensities $I_3$ obtained for the natural minerals are consistently smaller than glass specimens. No long component of positron lifetime was observed for quartz, which has high crystallinity.

It is found that a typical sedimentary rock of chert contains less nano pores than in volcanic glasses or chalcedony. Chert is known to be formed being more compact than other minerals. This compaction effect could reduce the amounts of nano pore during its formation process at underground. On the other hand, volcanic glasses are known to be formed by quenching the lava, producing porous structures macroscopically. Interestingly, this effect of quenching can be nanoscopically seen in the data of $I_3$ (~ 15 %),
which is significantly higher than other minerals. Chalcedony contains fine particles of quartz crystals with interstitial pores, resulting in slightly smaller density (2.55 ~ 2.64 gcm\(^{-3}\)) than in quartz crystal (2.65 gcm\(^{-3}\)). The interstitial pores are thus the most probable candidate for the explanation of higher \(I_3\) of ~ 10%.

Fig. 2 shows pore-size distributions obtained for chert, silicified wood, chalcedony, volcanic glass 1 taken at Tokachi, volcanic glass 2 taken at Wadatoge [13]. A variety of pore-size distributions can be seen. It is particularly interesting that two kinds of volcanic glasses exhibit entirely different size distributions, although essentially the same x-ray diffraction patterns (x-ray data not shown here). It is thus unlikely that the different size distributions are caused by chemical reaction of \(\alpha\)-Ps in volcanic glasses. We therefore conclude that the distinct pore size distributions obtained for two volcanic glasses are solely attributable to the difference of local atomic structures. Presumably, pore-size distributions are sensitively influenced by the environmental factor such as a cooling rate of the lava in their formation history.

Fig. 3 shows positron lifetime spectra measured for a synthetic saponite (a) under atmospheric condition, (b) under vacuum condition at \(\sim 10^{-5}\) Torr, and (c) after baking at 423 K for 8 h under the vacuum condition at \(\sim 10^{-5}\) Torr [5]. The measurement was again performed immediately after exposing to air (see the data (d)). The successive changes in positron lifetime spectra owing to hydration and dehydration can be clearly seen in Fig. 3.

Positron lifetime spectra obtained under atmospheric condition ((a) and (d)) were analyzed with respect to three components of positron lifetimes. On the other hand, four-component analyses are accomplished for the saponites measured (b) under vacuum condition at \(\sim 10^{-5}\) Torr and (c) after baking at 423 K for 8 h under the vacuum condition at \(\sim 10^{-5}\) Torr. The longest-lived component \(\tau_4\) and second longest-lived component \(\tau_3\) were attributed to pick-off annihilation of \(\alpha\)-Ps localized in the open nanospaces in the synthetic saponite. Table 1 lists positron lifetimes \(\tau_3\) and \(\tau_4\) together with their intensities observed in the present work. It is of interest
that very long positron lifetime $\tau_4$ of $\sim 24$ ns appears with the intensity of $\sim 8\%$ when the sample is evacuated at $\sim 10^{-5}$ Torr. The size of open nanospaces evaluated from the lifetime $\tau_3$ is $\sim 3$ Å in radius, whereas the size evaluated from the lifetime $\tau_4$ is $\sim 10$ Å. In light of the fact that the basal spacing of smectite clay minerals is $\sim 12$ Å, the larger spaces corresponding to positron lifetime $\tau_4$ arise from the interlayer spaces in the saponite. The open nanospace increases up to 13 % after baking at 150 °C for 8 h under the vacuum. We reasonably infer that desorption of water molecules from the interlayer spaces occurs in the vacuum and it further proceeds with baking treatment. Two positron lifetime spectrum measured under atmospheric condition ((a) and (d)) are essentially identical to each other. This demonstrates that the absorption of water molecules into the interlayer spaces occurs immediately after exposing to air. The present results imply that positron lifetime spectroscopy is a powerful tool for investigating hydration and dehydration behavior of interlayer spaces in clay minerals.

Table 1. Positron lifetimes $\tau_3$ and $\tau_4$ together with their intensities ($I_3$ and $I_4$) observed for a synthetic saponite.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$\tau_3$ [ns]</th>
<th>$I_3$ [%]</th>
<th>$\tau_4$ [ns]</th>
<th>$I_4$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) air 1</td>
<td>2.2</td>
<td>21</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(b) vacuum</td>
<td>3.2</td>
<td>7</td>
<td>21.7</td>
<td>8</td>
</tr>
<tr>
<td>(c) vacuum and baking</td>
<td>3.1</td>
<td>6</td>
<td>23.9</td>
<td>13</td>
</tr>
<tr>
<td>(d) air 2</td>
<td>2.2</td>
<td>22</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

To gain an insight into geological environment, open nanospaces in natural minerals and rocks were investigated by positron annihilation spectroscopy. It was found that positronium (Ps) formation occurs with ortho-positronium ($\omega$-Ps) intensities ranging from a few % to 20 %. Sub-nanoscale pores were evaluated from $\omega$-Ps lifetimes. The results suggest that sub-nanoscale pores in both natural minerals and rocks are closely correlated with the environmental factor in their formation history. Furthermore, hydration and dehydration processes occurring in nanoscale interlayer spaces of synthetic clay minerals are discussed.

Acknowledgments

This work was partially supported by a Grant-in-Aid of the Japanese Ministry of Education, Science, Sports and Culture and the Japan Atomic Energy Agency.

References


