Diffusion ellipsoids of anisotropic porous rocks calculated by X-ray computed tomography-based random walk simulations

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1[b] Water molecules and contaminants migrate in water-saturated porous strata by diffusion in systems with small Pe´clet numbers. Natural porous rocks possess the anisotropy for diffusive transport along the percolated pore space. An X-ray computed tomography (CT) based approach is presented to quickly characterize anisotropic diffusion in porous rocks. High-resolution three-dimensional (3-D) pore images were obtained for a pumice and three sandstones by microfocus X-ray CT and synchrotron microtomography systems. The cluster-labeling process was applied to each image set to extract the 3-D image of a single percolated pore cluster through which diffusing species can migrate a long distance. The nonsorbing lattice random walk simulation was performed on the percolated pore cluster to obtain the mean square displacement. The self-diffusion coefficient along each direction in the 3-D space was calculated by taking the time derivative of the mean square displacement projected on the corresponding direction. A diffusion ellipsoid (i.e., polar representation of the direction-dependent normalized self-diffusivity) with three orthogonal principal axes was obtained for each rock sample. The 3-D two-point autocorrelation was also calculated for the percolated pore cluster of each rock sample to estimate the pore diameter anisotropy. The autocorrelation ellipsoids obtained by the ellipsoid fitting to the high correlation zone were prolate or oblate in shape, presumably depending on the eruption-induced deformation of magma and regional stress during sandstone diagenesis. The pore network anisotropy was estimated by calculating the diffusion ellipsoid for uniaxially elongated or compressed rock images. The degree and direction of the geological deformation of the samples estimated by the pore diameter anisotropy analysis agreed well with those estimated by the pore network anisotropy analysis. We found that the direction of the geological deformation coincided with the direction of the major (or minor) principal axis of the prolate (or oblate) diffusion ellipsoid for each sample. Thus, it can be concluded that the deformation-induced pore structure anisotropy is responsible for the anisotropy of the diffusive transport properties.


1. Introduction

[b] Diffusion or random walk is a dominant mechanism of material transport in water-saturated porous strata systems with small Pe´clet numbers. Examples include the pore-scale water/rock interactions [e.g., Sorai et al., 2007] and meter-scale contaminant migration [e.g., Ohlsson and Neretnieks, 1995] in deep (~1 km) strata with small hydraulic head difference relevant to the underground CO2 storage [e.g., Gherardi et al., 2007] and high-level radioactive waste disposal [e.g., Madsen, 1998]. Because contaminants and water molecules diffuse along the microscopic pore space, pore-scale characterization is needed to understand the diffusive migration mechanism in porous rocks. Natural porous rocks often possess anisotropic diffusive transport properties [e.g., Farver and Yund, 1999]. Characterization of the pore-scale anisotropy is thus essential to understanding the diffusive transport properties of real porous rocks. Because conventional laboratory methods using diffusion cells or electron microscopy [e.g., Van Loon et al., 2004; Yokoyama and Nakashima, 2005] are time-consuming and exhausting, a new quick method should be developed to examine the direction-dependent diffusivity of anisotropic rocks. In relation to the diffusive anisotropy, there is a likely hypothesis that the pore structure anisotropy causes the anisotropic diffusive transport [Yokoyama and Nakashima, 2005]. For example, geometrically tortuous pipes in rocks lead to high diffusion tortuosity (i.e., low self-diffusion coefficient), as illustrated by Figure 1. This hypothesis needs to be tested to understand the cause of the diffusive anisotropy in rocks. The diffusion ellipsoid (i.e., polar representation of the direction-dependent normalized diffusivity) is usually convex ellipsoidal [e.g., Westin et al., 2002]. Recently, however, a few studies on the water self-diffusion for synthetic clay gels using nuclear magnetic
anisotropy study on rocks. Another point to be addressed in relation to the diffusion pinched-in ellipsoid has not been studied in detail, this is likely to occur also for natural porous samples. The convex constricted in the direction of minimum self-diffusivity (no longer convex ellipsoidal). This breakdown of the convex ellipsoid expression can be caused by the uniaxial compression in the vertical direction. An isolated pore, which cannot contribute to the long-distance material transport, is also shown.

resonance spectroscopy [Porion et al., 2001, 2003; de Azevedo et al., 2007] reported the unusual shape, namely constricted in the direction of minimum self-diffusivity (no longer convex ellipsoidal). This breakdown of the convex ellipsoid expression likely occurs also for natural porous rocks. Because the mechanism of the generation of this pinched-in ellipsoid has not been studied in detail, this is another point to be addressed in relation to the diffusion anisotropy study on rocks.

X-ray computed tomography (CT) is a powerful tool for obtaining accurate three-dimensional (3-D) images of microscopic pores rapidly [e.g., Auzerai et al., 1996; Lindquist et al., 2000; Karacan and Mitchell, 2003; Arns et al., 2004, 2005 Ketcham and Inrrino, 2005; Al-Raouush and Wilson, 2005; Altmann et al., 2005; Liu et al., 2005; Du et al., 2007; Goldstein et al., 2007; Jones et al., 2007], and isotropic diffusion has been simulated by random walk in digitized CT images of porous sandstones [e.g., Schwartz et al., 1994; Nakashima et al., 2004]. In the present study, we extended this CT-based method to the quick evaluation of anisotropic diffusion. Digital 3-D pore images were obtained by X-ray CT for one pumice and three sandstone samples. Nonsorbing lattice random walk simulations were performed in a percolated pore cluster of the CT images to calculate the mean square displacement along an arbitrary direction in 3-D space. The diffusion ellipsoid was calculated by taking the time derivative of the direction-dependent mean square displacement. The anisotropy of the pore structure of the geologically deformed samples was analyzed in terms of the pore diameter anisotropy and pore network anisotropy. The pore diameter anisotropy was estimated by computing the two-point autocorrelation ellipsoid of the pore cluster [Ikeda et al., 2000]. The pore network anisotropy was estimated by calculating the diffusion ellipsoid for uniaxially elongated or compressed rock images. To test the relationship between pore structure anisotropy and diffusive anisotropy, the deformation direction inferred from the analysis of pore diameter anisotropy and pore network anisotropy was compared with the direction of the principal axes of the diffusion ellipsoids. As for the unusual constriction of the diffusion ellipsoid, we first found that it occurs for natural porous rocks in the present study. To discuss the generation mechanism of this constriction, diffusion ellipsoids for highly anisotropic porous media were calculated using synthetic pore CT images produced by systematic uniaxial elongation/compression using affine transformation. The effect of the degree of the elongation/compression on the ellipsoid shape was examined.

2. Calculation of the Diffusion Ellipsoid by Random Walk in CT Images

We developed a Mathematica® version 6 program, DellipsoidM6.nb, to calculate a diffusion ellipsoid using a 3-D pore image set. The method for calculation of the diffusion ellipsoid by 3-D lattice random walk in the pore space using the program is described. The random walk simulation should only be performed in a percolated pore cluster responsible for the macroscopic or long-distance transport of materials (not in isolated small pores, see Figure 1). Thus, the raw 3-D CT images of porous samples need to be preprocessed by cluster labeling to exclude isolated pores [e.g., Ikeda et al., 2000; Nakashima and Kamiya, 2007]. The DellipsoidM6.nb program is available at http://staff.aist.go.jp/nakashima.yoshito/progeng.htm to facilitate the X-ray CT approach to the pore-scale analysis of anisotropic diffusive transport in porous media. For further information about data preparation including cluster labeling and program output, readers are requested to refer to the “readme” file available at the URL above.

DellipsoidM6.nb is an advanced version of Rwalk.nb developed by Nakashima and Kamiya [2007]. The random walk algorithm used is the nonsorbing 3-D lattice-walk on a percolated pore cluster in a simple cubic lattice image system with a periodic boundary condition using a mirror operation. An excellent pseudorandom number generator, Mersenne Twister, developed by Matsumoto and Nishimura [1998] was implemented in DellipsoidM6.nb. The random walker should be nonsorbing because the purpose is to calculate the geometrical tortuosity of the pore structure and the undesirable effects of the sorption of walkers on the solid surface should be eliminated. The difference between DellipsoidM6.nb and Rwalk.nb is that while the former can calculate the self-diffusivity along any direction in the 3-D space, the latter calculates the self-diffusivity only along the three orthogonal directions.

The self-diffusivity along any direction in the 3-D space is calculated as follows. Each 3-D random walk trajectory is projected on the α-axis originating from the center of the 3-D image system (Figure 2a). The displace-
ment on the $\alpha$-axis is used to calculate the walkers’ mean square displacement $\langle \alpha(\tau)^2 \rangle$ in the $\alpha$-direction

$$\langle \alpha(\tau)^2 \rangle = \frac{1}{n} \sum_{i=1}^{n} (\alpha_i(\tau) - \alpha_i(0))^2,$$

where $n$ is the number of random walkers, $\tau$ is the dimensionless integer time ($\tau = 0, 1, 2, 3, \ldots$), $\alpha_i(\tau)$ is the coordinate of the walker’s position on the $\alpha$-axis at time $\tau$ for the $i$th walker, and $\alpha_i(0)$ is the initial position of the $i$th walker. The exact solution for a lattice walk in free space (i.e., porosity = 100 vol %), $\langle \alpha^2 \rangle_{\text{free}}$, is given by $\langle \alpha^2 \rangle_{\text{free}} = \ell^2 \tau / 3$ where $\ell$ is the lattice constant of the simple cubic lattice (i.e., the dimension of a cubic CT voxel). The self-diffusion coefficient is proportional to the time derivative of the mean square displacement [e.g., Nakashima and Kamiya, 2007; Ohkubo, 2008]. “Normalized diffusivity” in the present study refers to the self-diffusivity in porous media divided by that in free space, and the tortuosity is its reciprocal. Thus, we have

$$\text{normalized diffusivity} = \frac{1}{\text{tortuosity}} = \frac{d\langle \alpha(\tau)^2 \rangle}{d\tau} = \frac{1}{\ell^2 \tau}$$

as $\tau \to \infty$.

The normalized diffusivity is unity for the random walk in free space, and less than unity for that in porous media owing to the obstructing effect of the solid. The asymptote value (i.e., $\tau \to \infty$) is essential because the normalized diffusivity can be overestimated owing to the short diffusion distance compared with the pore network size if the time derivative is taken at a small $\tau$ value [e.g., Nakashima and Watanabe, 2002]. For an identical set of random walk trajectories, the $\alpha$-axis is scanned on the upper-half plane of the 3-D polar coordinate system (Figure 2b) to express the directional mean square displacement as a function of the angles $\theta$ and $\phi$. Equation (2) is again applied to the mean square displacement to obtain the normalized self-diffusion coefficient depending on $\theta$ and $\phi$. Equation (3) is again applied to the mean square displacement to obtain the normalized self-diffusion coefficient depending on $\theta$ and $\phi$. Typically $\theta$ covers $0, 1, 2, \ldots, 90^\circ$, and $\phi$ covers $0, 1, 2, \ldots, 359^\circ$. Thus, the number of the data points we obtain for the normalized diffusivity is as large as $90 \times 360 + 1 = 32,401$, which is likely sufficient to evaluate the diffusive anisotropy of porous rocks.

[7] The normalized self-diffusion coefficient depending on $\theta$ and $\phi$ can be visualized by a polar representation, namely, diffusion ellipsoid [e.g., Westin et al., 2002]

$$\left(\frac{a}{A}\right)^2 + \left(\frac{b}{B}\right)^2 + \left(\frac{c}{C}\right)^2 = 1,$$

where $A$, $B$, and $C$ are the radii on the $a$-, $b$-, and $c$-axes, respectively (Figure 2c). The order of the three principal self-diffusion coefficient values is $A \leq B \leq C$. The data set

Figure 2. Principles of quantification of the anisotropic self-diffusivity using DelipsoiM6.nb. (a) A random walk trajectory is projected on the $\alpha$-axis originating from the center of the 3-D image system to calculate the walkers’ mean square displacement in the $\alpha$-direction. (b) The $\alpha$-axis is scanned on the upper-half plane of the 3-D polar coordinate system to express the directional mean square displacement as a function of $\theta$ and $\phi$. (c) The direction-dependent mean square displacement is converted into a diffusion ellipsoid. Generally, the principal axes (i.e., $a$-, $b$-, and $c$-axes) of the ellipsoid do not coincide with the $x$-, $y$-, and $z$-axes of the original 3-D CT image system.
of the normalized self-diffusion coefficients calculated by
equation (2) was then fitted to equation (3) in terms of the
second moment of the object as described by Ikeda et al.

First, the search for a principal axis yielding the minimum value of the second
moment was performed to assign it to the c-axis (i.e., the
major axis). Second, a principal axis yielding the maximum
value of the second moment (i.e., a-axis or minor axis) was
searched in the direction perpendicular to the c-axis. Finally,
the third principal axis perpendicular to both the a- and c-axes
was automatically chosen to be the b-axis (i.e., intermediate
axis). The distances from the origin of Figure 2c to the crossing
points of the ellipsoid (i.e., raw data on the normalized self-
diffusion coefficients calculated by equation (2)) and the
three principle axes were determined to be radii A, B, and C.

With respect to the determination method of the
principal axes and diffusivity eigenvalues, our method using
the second moment of the ellipsoidal object is basically
identical to the method conventionally used in diffusion-
tensor magnetic resonance imaging studies [e.g., Westin et
al., 2002]. However, there is a difference between the two
methods. The latter method a priori assumes that the
diffusion ellipsoid is convex (i.e., without constriction).
While this assumption is correct, only seven directions of
the magnetic field gradients including a zero gradient are
needed [e.g., Bhagat and Beaulieu, 2004]. However, the
assumption breaks down for highly anisotropic porous
rocks. Thus, directions as many as 90 × 360 + 1 = 32,401
were required for the α-axis scanning to measure the 3-D
shape of the normalized diffusivity accurately in the present
study. The simple shape-fitting method of the normalized
diffusivity to the convex ellipsoidal surface is inappropriate
for diffusion ellipsoids with constriction. It should be noted
that our search method for the principal axes works
properly even for diffusion ellipsoids having a constriction
because the fitting algorithm is based on the minimization/
maximization of the second moment (not ellipsoidal shape
fitting).

3. Application to CT Images of Pumice,
Sandstones, and a Bead Pack

DellipsoidM6.nb was applied to 3-D CT image sets of
four natural rocks having anisotropic pore structures (one
pumice from Ito and three sandstones from Berea,
Shirahama, and Tako) and a pack of synthetic monosized beads
to calculate the diffusion ellipsoid. The Ito pumice sample
from Kagoshima, Japan [Yamamoto et al., 1978] has an
elongated pore structure formed by deformation during
eruption. A cylindrical sample (diameter 6 mm, length

Figure 3. The Berea sandstone sample used in the present
study. The z-direction is normal to the bedding plane. (a) X-ray
CT image after the cluster-labeling process. Black areas are
the largest or percolated pore cluster, white areas are solid
mineral grains, and red areas are isolated pore clusters
(7379 isolated pore clusters were identified). The dimension
of the image system is 420³ voxels = 4.13 mm³. (b) Crossplot
of the volume and surface area of 7380 pore clusters. The
theoretical upper and lower limits [Nakashima and Kamiya,
2007] for sufficiently large clusters are shown by dotted lines.
(c) Wireframe rendering of the autocorrelation ellipsoid
projected on the x-z plane. The principal axes of the ellipsoid
from Table 1 are shown. Note that the shape of the ellipsoid is
prolate in the z-direction.
Figure 4
10 mm) was prepared so that the longitudinal direction of the cylinder would be parallel to the pore elongation direction. Three cylindrical sandstone samples from Berea (USA), Shirahama (Wakayama, Japan), and Tako (Gunma, Japan) of similar dimensions were cored normal to the bedding plane for CT imaging. Some petrophysical data on the sandstones (e.g., pore size distribution and mineralogy) have been published elsewhere [Xue et al., 1992; Lin and Takahashi, 2000]. A random pack of monosized beads (bead diameter 2.11 mm, porosity 37 vol %) was chosen as an analog of the unconsolidated well-sorted sandy sediment before diagenesis, which yields an isotropic diffusion ellipsoid (i.e., sphere).

Cylindrical samples of Ito pumice and Berea sandstone having a diameter of 6 mm were imaged by microfocus X-ray CT (Toscaner-30000, Toshiba IT and Control System Corporation) at a cubic voxel size of $\ell = 9.8 \, \mu m$ with 50 kV acceleration voltage and 0.35 mA tube current. The original reconstructed 3-D images (1024 $\times$ 1024 voxels, 691 slices) were trimmed to extract a cubic image system of $420^3$ voxels = $4.1^3$ mm$^3$. The two cylindrical sandstone samples with a diameter of 4 mm from Shirahama and Tako were imaged by the SP-$\mu$CT system (SPRing-8 synchrotron radiation facility [Uesugi et al., 2001]) at a cubic voxel size of $\ell = 5.8 \, \mu m$ with 25 keV monochromatic X-ray energy. The reconstructed original 3-D images (1000 $\times$ 1000 voxels, 700 slices) were trimmed to extract a cubic image system of $435^3$ voxels = $2.5^3$ mm$^3$. For the monosized bead pack sample, a 3-D cubic image system of $256^3$ voxels = $13.6^3$ mm$^3$, which was obtained by another microfocus X-ray CT scanner (Nittetsu Elex Co., Ltd.) and reported elsewhere [Nakashima and Watanabe, 2002], was reused in the present study.

Cluster labeling was applied to each trimmed cubic image system before the random walk simulations to eliminate isolated small pores (see, for example, Figure 1) and to extract a single percolated pore cluster responsible for the long-distance material transport. A threshold for voxel intensity is needed to distinguish the pore and solid in cluster labeling. We chose threshold values that yield an experimentally determined effective porosity (volume fraction of a percolated pore cluster) values measured by the weight difference between water-saturated and dried rock samples (i.e., 20, 12, 21, and 54 vol % for the Berea, Shirahama, Tako, and Ito samples, respectively).

[10] An example of cluster labeling is shown in Figure 3 for the Berea sandstone sample. The percolated pore cluster determined extends through the whole image system (Figure 3a), and serves as the 3-D network for diffusive transport. All pore clusters including the single percolated pore cluster and 7379 isolated small pore clusters are plotted in Figure 3b. The surface area in Figure 3b refers to the area sum of numerous squares (each dimension, $\ell \times \ell$) on the surface of each blocky pore cluster. The surface area value was calculated without considering the contribution of the pore faces exactly on the surface of the 4203 image system (i.e., “definition A” of Nakashima and Kamiya [2007]) because such pore faces disappear in random walk simulations with a mirror boundary condition employed. Cluster labeling revealed that the total porosity (i.e., sum of the volume fraction of a percolated pore and of numerous isolated small pores) is nearly equal to the effective porosity (21 versus 20 vol %), implying that almost all of the pores are connected to form a single large pore cluster in the Berea sandstone. Results of cluster labeling for other rock samples are shown in Figure 4. The Shirahama sandstone sample shows a finer pore structure than the Berea sample, as previously revealed by mercury intrusion porosimetry [Lin and Takahashi, 2000]. There are many prolate pores visibly elongated in the $z$-direction of the image of the Ito pumice sample. The Tako sample contains large pores partly filled with precipitated minerals [Nakashima and Kikuchi, 1992] and narrow throats connecting those large pores. The number of isolated pore clusters was as large as 245,985.
for Shirahama sandstone, 14,988 for Ito pumice, and 172,454 for Tako sandstone. However, the total porosity was nearly equal to the effective porosity (15 versus 12 vol % for Shirahama sandstone, 54 versus 54 vol % for Ito pumice, and 23 versus 21 vol % for Tako sandstone), implying again that almost all of the pores were connected to form a single large pore cluster.

[13] In accordance with Ikeda et al. [2000], the two-point autocorrelation was calculated for the percolated pore cluster images before random walk simulations. The voxel value of the largest (i.e., percolated) pore cluster was set to unity; that of the solid voxels and isolated pore voxels was zero. The two-point autocorrelation was calculated as (average of the product of the voxel value and the spatially shifted voxel value)/(effective porosity calculated by the volume fraction of the percolated pore cluster). The autocorrelation obtained, a function of the space shift, is a 3-D image, and its voxel value decreases from unity to the effective porosity value with increasing spatial shift. As used by Ikeda et al. [2000], an autocorrelation value of 0.5 was chosen as a threshold to extract a high correlation zone for the three sandstone samples and bead pack; the threshold was taken to be 0.7 for Ito pumice because the two-point autocorrelation value never decreased to 0.5 owing to the extraordinarily high porosity of pumice. We have confirmed that the results (i.e., the fitted $q$ and $f$ values and relative magnitude of radii of autocorrelation ellipsoids in Table 1) do not show a strong dependence on the chosen threshold value. The ellipsoid fitting algorithm using the second moment described above was applied to an object with a high correlation value of $\geq 0.5$ (or 0.7) to output the ellipsoid defined by equation (3). The fitting results are listed in Table 1, and shown in Figures 3 and 4. Although the cluster-labeled pore CT images of Figures 3 and 4 show no obvious pore anisotropy except for Ito pumice, the autocorrelation analysis (Table 1) clearly reveals that the four rock samples are all anisotropic in the $z$-direction (prolate for Berea and Ito, oblate for Shirahama and Tako).

[14] The comparison of the pore diameter in the labeled images (Figures 3–5) with $A$, $B$, and $C$ values in Table 1 for the two-point autocorrelation ellipsoid indicates that they are almost of the same order. Thus, the anisotropy inferred from the autocorrelation ellipsoid is the anisotropy of the pore diameter averaged over numerous individual pores. The degree of the deformation of the pore diameter can be estimated quantitatively using the autocorrelation data. It is reasonable to assume that initially the pore structure was as isotropic as that in the randomly packed bead pack ($f = 1$ in Figure 5), and was significantly elongated or compressed in the $z$-direction during the geological deformation processes. Then the deformation degree of the pore diameter, $f_0$, can be calculated by $f_0 = C(AB)^{-1/2}$ for prolate autocorrelation ellipsoids (Berea and Ito samples) and by $f_0 = A(BC)^{-1/2}$ for oblate autocorrelation ellipsoids (Shirahama and Tako samples). The geometric mean, $(AB)^{1/2} or (BC)^{1/2}$, was taken to conserve the volume of the ellipsoid. In general, the pore diameter anisotropy is not exactly identical to the pore network anisotropy (Figure 1) responsible for the diffusion anisotropy. It is thus difficult to connect the anisotropy of the autocorrelation ellipsoid directly to the diffusion anisotropy. However, there should be positive correlation between the pore diameter anisotropy and pore network anisotropy because they are degrees of geological deformation recorded in the same rock mass. The obtained $f_0$ values listed in Table 1 were used to discuss the diffusive anisotropy via pore network anisotropy.

[15] We examined the diffusion anisotropy of the porous samples as follows. The program DellipsoidM6.nb was run by importing each labeled CT image in Figures 3–4 to

Figure 5. Anisotropic pore structure of a bead pack elongated or compressed in the $z$-direction. The coloring rule of the 3-D image is identical to that of Figure 3a. The elongation/compression factor $f$ is indicated. The image systems for $f = 1.9$ and 0.54 are composed of $256^2 \times 486$ and $256^2 \times 138$ cubic voxels, respectively. The original image (i.e., $f = 1$) of $256^3$ cubic voxels = $13.6^3$ mm$^3$ having an isotropic pore structure is also shown.
Figure 6
Obtain the mean square displacement for nonsorbing walkers diffusing in the percolated pore cluster. The number of the random walkers $n$ in equation (1) was as large as 400,000 to reduce the undesirable stochastic fluctuation of the mean square displacement [Ohkubo, 2008]. The starting position of the random walk was chosen randomly among the voxels of the percolated pore cluster. A personal computer (PC) with an Intel Core2 Duo T7600 CPU (2.33 GHz) and 2 GB RAM running Windows XP was used for the random walk simulations. In order to avoid an undesirable overestimate of the normalized diffusivity due to the short diffusion distance compared with the pore network size [Nakashima and Kamiya, 2007], sufficiently long values were employed for the random walk duration to allow the walkers to travel long distances to obtain the linear (not convex) mean square displacement. The directional mean square displacement was obtained for a number of discrete integer $(\theta, \phi)$ pairs (i.e., $\theta = 0, 1, 2, \ldots, 90^\circ$ and $\phi = 0, 1, 2, \ldots, 359^\circ$) in Figure 2b. Then, the time derivative of the linear directional mean square displacement was calculated according to equation (2) to obtain the normalized diffusivity as a function of $\theta$ and $\phi$. The 3-D shell-like object obtained was the raw data on the diffusion ellipsoid, and was used for the ellipsoid fitting process as follows. A $(\theta, \phi)$ pair that minimized the second moment of this shell-like object was chosen as the c-axis; another $(\theta, \phi)$ pair that was normal to the c-axis and yielded the maximum second moment was taken to be the a-axis. The intermediate axis (b-axis) was automatically determined to be perpendicular to both the a- and c-axes. The distances from the origin of Figure 2c to the crossing points of the 3-D shell-like object and the a-, b-, and c-axes were taken to be the radii $A$, $B$, and $C$ in equation (3), respectively.

One of the purposes of the present study is to discuss the effect of pore structure anisotropy on the anisotropy of the diffusion through the percolated pore cluster. To this end, we calculated the diffusion ellipsoids for 3-D CT images systematically deformed by an affine transformation. The bead pack image [Nakashima and Watanabe, 2002] has no significant pore structure anisotropy in terms of the autocorrelation ellipsoid (Table 1), and yields a diffusion ellipsoid of an almost perfect sphere. We generated a series of synthetic bead pack images that were uniaxially elongated or compressed in the z-direction. The case of $f > 1$ implies elongation and $f < 1$ implies compression, where $f$ is the elongation/compression factor. Examples for some $f$ values are shown in Figure 5. The program DellipsoidM6.nb was applied to the image sets to obtain the diffusion ellipsoids averaged over 200,000 walkers for various $f$ values. We analyzed the results and discussed the effects of $f$ on the ellipsoid shape, focusing on the emergence of the constriction that has been reported for water self-diffusion in clay gels having anisotropic (nematic) pore structure.

We also applied an affine transformation in the $z$-direction with a factor of $f$ to the natural rock CT images in Figures 3 and 4. Unfortunately, according to the autocorrelation ellipsoid analysis shown in Table 1, all rock samples possessed intrinsic pore structure anisotropy with respect to the $z$-axis, presumably caused by geological processes during the diagenesis in sedimentary basins and eruption of magma. Thus, corrections must be made to estimate the true strain from the state having an isotropic pore structure. The isotropic pore state yields an isotropic diffusion ellipsoid (i.e., a sphere). Thus, if a diffusion ellipsoid becomes spherical (i.e., $A = B = C$) for a 3-D image that is elongated or compressed with a specific factor, $1/f$, in the $z$-direction, it is reasonable to assume that the 3-D pore image is in the no-strain, or isotropic, state. After some trial and error, we found the intrinsic elongation/compression factor, $f$, for each sample, as listed in Table 1. The product, $f_1 \times f$, was used to express the true degree of pore elongation/compression from the isotropic pore structure state.

The quantity, $f_1$, is an important measure to characterize the pore network anisotropy, which is responsible for the diffusive anisotropy. Because the isotropic pore image set was successfully obtained by the affine transformation applied in the $z$-direction, the direction of the rock deformation is the $z$-direction for all samples in terms of the pore network anisotropy. The estimated magnitude (i.e., $f_1$ values listed in Table 1) and the direction of the rock deformation were used to discuss the correlation with the diffusive anisotropy and pore diameter anisotropy.

Results for the Berea sandstone sample are shown in Figure 6. The fitted parameters of the diffusion ellipsoid are tabulated in Table 1. The CPU time of DellipsoidM6.nb required for the Berea sandstone sample was 4.4 h for the PC used. The mean square displacements along the $x$-, $y$-, and $z$-axes in Figure 3a, as calculated by equation (1), are shown in Figure 6a. Equation (1) becomes simple if the cubic voxel dimension, $\ell$, (9.8 $\mu$m for the Berea sandstone) is taken to be unity. Thus, $\ell = 1$ was assumed in Figure 6a, yielding a dimensionless mean square displacement. There is a slightly convex portion of the mean square displacement curve in the early stage (i.e., $\tau < 10,000$). This time interval is derived from the finite size of the pore network [e.g., Nakashima and Kamiya, 2007]. The pore network of most sedimentary rocks consists of large subspherical pools and narrow throats bridging the pools [Lindquist et al., 2000]. The percolated pore cluster of Figure 3a suggests that the

Figure 6: Results of the random walk simulation for the percolated pore cluster in Figure 3a (Berea sandstone). (a) Dimensionless mean square displacement along the directions of $x$-, $y$-, and $z$-axes averaged over 400,000 walkers as a function of $\tau$. (b) Snapshot of the 400,000 walkers at $\tau = 30,000$. The unit of the axes is the cubic voxel dimension (i.e., $\ell = 9.8 \mu$m for the Berea sandstone). The origin of the 3-D image is the starting position of the random walk of each walker. (c) Unwrapped expression of the Northern Hemisphere (i.e., $\theta \leq 90^\circ$) of the normalized diffusivity calculated by equation (2) as a function of $\theta$ and $\phi$ (in units of degrees). This is the raw data (i.e., before ellipsoid fitting) and normalized diffusivity values for 32,401 integer $(\theta, \phi)$ pairs (i.e., $\theta = 0, 1, 2, \ldots, 90^\circ$ and $\phi = 0, 1, 2, \ldots, 359^\circ$) are plotted. (d) Bird’s-eye-view of the wireframe rendering of the wrapped normalized diffusivity. The three principal axes $(a, b,$ and $c$) of the fitted diffusion ellipsoid are superimposed. (e) Wrapped diffusion ellipsoid viewed along the principal axes.
pool diameter is typically 10 to 30 voxels and the typical distance between the pools is 20 to 40 voxels. Random walkers should travel more than 40 voxels to reach the asymptote in terms of equation (2). On the other hand, the 3-D mean square displacement of the walkers, \( \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle \), is 1800 at \( \tau = 10,000 \) (Figure 6a). Thus, the characteristic travel distance of the walkers is 1800\(^{1/2} \approx 42 \) voxels at \( \tau = 10,000 \). Because 42 voxels are larger than the typical values of the pool diameter and the distance between pools, it is reasonable to conclude that the mean square displacement reaches the asymptote for \( \tau > 10,000 \). The undesirable early stage (i.e., \( \tau < 10,000 \)) having a convex mean square displacement should be eliminated from the calculation of normalized diffusivity because the time derivative (equation (2)) has not yet reached the asymptote value. Thus, to obtain a reliable diffusion ellipsoid, the time derivative was calculated using the very last portion of the mean square displacement time series data for all simulations of the present study, namely, the slope value of \( \langle x(t) \rangle \) between the maximum time step and 75% of it was employed. For example, the normalized diffusivity was calculated using the difference of \( \langle x(t) \rangle \) at \( \tau = 30,000 \) and \( 30,000 \times 0.75 = 22,500 \) for the Berea sandstone.

[20] Figure 6a suggests that the diffusion ellipsoid is prolate in the \( z \)-direction because the mean square displacement in the \( z \)-direction is significantly larger than those in the \( x \)- and \( y \)-directions. The final positions of all the walkers are shown in Figure 6b. The overall shape of the diffusion front can be seen. Although Table 1 indicates that the diffusion ellipsoid is prolate for the Berea sample, it is difficult to see the prolate nature in Figure 6b because the degree of the diffusive anisotropy is small (i.e., \( C \approx A \)). The unwrapped and wrapped diffusion ellipsoids are shown in Figures 6c and 6d, respectively. The prolate shape of the diffusion ellipsoid in Figure 6a is confirmed in Figures 6c and 6d. The prolate shape of the ellipsoid can be seen more clearly when it is viewed from the principal axes (Figure 6e).

[21] We carried out a random walk simulation in the free lattice space (i.e., porosity 100 vol %), which theoretically yields a complete sphere with a radius of unity for the diffusion ellipsoid. The results of DelloipsoidM6.nb showed that the fitted major and minor axis values of the normalized diffusivity ellipsoid averaged over 400,000 walkers were \( C = 1.01 \) and \( A = 0.99 \), respectively. These are very close to the theoretical value of unity, demonstrating that our random walk simulations were performed reliably.

[22] Results for the Shirahama sandstone sample are shown by Figure 7 and Table 1. The CPU time of DelloipsoidM6.nb required for this sample was 14 h for the PC used. The normalized diffusivity was calculated using the difference between \( \langle x(t) \rangle \) at \( \tau = 300,000 \) and 300,000 \( \times 0.75 = 225,000 \). The distinguishing feature of Figure 7 as compared with Figure 6 is that the oblate shape of the diffusion ellipsoid compressed in the \( z \)-direction. The oblate shape is evident from the significantly small mean square displacement in the \( z \)-direction as compared with those in the \( x \)- and \( y \)-directions (Figure 7a), from the oblate shape of the diffusion front (Figure 7b), from the small normalized diffusivity value at the high-latitude (i.e., low-\( \theta \)) zone (Figure 7c), and from the shape of the diffusion ellipsoid (Figures 7d and 7e).

[23] Results for the Ito pumice sample are shown in Figure 8 and Table 1. Because the pore size of the vesicular sample is much larger than that of the Berea sample, as many as 400,000 time steps were required to make the mean square displacement reach the asymptote line (Figure 8a). Figures 8a–8c show that the diffusion ellipsoid is prolate in the \( z \)-direction, as can be easily predicted by the clearly elongated shape of the individual pores in Figure 4c. The large elongation factor (\( f_0 = 2.32 \) and \( f_1 = 2.60 \), see Table 1) of the pores yields the following important point regarding the shape of the prolate diffusion ellipsoid. The constriction of the ellipsoid occurs in the direction of the minor and intermediate principal axes (i.e., \( a \)- and \( b \)-axes), as depicted in Figures 8d and 8e. Thus, the diffusion ellipsoid is no longer convex, like what has been reported for highly anisotropic porous clay gels [Porion et al., 2001, 2003; de Azevedo et al., 2007].

[24] Results for the Tako sandstone sample are shown in Figure 9 and Table 1. Figures 9a–9c show that the diffusion ellipsoid is oblate, compressed in the \( z \)-direction. The large degree of the compression (\( f_0 = 0.77 \) and \( f_1 = 0.61 \), see Table 1) of the sample reveals a remarkable feature of the shape of the oblate diffusion ellipsoid. The constriction of the ellipsoid occurs in the direction of the minor principal axis (i.e., \( a \)-axis), as depicted in Figures 9d and 9e. The diffusion ellipsoid is no longer convex, as in the case of the Ito pumice sample.

[25] Results for the bead pack sample without the affine transformation (i.e., \( f = 1 \)) are shown in Figure 10 and Table 1. The isotropic diffusion front in Figure 10b and the spherical diffusion ellipsoid in Figures 10d and 10e indicate that the pore structure of the bead pack is isotropic. Although Figures 10a and 10c show slight anisotropy, it is reasonable to neglect the anisotropy because \( A = 0.577 \) is very nearly equal to \( C = 0.595 \) (Table 1).

[26] A relatively simple thresholding in which all voxels below (or above) a chosen X-ray linear absorption coefficient value are assigned to pore space (or solid) was employed to extract a binary image set in the present study. Although there are more advanced methods for extracting a pore space [e.g., Oh and Lindquist, 1999; Arns et al., 2001], we chose this simple method because it yields acceptable pore characteristics as follows. Following Nakashima [2000], Polak et al. [2003], and Zhu et al. [2007], a medical (i.e., low-resolution) X-ray CT scanner was used to measure the tortuosity of each rock sample prepared from the identical block from which the small cylindrical CT sample was cored (Y. Nakashima, unpublished data, 2008). Invasion of nonsorbing iodine ions from a KI-bearing filter paper on one face of the water-saturated sample into the sample was monitored by the medical CT. For example, the Gaussian distribution of iodine concentration within the sample was fitted to obtain a tortuosity of \( \tau \approx 6 \) for the Berea sample. No significant anisotropy was detected, presumably owing to the inevitable low precision of this method. According to Table 1, the random walk simulations suggest that the tortuosity of the Berea sample falls within \( 1/C \approx 6.25 \) and \( 1/A \approx 7.04 \). Thus, results of the random walk simulations agree well with those of the laboratory diffusion test, indicating the spatial resolution and thresholding method of the present study are acceptable. As for the bead pack image set of \( \ell = 53 \) \( \mu \)m, we have shown that our thresholding
Figure 7. Same as Figure 6 but for the Shirahama sandstone and with snapshot of the 400,000 walkers at $\tau = 300,000$. 
Figure 8. Same as Figure 6 but for the Ito pumice and with snapshot of the 400,000 walkers at $\tau = 400,000$. 
Figure 9. Same as Figure 6 but for the Tako sandstone and with snapshot of the 400,000 walkers at $\tau = 600,000$. 
Figure 10. Same as Figure 6 but for a bead pack and with snapshot of the 400,000 walkers at $\tau = 50,000$. 
method and spatial resolution are sufficient to reproduce the experimentally measured tortuosity and surface-to-volume ratio values by the random walk simulations [Nakashima and Watanabe, 2002]. The laboratory KI diffusion tests for the Ito pumice sample showed that the tortuosity parallel to the pore elongation direction and that normal to the pore elongation direction were ~4 and ~13, respectively. According to the random walk simulations for the pumice sample (Table 1), the tortuosity values for the corresponding directions are $1/C \approx 2.1$ and $1/(AB)^{1/2} \approx 5.8$, respectively, which are less than those obtained by the laboratory tests. The discrepancy is probably derived from the simple thresholding method and relatively low spatial resolution of the CT system employed. Similar discrepancy of the tortuosity was also observed for Shirahama and Tako samples, suggesting that submicrometer pore structure was not accurately imaged. However, the maximum-to minimum diffusivity ratio by the KI diffusion experiment agrees well with the $(BC)^{1/2}/A^{-1}$ or $(AB)^{-1/2}$ values of the oblate/prolate diffusion ellipsoids in Table 1 ($\sim 13/4 \approx 3$ versus $5.8/2.1 \approx 2.8$ for the Ito sample, $\sim 2$ versus $1.7$ for the Shirahama sample, and $\sim 3$ versus $2.8$ for the Tako sample). Thus, it is reasonable to conclude that the gross anisotropy of the pore structure derived from the detectable large pores was successfully obtained by the employed CT apparatus with the simple thresholding method, which is sufficient for the present study because the purpose is to present the principle of the new method to calculate the diffusion ellipsoids quickly, to evaluate the general trends in the diffusive anisotropy in relation to the degree of the rock deformation, and to discuss the cause of the constriction of diffusion ellipsoids rather than to reproduce the individual diffusivity values measured by the laboratory experiments.

[27] When the bead pack image was elongated or compressed by a factor $f$ in the $z$-direction, as shown in Figure 5, the spherical diffusion ellipsoid of Figure 10d broke down. The dependence of the shape of the diffusion ellipsoid on the $f$ value is shown in Figure 11. The direction of the affine transformation is along the $z$-direction. Therefore, the resultant diffusion ellipsoid for the transformed CT image should be symmetric with respect to the $z$-axis, and independent of $f$. The $\theta$ dependence of the ellipsoid averaged over $\phi$ values is shown in Figures 11a and 11b for elongation and compression, respectively. The polar representations of the diffusion ellipsoids, Figures 11a and 11b, clearly show that the sphere becomes distorted (prolate or oblate) if the $f$ value differs from unity. It should be noted that when the $f$ value exceeds a critical value, the constriction of the ellipsoid appears in the direction of minimum diffusivity (i.e., $\theta = 90^\circ$ for Figure 11a and $0^\circ$ for Figure 11b). We express the deviation of the shape of the ellipsoid.

Figure 11. Diffusion ellipsoid for random walk in the percolated pore cluster of the bead pack for various $f$ factors. The ellipsoid was averaged over 200,000 walkers. (a) Polar representation of the averaged diffusion ellipsoid for the elongated (i.e., $f = 1.0, 1.3, 1.9, 2.9,$ and 5.0) bead pack images. (b) Polar representation of the averaged diffusion ellipsoid for the compressed (i.e., $f = 0.2, 0.3, 0.4, 0.54,$ and 0.7) bead pack images. (c) Degree of anisotropy of self-diffusivity $D_z/D_{xy}$ plotted for various values of elongation/compression $f$ for the bead pack CT image. The case for $f = 1$ (i.e., Figure 10) is indicated by an arrow. The solid line is a guide for the eye. The four ellipsoid regimes with three boundaries (horizontal broken lines) are illustrated.
diffusion ellipsoid from the isotropic sphere by a single quantity, $D_z/D_{xy}$, where $D_z$ is the normalized diffusivity in the $z$-direction (i.e., normalized diffusivity for $\theta = 0^\circ$) and $D_{xy}$ is the normalized diffusivity averaged on the $x$-$y$ plane (i.e., normalized diffusivity averaged over $\phi = 0$ to $359^\circ$ at $\theta = 90^\circ$). The quantity, $D_z/D_{xy}$, is greater than unity for image elongation, and less than unity for image compression. The $D_z/D_{xy}$ versus $f$ relationship is shown in Figure 11c for a wide range of $f$ values. Four regimes were identified in terms of the shape of the diffusion ellipsoid. The ellipsoids for $f = 1.9$ and 0.54 in Figure 5 are located at the boundary of the regimes for with and without constriction.

Results for rock samples having nonunity $f_1$ values are shown in Figure 12. Both the direction of the intrinsic pore diameter anisotropy inferred from the autocorrelation ellipsoid (Table 1) and the direction of the affine transformation lie along the $z$-direction. Thus, it is reasonable to characterize the diffusion ellipsoid shape of the rock samples using the same quantity, $D_z/D_{xy}$, as in Figure 11. The pore structure, and hence the $D_z/D_{xy}$ versus $f_1 \times f$ curves, differ from sample to sample. However, all curves include $(f_1f, D_z/D_{xy}) = (1, 1)$ owing to the properly chosen $f_1$ values listed in Table 1. All rock samples showed a common feature: the same four regimes as in Figure 11 appeared depending on the $f_1f$ values. It is noteworthy that the regime transition occurs at a common value with respect to $D_z/D_{xy}$.

The transition from the prolate ellipsoid without constriction to that with constriction occurs at $D_z/D_{xy} = 1.49, 1.50, 1.54, 1.37$ for the bead pack, Berea, Ito, Shirahama, and Tako samples, respectively (average 1.5). The transition from the oblate ellipsoid without constriction to that with constriction occurs at $D_z/D_{xy} = 0.64, 0.66, 0.68, 0.60,$ and 0.67 for the bead pack, Berea, Ito, Shirahama, and Tako samples, respectively (average 0.65). The boundaries at $D_z/D_{xy} = 1.5$ and 0.65 are indicated in Figure 12. Because the reciprocal of 0.65 is nearly equal to 1.5, we can conclude that the constriction occurs when the maximum to minimum diffusivity ratio of the diffusion ellipsoid exceeds $\sim 1.5$.

5. Discussion

One of the purposes of the present study is to confirm the hypothesis [Yokoyama and Nakashima, 2005] that the pore structure anisotropy is responsible for the anisotropic diffusivity. It should be noted that there are two independent measures for the pore structure anisotropy of porous media: anisotropy of the pore diameter and that of the pore network. For example, in Figure 1, the former is the anisotropy of the pipe diameter, and the latter is the anisotropy of the geometrical tortuosity of the pipes. The two measures can be expressed as $f_0$ and $f_1$, respectively. The pore network anisotropy (not pore diameter anisotropy) is responsible for the long-distance diffusive anisotropy calculated by the asymptote of equation (2). It is reasonable to assume that initially the pore diameter and pore network were as isotropic as those in the randomly packed bead pack, and were significantly elongated or compressed in the $z$-direction during the geological deformation processes. This assumption is reasonably supported by that (1) the $f_0$ value is almost identical to $f_1$ value for each sample (Table 1) and (2) the direction of the elongation/compression of the autocorrelation ellipsoid is the $z$-direction identical to the direction of the pore network deformation. Thus, it can be concluded that the pumice and sandstone samples are elongated or compressed in the $z$-direction, and the degree of the geological deformation is given by the almost identical values $f_0$ and $f_1$.

The hypothesis that the pore structure anisotropy is responsible for the anisotropic diffusivity predicts that the direction of the geological deformation agrees with the direction of the major (or minor) principal axis of the prolate (or oblate) diffusion ellipsoid. As described, the direction of the geological deformation is the $z$-direction for all rock samples. The parameters of the diffusion ellipsoids listed in Table 1 clearly show that the direction of the major or minor principal axis of the diffusion ellipsoid is almost parallel to the $z$-direction (i.e., $\theta \approx 0^\circ$). For example, $\theta = 19^\circ$ for the major axis of the Berea sample, $\theta = 1^\circ$ for the minor axis of the Shirahama sample, $\theta = 1^\circ$ for the major axis of the Ito sample, and $\theta = 2^\circ$ for the minor axis of the Tako sample.
The anisotropy of the sandstone samples is not very obvious by visual inspection in the 3-D CT images in Figures 3 and 4. However, we clearly detected the anisotropy of the pore structure, which is seen to be oblate or prolate with respect to the bedding plane in Figures 6, 7, and 9 and Table 1. For example, a prolateness in diffusion of as small as \((C - A)/C = 11\%\) was successfully detected for the Berea sandstone sample. The smooth \(D_z/D_{xy}\) versus \(f_1 f_2\) curves of Figure 12 free of undesirable stochastic fluctuation show that a much lower anisotropy can be detected if a sufficiently large number of random walkers are employed. This high sensitivity to pore anisotropy suggests that the present CT-based method would be particularly effective in evaluating rocks with relatively low anisotropy, for which the conventional technique [e.g., Ohlsson and Neretnieks, 1995] fails to detect the anisotropy because of the low accuracy.

A diffusion ellipsoid with constriction was observed for water self-diffusion in synthetic clay gels using nuclear magnetic resonance spectroscopy [Porion et al., 2001, 2003; de Azevedo et al., 2007]. However, the mechanism of the generation of this pinched-in ellipsoid has not been studied in detail. In the present study, we report for the first time that the constriction occurs for natural porous rocks as well. We also discuss the generation mechanism in detail by analyzing highly anisotropic pore CT images produced by systematic uniaxial elongation/compression operations using affine transformation. According to Table 1, the diffusion ellipsoid constriction occurs for samples with a very large \(f_1\) value (Ito pumice) or very small \(f_2\) value (Tako sandstone). This suggests that the constriction appears when the pore is substantially elongated or compressed. This is strongly supported by the systematic calculations of diffusion ellipsoids for uniaxially deformed pore images (Figures 11 and 12). Figures 11 and 12 demonstrate that (1) the constriction occurs in the direction of the minor principal axis even for the Berea, Shirahama, and bead pack samples when they are elongated or compressed significantly and that (2) the constriction occurs when the maximum to minimum self-diffusivity ratio of the diffusion ellipsoid exceeds a critical value of \(\sim 1.5\). Thus, the constriction is not particular to the Ito and Tako samples, but can be found in any porous geomaterial showing strong diffusive anisotropy.

On the basis of the conventional magnetic resonance imaging studies, a microscopic approach (i.e., pore-scale random walk simulating self-diffusion) was employed in the present study for the evaluation of the diffusion anisotropy. There is another possible approach for the diffusion anisotropy study, namely, macroscopic or continuum method using a parabolic partial differential equation with a diffusion tensor of rank 2 [e.g., Crank, 1975]. In the latter approach, the directional mean square displacement is not calculated, but a macroscopic concentration gradient is introduced as a boundary/initial condition to drive the diffusion. The introduced concentration gradient would bias the movement of diffusing species to follow the gradient, and thus care must be taken when one compare the random walk method with the continuum method. For example, it is possible to obtain an anisotropic diffusion front without constriction such as Figure 8b by numerically solving the parabolic partial differential equation. However, it is difficult to calculate the 3-D shell of the direction-dependent diffusivity with constriction (e.g., Figure 8d) by the continuum method because the macroscopic concentration gradient distorts the direction of the diffusion flux vector.
[35] Thermal diffusivity or thermal conductivity also is an important transport property of rocks [e.g., Gueguen and Palciauskas, 1994]. The thermal energy diffuses through rock-forming minerals, and the thermal diffusivity differs among minerals and pores. The thermal conduction phenomenon obeys a parabolic partial differential equation as well as the material diffusion phenomenon. Thus, the present study predicts that ellipsoid constriction of thermal diffusivity also would occur if the material possesses high anisotropy with respect to thermal conductivity. Examples include pumice made of volcanic glass (conductor) and air-filled pore (insulator) and graphite schist made of graphite (conductor) and silicate (insulator). Assuming zero conductivity for the air-filled pore, a preliminary random walk simulation on the conductive solid framework was performed for the Ito pumice image set of Figure 4c using the same number of walkers and same time steps as Figure 8. The obtained ellipsoid of the thermal diffusivity clearly showed the constriction in the direction normal to the z-axis, supporting the prediction.

[36] It should be noted that the CT-based method for anisotropy evaluation requires much less time than the conventional laboratory method [e.g., Van Loon et al., 2004; Yokoyama and Nakashima, 2005] using a diffusion cell and cut samples. For example, as many as 90 × 360 + 1 = 32,401 diffusivity data points were acquired in 4.4 h for Figure 6. It is practically impossible to obtain a data set of the same magnitude by conventional laboratory diffusion tests using a diffusion cell and cut samples. Unfortunately although synchrotron-based submicrometer imaging systems are being developed [Promentilla et al., 2008], the current state of the art of X-ray CT is not always satisfactory in terms of the spatial resolution. Thus, the conventional diffusion cell method would not be immediately replaced with the CT-based method described in this study. However, the current CT technology enables us to accurately image rock pores larger than several or several tens of micrometers. Thus, the CT-based method can contribute to the quick analysis of the anisotropy of the diffusion through relatively large pores.

6. Conclusions

[37] High-resolution 3-D pore images were obtained by microfocus and synchrotron X-ray CT for one pumice and three sandstone samples. Nonsorbing lattice random walk simulations were performed in a percolated pore cluster of the CT images to calculate the mean square displacement along an arbitrary direction in 3-D space. Direction-dependent self-diffusion coefficients were calculated by taking the time derivative of the mean square displacement projected on any given direction. The second moment was computed for the direction-dependent self-diffusivity data to obtain the principal axes of the diffusion ellipsoid. The two-point autocorrelation ellipsoid was also calculated for the percolated pore cluster of each rock sample to estimate the pore diameter anisotropy. The pore network anisotropy was estimated by calculating the diffusion ellipsoid for uniaxially elongated or compressed rock images. The degree and direction of the geological deformation of the samples estimated by the pore diameter anisotropy analysis agreed well with those estimated by the pore network anisotropy analysis. We found that the direction of the geological deformation coincided with the direction of the major (or minor) principal axis of the prolate (or oblate) diffusion ellipsoid for each sample. Thus, it can be concluded that the deformation-induced pore structure anisotropy is responsible for the anisotropy of the diffusive transport properties. For the highly anisotropic Ito pumice and Tako sandstone samples, the shape of the diffusion ellipsoid was significantly distorted (constricted in the direction of minimum diffusivity), and no longer convex ellipsoidal. Systematic calculations of the diffusion ellipsoids for synthetic 3-D rock images uniaxially elongated or compressed using the affine transformation were performed to explore the generation mechanism of this remarkable constriction of the diffusion ellipsoid. The results revealed that the constriction is not particular to the Ito and Tako samples, but can occur for any rocks when the maximum to minimum self-diffusivity ratio of the diffusion ellipsoids exceeds a critical value of ~1.5. We offer the DiffellipsoidMrob program used to calculate the diffusion ellipsoids on the Internet to facilitate the X-ray CT approach to groundwater hydrology.

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