Japan Association of Mineralogical Sciences

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RESEARCH TOPIC FROM JAMS: ANALYSES OF DYNAMICS AND STRUCTURES OF SILICATE LIQUIDS AND GLASSES VIA CLASSICAL MOLECULAR DYNAMICS SIMULATIONS.

Fumiya Noritake[1]

Silicate liquids are not minerals but interest mineralogists sometimes. However, their lack of periodicity makes it difficult to investigate their dynamics and structural properties. Molecular dynamics simulation (MD) is not real, just numerical simulations, but enables us to approach the behaviour of atoms in silicate liquids.

It has been more than 40 years since force-field MD simulations of silicate liquids were conducted (Woodcock et al. 1976; Matsui and Kawamura 1980). At that time, the systems consisted of several hundreds of particles, as in the recent ab-initio MD simulations (Ho et al. 2023). Force-field MD simulation recently can handle 10^{4-5} particles even though simulations are performed on "personal" computers. An increase in system size enables us not only to avoid finite-size effects but also to obtain well-statistically averaged data even with slightly complex properties. Here, I introduce some analysis of dynamics and structural properties from MD simulation data of simple silicate liquids/glasses.

Diffusion dynamics of network-forming elements in silicate liquids

Elemental processes of diffusion in silicate liquids are complicated, especially for network-forming elements. Diffusion of network modifying elements, such as alkali ions, is considered to take place by thermal hopping events (Horbach et al. 2001). However, network-forming elements such as Si and O, seem to have several processes for diffusion.

I have performed MD simulations of $Na_2O{\cdot}nSiO_2$ (n = 1, 2, 3, and 4) liquids to analyze the diffusion mechanism of network-forming elements (Noritake 2021). Note that the system consists of approximately 10^4 particles. Many interesting insights about diffusion mechanisms have been obtained, here are the most important results. Mean square displacement (MSD) is used to calculate self-diffusivity. The MSD increases linearly at first. This time region is called the ballistic regime and represents thermal vibration. After the regime, MSD becomes constant for some time. This time region is called the cage regime. After that, the atom starts to diffuse. Usually, the MSD for diffusivity calculation is averaged over time, however, we can clarify the diffusion mechanism by averaging specific groups. FIGURE 1 shows the difference in the mean square displacement of silicon with or without a bond-exchange event in metasilicate and tetrasilicate liquids. In metasilicate, Si atoms can diffuse to some extent without bond-exchange events like the reptation of organic polymers. In contrast, Si atoms in tetrasilicate cannot diffuse without the bond-exchange events. The MSD value of an after-bond exchange Si atom in the cage regime is higher than that of the overall average. Thus, Si diffuses via bond-exchange events in acidic silicate liquids, while reptation also contributes to diffusion in basic silicate liquids.

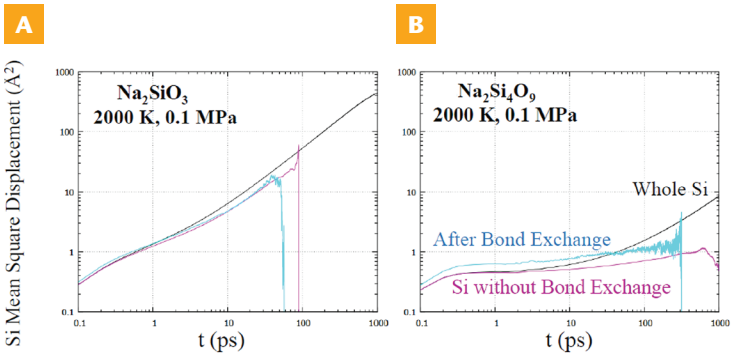

FIGURE 1 Plots of mean square displacement of Si in (**A**) sodium metasilicate and (**B**) sodium tetrasilicate liquids. Black and magenta lines represent whole Si atoms and Si atoms with no bond-exchange events. The cyan line represents mean square displacement with setting the origin time as the end of bond-exchange events.

Geometrical approach to diffusion pathway of alkali ion

Alkali ions in silicate glass are considered to diffuse via certain pathways (Greaves 1985). The mixed alkali effect, which decreases the diffusivity of alkali elements in silicates with two or more alkali species, is a well-known anomaly in silicate liquids. Habasaki et al. (1995) found that the site exchange between different types of alkali ions is significantly slower than the distinct-part of the van Hove function. If the "blocking" is the cause of the mixed alkali effect, each alkali ion should homogeneously exist in the pathway. In this case, the subdivision method of space is effective. The Voronoi diagram is frequently used in MD studies; however, here I show the interesting result using the Delaunay diagram, the dual graph of the Voronoi diagram. I have performed MD simulations of $0.3x{Na_2O}{\cdot}0.3(1-x){K_2O}{\cdot}0.7SiO_2$ glasses to analyze the geometrical information of the diffusion pathway. The simulation space is subdivided into tetrahedra considering oxygen atoms as discrete points. The circumscribed sphere of a tetrahedron includes R cation, a sphere denoted as a simplex sphere R_O. If two simplex spheres share the same R cation, they are considered connected. More details of the MD simulation can be found in Noritake and Naito (2023).

FIGURE 2 shows snapshots of Na_O simplexes in sodium-potassium silicate glass. The snapshots are made using VESTA 3 (Momma and Izumi 2011). Garnet red and yellow simplex spheres represent whether or not they

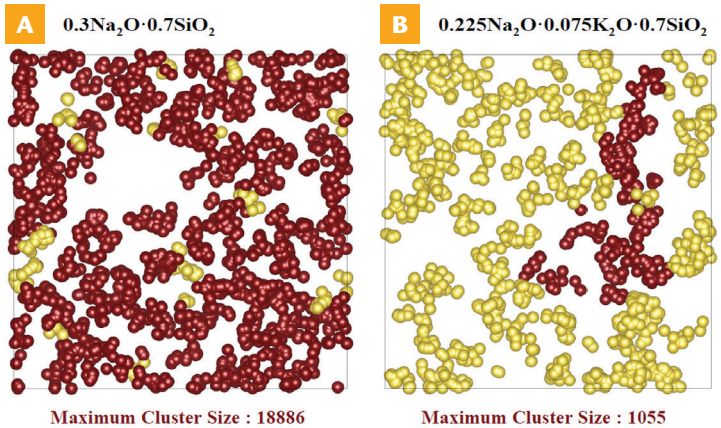

FIGURE 2 Snapshots of distribution of Na_O simplex in two compositions. Red and yellow spheres represent simplex spheres that belong to the dominant cluster or not, respectively. Sphere size represents the average simplex sphere radius. Only simplex spheres in the region of 0.8 to 1.0 depth are shown.

1 Graduate Faculty of Interdisciplinary Research, University of Yamanashi
Email: fnoritake@yamanashi.ac.jp

Swiss Geological Society

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SWISS GEOLOGICAL SOCIETY

It is a pleasure to recognize excellent work by young scientists. This provides a glimpse where the future of research might be going and how young talents tackle a wide range of problems. The "Best Master's Thesis Award" from the Swiss Geological Society and the "Paul Niggli Medal" are two prizes that are awarded annually during the Swiss Geoscience Meeting. The Swiss Geoscience meeting was held in Mendrisio on November 17th and 18th, 2023. Since the 100th birthday of Paul Niggli in 1988, the "Paul Niggli Medal" has been awarded by the Paul Niggli Foundation. This medal is Switzerland's most prestigious "young scientist award" in Earth Sciences; it is open to researchers that are up to 35 years old or have received their doctorate in the last 6 years, and work in the field of mineralogy, geochemistry, petrology, resource geology, or solid-earth geophysics. For further information, see the awards page on the SGS website at https://geolsoc.ch/en/awards/.

Below are short citations of the awardees. The committees of the two awards are looking forward to receiving again nominations of outstanding young scientists for these prizes.

With best wishes

Jörg Hermann (President of the Swiss Geological Society)

Cont'd from page 274

belong to the dominant cluster or not, respectively. In sodium silicate glass, about 90% of NaO simplexes belong to the dominant cluster. However, the clusters are divided into subclusters by substituting sodium quarter by potassium. The maximum size cluster becomes less than 10% of simplexes. Thus, potassium ions distribute homogeneously in sodium silicate glass and disconnect the diffusion pathway of sodium ions.

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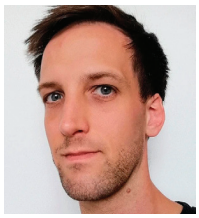
CHRISTIAN RENGGLI RECEIVES THE 2023 PAUL NIGGLI MEDAL



The Board of the Paul Niggli Foundation decided, in their annual meeting of June 19, 2023, to award the Paul Niggli Medal for the year 2023 to Christian Renggli in recognition of his outstanding research using experimental methods to understand the properties of gas–solid reactions in volcanic systems on Earth, the Moon, and Mercury.

Maria Schönbächler (ETH Zürich)
On behalf of the Foundation Council of the Paul Niggli Stiftung

The Paul Niggli Medal is Switzerland's most prestigious award for young earth scientists who made outstanding contributions in the research fields of mineralogy, geochemistry, petrology, resource geology, or solid-earth geophysics. The Paul Niggli Medal honours and supports young ambassadors of Swiss geoscience, who are either Swiss citizens or obtained at least two of their academic degrees in the Swiss university system (BSc or MSc and usually their PhD).

The laudatio from Prof. Dr. Stephan Klemme (Universität Münster) and response of Dr. Christian Renggli (Max-Planck Institute for Solar System Research, Göttingen) can be found in the Swiss Journal of Geosciences volume 117 (1), and is freely available at https://doi.org/10.1186/s00015-024-00451-w.

2023 BEST THESIS AWARD

The winner of the 2023 Best Thesis Award from the Swiss Geological Society is **Jonathan Pople** from the University of Lausanne, Switzerland, for the work: **"Epibionts and trace fossils on stem- and crown-group euarthropod carapaces from the Early Ordovician Fezouata Shale."** The committee was impressed with the comprehensive and modern approach to this topic, the exceptional graphic display, and the wider implications for the evolution of life. The following is a citation from the nomination letter of supervisor Professor Allison Daily:

"Jonathan made a comprehensive and coherent assessment of both the paleoecological and taphonomic implications of these important fossils. For example, he develops a logical and convincing argument for the syn-vivo relationship between sessile filterfeeding brachiopods and a giant swimming arthropod, with these attached brachiopods basically getting a free ride on the cephalic carapaces of living radiodonts. This is a highly uncommon symbiosis for brachiopods and is a unique systematic association in the fossil record. He was also able to conclude that the epibiotic behaviour of many Fezouata Shale organisms was likely the result of the seafloor being quite soft and muddy with only rare stable solid substrates, creating an evolutionary pressure for epibiotic and symbiotic behaviour, supported both by his fossil data and sedimentary observations. Jonathan not only identified and quantitatively characterised the trace fossils, but also a developed a fascinating model for their unusual preservation, based on his observations and data, and comparison with similar trace fossil assemblages known from other Cambrian lagerstätten."

Jörg Hermann (SGS president)