Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

U04-01 Room:IC Time:May 27 09:15-09:45

Sub-seafloor methane biogeochemistry and unseen archaeal methanotrophic processes

TAKANO, Yoshinori[1]*

[1] JAMSTEC

Microorganisms play a central role in the global methane cycle for both production and consumption. Methanogenic archaea (methanogens) are a phylogenetically diverse group of strictly anaerobic Euryarchaeota, which grow with the enzymatic formation of methane from H2 plus CO2, acetate, and C1 compounds (e.g. methanol, methylamine) present in anaerobic environments. Kaneko et al. (2014) reported the analytical development for coenzyme factor 430, critical cofactor for biological methanogenesis and reverse-methanogenesis (occasionally), by using high performance liquid chromatography / electrospray ionization mass spectrometry (HPLC/ESI-MS/MS) on the optimized multiple reaction monitoring method during the order of 0.1-1.0 femto mol.

On the other hand, the anaerobic oxidation of methane (AOM) in marine sediments is an important microbial process in the carbon cycle and also greenhouse gas emission constraints. Since the first report of 13C-depleted lipids mediated by modern anaerobic methanotrophic archaea (ANME) consortium, the molecular carbon isotopic signatures have been recognized as an indicator of ongoing microbial methanotrophy [e.g., Hinrichs et al., 1999; Elvert et al., 1999]. Cold seep ecosystems, a biological hot spot for ANME communities, is an ideal natural laboratory for the study of methane biogeochemistry and microbial anaerobic methanotrophy driven by modern ANME communities [e.g., Knittel and Boetius, 2009 and literatures therein]. Since laboratory-based culture and isolation of ANME are currently difficult, the fate of sub-seafloor 13C-depleted methane emission is still unclear on their biosynthetic pathways during anaerobic oxidation process.

[References]

Elvert et al., 1999. Anaerobic methane oxidation associated with marine gas hydrates: superlight C-isotopes from saturated and unsaturated C-20 and C-25 irregular isoprenoids. Naturwissenschaften, 86, 295-300.

Kaneko et al., 2014. Quantitative analysis of coenzyme F430 in environmental samples: a new diagnostic tool for methanogenesis and anaerobic methane oxidation. Analytical Chemistry, 86, 3633-3638.

Knittel, K., Boetius, A., 2009. Anaerobic oxidation of methane: progress with an unknown process. Annual Review of Microbiology 63, 311-334.

Hinrichs et al., 1999. Methane-consuming archaebacteria in marine sediments. Nature, 398, 802-805.

Keywords: Sub-seafloor methane biogeochemistry, global methane cycle, Archaea, ANME (ANaerobic MEthanotroph)

U04-02 Room:IC Time:May 27 09:45-10:15

Exploring life at its limits in the subseafloor biosphere through scientific ocean drilling

INAGAKI, Fumio[1*] ; HINRICHS, Kai-uwe[2] ; D'HONDT, Steven[3] ; IODP, Expeditions 329 and 337 scientists[4]

[1]Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology, [2]MARUM and Department of Geosciences, University of Bremen, [3]Graduate School of Oceanography, University of Rhode Island, [4]IODP Expedition 329 and 337 Scientists

Deep drilling of marine subsurface offers unique opportunities to explore how life persists and evolves in the Earth's interior ecosystems. There are very few natural environments on Earth's surface where life is absent; however, the limits to life are expected in the subsurface world. Processes that mediate genetic and functional evolutions of the deep life may be very different to those in the surface ecosystems on our planet. Previous studies of the subseafloor sedimentary biosphere have demonstrated that activity of microbial communities is generally extremely low, mainly because of the limit of nutrient and energy supply. However, the limits and habitability in deep subseafloor sediments have still remained largely unknown; subseafloor microbial biomass, activity and functional/taxonomic/physiological diversity are possibly constrained significantly by each or the combination of multiple geophysical and geochemical factors, such as temperature, pH, pressure, salinity, porosity, and availability of nutrient and energy. In addition, understanding of the limits and habitability of life in the deep subseafloor biosphere may hold the clue to the issue regarding the origins and evolution of subseafloor life and its ecological consequences in Earth's history.

The Integrated Ocean Drilling Program (IODP) Expeditions 329 and 337 were the microbiology and biogeochemistry-dedicated scientific ocean drilling, targeting on very distinct oceanographic settings; in 2010, using the *JOIDES Resolution*, Expedition 329 explored deep-water sediments (water depth: 3,740~5,695m, sediment depth: ~131m) down to the basement at 7 sites in the ultra-oligotrophic South Pacific Gyre. During Expedition 337 in 2012, the *Chikyu* explored ultra-deep sediments (water depth: 1,180m, sediment depth: ~2,466m) associated with deeply buried coalbeds in the northwestern Pacific coast. The samples and data collected during these drilling expeditions, as well as rapid technological developments, provided unprecedented opportunities to study the limits and habitability of life in the subseafloor sedimentary biosphere.

The number of microbial cells is measured by newly developed cell separation and fluorescent image-based cell count techniques, revealing that cell abundances in both ultra-oligotrophic and deep coalbed-associated sediment samples are several orders of magnitude lower than those previously observed in shallow sediments of the ocean margins. The finding of very small microbial populations under two distinct extreme subseafloor conditions leads to subsequent questions: What are the environmental constraints for habitability of subseafloor life? What are ecological roles of subseafloor microbial activity in biogeochemical carbon and other elemental cycles? What are genetic and metabolic functions and its diversity of microbial communities? How and why can they live in such deep and extremely energy-limited conditions?

Keywords: IODP, The deep subseafloor biosphere

U04-03 Room:IC Time:May 27 10:15-10:45

Unprecedented Zipangu Underworld of the Moon/Mars Exploration (UZUME)

HARUYAMA, Junichi[1*] ; KAWANO, Isao[1] ; IWATA, Takahiro[1] ; YAMAMOTO, Yukio[1] ; NISHIBORI, Toshiyuki[1] ; ISHIHARA, Yoshiaki[1] ; YAMAMOTO, Keiko[1] ; NAGAMATSU, Aiko[1] ; MOROTA, Tomokatsu[2] ; NISHINO, Masaki[2] ; SAIKI, Kazuto[3] ; HASHIZUME, Ko[3] ; KOBAYASHI, Kensei[4] ; YOKOBORI, Shin-ichi[5] ; HASEBE, Nobuyuki[6] ; HASENAKA, Toshiaki[7] ; MIYAMOTO, Hideaki[8] ; SHIMIZU, Hisayoshi[8] ; KOMATSU, Goro[9] ; SHIRAO, Motomaro[10] ; OSHIGAMI, Shoko[11] ; MICHIKAWA, Yuichi[12] ; YAMAMOTO, Satoru[13] ; YOKOTA, Yasuhiro[13] ; KOBAYASHI, Takao[14] ; MICHIKAMI, Tatsuhiro[15]

[1]Japan Aerospace Exploration Agency, [2]Nagoya University, [3]Osaka Univeristy, [4]Yokohama National University, [5]Tokyo University of Pharmacy and Life Sciences, [6]Waseda University, [7]Kumamoto University, [8]University of Tokyo, [9]Universita d'Annunzio, [10]Institute of Planetary Geology, [11]National Astronomical Observatory of Japan, [12]National Institute of Radiological, [13]National Institute for Environmental Studies, [14]Korea Institute of Geoscience and Mineral Resources, [15]Kindai University

Japanese lunar explorer SELENE (Kaguya) discovered gigantic vertical holes/pits of several 10 m to 100 m in diameters and depths in the Marius Hills, Mare Tranquillitatis, and Mare Ingenii of the Moon. These holes are possibly skylights of underground large caverns such as lava tubes. Similar hole/pit structures have been also found on the Mars. The caverns connecting to the Martian holes may be the best place for Martian lives to emerge, evolve and survive because of their safer conditions than the Martian surface.

Exploration into the lunar/Martian holes/pits and underlying subsurface caverns will probably provide valuable information about emergence and evolution of terrestrial and extra-terrestrial lives. We are now studying the missions and systems to investigate lunar and Martian holes and furthermore subsurface caverns associating to the holes/pts. We will realize projects to explore the holes and caverns. We have named the series of the projects as UZUME (Unprecedented Zipangu Underworld of the Moon/Mars Exploration).

Keywords: Moon, Mars, vertical hole, cavern, life exploration, UZUME

U04-04 Room:IC Time:May 27 11:00-11:15

Challenges to Predict the Long-Term Uranium Migration in Deep Terrestrial Crust

KOUDUKA, Mariko[1] ; SUZUKI, Yohey[1*]

[1]Department of Earth and Planetary Science, The University of Tokyo

Our understanding of uranium mobility in the near surface environment has been rapidly expanding in the past decades, especially due to problems associated with environmental remediation of U-contaminated sites. After Fukushima Daiichi nuclear disaster, it is becoming important to study the environmental behavior of U even in Japan, because meltdown debris mainly composed of UO_2 need to be disposed of in a deep geological repository. Recently, it has been demonstrated that our understanding of U in deep granitic rocks is limited, as exemplified by an unexpected finding of high concentrations of uranium in reducing deep granitic groundwater at a Swedish geological disposal site. As Japan is located at tectonically active plate boundaries, geological factors influencing the mobility of uranium remain to be clarified.

Biogeochemical processes mediated in the deep granitic aquifer at the Mizunami underground research laboratory (URL) were studied in details and published in Suzuki et al. (2014). Briefly, large extents of sulfur isotopic fractionation between sulfate and sulfide and zinc sulfide precipitation clearly indicate that the aquifer is under sulfate-reducing conditions. Groundwater concentrations of U were measured to be exceedingly low at the ppt level. To constrain factors determining the low U concentrations, fracture-filling minerals were investigated by scanning electron microscopy (SEM) coupled to energy dispersive X-ray spectroscopy (EDS) for focused ion beam (FIB) fabricated samples. At 300 meter below ground level (mbgl), pyrite and chlorite were associated with U-bearing loci. One of the samples was FIB fabricated for transmission electron microscopy coupled to EDS, and selected area electron diffraction (SAED) patterns, chemical compositions and spacings of lattice fringes were all indicative of the formation of a U(IV) silicate mineral called coffinite. High-resolution TEM observations also revealed that coffinite was crystalline. The solubility of crystalline coffinite was thermodynamically calculated by Phreeq C with our selected database and consistent with the U concentrations in the deep granitic aquifer. It is therefore concluded that U is stable as its reduced state and immobile in the present groundwater.

Tono uranium ore deposits are adjacent to the Mizunami URL, and geological settings of the two sites are almost the same. 10 Ma U mineralization occurred in the overlying sedimentary formation where lignite is a reducing agent for U(VI). It is well established that U is mobilized from granite under oxidizing conditions and transported to downstream ore bodies with abundant reductants such as organic matter and pyrite. However, the current redox state of granitic groundwater at the Mizunami ULR is under stably reducing conditions, and the established concept involving oxidizing groundwater appears not to be a case. As a significant transgression event is known to have occurred 10 Ma, there is the possibility that the intrusion of seawater into the freshwater aquifer might be important as suggested for the Swedish repository site after the last glacial maximum. We investigated the paragenesis of cofinite, pyrite and chlorite within calcite grains formed during the 10 Ma transgression by SEM-EDS, carbon and oxygen stable isotope measurements of microdrilled calcite and field emission elemental probe microanalysis (FE-EPMA). Results will be shown to discuss about the reconstruction of geological events and their influences on U migration in the deep granitic rock.

Suzuki, Y, Konno, U., Fukuda, A., Komatsu, D. D., Hirota, A., Watanabe, K., Togo, Y., Morikawa, N., Hagiwara, H., Aosai, D., Iwatsuki, T., Tsunogai, U., Nagao, S., Ito, K., Mizuno, T. (2014) Biogeochemical Signals from Deep Microbial Life in Terrestrial Crust, PloS one, 9(12), e113063.

U04-05 Room:IC Time:May 27 11:15-11:45

Biomineralization of corals and paleoenvironmental studies

YOKOYAMA, Yusuke[1*] ; BELL, Tomoko[1] ; HIRABAYASHI, Shoko[1] ; MIYAIRI, Yosuke[1] ; KUBOTA, Kaoru[1] ; SEKI, Arisa[1] ; IGUCHI, Akira[2] ; SUZUKI, Atsushi[3]

[1]Atmosphere and Ocean Research Institute, University of Tokyo, [2]Department of Bioresources Engineering, Okinawa National College of Technology, [3]Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology

Coral skeleton is a unique archives that recoding paleoclimate since the chemical compositions are fingerprinting the temperature as well as water chemistry including pH. Recent advance in analytical chemistry as well as biological experimental techniques enables us to assess the reliability of individual proxy to better picturing environmental changes. This provide strong platforms to analyzing paleoenvironment and paleoecological studies. In this presentation, we will introduce our approach to address these issues using geochemistry and bioinformatics. We will introduce our recent study to understand adaptation of corals both temperature and pH changes throughout the last deglaciation when the large environmental change was naturally occurred.

Keywords: Biomineralization, Geochemistry, Coral, Paleoclimate

U04-06 Room:IC Time:May 27 11:45-12:15

Ultra-high resolution past environmental reconstruction-Insolation extracted from giant clam shells-

SANO, Yuji[1]*

[1] Atmosphere and Ocean Research Institute, University of Tokyo

Marine biogenic calcium carbonate such as coral skeleton and bivalve shell may record past environmental and/or ecological information as the chemical and isotopic compositions. These past information have been studied by the analyses of modern and fossil materials [1]. Past climate reconstruction from the carbonate greatly contributes to understanding of the climate system and global warming. However, the climate change of tropical and sub-tropical region is relatively unknown due to the limited instrumental observation, luck of historical documents and insufficient dendrochronology. The aim of this study is to reconstruct the past marine environment at ultra-high resolution by the analysis of biogenic calcium carbonate using state-of-the-art micro-analytical technique (NanoSIMS). The NanoSIMS is capable to analyze the solid sample surface with a high sensitivity and a high precision at sub-micron scale. Initial stage of this project comprised with the matrix-matched standard reference materials, and development of new analytical procedures at a few micron [2].

We have measured minor (Mg and Sr) and trace (Ba) elements of living giant clam and fossil clam shells. Living sample (Tridacna derasa) was cultivated from March 2002 to October 2005 at Kabira coral reef of Ishigaki Island in the southwestern part of the Ryukyu Archipelago, southern Japan. A clear seasonal variation in Sr/Ca ratio is observed in longer set of measurements with 50 micron resolution. In addition the ratio exhibits striking diurnal variations by 2 micron resolution, reflecting the daily light cycle. Light-enhanced calcification and elemental transportation processes, in giant clam and symbiotic algae, may explain these annual and diurnal variations [3]. About 5000 years old fossil sample (Tridacna gigas) was collected in August 2007 at Shiraho coast of the same island. The Sr/Ca ratios in the winter layers of the sample are characterized by a striking diurnal cycle consisting of narrow growth lines with high Sr/Ca ratios and broad growth bands with low Sr/Ca ratios. These variations, which are consistent with those of the cultivated clam shell, indicate the potential for the reconstruction of the variation in solar insolation during the middle Holocene at a few hours resolution [4].

[Reference]

[1] Henderson (2002) *Earth Planet. Sci. Lett.* 203, 1-3. [2] Sano et al. (2005) *Anal. Sci.* 21, 1091-1097. [3] Sano et al. (2012) *Nature Commun.* 3, 761. [4] Hori et al. (2015) *Scientific Reports*, in press.

Keywords: past marine environment, insolation, NanoSIMS, giant clam shell

U04-07 Room:IC Time:May 27 12:15-12:45

Full-Depth Biogeosciences for Profound Life in Ultradeep Terrain of Ocean (PLUTO)

TAKAI, Ken[1*]

[1] JAMSTEC

t has been long believed that hadal zone is extraordinary geological and oceanographic place and biosphere in global ocean environment and represents some exceptional and specific geological, oceanographic and biological processes in the modern and even the past earth due to its quite limited space as compared to expansion of ocean. However, recent geological and geophysical investigations have revealed that ultradeep trench with hadal zone would be characterized by dynamic tectonic, seismogenic and even magmatic processes. The new image of ultradeep trench and hadal water and seafloor provokes that such geodynamic environments could host active biosphere. Nevertheless, many (micro)biologists still feel that ultradeep trench and hadal water and seafloor represent very quiet (inactive) biosphere simply as the last sinking stage of photosynthetic biological production into the earth interior.

To these unexplored deepest ocean environments, engineering and technological challenges have preceded scientific investigations. In 1989, JAMSTEC developed and launched a human occupied submersible vehicle (HOSV) Shinkai 6500 and conducted the scientific exploration of hadal water and seafloor. In 1995, a remotely operative vehicle (ROV) Kaiko of JAMSTEC successfully reached the world deepest ocean bottom at the Challenger Deep, Mariana Trench, for the first time after the adventure of Jacques Piccard and Don Walsh using a bathyscaphe, Trieste, in 1960. Once Kaiko lost in 2002, descendant JAMSTEC ROVs Kaiko 7000 and ABISMO and WHOI HROV Nereus have continued to explore the ultradeep trenches and hadal biospheres. In particular, yet-limiting but increasing studies have renewed our view of such ultradeep trench environments and extant hadal biospheres.

Historically, the hadal water and seafloor are characterized by quite little elemental and nutrient input from surface ocean and biological production. The extinction-to-consumption organic matters host quite low biomass and diversity of planktonic and benthic heterotrophic prokaryotes and thus narrower food web and lower biomass and diversity of faunal communities. However, recent (micro)biological investigations have indicated that not only vertical sinking of nutrients from surface and coastal waters and ecosystems but also episodic and continuing inputs of energy sources and nutrients by crustal fluid flows through the underlying crusts of the subduction zone sustain the active hadal ecosystems. Surprisingly, recent geochemical and microbiological investigations have pointed that the hadal biosphere is highly independent of other planktonic and benthic ecosystems in terms of the community- and species-level composition and genetic connectivity despite no apparent physical and chemical signatures for the environmental isolation. The existence of hadal biosphere and ecosystem is likely associated with the anaplelotic input of pooled nutrients of past coastal and surface ecosystems in the trench slope sediments with the decomposition and turbulence.

These challenges for ultradeep trench and hadal biosphere have been lead by technology and biogeosciences in Japan and are going to establish a kind of paradigm shift. To push the revolutionary paradigm shift for ultradeep trench and hadal biosphere, a Japanese multidisciplinary research project is now being assembled with a leadership of JAMSTEC biogeoscientists and me. Here, I would like to overview the scientific background of exploration of ultradeep trench and hadal biosphere and introduce the new multidisciplinary science stream and the leading project that has been just launched.

Keywords: Hadal zone, tectonic errosion, subduction zone, slope decomposition, crustal fluid, organic matter

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

U04-08 Room:201A Time:May 27 14:15-14:45

Searching for habitable worlds in the solar system

SEKINE, Yasuhito[1*]

[1] Department of Earth and Planetary Science, University of Tokyo

New observations from spacecraft missions enable us to examine habitability in the solar system. The icy satellites with geological activity, Europa and Enceladus, are considered to possess subsurface liquid oceans beneath the icy crusts. Recent findings of water-rich plumes erupting from Enceladus would allow us to investigate biogeochemistry of the subsurface ocean. Mars is also highly likely to have been another habitable terrestrial planet in the first several hundred million years after its formation. The combinations of in-situ geological and geochemical analyses by the rovers and high-resolution remote sensing by the orbiters help us to understanding the drastic environmental changes on early Mars. Future explorations of these habitable worlds in the solar system would provide insights into understanding not only the possibility and variety of life in the universe but also the concrete pathways of chemical evolution toward life, which was occurred on early Earth. Here, I will review recent progresses in the search for habitable worlds in the solar system and discuss the scope for the assessment of planetary habitability by spacecraft missions.

Keywords: Mars, icy satellite, chemical evolution, origin of life, planetary exploration

U04-09 Room:201A Time:May 27 14:45-15:15

Geochemistry of trace elements at the seawater/ferromanganese oxide interface

KASHIWABARA, Teruhiko[1]*

[1]JAMSTEC

Chemical reaction on the surface of ferromanganese oxides, which are widely present in a variety of forms such as crusts, nodules, and precipitate particles, strongly affects geochemical behaviors of trace elements in the marine environment. Accumulation of some valuable metals into ferromanganese oxides is closely related with the formation of mineral deposits including Co-rich crust, Mn nodules, and REY-rich mud, whereas scavenging of trace elements from seawater sometimes controls their concentrations and isotopic compositions in seawater. Molecular structures reveled by synchrotron X-ray analysis can explain the mechanisms of incorporation and isotopic fractionation of trace elements at the seawater/ferromanganese oxide interface. For example, the extreme enrichment of Te among oxyanions can be explained by structural substitution into Fe (oxyhydr)oxides via coprecipitation reaction because its molecular geometry is similar to Fe octahedron, in contrast to other oxyanions incorporated via adsorption reaction. In the adsorption reaction, on the other hand, the mode of attachment (inner- or outer-sphere) is an important factor, where the formation of inner-sphere complex causes the larger adsorption than outer-sphere complex, as observed in the case of Mo, W, As, Sb, and Se. We found the correlation between these molecular structures at the seawater/ferromanganese oxide interface and chemical properties of elements including pKa, and pKOH, which can lead to the systematic understanding of variable behaviors of elements. In this presentation, I will talk about the chemistry of trace elements at the seawater/ferromanganese oxide interface and its significance in the study of marine environment and submarine resources.

Reference

[1] Hein, J.R., Koschinsky, A., Halliday, A.N. (2003) *GCA* **67**, 1117-1127.
[2] Kashiwabara T., Oishi Y. Sakaguchi A., Sugiyama T., Usui A. and Takahashi Y. (2014), *GCA* , **131**, 150-163.
[3] Kashiwabara T., Takahashi Y., Tanimizu M., and Usui A. (2011), *GCA* , **75**, 5762-5784.
[4] Kashiwabara T., Takahashi Y., Marcus M. A., Uruga T., Tanida H. Terada Y., and Usui A. (2013), *GCA* , **106**, 364-378.

Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

U04-10 Room:201A Time:May 27 15:15-15:45

Microscopic analyses of radioactive contamination in Fukushima soil

MUKAI, Hiroki[1*] ; MOTAI, Satoko[1] ; KOGURE, Toshihiro[1]

[1]Graduate School of Science, the University of Tokyo

Since the accident at Fukushima Daiichi Nuclear Plant in 2011, it has been required to trace the behavior of the released radionuclides, particularly the radioactive cesium, in the natural environment. However, in the actual contaminated soil, the radioactive cesium presents in extremely low concentration (˜0.1 ppb) which makes it difficult to locate it chemically. Last year, we could successfully identify the radioactive particles in the actual soil using autoradiography with micro-processed imaging plates (IP), and revealed the adsorbents of the radioactive cesium mainly by electron microscopy (Mukai et al., 2014). We are now investigating the distribution of the radioactive cesium in the particles by the combination of autoradiography and micro-processing using focused-ion-beam (FIB). In this talk, these results will be presented.

Keywords: Fukushima nuclear accident, Contaminated soil, Radioactive cesium, Electron microscope

U04-11 Room:201A Time:May 27 15:45-16:00

Effect of pore size on ion adsorption properties of nanoporous silica

NISHIYAMA, Naoki[1]* ; YOKOYAMA, Tadashi[2]

[1]National Institute for Materials Science, [2]Osaka University, Graduate School of Science, Department of Earth and Space Science

Understanding the ion adsorption on mineral surfaces is of importance in predicting the transport and accumulation of toxic elements and resources. Nanoscale pores (referred to as nanopores) are often seen as the etch pits formed by weathering and hydrothermal alteration and in the aggregates of fine clay or iron (hydro)oxide particles. The behavior of ion adsorption is intimately connected to the structure of the electric double layer which spreads to a distance (<1 μm) at a mineral/water interface. However, the distance of electric double layer spreading in a nanopore is expected to be limited to its pore size, and the ion adsorption on the nanopore surfaces may change with pore size. In this study, we evaluated the influence of pore size on the surface charge density and the amount of adsorbed ion.

We used two different nanoporous silica powders (CARiACT Q; Fuji Silysia) with pores of 25 nm radius and 1 nm radius. In order to measure the charge density of nanopore surfaces, the acid/base titration experiment was conducted using the silica powder of each pore radius suspended in a 1 mM solution of NaCl. The surfaces of silica in contact with a neutral or alkaline solution usually have negative charges by the protonation-deprotonation of silanol groups ($>$Si-OH $\leftrightarrow$ $>$Si-O$^-$ + H$^+$) and the adsorption-desorption of Na$^+$ ($>$Si-OH + Na$^+$ $\leftrightarrow$ $>$Si-O$^-$ $\cdots$ Na$^+$ + H$^+$). Comparison of surface charge densities of silica with pores of 25 nm radius and those of 1 nm radius reveals that the surfaces of narrower pores are less negatively charged. This finding means that the surface silanol groups on narrower nanopores less desorb H$^+$.

In order to evaluate the effect of pore size on the amount of adsorbed ion, the adsorption experiments for K$^+$ were performed using silica with different pore sizes. Silica powder was added to a 0.1 mM NaCl solution containing 0.006 mM KCl. The pH of the mixture was adjusted to 4.0, 4.5, 5.6, 6.4, 7.3, 8.2, and then stirred for 30 minutes. The small volume of supernatant was collected and filtered by 0.2 μm membrane filter, and then the concentration of K$^+$ was measured by a liquid chromatography. The amounts of adsorbed K$^+$ ion for pores of 1 nm radius was up to more than 50% less than those of 25 nm radius, which is consistent with the result of titration experiments that the surfaces of narrower pores have less negative charges. Our results demonstrate the importance of pore size for a better understanding of the ion adsorption properties.

Keywords: Ion adsorption, Surface charge, Electric double layer, Silica, Nanopore