

## Division for Chronological Research



- Anthropogenic history and geochronology
- Accelerator mass spectrometry
- Electron probe microanalysis
- Paleoclimate reconstruction and future Earth
- Geosphere stability
- Isotope geoenvironmental chemistry
- CHIME dating
- Development of new analytical methods

Short- and long-term forecasts of global environmental changes and their countermeasures are urgent issues. Determining when an event occurred in the past, via “dating,” is important for understanding the present state of the Earth and predicting its future. We promote chronological studies on a broad range of subjects, from events in Earth’s history, spanning 4.6 billion years, to archeological materials, cultural properties, and modern cultural assets.

The Division for Chronological Research conducts interdisciplinary research involving radiocarbon ( $^{14}\text{C}$ ) dating using accelerator mass spectrometry to understand changes in the Earth’s environment and the cultural history of humankind from approximately 50,000 years ago to the present day, as well as research on and development of new  $^{14}\text{C}$  analyses and dating methods. In addition, the laboratory studies near-future forecasts of Earth and space environments, focusing on spatio-temporal variations in cosmogenic nuclides, such as  $^{14}\text{C}$  and  $^{10}\text{Be}$ , and conducts research that integrates art and science through collaborations between researchers in archeology, historical science, and other fields. Furthermore, using the chemical U-Th total Pb isochron method (CHIME), which was first developed at Nagoya University, and radiometric dating of long-half-life radioisotopes (Sr-Nd-Hf), we have shed light on events in Earth’s history from its formation 4.6 billion years ago to approximately 1 million years ago. An electron probe microanalyzer (EPMA) has been used to perform nondestructive microanalyses of rocks and other materials to reveal records of complex events recorded in zircon, monazite, and other samples.

### Main Activities in FY2022

#### Validation of the stability of the West Antarctic ice sheet of the Amundsen Sea sediment core

A sector of the West Antarctic ice sheet draining into the Amundsen Sea is currently experiencing the largest ice loss in Antarctica, and there is serious concern regarding a large-scale ice collapse in this area caused by global warming. The International Ocean Discovery Program Expedition 379 drilled two sites in the Amundsen Sea area of the Southern Ocean using the D/V JOIDES Resolution. The shipboard physical properties and sedimentological data of sediment cores demonstrated strongly variable physical properties, high diatom abundance, and ice-rafted debris occurrence from 4.2 to 3.2 million years ago. This was interpreted to have been caused by the dynamic West Antarctic ice sheet during an extended warm period (Gohl et al., 2021; Wellner et al., 2021; Gille-Petzoldt et al., 2022). Further research is expected to elucidate the stability of the West Antarctic ice sheet and the linkage between West Antarctic ice sheet changes and climate change.



An ice sheet in the Amundsen Sea, West Antarctica

## Radiocarbon dating of Ezo-Nishiki silk fabrics

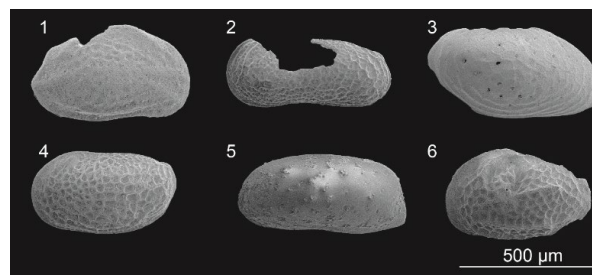
In Japan, silk fabrics, known as Ezo Nishiki, are distributed throughout the Hokkaido and Tohoku areas of the Honshu Islands. On Ezo Nishiki, elegant designs of dragons, huge snakes, peonies, and other animals or plants are laced with gold, silver, and other color threads. Although silk fabrics were originally made in China as cloth for the uniformity of government officials, they were also given to the chieftains of the tribes and Amur Basin villages and imported into Sakhalin Island over the Mamiya Strait. Trade was performed by indigenous peoples in the Amur Basin and Sakhalin Island, including the Nivkh, Nanai, and the Ul'ch. Santan is a generic name for the indigenous people living in the Amur Basin and Sakhalin Island. Silk fabrics were then spread southward into Hokkaido Island by the Ainu people living on Sakhalin and Hokkaido islands. Silk fabrics were brought to Honshu Island in Japan through the trade between the Ainu and Matsumae clans, which ruled the southwest edge of Hokkaido. The route in which the Ezo Nishiki was introduced from China to Japan via the Amur Basin and Sakhalin Island is called “the Silk Road of Northeast Asia” and the trade is called the Ezo-NishikiSantan trade. Although the origin of the trade was obscure, Ezo-Nishiki radiocarbon dating indicated that it began at the end of the 14th century or the early 15th century, when Emperor Yongle of the Ming Dynasty (1368–1644) expanded their territory.



The Ezo Nishi silk wrapping cloth was owned by the Esashi Town Board of Education (photograph presented by the Esashi Town Board of Education)

## The analysis of fossil ostracod assemblage from the Sakari Shell Mound in Minamichita Town, Chita District, Aichi Prefecture

The melting of glacier ice and ice sheets has been reported to increase the sea level associated with global warming since the 20th century, and the rise in sea level after several hundred years has been estimated by several researchers. Estimating sea-level changes in the future based on these data on the paleo-environment and sea level is important to predict the highly sensitive sea level. To reconstruct the paleo-environments and sea-level changes, we studied the reconstruction of the sea-level curve using fossil ostracods during the Holocene around Japan. In this study, a borehole core was excavated from the Mazukari shell mound in Minamichita to reconstruct its paleoenvironment and paleowater depth based on fossil ostracod assemblages. Six species belonging to five ostracods genera were found in a sample at approximately 9,600–8,600 cal BP. Meanwhile, the paleo-water depth was estimated to be 12 m based on a comparison with the fossil ostracod assemblage in this study and modern ostracod assemblages from Ise Bay. (In this sample, we used the part of the archival document “Mazukari shell mound unearthed information materials” of the Minamichita town board of education.)



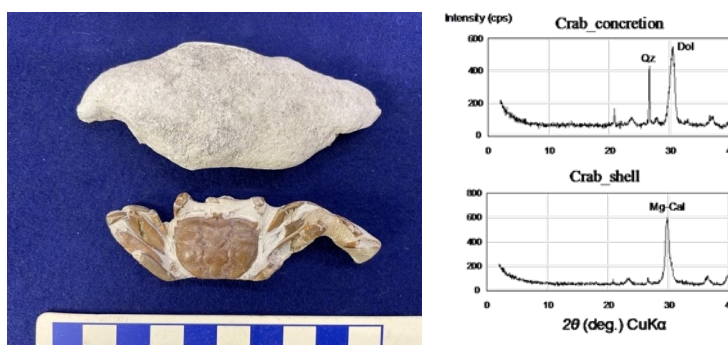
GSEM photographs of the selected ostracod species

## Radiocarbon dating to bronze implement

Radiocarbon dating is a useful method for samples containing carbon derived from CO<sub>2</sub> in the atmosphere. Verdigris, CuCO<sub>3</sub> and Cu(OH)<sub>2</sub>, is the rust produced on bronze implements. The reactants used were bronze, copper, and CO<sub>2</sub> in the atmosphere. When a verdigris is formed, it is a closed film that restrains the generation of new rust. Therefore, the verdigris should preserve atmospheric carbon when formed. We improved the carbon extraction method using CuCO<sub>3</sub> and Cu(OH)<sub>2</sub>. We then applied this method to archaeological samples of known age, measured radiocarbon ages, and accumulated examples of verdigris radiocarbon dating to demonstrate that verdigris is suitable for radiocarbon dating.

## Radiocarbon age of Holocene carbonate concretions at Nagoya and Shimizu port

Carbonate concretions occur in diverse geological formations worldwide. We studied carbonate concretions from Nagoya and Shimizu ports. Concretion samples often contain biological remains, and organic matter, such as organisms, and is thought to be involved in the formation of concretion. To elucidate the formation process of concretions, it is important to conduct geochemical evaluations of concretions with known formation ages. In this study, to elucidate the formation rate of concretions, we measured  $^{14}\text{C}$  and  $\delta^{13}\text{C}$  ages of the shell and concrete parts of concretion samples collected from the Nagoya and Shimizu ports. The  $^{14}\text{C}$  ages of the shells are approximately 7850–7600 cal BP (Nagoya port) and 7700–7500 cal BP (Shimizu port), and the  $^{14}\text{C}$  ages of the Shimizu port concretion are approximately 7840–7620 cal BP. Conversely, the  $^{14}\text{C}$  age of the Nagoya port concrete part was older than the  $^{14}\text{C}$  age of the encapsulated shell; however, after age correction by estimating the contribution of soil organic carbon with old age from the  $\delta^{13}\text{C}$  value, the age was close to that of the shell (8000–7800 cal BP). Oyama (2009) reported that the area near the mouth of the Nagoya port changed from marine transgression to regression at 7800–7300 cal BP, suggesting that the carbonate concretions in the Nagoya and Shimizu ports formed rapidly after the death of organisms in an environment with the highest sea level and stagnant currents. Further research is expected to estimate sea level and paleoenvironmental changes during the sea level rise of the Jomon period. (Minami, Kuma et al., 2022, *Journal of Geology*, 128, 239-244.)

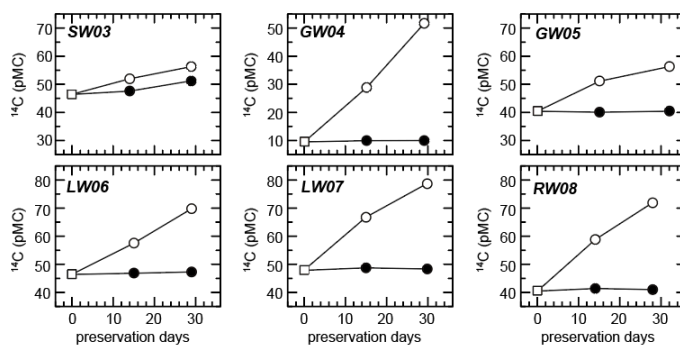


Left: Concretions and inclusions of crab fossils collected from the Nagoya port  
Right: Mineral composition of crab shell and concrete (Qtz: Quartz, Cal: calcite, Dol: dolomite) From Minami et al. (2022)

## Effect of benzalkonium chloride addition on $^{14}\text{C}$ analysis of dissolved inorganic carbon

The  $^{14}\text{C}$  concentration of dissolved inorganic carbon (DIC) in water is an important indicator of the actual state of biological activity and other conditions in seawater and terrestrial water. However, after sample collection and storage, the  $^{14}\text{C}$  concentration may change owing to DIC formation or decomposition by microbial activity in the sample water. Sterilization with  $\text{HgCl}_2$  is commonly used to prevent DIC changes due to microbial activity; however, the use of mercury, which has a high environmental impact, is highly restrictive. Therefore, we investigated benzalkonium chloride (BAC) as a disinfectant that can be used to disinfect medical devices and that is easy to handle.

We investigated the changes in  $^{14}\text{C}$  concentrations in DIC due to microbial activity during water storage and found that  $^{14}\text{C}$  concentrations in natural waters (groundwater, seawater, river water, and lake water) without BAC increased considerably in two weeks, whereas all BAC-added water samples, except seawater, demonstrated no change in  $^{14}\text{C}$  concentrations. Furthermore, the incorporation of carbon into the water sample due to the BAC decomposition or microbial degradation by BAC was negligible in the  $^{14}\text{C}$  analysis. These results indicate that BAC is very effective in  $^{14}\text{C}$  analysis of freshwater samples as an inhibitor of DIC changes, although to a lesser extent in seawater samples. (Takahashi and Minami, 2022, *Limnol. Oceanogr.: Methods*, 20, 605–617)



$^{14}\text{C}$  concentrations in natural water samples (seawater: SW03; groundwaters: GW04, GW05; lake waters: LW06, LW07; river water: RW08) for approximately 15-d and 30-d preservation periods (□ : initial water, ○ : BAC-free water, ● : BAC-added water)



## Direct search for dark matter using minerals

Approximately a quarter of the universe is thought to be occupied by an unknown elementary particle called dark matter. Dark matter is an unknown elementary particle with mass that hardly interacts with ordinary matter and cannot be directly observed optically. Diverse studies have been performed to detect dark matter.

In recent years, a direct search for unknown elementary particles, such as dark matter, using minerals has attracted attention. When dark matter interacts with atoms in minerals, it leaves tracks in the crystals. Using minerals on a geological timescale, it is possible to realize a sensitivity exceeding that of large-scale experiments, even with small samples. For example, 100 mg of a 100-million-year-old mineral has a sensitivity equivalent to that of a 10-year experiment with 1 t material (e.g., liquid xenon).

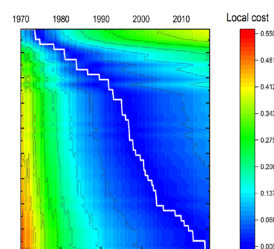
In FY2022, a feasibility study of the optical readout of tracks was performed by focusing on muscovite. Additionally, we obtained muscovite specimens for which a sufficient number of samples were available for future proof of principle. We carried out dating of the muscovite sample using the K-Ar method, and an age of approximately 650 million years was obtained. In the future, we will aim to directly search for unknown elementary particles using diverse minerals, including the muscovite sample.



Muscovite sample

## A growth curve estimate of Christ's thorn jujube in Northcentral Oman determined by a series of radiocarbon measurements

*Ziziphus spina-christi*, also known as Christ's Thorn Jujube, is a deciduous species. It is distributed in warm-temperate and subtropical regions, including North Africa, Southern Europe, the Mediterranean, Australia, tropical America, Southeast Asia, and the Middle East. This tree was used as a medicinal plant in ancient Egypt. Due to its extensive range of applications in human health, its commercial demand is increasing. Recently, habitat area expansion was observed in the Mediterranean region. It is speculated that this expansion may have been facilitated by the rise in temperature caused by global warming, although the exact cause remains unknown. This study was performed to comprehend the effects of temperature and precipitation on the growth of mature *Ziziphus spina-christi* trees and to gain insights into their future geographical distribution. To construct the growth curve of *Ziziphus spina-christi*, which lacks clear annual rings, a 24 cm-long core sample was collected from Northcentral Oman and subjected to radiocarbon dating. Time-series data comprising approximately 100 radiocarbon measurements were compared with a carbon-14 calibration dataset using the dynamic time wrapping (DTW) method. By aligning the data, we were able to determine temporal changes in the growth rate of *Ziziphus spina-christi* and shed light on how it is affected by climate change.



Estimating growth curve of Omani Christ's Thorn Jujube using DTW method

## A special support project for regional contribution in FY2022, "How do we determine the ages of rocks and archeological sites?"

On March 18 and 25, 2023, an experiential learning program targeting upper elementary school students was implemented. On the first day, a large bus was chartered to visit the Nakatsugawa City Mineral Museum, where students learned about the formation of granite and quartz. They also used a portable radiation detector to measure the radiation levels in rocks and minerals. Additionally, they had the opportunity to create micromounted quartz specimens. On the second day, the program took place at Nagoya University, where students learned about radioactive materials, radiation, natural radiation levels, and radiometric dating. Each student created a cloud chamber and observed the emission of radiation by placing a pitchblende sample inside. This experiential learning provided a valuable experience that could not be obtained through regular school life and served as a catalyst for increasing interest of children in natural and earth science.



Children measuring radiation levels in Naegi granite