Division for Chronological Research

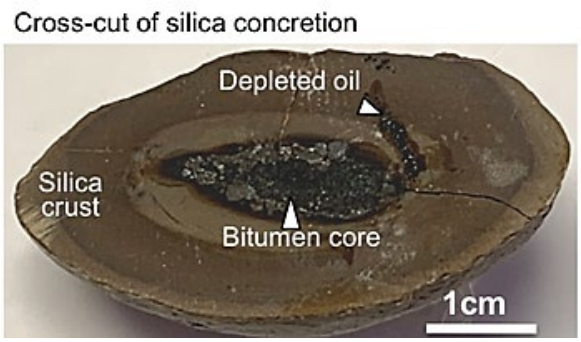
- Anthropogenic history and geochronology
- Accelerator mass spectrometry
- Electron probe microanalysis
- Paleoclimate reconstruction and future Earth
- Geosphere stability
- Isotope geoenvironmental chemistry
- CHIME dating
- Development of new analytical methods

Short- and long-term forecasts of global environmental changes and their countermeasures are issues of great urgency. Determining when an event occurred in the past, via "dating," is important for understanding the present and predicting the future state of the Earth. 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 Tandetron dating group conducts interdisciplinary research involving radiocarbon (^{14}C) dating using accelerator mass spectrometry to understand changes in the Earth's environment and the cultural history of humankind from approximately 50000 years ago to the present day. In addition, the group studies near-future forecasts of Earth and space environments, focusing on spatio-temporal variations in cosmogenic nuclides, such as ^{14}C and ^{10}Be, and conducts research that integrates art and science through collaborations between researchers in archeology, historical science, and other fields. The microscale spatial dating group uses the chemical U-Th total Pb isochron method (CHIME), which was first developed at Nagoya University, to shed light on events in Earth's history from its formation 4.6 billion years ago up 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 FY2020

Elucidation of the formation of silica concretions containing petroleum

In collaboration with Dr. Yoshida's group at the Nagoya University Museum, this research division studies the formation mechanisms of spherical concretions made of calcium carbonate or iron oxide. This research investigated the formation process of spherical silica concretions (SiO_2) containing petroleum from Utah, USA. Silica dissolved in groundwater precipitated rapidly by the neutralization reaction of alkaline groundwater in the stratum around fish feces (organic matter) acidified through corrosion and the trapped organic matter was converted into petroleum during subsequent geological maturation. Until now, the exact cause and formation timing of silica-based concretions have been unknown; however, this study revealed that the corrosion of biogenic organic matter and the associated neutralization reaction are essential for silica concentration. The results of this study have been published in Scientific Reports (Yoshida et al., 2021).



Photograph of the cross-cut of spherical silica concretion. The black area in the center is the organic core containing petroleum (Yoshida et al., 2020).

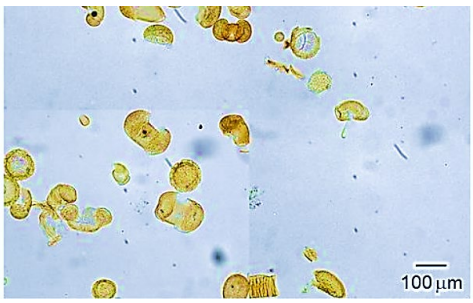
ICP-MS analysis of trace elements in mantle-derived olivine

Hand-picking of olivine grains from crashed rock-sample under an optical microscope.

Chemical characterization of trace elements in the mantle is important for understanding the mantle-crust interactions associated with subduction and igneous activity. Quantitative analysis of trace elements by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been reported (De Hoog et al., 2010); however, the number of target elements is limited. In particular, Pb, Th, and U have low abundance in olivine and are difficult to quantify by LA-ICP-MS; thus, their concentration ranges remain unknown. Quantitative analysis of trace elements, including Pb, Th, and U, in olivine was performed with ICP-MS using the solution method. Mantle-derived olivine was separated under an optical microscope after rock crushing. The Pb, Th, and U concentrations in olivine were low, ranging from 5 to 61 ng/g, 0.1 to 67 ng/g, and 0.1 to 38 ng/g, respectively, and all olivine contained measurable amounts of these elements. Therefore, U and Pb measurements of olivine, combined with high-precision analysis of Pb isotope ratios, might allow us to estimate the formation ages of olivine, the major constituent mineral of the mantle (Kozaka et al., submitted).

Fossil pollen sorting for radiocarbon dating using a newly developed large particle on-chip sorter

Radiocarbon dating of plant remains, such as seeds and wood chips, is effective for building the chronology of lake sediment cores. However, plant remains used for radiocarbon dating are not preserved in sediment cores (e.g., from Lake Biwa). A novel on-chip sorting method utilizing traveling vortices generated by on-demand micro-jet flows was developed in collaboration with the Department of Micro-Nano Mechanical Science and Engineering, Nagoya University. Using this new sorting method, we succeeded in sorting pollen particles in sediments. Radiocarbon dates of fossil pollen concentrates derived from sorting are a good method to enhance building of chronologies for paleoenvironmental records. The method can also address the urgent need for high-throughput large particle sorting in genomics, metabolomics, and regenerative medicine.



Photograph of pollen particles sorted by on-chip sorting method.

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Source changes in atmospheric PM2.5 carbon components before and after refraining from going outside due to coronavirus infection spread

Among carbonaceous aerosol particles, which are the main component of atmospheric PM2.5, secondary organic aerosol particles (secondary OA) have a tremendous environmental impact. However, their sources and formation mechanisms remain unclear. Because of the complexity of their sources and formation mechanisms, detailed domestic sources of OA and their contribution to transboundary pollution are not well understood. Carbon-14 analysis is a powerful method that can divide OA into two origins (biogenic and fossil fuels) and quantify them. In April 2020, the spread of the new coronavirus infection led to a worldwide request to remain indoors. The transboundary pollution of OA and the impact of regional human activities were reduced. Because the amount of OA has been continuously observed in Nagoya from approximately 2017 to the recent refraining from going outside, it is possible to examine in detail the changes in the contribution rates of biogenic and fossil fuel OA sources before and after the voluntary restraint following the coronavirus outbreak by measuring the monthly carbon-14 in PM2.5. The carbon analysis results showed that the OA concentration in Nagoya was lower than usual from January to September 2020. The ratio of fossil to biogenic OA did not change significantly after March 2020, when the new coronavirus infection spread in Japan. Therefore, there was no significant decrease in anthropogenic fossil fuel carbon.

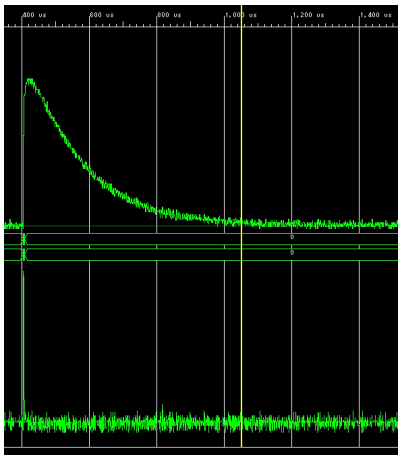
Validation of the stability of the West Antarctic ice sheet using geochemical analysis of the Amundsen Sea sediment core

A sector of the West Antarctic ice sheet draining into the Amundsen Sea is experiencing the largest ice loss in Antarctica today, and there is a serious concern of 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 in the Southern Ocean using the D/V *JOIDES Resolution* from January to March 2019. We reconstructed the melting history of the West Antarctic ice sheet using the fluctuation of beryllium-10 concentration in the sediment core, and verified the stability of the ice sheet during the past warm periods. Further research in the future should clarify the linkage between the West Antarctic ice sheet changes and climate change.

Iceberg in the Amundsen Sea.

Development of a low-noise X-ray detection system for the EPMA

In the wavelength-dispersive spectrometer of the EPMA, the output of the proportional counter was processed using a charge-sensitive amplifier and waveform shaper. The observed signal is the sum of characteristic X-rays, continuum X-rays, and noise. According to the manufacturer's specifications, the noise must be less than 1 cps. During analysis of trace elements, the characteristic X-ray intensity might be of the order of 1 cps or less. Under such conditions, the required signal is buried in the noise and cannot be detected. Therefore, we used a waveform shaper based on a digital circuit to reduce the noise. The original waveform shaper is a pseudo-Gaussian filter without undershoot compensation using an R-C circuit with an operational amplifier. In this case, the S/N was approximately 1.8 times worse than that of an ideal cusp-type filter. We decided to use a trapezoidal filter to convert the output of the charge-sensitive amplifier to A/D. With a trapezoidal filter, the S/N can be suppressed to approximately 1.1 times lower than a cusp-type filter. The filter circuit was implemented on an FPGA. The prototype device was connected to an existing JEOL JCXA-733 and applied to the FY2020 joint research project. We succeeded in quantitatively analyzing the aluminum contained in quartz formed near the solidus temperature of granite magma with sufficient accuracy.



Input signal (upper) and output signal (lower) of the pulse-shaper.

Radiocarbon dating of samples at the Middle to Upper Paleolithic transition

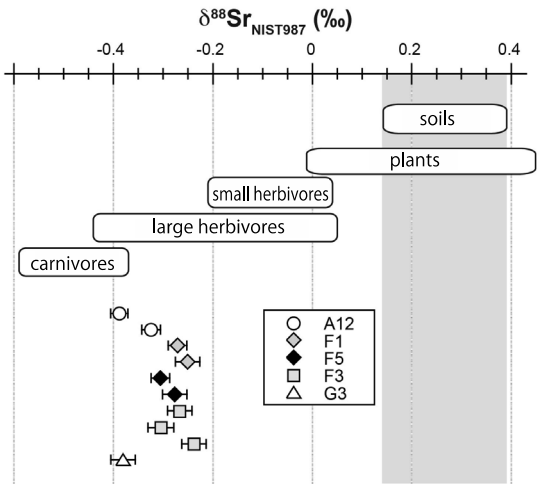
The Middle to Upper Paleolithic transition dates back to ~40000 years ago, corresponding to the timing of the replacement of Neanderthals by modern humans. Radiocarbon dating of samples during this period requires a scrupulous pretreatment method because this period is close to the measurement limit of radiocarbon dating (~50,000 years ago). In the framework of the PaleoAsia project, archeological excavations in the Arabian Peninsula, Central Asia, Southern Asia, and Northern Asia have been conducted. We applied cutting-edge radiocarbon dating methods to samples collected from this project and evaluated the reliability of the radiocarbon dating results. We contribute to a deeper understanding of the cultural history and migration of modern humans to Asia through the construction of a more reliable chronology.

Establishment of a new method for high-precision carbon-14 analysis of water samples

The carbon-14 concentration of dissolved inorganic carbon (DIC) in water samples is an important indicator for understanding carbon dynamics in the environment, especially the anthropogenic carbon cycle and for water dating. In the carbon-14 analysis of DIC in this research division, we used a method in which DIC is precipitated as carbonate and reacted with phosphoric acid to extract CO_2. However, this method is complicated, time-consuming, and sometimes fails to produce precipitation, which is easily contaminated by atmospheric CO_2. In this study, we improved the headspace method, which has been widely used in recent years for the $\delta^{13}C$ measurement of DIC, to suit the actual situation and a processing system that can be applied to water samples with a wide range of DIC concentrations to extract CO_2 efficiently without using a carrier gas. Basic experiments were performed to verify the reproducibility of the analytical values, the change in analytical values due to differences in extraction efficiency, and the background, and established a new method that is simple, efficient, and highly reliable with low background and no atmospheric CO_2 contamination. This has established a new foundation for the research department for carbon-14 analysis of water samples (submitted to *Radiocarbon*).

Multi-Sr isotope analysis of cremated bones reveals food habits and settlement areas

This research group has been conducting research to clarify the residential area and food habits of buried people using high-precision analysis of multi-Sr isotope ratios, including radiogenic Sr isotopes ($^{87}Sr/^{86}Sr$) and stable Sr isotopes ($\delta^{88}Sr$) of bioapatite, which is an inorganic component of bones excavated from archeological sites. This year, we conducted research on cremated bones excavated from the Ishibotoke-dani grave site at the Binman-ji Temple in Taga Town, Shiga Prefecture (multiple graves exist in eight research areas from A to G). Based on the type of pottery excavated and descriptions in ancient documents, it was estimated that the monks of Binman-ji and local residents were buried in the Ishibotoke-dani grave site during the 12th–15th centuries. The results of the multi-Sr isotope analysis of the cremated bones revealed that people who lived around Binman-ji Temple were buried in the Ishibotoke-dani site, and that people buried in Sections A and G were more carnivorous than those buried in Section F. Because the ^{14}C ages and grave styles differed depending on the study area, this difference in diet may indicate age or status differences. The results obtained in this study suggest that multi-Sr isotope analysis of cremated bone bioapatite is useful as an indicator for reconstructing diet and residential areas. In Japan, where many cremated bones have been excavated from archeological sites, multi-Sr isotope analysis of cremated bones will be a powerful tool for reconstructing historical living environments (Sawada et al., Presentation at the 2020 Annual Meeting of the Geochemical Society of Japan; Minami and Wakaki, Report on the investigation of cremated bones excavated from the Ishibotoke-dani site, Binman-ji Temple).



Sr stable isotope ratio ($\delta^{88}Sr$) of cremated bones excavated from the Ishibotoke-dani grave site.