**Highly-sensitive LA-ICP-MS approaches for the determination of ultra-trace rare earth elements (REEs) and U-Th isotopes in stalagmites**

**Chung-CheWu**1,2 (吳忠哲)

1Associate Professor, College of Marine Sciences and Engineering, Nanjing Normal University, China

2Foreign Researcher, Atmosphere and Ocean Research Institute (AORI), The University of Tokyo, Japan

**Keywords:** Highly-sensitive, LA-ICP-MS, REE, U-Th dating, Stalagmites

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has become one of the widely applied techniques for solid sample analyses in a variety of fields, such as geology, biology, archaeology, and material sciences. LA-ICP-MS can provide several advantages over conventional solution-based ICP-MS methods: (i) spatially resolved analyses at 10–100 μm; (ii) high sample throughout; and (iii) the reduction of polyatomic interfaces from the solvent. However, due to the lower sensitivity and precision of LA-ICP-MS, the overall applications remained restricted. Here we demonstrate two advanced LA-ICP-MS approaches and their applications by means of improved sensitivity using a “jet” interface setup.

The first case study1) is the determination of ultra-trace rare earth elements (REEs) in carbonate stalagmites. Since REEs are enriched in igneous rocks but depleted in carbonates, REE series preserved in stalagmites are a valuable indicator to reconstruct past gigantic volcano eruptions. Nevertheless, due to typically low REE abundances (ng/g or less), the access to REE profiles in stalagmites are still challengeable. By adopting the “jet” interface and N2 gas addition, the sensitivity could be enhanced by 20-40 times compared to the conventional interface. Limits of detection (LOD) in the sub-ng/g range could be achieved for most REEs in stalagmite samples. Spatially resolved analysis of a stalagmite collected from East Timor revealed at least two abrupt elevations in light rare earth elements (LREEs), possibly contributed from the volcanic tephra.

The second case study2) used LA-ICP-MS for the determination of U and Th isotopes in stalagmites. The U-Th absolute dating system (also called 230Th or 238U-234U-230Th-232Th) has been widely exploited to determine the timing and the processes of Earth’s geological, environmental, and biotic evolution, based on materials as young as few years to over the last 600 thousand years (ka). In this study, we utilized the detection efficiency of 1-2% to detect sufficient amounts of the low abundant 230Th+ (101-103 pg/g). Online-addition of a 229Th-233U-236U triple spike to the laser-generated aerosol, allowed for correction of instrumental mass discrimination and U/Th elemental fractionation. With this approach, the 234U/238U and 230Th/238U activity ratios of a flowstone sample in secular equilibrium could be accurately reproduced as unity. The method could furthermore successfully determine the formation ages of individual layers in natural stalagmites ranging between 210 to 1 ka. Particularly, Holocene stalagmites, as young as 1 ka, could be accurately dated with 2 standard error of ± 76 years.

The highly-sensitive LA-ICP-MS approach with “jet” interface setup is suitable for materials and subjects such as: low contents trace to ultra-trace elements analyses; dating of thin-layers; slow growing rate samples, where the spatial resolution is crucial; or small, archaeological samples, where sample consumption needs to be minimized. We expect these two highly-sensitive LA-ICP-MS approaches can make substantial contributions to various fields in paleoclimatology, oceanography, environmental science, and archaeology.

**References**

1. C.-C.Wu *et al*., Anal. Chim. Acta, **1018,** 54-61 (2018).
2. C.-C.Wu *et al*., Anal. Chem., **96,** 12640-12648 (2024).

報告人簡介：

吳忠哲，博士，歐盟居禮夫人獎學金(Marie-Curie Fellowships)得主，目前擔任中國南京師範大學海洋科學與工程學院副教授，兼日本東京大學大氣海洋研究所外國人研究員。 大學畢業於國立中央大學地球科學系，博士畢業於國立臺灣大學地質科學系，並以臺大理學院院長獎畢業。2019-2022年，在瑞士蘇黎世聯邦理工學院(ETH)從事博士後研究。研究興趣包括古氣候古環境變遷、同位素分析技術開發、海洋微量元素分析。至今學術成果：學術專著1本，論文總數52篇，其中，一作、通訊作者文章10篇（全部他引次數2152, H指數：22）。