Contribution ID: **28** Type: **Talk**

2D X-ray Absorption Spectroscopy and Diffraction mapping of complex dendritic structures found in ancient Chinese glazed ceramics at ESRF

Friday, November 24, 2023 9:35 AM (25 minutes)

Black-to-brown glazed ceramics manufactured during the Song Dynasty (960-1279 A.D.) constitute a highly regarded family in Chinese ceramics history, as illustrated for instance by the imperial praise given to several of the productions during the time of their manufacturing [1] and the fact that well preserved bowls are considered national treasure in Japan today [2]. The most famous are the bowls fired in the Jian kilns (Fujian province, China), with iron-rich glazes displaying brown to silvery patterns on a black background, which appear spontaneously during the cooling.

These characteristic patterns are formed by micrometric dendritic structures composed mainly of the rare ε-Fe2O3 polymorph, sometimes mixed with hematite [3]. Additional degrees of complexity are also commonly found, for instance in flower-like clusters of several hundreds of micrometers composed of smaller iron oxide crystals and mullite [4]. Better understanding of Fe speciation (nature and in-depth distribution) and crystal orientations are highly desirable to document the chemistry that lead to such structures, which provides key clues for the comprehension of the manufacturing processes of these ceramics. Due to their scale and complexity, synchrotron radiation-based micro-analyses are perfectly adapted to their investigation, being able to reach at the same time relevant spatial resolution and wide-enough field of view thanks to the high brightness enabling fast acquisition.

This study focuses on sherds from the Luhuaping archaeological site of the Jian kilns (Shuiji town, Jianyang district, Fujian province, China) provided by the Nanping Jian Kilns Ceramics Research Institute (Nanping, Fujian province, China). Samples of the surface of the glaze and cross sections were analysed at the ID13 and ID21 beamlines in ESRF (Grenoble, France). These beamlines allow 2D µXRD and µXRF/µXANES mapping respectively, both offering a wide field of view together with a spacial resolution suiting the scales of the structures of interest in a reasonable time thanks to the high brightness and coherence of the beam provided by the EBS (Extremely Brilliant Source) upgrade of the ESRF implemented in 2020 [5]. µXRD maps give the identification of the crystalline phases and information about their orientation, while µXANES at the Fe edge provides information of the Fe oxidation state even in the amorphous glassy matrix, making their combination very relevant and complementary.

µXRD maps up to 800 x 800 µm² were recorded with a spatial resolution of 2 µm. They highlight the obvious specific orientations of the structures at the surface of the glaze, with the bigger structures sometimes displaying different orientations suggesting an independent growth of several dendrite branches on a single base. µXANES maps were obtained from successive maps acquired in transmission over around 140 energies over the Fe K-edge, with sizes up to 100 x 100 µm² and spatial resolutions of 1 µm for surface samples and 2 µm for cross sections. The spectra of all the pixels were extracted and processed using workflows and statistical tools. Even if results on the surface samples are altered by the glaze underneath, small differences in the spectra are still correlated with structural features. Furthermore, data recorded on cross-sections show a significant gradient in the oxidation state of iron: almost exclusively Fe3+ toward the surface and a mixture of Fe2+ and Fe3+ deeper in the glaze, clearly visible both on the pre-peak and the white line position.

These results offer new insight on the growth of the complex dendritic structures found in the black-to-brown glazed ceramics and on their firing processes.

[1] M. Huang, translation of Dà Guān Chá Lùn from Emperor Huīzōng (1107), Global Tea Hut. 51 (2016) 35–48.
[2] Song Ceramics - Exhibition catalogue of Tobu bijutsukan (Tokyo), Osaka Shiritsu Tôyô Tôji Bijutsukan (Osaka) et Yamaguchi kenritsu Hagi bijutsukan Uragami kinenkan (Hagi), Tokyo, Osaka, Habi, 1999.
[3] C. Dejoie et al., Learning from the past: Rare ε-Fe2O3 in the ancient black-glazed Jian (Tenmoku) wares, Sci. Rep. 4 (2014) 4941.
[4] Q. Hoo et al., Millimeter-sized flower-like clusters composed of mullite and ε-Fe2O3 on the Hare's Fur Jian Ware, J. Eur. Ceram. Soc. 40 (2020) 4340–4347.
[5] https://www.esrf.fr/about/upgrade.

Primary authors: HOLÉ, Clément; COTTE, Marine (ESRF / LAMS); Prof. SCIAU, Philippe (CNRS, CEMES, Toulouse University)

Co-author: Dr WANG, Tian (Institute of Silicate Cultural Heritage, School of Material Science and Engineering, Shaanxi Key Laboratory of Green Preparation and Functionalization for Inorganic Materials, Shaanxi University of Science and Technology)

Presenter: HOLÉ, Clément

Session Classification: Production Techniques

Track Classification: Default track