

DEVELOPMENT OF A NON-DESTRUCTIVE ANALYSIS METHOD FOR OBSIDIAN ARTIFACTS USING WD-XRF

Atsushi Kamei¹

¹ Interdisciplinary Faculty of Science and Engineering,
Shimane University, Japan
E-mail: kamei-a@riko.shimane-u.ac.jp



Introduction

Archaeological provenance studies aim to identify the geological sources or production sites of raw materials used for artifacts such as stone tools, magatama beads, pottery, and metal implements. Determining provenance contributes to understanding ancient human mobility and social structures, making it a crucial field within archaeology. In the case of obsidian artifacts, visual characteristics such as color, luster, and texture were traditionally used as indicators. However, interpretations often varied among researchers, and objective chemical analyses have become increasingly important.

In Japanese archaeology, energy-dispersive X-ray fluorescence (ED-XRF) spectrometry has been widely used for obsidian analysis (e.g., Mochizuki et al., 1994) because it allows non-destructive measurements. However, ED-XRF has limitations in analytical precision and often neglects surface irregularities of stone tools (e.g., Kamei et al., 2016). Internationally, non-destructive wavelength-dispersive XRF (WD-XRF) methods for a limited set of elements (Rb, Sr, Y, Zr, Nb) have been developed (e.g., Acquafredda et al., 2018). Furthermore, recent studies have increasingly adopted laser ablation ICP-MS (LA-ICP-MS), which enables micro-destructive sampling and provides high-precision trace element data (e.g., Kim and Chang, 2021).

Thus, the development of non-destructive analytical methods has reached something of a plateau, whereas internationally, research is shifting toward micro-destructive techniques that enable high-precision analyses. This study aims to develop a non-destructive yet high-precision WD-XRF method that achieves analytical performance comparable to destructive approaches for obsidian artifacts.

Samples and Instrumentation

Obsidian raw materials collected from volcanic regions across southwestern Japan were used for developing the analytical method. In addition, Jomon-period artifacts housed at the Ashical Museum, Shimane University, and Yayoi-period artifacts curated by the Shimane Prefectural Archaeological Center were used for test analyses. In this study, the Rigaku Primus IV WD-XRF spectrometer at Shimane University was employed.

Development of Analytical Procedures

This study focused on two key issues: (1) constructing calibration curves for direct WD-XRF analysis of obsidian, and (2) overcoming analytical errors caused by uneven artifact surfaces.

(1) Calibration curve construction:

In WD-XRF, a calibration curve represents the relationship between the known concentration of an element (x-axis) and its X-ray fluorescence intensity (y-axis) using standard materials. The element concentration of unknown samples can then be derived from the measured intensity. In this study, chemically characterized obsidians were prepared as standards at the first step.

In conventional XRF rock analysis, powdered rock samples are fused with lithium tetraborate to form glass beads (>1000 °C). Therefore, each raw obsidian sample was split in half: one half was used for destructive WD-XRF glass bead analysis to determine chemical composition, while the other was polished into a flat-surfaced standard sample. Using these polished standard obsidians, calibration curves were constructed for ten major elements (wt%) and eight trace elements (ppm), enabling direct quantitative analysis of polished obsidian surfaces.

(2) Correction for surface irregularities:

Accurate XRF measurements require flat sample surfaces. To evaluate the effect of surface roughness, one obsidian nodule from Mt. Koshidake, Saga Prefecture, was randomly fractured to produce samples with varying surface irregularities. These were quantitatively analyzed using the newly developed calibration curves. The Primus IV allows horizontal sample rotation during measurement, thereby averaging fluorescence intensity variations due to X-ray incident angles. Consequently, the analytical results depend mainly on the degree of surface irregularity. As shown in Figure 1, both the concentration of each element and the total concentration of major elements decrease with increasing surface roughness, exhibiting a linear relationship. This trend was consistent across all analyzed elements. All obsidian samples contain SiO₂, TiO₂, Al₂O₃, Fe₂O₃(T), MnO, MgO, CaO, Na₂O, K₂O, and P₂O₅ as major elements, and their total concentrations sum to approximately 100 wt%. Therefore, the total major-element value serves as a reliable indicator of surface roughness. Based on the relationships shown in Figure 1, correction equations were established for all elements to compensate for the effects of surface irregularities.

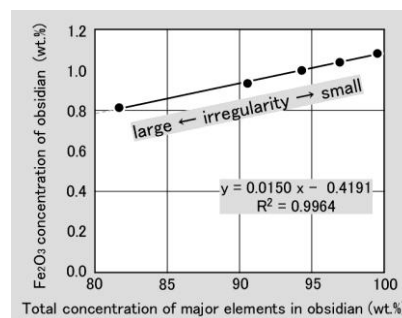


Fig. 1. Compositional variations in obsidian samples with surface irregularity.

Test Analyses of Artifacts

Obsidian artifacts excavated from Jomon and Yayoi sites in Shimane Prefecture were analyzed using the developed method. The results indicate that these artifacts originated from the Kumi and Sai sources on the Oki Islands.

The features of this developing method are:

1. Completely non-destructive analysis
2. Analytical precision equivalent to glass-bead WD-XRF methods
3. Ease of access for any field of researchers

Artifacts that fit into a 7 cm sample holder and have an X-ray irradiation area of at least 1 cm can be analyzed. A measurement requires approximately 20 minutes, and up to 48 samples can be automatically analyzed by Primus IV overnight, allowing for a large amount of data acquisition.

Acknowledgements

Thanks to Dr. Takashi Iwamoto of Shimane University and Mr. Yosuke Inata of the Archaeological Research Center, Shimane Prefecture, for kindly providing the obsidian artifacts used for analysis.

References

- ACQUAFREDDA, P., MUNTONI, I.M., PALLARA, M.: Reassessment of WD-XRF method for obsidian provenance shareable databases. *Quaternary International* 468, 169-178. 2018.
- KAMEI, A., KAKUBUCHI, S., SUDA, Y., OYOKAWA, M., SHIBA, Y., INATA, Y., OHASHI, Y., FUNAI, K., ICHIMOTO, N., OCHI, Y., KOSHIDAKE OBSIDIAN SOURCES RESEARCH GROUP: Whole rock geochemistry of the Koshi-dake series obsidian, Saga prefecture, Japan. *Palaeolithic Research* 12, 155-164. 2016.
- KIM J.C., CHANG Y. : Evidence of human movements and exchange seen from curated obsidian artifacts on the Korean Peninsula. *Journal of Archaeological Science: Reports* 39, 103184, 2021.
- MOCHIZUKI, A.: Identification of source of obsidian found in chuubu and Kanto districts by X-ray fluorescence analysis. *Advances in X-ray Chemical Analysis Japan* 28, 157-168 1997 (in Japanese with English abstract).