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Application of prompt gamma activation analysis to provenance study of the Korean obsidian artefacts

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ABSTRACT

Prompt gamma activation analysis (PGAA) is a non-destructive nuclear analytical method and is useful to obtain the bulk elemental composition of materials. We conducted PGAA for the source rocks of Korean obsidian artefacts. It has been reported that there exist lots of microlites inside the obsidian artefacts. When the uneven distribution of microlites is prominent, bulk analysis rather than spot analysis is preferable to the provenance study of obsidian artefacts. We compared two bulk analytical methods for obsidian: the correlation between the analytical results of PGAA and wavelength dispersive X-ray fluorescence analysis (WDXRF) has been examined. We have found that the major oxide contents from the PGAA are in good accordance with those from the WDXRF except for MnO. Using the PGAA data, we investigated the geochemical contrast between the two kinds of source rocks of the Korean obsidian artefacts and found out that the bulk PGAA data can be used as a good discriminator of the two distinct sources.

1. Introduction

Provenance study of prehistoric obsidian artefacts provides a clue to understanding various aspects of the ancient culture in consideration. So far, estimation of the source of the obsidians found in archaeological context has usually been made by analyzing their geochemical characteristics. Before conducting geochemical analysis for obsidian artefacts, there are some important factors to be taken into account to select an analytical method for obsidian samples: amount and preservation (non- or micro-destructive techniques) of samples, accuracy, precision and sensitivity (level of detection) of the techniques (Falcone et al., 2006).

Geochemical information has been acquired by such analytical methods as pXRF, PIXE, ICP-MS, SEM/EDX, WDXRF, etc., and these methods can be divided into two types according to the analytical area of the sample: spot analysis and bulk analysis. The spot analysis provides the elemental composition for the small limited area (several micrometres to a centimetre in diameter) of samples, for example, EPMA, portable XRF, PIXE and so on. The bulk analysis is conducted for a certain amount (at least several grams) of whole-rock samples, for example, laboratory-based XRF (EDXRF, WDXRF), ICP-MS and so on. It is noticeable that many researchers have reported remarkable disagreement between the compositional results of obsidian artefacts derived from spot analysis (portable XRF) and laboratory-based bulk XRF (EDXRF and WDXRF) analysis (Craig et al., 2007; Nazaroff et al., 2009; Jia et al., 2010). This kind of disagreement could have come from the non-homogeneous internal texture of the obsidians. If the internal texture of obsidian is not homogeneous, the spot analysis will give us information only on a small analyzed area, not on the whole sample. We introduce the internal heterogeneity of Korean obsidian artefacts and discuss the advantage of bulk analysis for the provenance study of the obsidian artefacts.

It is also well known from the literature that Instrumental Neutron Activation Analysis (INAA or NAA) is a powerful tool to apply for provenance studies of archaeological obsidian (Williams-Thorpe et al., 1984; Kilikoglou et al., 1996; Kuzmin et al., 2002). Lynch et al. (2016) have been compared the analytical capabilities of NAA, ICP-MS and EPMA, using Geological Reference Materials, whereas Suda et al. (2018) have compared the analytical capabilities of WDXRF, EDXRF, ICP–MS, NAA and PGAA on Japanese origin geological obsidian.

With NAA, a series of major- and trace elements can be quantitatively determined with high sensitivities, including Na, K, Mn, Fe, Rb,

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Sr, Cs, Ba, Sc, Co, Zn, Zr, Hf, Ta, Sb, La, Ce, Sm, Eu, Tb, Yb, Lu, Th and U. From these elements, for instance, linear combination of Sc, Cs, Ta, Ce, La, Th and Rb vs. linear combination of Sc, Fe and Co can be used as discriminative factors in provenance studies of archaeological obsidian (Williams-Thorpe et al., 1984; Kilikoglou et al., 1996).

Recently prompt gamma activation analysis (PGAA) is proved to be a useful non-destructive bulk method to determine the concentration of most major and on some trace elements in obsidian samples (Kasztovszky et al., 2008; Kasztovszky et al., 2017). Since PGAA has been successfully applied to provenance research on Carpathian obsidians (Kasztovszky et al., 2014), we decided to examine the applicability of the PGAA to study of the provenance of Korean obsidian artefacts. We compare the geochemical data of obsidians acquired from two bulk analytical methods, PGAA and WDXRF.

Comparing the number of chemical elements determined by PGAA vs. NAA, one can say that PGAA enables to quantify all the major geochemical components, except Mg, which is usually under the quantification limit in obsidian. In addition, a few minor and trace elements, such as H, B, Cl, Nd, Sm and Gd can be measured with high sensitivity, from which quantitative determination of H, B and Cl is a unique feature of PGAA.

On the other hand, with NAA a relatively larger number of trace elements can be measured. Nevertheless, the indisputable advantage of PGAA over NAA in Cultural Heritage studies is that PGAA does not require sampling of the investigated objects, thus valuable museum objects can be studied in a non-invasive way (Kasztovszky et al., 2014).

2. Obsidian sources around Korea

In South Korea, obsidian artefacts are known at many prehistoric sites, if limited in quantity (Fig. 1). All of the sites in this figure are representative open-air localities dated between c. 25–30 ka and 5–6 ka. Regarding the provenance of the obsidian artefacts, there currently are a couple of contrasting opinions among the researchers. One is that they are mostly from the Baekdusan area (the obsidian artefacts from Hahwagyeri, Hopyeongdong, Jangheungri, Sangmuryongri, Samri, and Suyanggae sites in Fig. 1; Sohn, 1989; Kuzmin, 2004; Kim et al., 2007). The other is that other materials are present, whose sources must be delineated (Gigok, Sangsari, Shinbuk, and Wolseongdong sites in Fig. 1; Cho et al., 2006; Jang et al., 2007; Cho and Choi, 2010, 2012). Obsidian artefacts from the southern part of South Korea demonstrate genetic similarity to the Kyushu obsidians (Dongsamdong, Tongyeong, and Yeosu sites in Fig. 1; Cho et al., 2006; Jang et al., 2007; Kim et al., 2007). Since the petrological and geochemical characteristics of both the Baekdusan and Kyushu obsidians are not well known, it is important to understand the compositional contrast between the two types of obsidians in clarifying the provenance of the Korean obsidian artefacts.

3. Microlite effect on spot analysis

Obsidian stands for rhyolitic glass in geological nomenclature. The glass is thought to be a homogeneous non-crystalline material, but it is not completely homogeneous in its composition and texture due to internal impurities. The impurity comes from the very tiny micrometre-sized crystals, called microlites. In Korean obsidian artefacts there exist lots of microlites which were produced from quenching of acidic magma under disequilibrium condition (Fig. 2; Jin et al., 2014; Jwa and Yi, 2016; Hwang and Jwa, 2017).

According to the morphological discrimination of the microlites compiled by Clark (1961), the most abundant morphological features in the Baekdusan and Kyushu obsidians are trichites acicular and asteroidal, arculites, crenulites, lath-crystal and so on (Jin et al., 2014; Hwang and Jwa, 2017), which are well observed under high magnification of the optical microscope. However, if we examine the microlites through high-resolution scanning electron microscope, they show very distinct mineral assemblage and/or mineral paragenesis (Hwang and Jwa, 2017). For example, the microlites in the Baekdusan and Kyushu obsidians represent different mineral paragenesis. In other words, Fe-oxides in the Baekdusan obsidians occur within the clinopyroxenes, showing poikilitic texture (Fig. 2B and C). On the other hand, the clinopyroxene microlites in the Kyushu obsidians are overgrowing around the Fe-oxides. The most contrasting mineral assemblage between the Baekdusan and Kyushu obsidians is that the biotite microlites exclusively occur in the Kyushu obsidians.

Microlites are ubiquitous and unevenly distributed in obsidian; thus the internal texture of obsidian is usually divided into the microlites and glassy host matrix (Swanson et al., 1989). Also, the microlites have various compositions such as Fe−Ti oxides, clinopyroxene, plagioclase etc. (Castro and Mercer, 2004; Befus et al., 2014). It can be, therefore, hardly said that composition from a small area of the obsidian represents the bulk composition of it.

In other words, it seems likely to be a critical factor in the geochemical analysis for obsidian how many microlites are distributed and what kinds of them are occurred in obsidian. It is necessary to avoid the unexpectable effect of microlites in geochemical consideration of obsidian source. Thus it is highly recommended to get bulk data and use the data for discussion on provenance.

4. Materials and analytical methods

We analyzed nine natural obsidian samples; three obsidians collected from the Baekdusan and six from the Kyushu volcanic fields (Fig. 1). The obsidians from both areas have been known for the contrasting sources of the prehistoric obsidian artefacts in Korean Peninsula. (Kim et al., 2007; Chang, 2013; Yi and Jwa, 2016). The obsidians are black to dark color and show conchoidal surface fracture. About 5 to 10 g of the samples were ground in an agate mill and well mixed during pulverization. The sample powders were directly used for PGAA and used to prepare glass beads for XRF analysis.

4.1. PGAA

Nine samples of geological obsidian have been analyzed by PGAA at the Budapest PGAA Laboratory. PGAA is a nuclear analytical technique for non-destructive quantitative determination of elemental compositions (Révay and Belgya, 2004). The sample is irradiated in a guided neutron beam, and the gamma-rays originated from the radiative capture, i.e., from the (n,γ) reaction are detected. In principle, every chemical element can be measured, without any prior information on the analyte. However, the sensitivities vary within a wide range. The energies and intensities of the peaks are independent of the chemical state of the material; hence the analytical result is free of matrix effects. Both neutrons and gamma-rays are highly penetrating; therefore, the average composition of the illuminated volume is obtained. The evaluation can be described with statistical methods, and the uncertainties of the concentrations can be estimated already from a single measurement.

Powdered forms of all the samples have been packed in thin FEP film and placed in fixed sample position. The neutron flux at the sample position of the PGAA station was $9.6 \times 10^7\ cm^{-2}\ s^{-1}$. The cross-section of the neutron beam was changed between 100 mm^2 and 400 mm^2, to ensure that the whole sample is placed in the neutron beam. The acquisition time has been set to be between 2000 s and 19,000 s, to collect statistically significant counts in the spectra. The gamma radiation from the radiative neutron capture was detected with a High-Purity Germanium (HPGe) detector, surrounded by a Bismuth Germanate (BGO) scintillator and lead shielding; the signals were processed with a Canberra AIM 556A multichannel analyzer. The facility has been described in details in an earlier publication (Szentmiklósi et al., 2010). The spectra were evaluated with Hypermet-PC gamma spectroscopy software. The element identification was made with the program ProSpeRo (Révay, 2009), utilizing our prompt-gamma analysis library