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Inter-laboratory validation of the WDXRF, EDXRF, ICP–MS, NAA and PGAA analytical techniques and geochemical characterisation of obsidian sources in northeast Hokkaido Island, Japan

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ABSTRACT

Obsidian provenance studies, based on geochemical signatures, are important for determining the source regions of obsidian artefacts. Such research depends on the availability of reproducible geochemical data. An inter-laboratory study was conducted to validate analytical methods applied to samples from four obsidian sources in northeast Hokkaido Island (Shirataki, Rubeshibe, and Oketo regions). The methods applied were Wavelength-Dispersive X-ray Fluorescence (WDXRF), Energy-Dispersive X-ray Fluorescence (EDXRF), Inductively Coupled Plasma–Mass Spectrometry (ICP–MS), Neutron Activation Analysis (NAA) and Prompt-Gamma Activation Analysis (PGAA). Eight laboratories in Japan, the Russian Federation, Republic Korea, Hungary, Canada, and the USA took part in the trials. Results indicate discrepancies between laboratories, but compositional data for 53 elements were successfully compiled, and reference compositions for 16 elements in each sample defined. Based on these data, a new chemical discrimination scheme is proposed for obsidian sources in the Shirataki, Rubeshibe, and Oketo regions. This scheme is applicable to the discrimination of obsidian sources using semi-quantitative EDXRF analysis, with this being important in non-destructive provenance studies of artefacts. This study fosters the further establishment of reference materials for obsidian sources in the Hokkaido region, and the sharing of such materials.

1. Introduction

The need for consistent obsidian source data has been highlighted by increasing international collaboration in obsidian provenance studies within Northeast Asia during the past two decades (e.g., Doelman et al., 2008; Glascock et al., 2011; Hall and Kimura, 2002; Jia et al., 2010, 2013; Kim et al., 2007; Kuzmin and Glascock, 2010; Kuzmin et al., 2002, 2008, 2013; Lee and Kim, 2015; Ono et al., 2014;

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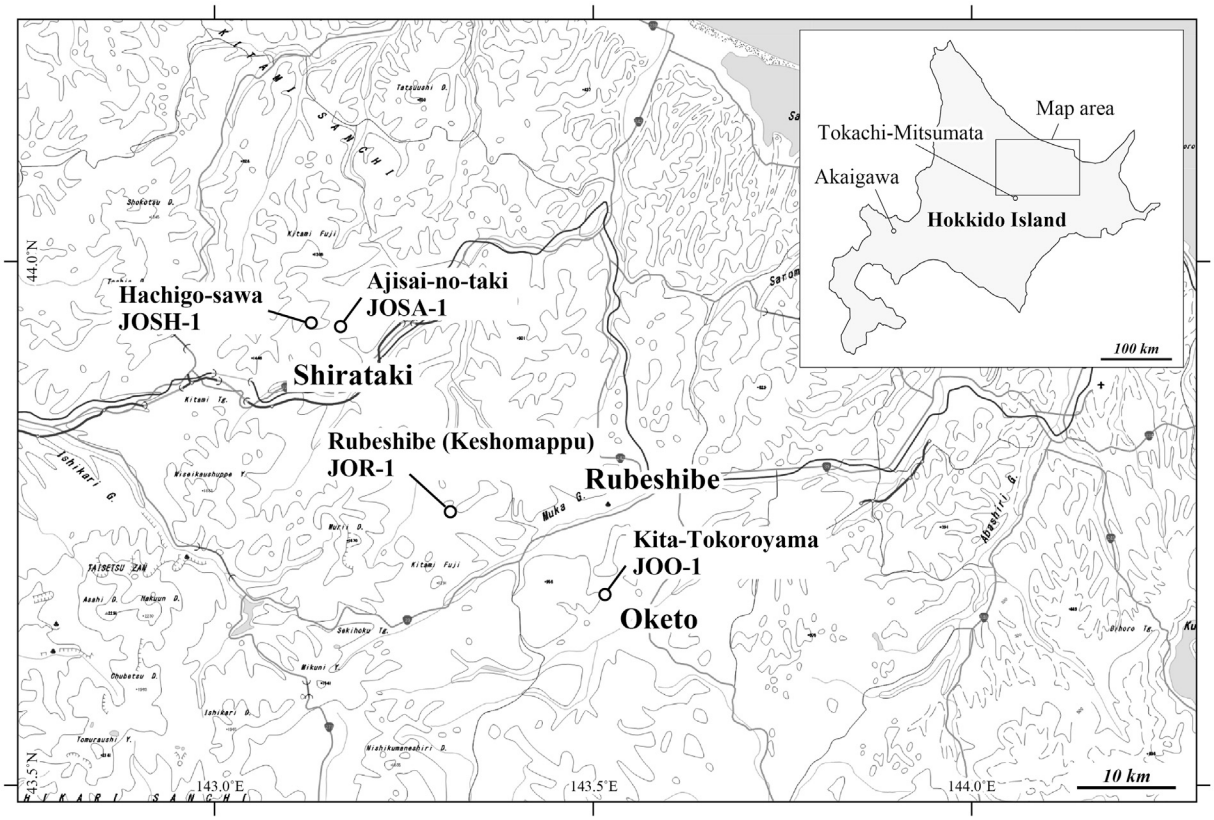

Fig. 1. Locations of obsidian samples analysed in this study, from Ajisai-no-taki (JOSA-1) and Hachigo-sawa (JOSH-1) in the Shirataki region, Rubeshibe (Rubeshibe or Keshomappu) in the Rubeshibe region, and Kita-Tokoroyama (JOO-1) in Oketo region, northeast Hokkaido Island, Japan.

Popov et al., 2005, 2008; Yoshitani et al., 2003). Limitations imposed by determination of a small number of elements were demonstrated by Warashina (2004) who was unable to distinguish between two obsidian sources from Hokkaido Island, Japan: Akaigawa, and Tokachi-Mitsumata (Fig. 1), using Energy-Dispersive X-ray Fluorescence (EDXRF) analysis of 12 elements (Izuho and Hirose, 2010). This distinction was possible only through use of Neutron Activation Analysis (NAA) of 28 elements (Kuzmin and Glascock, 2007; Kuzmin et al., 2013).

Obsidian is a natural glass, with a relatively homogeneous composition and texture compared with other lithic materials such as chert, flint, shale, phyllite, and serpentinite. Moreover, obsidian sources have distinctive and unique “fingerprints” of trace elements that vary according to circumstances of their formation. Therefore, obsidian is perhaps the best material for use in studies of prehistoric human interaction and migration. It is vital, however, that provenance studies of obsidian composition are undertaken with great care in terms of systematic methodology, selection of analytical techniques, and standardisation.

The characterisation of obsidian sources begins with the observation of their appearance, including colour, transparency, and surface texture. The subjective nature of such characterisation means that descriptions inevitably vary among observers. Chemical analysis by X-ray Fluorescence (XRF) method has therefore been employed since the 1960s (e.g., Shackley, 2005, 2011) in order to improve consistency. Analysis techniques advance over time, but the basic methodology of provenance studies for archaeological obsidian is based on comparisons between artefacts and geological obsidians, and remains unchanged. Indeed, the aim of provenance studies is the comparison of archaeological obsidian with reference data for geological obsidian. Therefore, obsidian source studies require an archive of reference materials from various sources, and a compilation of their chemical characteristics obtained by instrumental analysis. Ideally, all analyses for both geological and archaeological obsidians should be carried out by the same laboratory, because data consistency cannot be adequately verified with different facilities using a variety of analytical methods and reference materials. However, validation of data through laboratory intercomparisons is rarely undertaken (e.g., Bellot-Gurlet et al., 2005; Glascock, 1999, 2011), despite the clear rationale for doing so (e.g., Golitko, 2015).

The present study originated from a field excursion in the Shirataki region of northeastern Hokkaido Island, Japan, during November 2011 (Fig. 1; Ono et al., 2014), which provided an opportunity for collection of high-quality obsidian from several previously studied sources, followed by a comparison of data from different laboratories and analytical methods (e.g., Ferguson et al., 2014; Suda, 2014; Wada et al., 2014). Here we describe the geological background of the obsidian sources in Shirataki, Rubeshibe and Oketo regions, and petrological properties of obsidian revealed by microscopic analysis including Electron Probe Microprobe Analyser (EPMA). Analytical procedures and results of whole-rock analyses at different laboratories are presented, including the following methods: Wavelength-Dispersive X-ray fluorescence (WDXRF), EDXRF, Inductively Coupled Plasma Mass Spectrometry (ICP–MS), NAA, and Prompt-Gamma Activation Analysis (PGAA). Analytical results obtained by both quantitative and semi-quantitative analyses were compared between laboratories, and a geochemical characterisation scheme is proposed for obsidian sources in studied regions.

2. Sampling locations

The Shirataki, Rubeshibe and Oketo regions in northeastern Hokkaido are well known as a major cluster of obsidian sources (Fig. 1; e.g., Izuho and Sato, 2007; Kuzmin et al., 2013). Obsidian is closely associated with Pliocene volcanic rocks, and occurs in outcrops of rhyolite lavas and as nodules in pyroclastic deposits (Konoya et al., 1964; Nochi et al., 1967; Wada et al., 2014). A whole-rock K–Ar age of