

Sourcing Obsidian: a comparison of pXRF, INAA, ICP-MS and Electron Probe Microanalysis

Sean C. Lynch¹; M. John. M. Duke²; Andrew J. Locock³; Andrzej. W. Weber¹

1. Department of Anthropology, University of Alberta, Edmonton, Alberta, Canada

2. SLOWPOKE Reactor Facility, University of Alberta, Edmonton, Alberta, Canada

3. Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta, Canada

Modern Trends in Activation Analysis, Delft, Netherlands 2015

Introduction

Provenance studies of obsidian from Hokkaido, Japan, have focused on determining benchmark geochemical data through the use of well-established, multi-element, analytical techniques [1,2,3,4].

Few studies have addressed the potential of portable X-ray fluorescence (pXRF) for such characterization [5,6]. The work described here compares pXRF to laboratory-based techniques including instrumental neutron activation analysis (INAA), inductively-coupled-plasma mass spectrometry (ICP-MS), and electron probe microanalysis (EPMA) in order to demonstrate the suitability of pXRF for distinguishing archaeological sources of obsidian from Hokkaido [6].

Hokkaido Obsidian

Hokkaido is the most northerly island in the Japanese archipelago. Obsidian from the 21 known sources (and sub-deposits) on the island has been used to make stone tools since at least ~30,000 BCE (Fig. 1). Obsidian from Hokkaido was transported by prehistoric peoples up to 1000 km from its origin [1,2]. The most prominent sources of obsidian on Hokkaido are Shirataki, Oketo, Akaigawa and Tokachi-Mistumata (Fig. 2).



Figure 1. Tools made from Hokkaido obsidian, circa 4500 BCE.

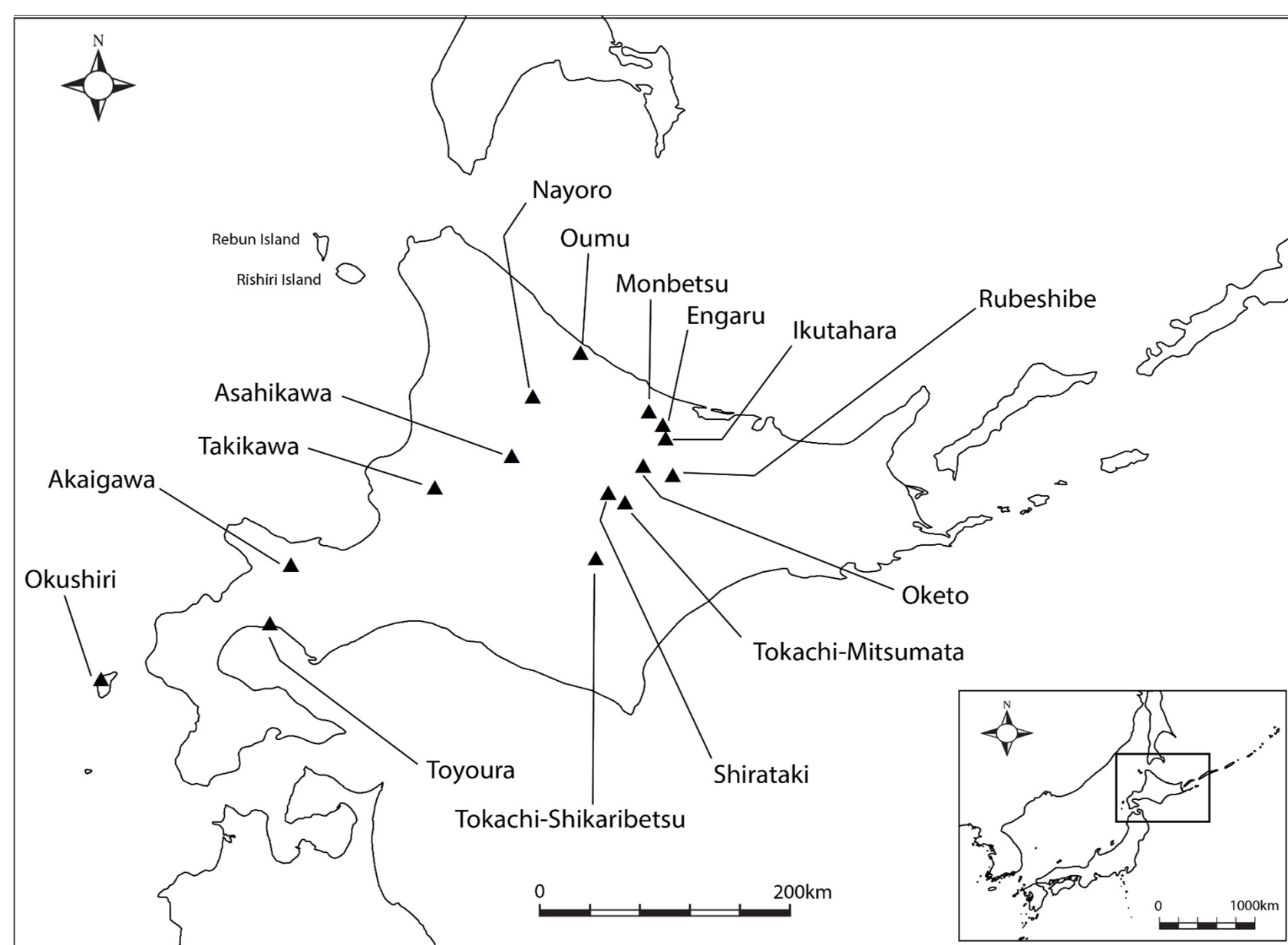


Figure 2. Obsidian source locations in Hokkaido, Japan.

Materials

Specimen JPN-1 is from the Shirataki-Akaishiyama sub-deposit, and was chosen because of the significant amount of published geochemical data for this locality [1,2,3,4]. The USGS reference material RGM-1 [7] was used to estimate the accuracy of the INAA and ICP-MS methods (Table 1).

Table 1. Consensus and measured values for RGM-1.

Element	USGS [7]	INAA U-Alberta	ICP-MS
Mn (µg/g)	282 ± 30	292	421
Fe (%)	1.30 ± 0.04	1.27	1.37
Zn (µg/g)	32 ± 6	35	29
Ga (µg/g)	15 ± 2	n.d.	18
Rb (µg/g)	149 ± 8	147	147
Sr (µg/g)	108 ± 10	99	106
Y (µg/g)	25 ± 4	n.d.	21
Zr (µg/g)	219 ± 20	214	219
Nb (µg/g)	8.9 ± 0.6	n.d.	11
Th (µg/g)	15.1 ± 1.3	14.2	27

Not determined: n.d.

Methods

pXRF: Sample JPN-1 was repeatedly analysed (28 replicates over 8 weeks) with a Bruker AXS Tracer III-SD handheld XRF spectrometer at 40 kV and 30 µA, using a polycrystalline filter (0.3047 mm Al, 0.0254 mm Ti, 0.1523 mm Cu), and 300 s live-time count. Intensities were calculated as ratios to the Compton peak of Rh and converted to µg/g.

INAA: Three powdered aliquots of JPN-1, together with a sample of RGM-1 (each weighing ~500 mg), were analysed at the Univ. of Alberta SLOWPOKE Facility. Short-lived radionuclide producing elements were determined following a 240 s irradiation at a nominal thermal neutron flux of $1 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$, while the majority of the reported elements were determined following a 2 h irradiation at $5 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ and various decay times. Counting was performed using a 40%-relative-efficiency ORTEC FX-Profile hyperpure Ge detector with carbon window, attached to an ORTEC DSPEC-Pro digital spectrometer.

ICP-MS: Three powdered aliquots of JPN-1, each weighing ~200 mg, were weighed and digested in sealed vessels with 8 mL HF and 2 mL HNO₃ at 130°C. Diluted solutions were run in triplicate on a Perkin Elmer Elan 6000 quadrupole ICP-MS at a flow rate of 1 mL/min, 35 sweeps per reading, with 3 replicates. ICP RF power was 1300 W and the instrument was run in dual detector mode with the auto lens on; 4-point calibrations were used for each element.

EPMA: For the glass matrix of JPN-1, 270 points were analyzed on a JEOL 8900R electron microprobe, run at 15 kV and 10 nA with a beam diameter of 10 µm and peak count times of 20 s. Wavelength-dispersive spectrometry was used to measure the K α lines of Na, Mg, Ca, Al, Si, K, Ti, Mn, and Fe. Natural minerals and glasses were used as standards, and the data were reduced using CITZAF. Back-scattered-electron (BSE) mapping was used to examine JPN-1 for the presence of micro-inclusions.

Results

The INAA data collected at the University of Alberta for JPN-1 are compared in Figure 3 with the data of Kuzmin *et al.*, 2013 [2] for obsidian from the same sub-deposit. The data are in excellent agreement (except Co), demonstrating the consistency for a wide range of elements of both Shirataki-Akaishiyama sub-deposit obsidian and the two laboratories.

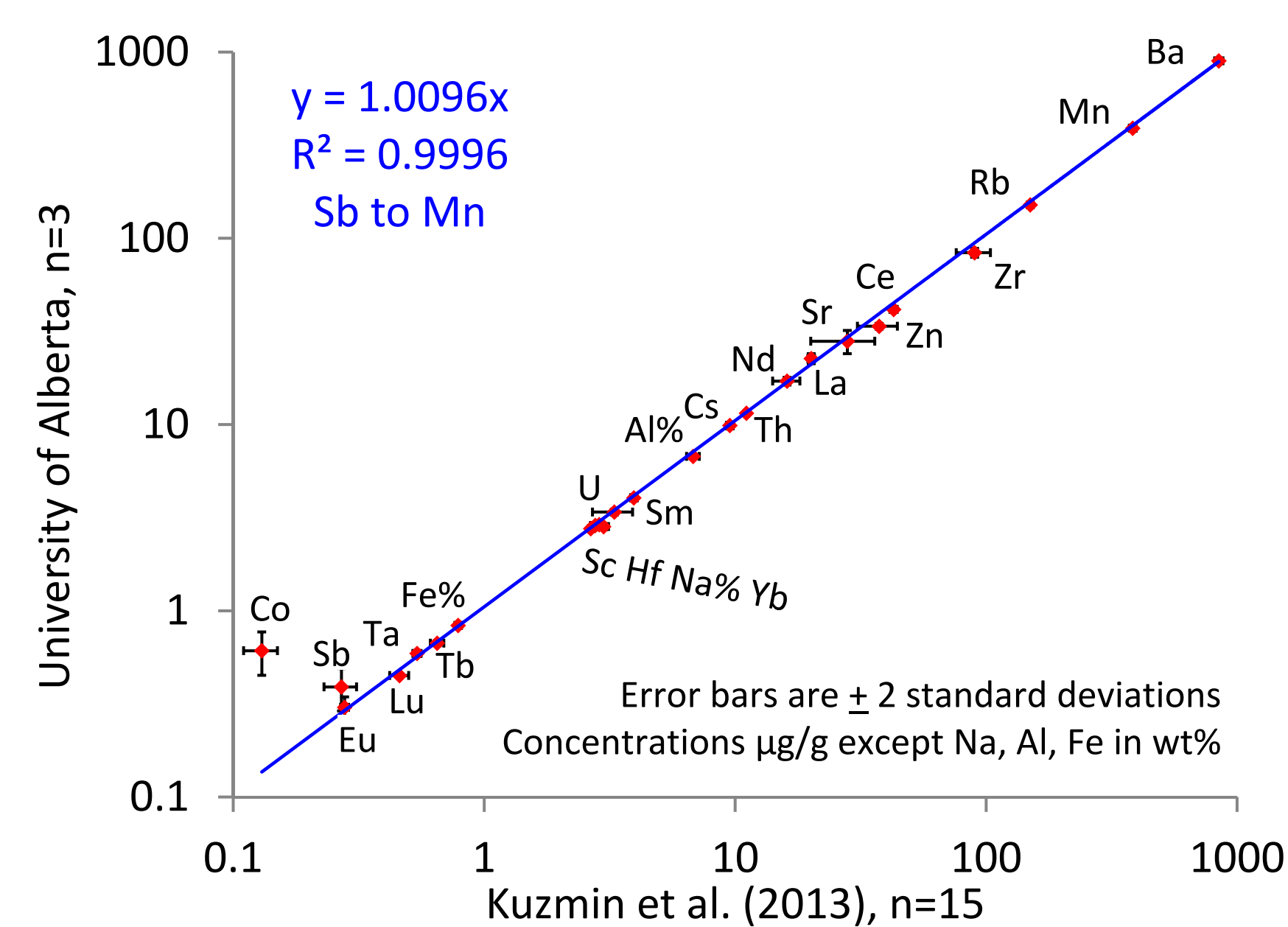


Figure 3. Comparison of Shirataki-A (JPN-1) INAA data.

The pXRF data for 10 elements are compared with INAA and ICP-MS data for JPN-1 in Figure 4. The results from pXRF for the petrologically important elements Rb, Sr, and Zr are in very good agreement with the benchmark data from these other methods. Some of the other elements do not agree as well (Mn, Zn), but these are less important in characterizing obsidian sources.

The present EPMA results (Table 2) of the glass matrix of JPN-1 are similar to published micro-analytical data for Shirataki obsidian [4], but has a lower Fe content (0.26 wt% Fe, as element) from present (Fig. 4) and previous whole-rock data [3].

Table 2. EPMA data for JPN-1 glass matrix (n=270 points).

	SiO ₂	TiO ₂	Al ₂ O ₃	MnO	FeO	MgO	CaO	Na ₂ O	K ₂ O	Sum
wt %	77.11	0.04	13.26	0.05	0.33	0.03	0.54	3.68	4.42	99.46
σ	0.33	0.02	0.09	0.02	0.12	0.01	0.04	0.16	0.08	0.42

Results, continued

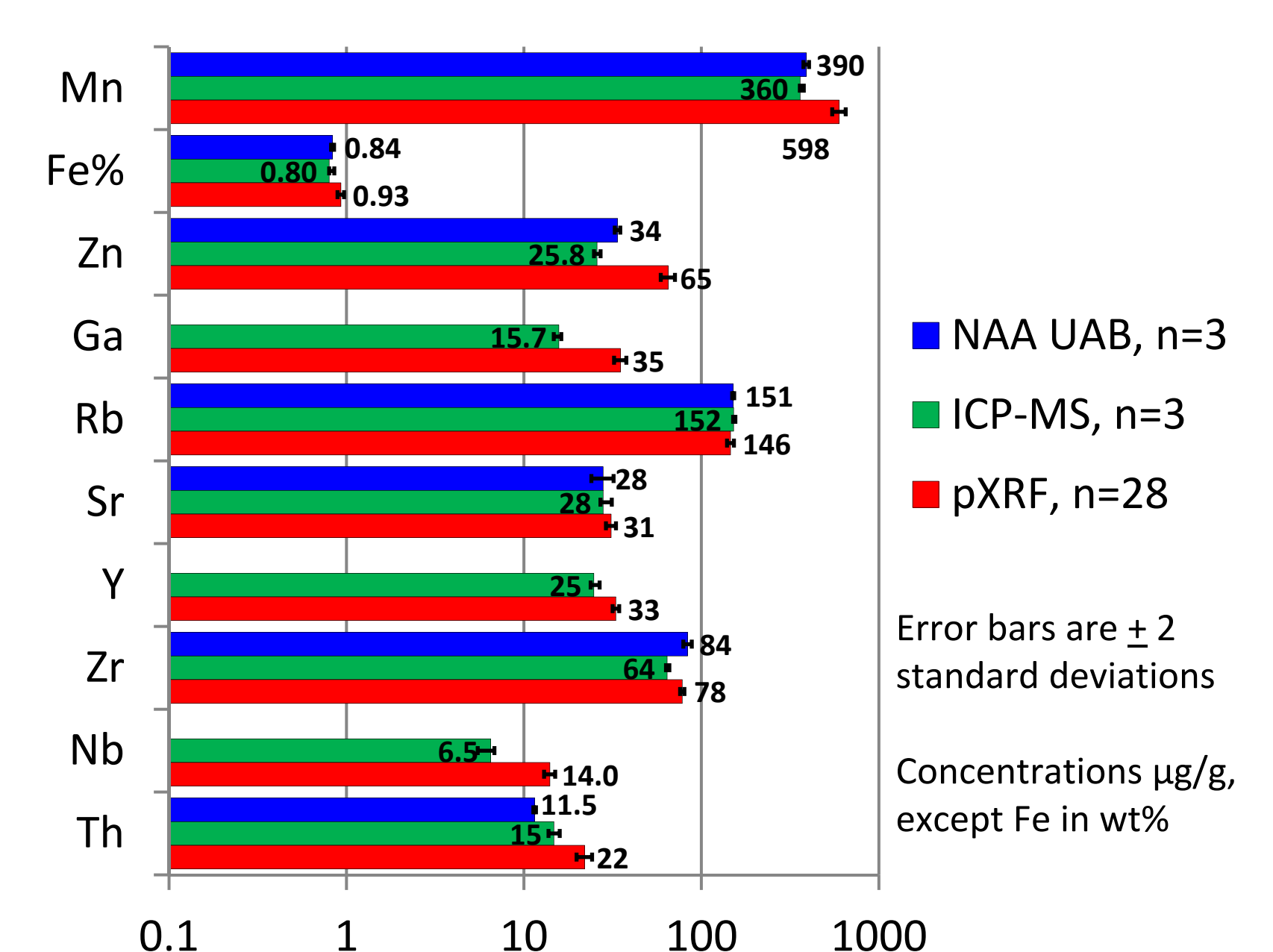


Figure 4. pXRF data for JPN-1 compared with other methods.

Back-scattered-electron (BSE) mapping revealed micro-inclusions of iron oxides throughout JPN-1 (Fig. 5). These range from less than 0.5 to 50 µm in diameter, and constitute about 0.4% by volume of the sample. This volume estimate is based on the dissimilarity between the Fe-content of the bulk rock (0.80 to 0.93 wt% Fe, Fig. 4) and that determined for the glass matrix by EPMA (0.26 wt% Fe).

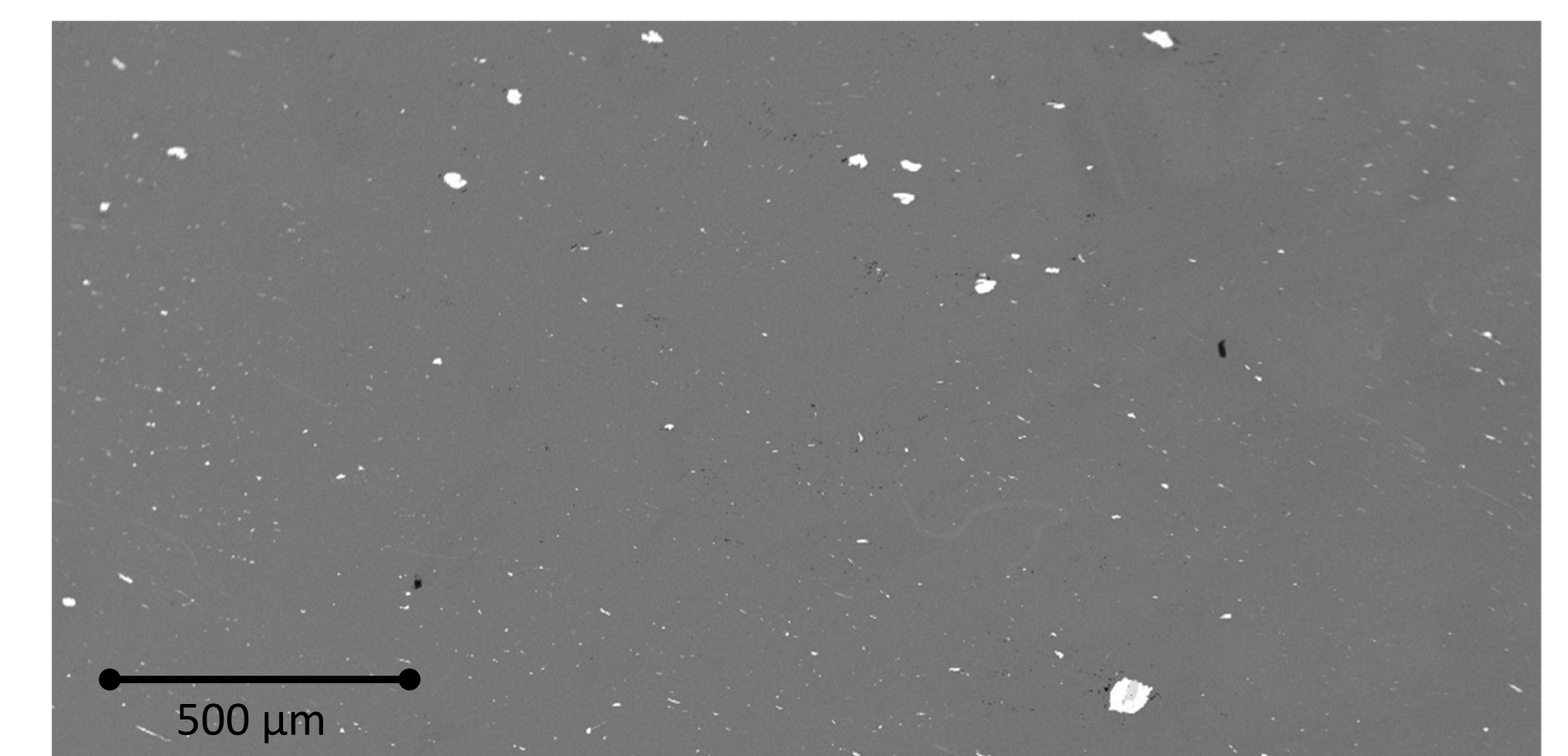


Figure 5. BSE image of JPN-1; white spots are iron oxides.

Discussion and Conclusions

This study demonstrates the consistency of pXRF data with INAA and ICP-MS for select trace elements (Rb, Sr, and Zr) that are important for obsidian source determination. In contrast, the results for the concentrations of elements such as Mn and Zn are only in fair agreement with those established by the other techniques.

The inaccuracy of the pXRF data for these latter elements may be partly attributed to the uneven surface of the JPN-1 sample examined. In the case of an uneven (rough) sample, the geometry of X-ray fluorescence (absorption of incident radiation and excitation of characteristic X-rays) becomes irregular [8]. The calibration, based on a regular geometry, when applied to such data appears to result in over-estimation of lower energy X-ray emission lines (Mn to Ga, in this case).

Flat or polished samples are ideal for pXRF analysis. However, prehistoric obsidian artifacts are typically irregular and lack flat surfaces (Fig. 1). Thus the JPN-1 sample selected for this study is morphologically irregular, reflecting the common real-world experience. Despite this complication, the petrologically important trace elements that assist with obsidian source determination (Rb, Sr, Zr) were accurately quantified by pXRF.

The advantages of pXRF for obsidian source determination are its completely non-destructive nature, rapidity of analysis, and portability. The other methods used here all require some degree of sample preparation, whether sizing to fit in a reactor vial (INAA), polishing of a thin section (EPMA), or dissolution of a representative powder (ICP-MS). The pXRF method is more rapid, if the sample preparation time for these other methods is taken into account. And, of course, pXRF is portable, and can be used easily in the field, museum, or laboratory.

Thus, despite the limitations on the accuracy of some elements, pXRF should be a powerful method for rapid obsidian source determination.

Acknowledgements

Purchase of the portable X-ray fluorescence spectrometer was made possible through funding to A.W.W. by the Canada Foundation for Innovation. Logistical support in Hokkaido was provided H. Kato.

Contact

Sean C. Lynch
University of Alberta
Email: sclynch@ualberta.ca
Website: <http://bhap.artsrn.ualberta.ca/>

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