



Quantitative EDXRF Studies of Obsidian Sources in Northern Hokkaido

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Quantitative trace element data from six obsidian sources on the Japanese island of Hokkaido is presented. Previous work by Japanese scholars has utilized neutron activation analysis (NAA) focusing on the rare earth elements, or qualitative energy dispersive X-ray fluorescence (EDXRF). In this study, non-destructive EDXRF is used to generate trace element data for 9 elements. Bivariate plots of the incompatible trace elements (Ba, Rb, Sr, Y, and Zr) can be used to separate the obsidian sources in this study. Source separation was confirmed by using linear discriminant analysis. Stepwise discriminant analysis indicates that Ba, Sr, Rb, Ti, Y, and Zr are the most discriminating elements.

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Introduction

Pioneering studies on sourcing Japanese obsidian, utilizing neutron activation analysis (NAA) and fission track dating, were done by Suzuki (1973a, 1973b, 1983, 1984), followed by Ninomiya (e.g., 1985), Okimizu (e.g., 1988), Osawa (1991) and Osawa *et al.* (1977). The focus of Suzuki's research was primarily on the obsidian sources in the Izu peninsula, Izu islands, and Nagano prefecture, and artifacts discovered in the Chubu and Kanto regions. In the later work, Okimizu and Osawa greatly expanded the number of samples and geographic regions covered. The primary disadvantage to this work is that the current method of NAA in Japan requires a destructive sample to be taken.

Warashina (e.g., Warashina, 1998; Warashina & Highashimura, 1983), and Mochizuki (e.g., Mochizuki n.d.; Takahashi, Mochizuki & Kamate, 1998), have published non-destructive, qualitative X-ray fluorescence (XRF) analyses of obsidian artifacts and sources from throughout the Japanese archipelago. While there is an exceedingly large database from each of their respective research programmes, the usefulness of this data to other researchers elsewhere is

exceedingly limited. They only report average peak-ratio data. As noted by Davis *et al.* (1998), raw peak-ratio data often varies from instrument to instrument. Second, barium and thorium, important incompatible elements for island arc volcanics, are not measured by these two research groups. Finally, for both of these groups, the sampling strategy and the geographic coverage for the source reference samples is not explained.

The primary purpose of this paper is to provide researchers with quantitative trace element data from several primary and secondary obsidian sources in northern Hokkaido. All these sources produce stone tool quality obsidian that was believed to have been exploited in antiquity. Geochemical data from two of the obsidian sources, Tokachiishikawa and Tokoro mountain, have never been published before. This data will allow researchers at other institutions using not only EDXRF, but also other chemical techniques, to also participate in Japanese obsidian studies. Second, following the work of Fralick *et al.* (1998), Glascock *et al.* (1999), Hughes (1988, 1994), and Shackley (1995, 1998a, b), a preliminary investigation into the chemical variability of three sources within the Shirataki valley is made.

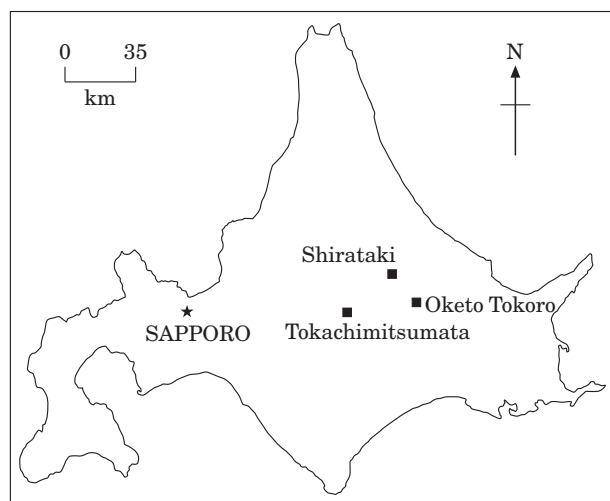


Figure 1. Map of Hokkaido with the obsidian sources noted.

Geochemistry and Geology of the Study Area

The northern half of Hokkaido (see Figure 1) is part of the Kurile volcanic arc. Reviews in English of the geology of this area can be found in Bailey *et al.* (1989), Gribenko *et al.* (1995) and Takagi *et al.* (1999). The volcanically active Kurile arc extends from Hokkaido in the south to the tip of Kamchatka in the north. Hokkaido forms the back-arc side of the arc complex. Coeval andesites, basalts, granites and rhyolites are all found within central and northern Hokkaido (Japanese Geological Survey, 1982; Takagi *et al.*, 1999). K-Ar dating places the first phase of volcanic activity to 10–15 million years ago (Mya), while the second phase is dated to 2–9 Mya (Okimizu, 1988; Takagi *et al.*, 1999).

As volcanic rocks elsewhere, the trace element chemistry of Hokkaido's volcanics reflects the geologic processes and materials involved. Factors such as magma source composition, the degree of melting and fractional crystallization, and mixing and assimilation all influence the trace element concentrations. For a review of these topics, the reader is referred to Christiansen & Keith (1996), Hyndman (1985), Kerrich & Wyman (1996), Mahood & Stimac (1990), Pearce (1996), and Pearce & Peate (1995). Generally though, volcanic arc magmas and their resultant products are characterized by an enrichment of large ion lithophile elements (LILE) such as Ba, Rb, Sr, and a relative depletion of high field strength elements (HFSE) such as Ti, Nb, Y, Zr, and the rare earth elements (REE) (Pearce & Peate, 1995; Kelman *et al.*, 1993). The HFSE and LILE are also called incompatible trace elements since they concentrate in the melt and enter into only select crystalline phases.

Major and select trace element data for the volcanic rocks from the Tokachimitsumata region and elsewhere in northeastern Hokkaido were presented by Ando (1972), and Katsui & Takahashi (1960). Their

work indicated that the Tokachimitsu volcanics were richer in alkali elements than the volcanics in north-eastern Hokkaido. Major element data for andesites, basalts, pumice, and rhyolites from the Kurile arc was summarized in Aramaki & Ui (1978). The data collected by them shows a trend of tholeiitic and calc-alkaline rocks in eastern Hokkaido with a gradual transition to alkali and calc-alkaline volcanics in western Hokkaido.

Detailed trace element data, particularly focussing on the incompatible elements, was presented in Bailey *et al.* (1989), Masuda *et al.* (1975) and Takagi *et al.* (1999). Masuda's research group found that the incompatible elements generally increased as one went from east to west across the Kurile arc. Furthermore, using the REE ratios, they argued the basaltic rocks and rhyolites were derived from the same magmas through fractional crystallization. On the basis of geochemical analyses on basalts from the Kurile islands, Bailey *et al.* (1989) advanced the idea that the volcanic rocks in the Kurile arc were the result of the melting of heterogeneous mantle sources. They also advanced the idea that both fluid melt and metasomatism were responsible for the differences in LILE concentrations between basalts. The geochemical and petrological research by Takagi *et al.* (1999) focussed specifically on the rhyolites of northern Hokkaido. On the basis of the minor and trace element data, they could not fully rule out fractional crystallization of a basaltic magma as the source of the rhyolites. They did argue that a metasomatized, partially melted mantle wedge could also be the source of the rhyolitic magmas.

Methodology

Collection areas

Except for the Tokachimitsumata samples, the authors collected all geologic samples during the summer of 1999. Figures 1 and 2 show the collection areas. Differential GPS coordinates were taken at most every collection location (see Table 1).

For all sources except the Shirataki outcrop, obsidian was collected over at least one transect 500 metres in length. At the Shirataki outcrop, collection was done on the ledge along the outcrop. Its physical layout does not allow transects to be walked. At Tokachiishikawa, the obsidian was collected from a single transect that followed the streambed. At Tokoro Mountain, collection was from a single transect next to the road. Bears and heavy vegetation prevented multiple transects from being collected. The Tokachimitsumata samples were obtained from the Hokkaido Cultural Properties Center in Ebetsu.

A brief description of the obsidian from each source is also contained in Table 1.

Analytical procedure

The obsidian samples were analysed on a Philips PV9550 EDXRF machine equipped with a rhodium

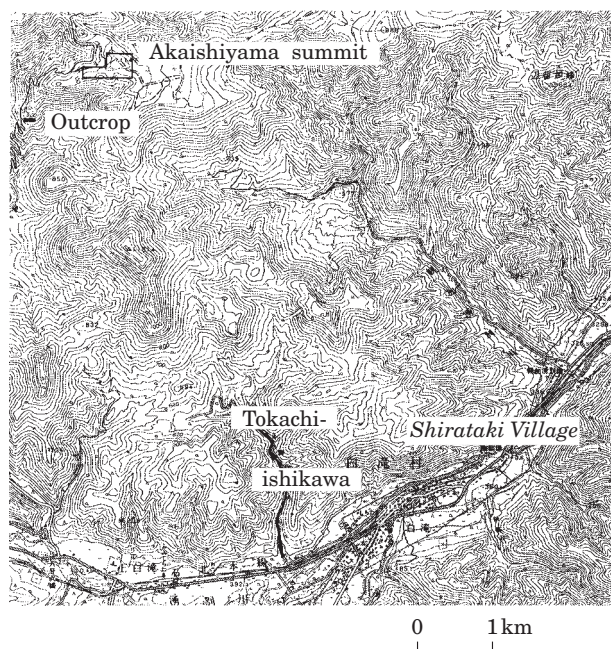


Figure 2. Map of collection locations in the Shirataki valley. The map was based on the 1:50,000 scale map from Kokudo Chiriin (1993). The collection zone for the summit of Akaishiyama is enclosed by a rectangular box. The Tokachi-ishiikawa drainage collection area is denoted by a heavy black line.

X-ray tube, a 0.1 mm silver filter and an EDAX DX-4 X-ray analyser located at the National Museum of Japanese History. The X-ray tube was operated at 50 kV, 100 μ amps at 500 s livetime to generate X-ray intensity data. The incident X-ray beam is approximately 1 cm in diameter. The K_{α} and L_{α} intensity data was collected for the following elements: barium (Ba), cerium (Ce), gallium (Ga), iron (Fe), niobium (Nb), rubidium (Rb), strontium (Sr), thorium (Th), titanium (Ti), yttrium (Y), and zirconium (Zr). The X-ray

Table 2. Concentration, in parts per million (ppm), of select trace elements in the obsidian collected from the summit of Akaishiyama, Shirataki valley. Cerium was not reported for the samples here since it was below the detection limit for the majority of them. Sample numbers ending in letters (i.e., a, b) indicate that the specimens were from the same piece of obsidian. These pieces weighed several kilograms and were over 30 cm in length. Sample numbers marked by an asterisk indicate that the specimens are a black obsidian found on the summit. All others are a reddish-brown or red and black variegated obsidian

Sample	Ti	Fe	Ga	Th	Rb	Sr	Y	Zr	Ba
ak001a*	3541	10,992	29	19	175	31	32	87	3030
ak001b*	3541	11,258	24	17	189	30	32	92	2873
ak002*	3541	12,157	22	15	191	34	31	96	2982
ak003*	2863	11,142	28	19	185	34	31	91	2831
ak004*	3270	10,991	24	18	187	32	31	88	2825
ak005*	2725	10,886	21	18	190	33	30	89	2560
ak006*	2819	10,757	21	16	185	35	29	91	2904
ak007*	2579	10,720	24	16	189	31	30	89	2785
ak008*	3512	11,038	24	19	182	29	30	86	2945
ak009	2750	11,070	21	18	190	31	32	95	2999
ak010	3102	11,473	27	21	184	30	31	88	2931
ak011	3226	10,837	22	19	194	33	30	88	2939
ak012*	4404	11,438	59	21	163	31	33	80	3222
ak013	3067	10,815	22	19	187	31	27	92	2978
ak014	3043	10,836	23	17	184	29	30	90	3006
ak015	3395	11,057	27	18	184	30	30	87	2872
ak016	3015	11,168	22	18	186	32	31	92	2916
ak017	3092	11,470	25	19	192	32	29	95	2873
ak018	3004	10,786	32	16	176	29	30	86	2794
ak019	3001	10,890	22	18	190	34	32	88	2409
ak020	4621	11,160	29	24	195	36	36	95	2857
ak021	3229	11,718	23	20	196	33	31	91	2954
ak022	3120	11,567	23	20	192	34	33	92	2955
ak023	3064	11,774	22	21	198	34	32	92	2679
ak024	3341	11,370	30	18	193	33	32	103	2939
ak025	2948	11,360	27	17	194	34	37	91	2895
ak026	3125	11,803	31	20	197	34	34	93	2921
ak027	2470	10,546	23	17	188	32	35	95	2402
ak028	2922	10,773	26	18	192	33	30	96	2811
ak029	3087	10,923	28	19	192	36	33	94	2875
ak030	2832	10,679	21	15	193	31	33	96	2619
Mean	3169	11,144	26	18	188	32	32	91	2857
S.D.	449	387	7	2	7	2	2	4	172

Table 1. Description and location of the obsidian sources studied in this paper

Location	Coordinates	Description
Akaishiyama summit, Shirataki valley	43° 56' N 143° 08' E Elev. = 1140 m asl	The obsidian ranges in size from small pebbles a few centimeters in size to large boulders several meters across. The obsidian in the western part of the summit is reddish-brown with black flecks. Flakes from this material are completely opaque. The obsidian on the eastern side of the summit is completely black. Flakes from this material are translucent.
Outcrop source on Akaishiyama, Shirataki valley	43° 56' N 143° 07' E Elev. = 850 m asl	The outcrop is approximately 3 metres in height. Spalling produces chunks of obsidian of varying size. Obsidian from this part the mountain contains phenocrysts of varying size. Flakes from this material are translucent.
Oketo	43° 41' N 143° 32' E Elev. = 400 m asl	Along the slopes and summit of the mountain, nodules approximately 5 cm in diameter can be found. Some variegated red and black obsidian is present.
Tokachiishikawa, Shirataki valley	N/A	Nodules ranging from a few centimeters to almost a meter in diameter can be found in this secondary deposit. The obsidian is a dull black with sub-millimeter voids in it.
Tokachimitsumata	N/A	A shiny black obsidian.
Tokoro	43° 40' N 143° 31' E Elev. = 425 m asl	Nodules 5–10 cm in length are found on the slopes of this mountain. It is a shiny black obsidian with some faint grey striations in it.

Table 3. Trace element concentrations (in ppm) from the outcrop source at Akaishiyama. Samples ending in letters (i.e., a, b, c) are from the same piece of obsidian. These pieces weighed several kilograms and were over 30 cm in length

Sample	Ti	Mn	Fe	Ga	Th	Rb	Sr	Y	Zr	Ba
h001	3303	752	11,225	35	19	185	31	31	94	2986
h002	3469	676	11,116	21	19	182	29	30	88	3128
h003	3575	792	11,790	31	23	179	32	31	85	3042
h004a	2552	619	10,530	21	17	182	29	31	87	2646
h004b	2640	671	10,846	23	16	188	31	33	89	2663
h005	3265	683	11,188	19	19	190	32	31	91	2867
h006	2437	657	10,896	18	19	188	33	33	92	2572
h007	3662	783	11,743	35	21	186	31	32	88	2989
h008	2385	658	10,728	21	17	188	31	30	96	2531
h009	3415	650	11,208	31	16	186	36	28	92	2925
h010	3131	733	11,598	22	20	193	33	32	90	2969
h011	3212	630	11,148	23	17	181	30	29	91	2931
h012a	3430	660	10,632	21	18	179	30	30	85	3016
h012b	3040	719	11,410	24	17	187	33	29	89	3002
h012c	3095	698	11,280	26	19	188	31	30	90	3009
h013a	3346	762	10,756	24	20	177	28	31	88	2973
h013b	2899	622	11,326	27	19	189	31	30	90	2855
h013c	3017	773	11,419	21	20	194	33	31	92	2880
h013d	2706	650	10,624	20	18	188	29	27	93	2969
h013e	2042	639	10,901	21	18	191	32	33	92	2299
h014	2772	610	10,941	21	19	192	31	28	94	2605
h015	2865	684	10,649	23	18	183	29	30	88	2793
h016	3011	605	9834	24	16	176	30	29	88	2951
h017	3276	745	11,056	26	18	178	31	33	87	3062
h018	3310	731	11,062	26	18	183	31	30	89	2925
h019	3329	720	10,913	27	19	184	29	31	86	2968
h020	2812	634	11,093	30	17	183	32	31	89	2859
h020b	3340	778	12,134	32	22	191	36	30	90	2932
h021	3693	694	11,156	50	16	169	30	30	81	3072
h022	3138	743	11,050	28	20	188	30	29	90	3015
Mean	3072	692	11,075	26	19	185	31	30	89	2881
S.D.	391	56	430	6	2	6	2	1	3	186

intensities are converted to concentration values using a Compton scatter matrix correction and the linear regression of a set of Geological Survey of Japan (GSJ) standards. Inter-element effects are accounted for by using a Lucas-Tooth and Price correction. The detection limits are listed in Appendix 1.

To monitor the operation of the EDXRF unit, standards of known composition were run with the unknowns. The results of these runs are also presented in Appendix 2. Depending on the concentration level and the element, the coefficient of variation (CV) ranges from 2–50%. The accuracy, depending on the element and its concentration level, varies from 0.5–21%. Generally, when elements are close to their detection limit they have a high CV and their accuracy is mediocre.

Measurements were taken on the surface of freshly broken nodules and flakes. After breaking open a nodule or making a flake, the surface to be analysed was washed with ethanol. No polishing was done on the surface. The majority of the surfaces were slightly concave or convex; none were absolutely flat. Samples thickness ranged from approximately 5 mm to 5 cm.

Table 4. Concentration, in parts per million (ppm), of select trace elements in the Oketo obsidian samples. Sample numbers ending in letters (i.e., a, b) indicate that the specimens were from the same, large piece of obsidian. Sample numbers marked by an asterisk indicate that the specimens are a red and black, variegated obsidian

Sample	Ti	Fe	Ga	Th	Rb	Sr	Y	Zr	Ba	Ce
ok001	3391	12,951	23	16	125	96	22	158	2518	25
ok002	1973	11,367	17	11	128	100	23	164	1733	bdl
ok003a	2953	12,967	26	16	130	98	22	172	2514	23
ok003b	3712	12,287	28	17	123	96	24	154	2587	31
ok004	2800	12,853	17	13	131	105	22	165	2214	bdl
ok005	3205	12,444	25	15	123	96	24	159	2476	28
ok006	3258	13,228	21	17	126	102	25	171	2488	22
ok007	3198	12,513	26	14	124	95	22	154	2503	25
ok008	3097	12,334	18	12	122	99	21	158	2315	20
ok009	3285	12,620	26	16	125	100	23	161	2524	26
ok010	3600	13,118	20	16	129	97	21	167	2561	27
ok011	3209	12,605	26	14	131	98	22	157	2549	25
ok012a	3388	12,543	22	19	124	92	22	157	2561	35
ok012b	3299	12,312	25	13	122	97	20	155	2536	26
ok013	3350	12,687	34	18	132	97	24	157	2380	24
ok014	3667	12,912	21	12	125	95	23	157	2644	27
ok015	3084	13,124	19	18	133	102	22	164	2439	21
ok016*	3556	13,639	25	13	125	95	22	163	2521	24
ok017*	3975	18,385	19	15	143	106	23	171	2687	23
ok018	3128	12,629	28	14	130	96	22	160	2476	24
ok019	3194	12,549	19	15	126	97	22	159	2543	22
ok020	3275	11,480	21	14	118	91	20	145	2534	28
ok021	3432	13,027	24	14	125	99	22	155	2564	26
ok022	3766	12,294	30	17	123	92	23	151	2542	31
ok023a	3406	12,454	22	15	125	95	23	156	2237	22
ok023b	3834	12,653	21	17	123	91	20	158	2722	35
ok024*	2780	11,888	25	16	117	93	25	149	1834	bdl
ok025*	3499	13,509	21	16	128	101	21	164	2595	26
ok026	3306	12,985	25	15	128	98	24	167	2528	23
ok027*	4229	18,340	34	19	139	104	24	160	2539	24
ok028*	2822	12,357	20	14	124	98	24	160	2307	bdl
Mean	3312	13,002	23	15	127	97	22	160	2457	26
S.D.	414	1514	4	2	5	4	1	6	213	4

bdl, below detection limit.

The sample width was large enough to fill the entire beam path.

Results and Discussion

Tables 2 to 7 contain the trace element concentration data from the geologic sources. All values are in parts per million (ppm). Cerium is listed for the samples where it occurs above the detection limit of the EDXRF unit. Niobium is omitted since it was below the detection limit of the EDXRF unit for the majority of the samples.

Bivariate plots of the incompatible trace elements separate the majority of the obsidian sources quite well. In these plots, for elements below their detection limit, such as Sr, 0.55 times the detection limit is used (Sanford *et al.*, 1993). Figure 3 shows a plot of the Zr content versus the Rb content. As can be seen in Figure 3, in addition to the overlap between the Akaishiyama sources, there is some slight

Table 5. Concentration, in parts per million (ppm), of select trace elements in the Tokachiishikawa, Shiritaki obsidian samples. Sample numbers ending in letters (i.e., a, b) indicate that the specimens were from the same, large piece of obsidian

Sample	Ti	Fe	Ga	Th	Rb	Sr	Y	Zr	Ba	Ce
tok001a	3820	11,103	32	22	207	bdl	38	75	1175	60
tok001b	2711	10,523	21	18	211	bdl	35	75	1093	50
tok002	1607	9896	17	12	219	bdl	36	79	722	35
tok003	2458	10,236	23	16	212	bdl	37	76	1029	48
tok004	2040	10,174	18	15	214	bdl	37	78	907	40
tok005	2793	11,114	23	20	211	bdl	38	80	1095	53
tok006	2765	9949	17	18	205	bdl	35	74	1074	49
tok007	2907	10,508	28	16	212	bdl	36	74	1083	52
tok008	2691	10,609	24	16	212	bdl	35	76	987	43
tok009	3275	10,475	34	16	198	bdl	37	72	1197	58
tok010	2822	9695	20	16	193	bdl	34	70	1035	49
tok011	5433	13,559	43	24	181	10	33	64	1982	bdl
tok012	3493	11,573	28	20	223	bdl	41	79	1124	50
tok013	4391	13,814	38	20	227	bdl	36	77	1508	bdl
tok014	3250	10,228	23	17	194	bdl	33	73	1127	61
tok015	2876	11,124	21	18	216	bdl	37	78	1074	50
tok016	2760	10,839	25	19	219	bdl	38	83	1056	48
tok017	2840	10,561	24	20	213	bdl	38	78	1104	53
tok018	3478	10,748	37	19	202	bdl	41	77	1162	56
tok019	2672	10,731	23	19	219	bdl	38	79	1053	48
Mean	3054	10,873	26	18	209	na	37	76	1129	50
s.d.	819	1068	7	3	11	na	2	4	247	7

bdl, below detection limit; na, not applicable.

Table 6. Select trace element concentration of the Tokachimitsumata obsidian samples. Ce was not detected by the EDXRF unit

Sample	Ti	Fe	Ga	Th	Rb	Sr	Y	Zr	Ba
t001	2935	10,504	25	22	179	54	39	96	3072
t002	3110	11,239	25	21	183	61	34	103	3133
t003	3020	10,918	25	18	180	62	32	107	3054
t004	3094	33,887	25	21	199	59	37	100	3143
t005	2617	10,281	19	16	184	53	35	95	2771
Mean	2955	15,366	24	20	185	58	35	100	3035
s.d.	201	10,360	3	3	8	4	3	5	152

overlap between the Akaishiyama sources and the Tokachimitsumata source. Separation of the Akaishiyama and Tokachimitsumata sources is enhanced in the plots of the Sr content versus the Zr content (Figure 4) and the Sr content versus the Y content (Figure 5).

For the elements measured here, the obsidian from the outcrop and summit of Akaishiyama contain the same incompatible trace element chemistry. Given their proximity, they are probably from the same magma chamber and underwent the same geologic processes. Despite their differences in appearance, geochemically they belong to the same group.

Linear discriminant analysis (LDA) with cross-validation is done to assess the separation and variability between groups. The concentrations in ppm for the Ba, Fe, Ga, Th, Rb, Sr, Ti, Y, and Zr are used in

Table 7. Trace element concentration of the Tokoro Mountain obsidian. All values are in ppm

Sample	Ti	Fe	Ga	Th	Rb	Sr	Y	Zr	Ba
ty001	3404	11,448	23	19	177	83	23	133	3218
ty002	3342	11,342	23	17	172	78	24	128	3293
ty003	3602	11,430	24	16	175	81	21	129	3349
ty004	4081	11,146	25	16	158	71	22	120	3907
ty005	3769	10,555	30	18	167	79	25	123	3214
ty006	4756	11,264	61	20	148	72	27	117	3556
ty007	3267	11,329	22	19	166	78	26	126	3402
ty008	3374	10,826	21	18	169	78	24	125	3374
ty009	3526	11,724	23	19	172	82	22	127	3229
ty010	3092	10,854	20	18	175	79	23	129	3270
ty011	3759	10,889	23	18	158	72	23	125	3634
ty012	3446	11,266	29	17	162	75	23	122	3424
ty013	2942	11,200	21	20	182	88	26	131	2987
ty014	3542	11,441	24	19	179	84	25	130	3210
ty015	3582	12,096	20	19	180	86	26	134	3409
ty016	3809	11,534	24	18	170	80	26	124	3510
ty017	3964	11,753	28	19	173	84	26	125	3413
ty018	4407	14,958	36	23	189	91	27	136	3854
ty019	2856	10,773	21	16	175	83	26	131	2928
ty020	3387	11,122	22	17	175	80	26	130	3325
Mean	3595	11,448	26	18	171	80	25	127	3375
s.d.	461	905	9	2	9	5	2	5	241

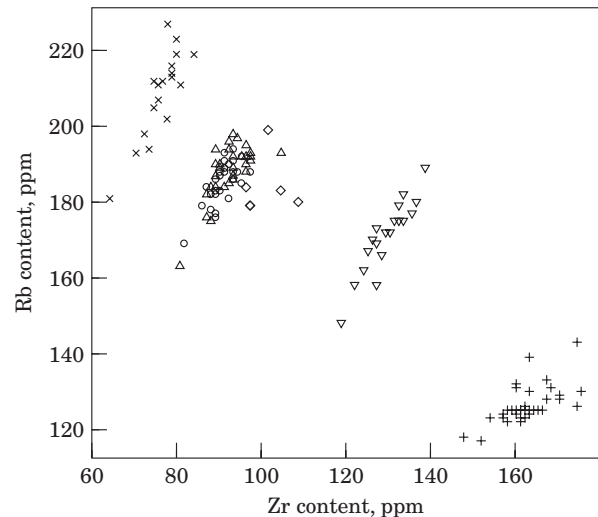


Figure 3. Plot of the rubidium content versus the zirconium content. The symbols represent the following collection points: \triangle = Akaishiyama (summit); \circ = Akaishiyama (outcrop); + = Oketo; \times = Tokachiishikawa; \diamond = Tokachimitsumata; and ∇ = Tokoro Mt.

the LDA. In most geological studies, before analyzing a data set with multivariate statistics, the data is log transformed. This is done to scale the data so that the variables are equally weighted, and “normalize” the data. Shackley (1995) has noted though, that the log transformation could reduce the variability that allows the groups to be discriminated. With this in mind, the untransformed data is used in the linear discriminant analysis.

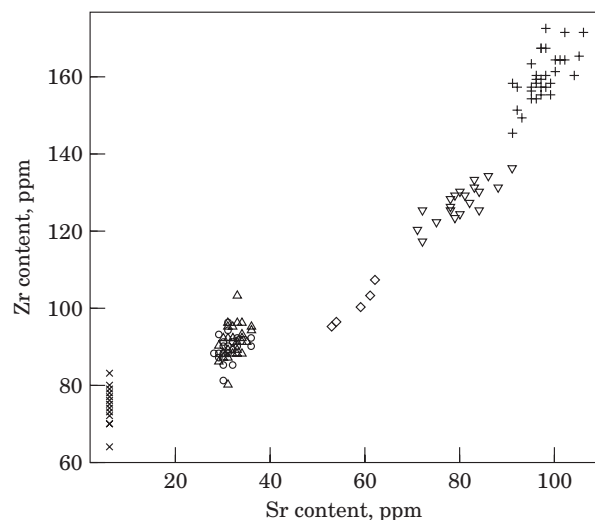


Figure 4. Plot of the zirconium content versus the strontium content. Same key for the symbols as in Figure 3.

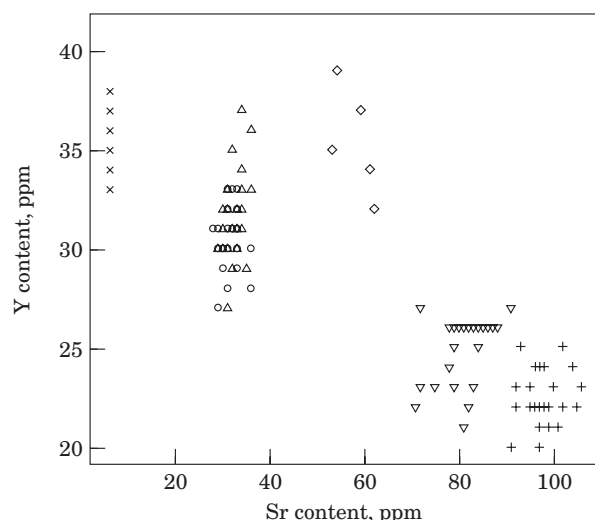


Figure 5. Plot of the yttrium content versus the strontium content. Same key for the symbols as in Figure 3.

LDA with cross-validation correctly classifies 99.3% of the cases; only sample t004 is mis-classified. A plot of the first two discriminant functions is in Figure 6. Step-wise discriminant analysis (SDA) with cross-validation correctly classified 100% of the cases. SDA identified Ba, Sr, Rb, Ti, Y, Zr as the most discriminating elements.

Conclusions

Both the bivariate plots and the LDA indicate that there are five obsidian sources in the samples under study. These five obsidian sources are from different magma chambers with different crystallization and solidification histories. Isotopic studies could shed

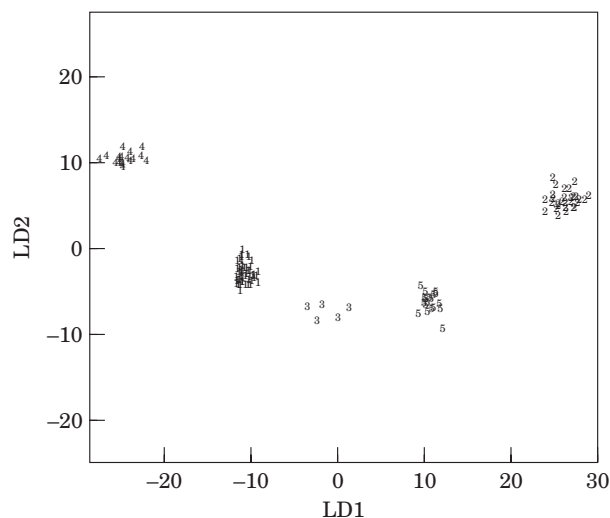


Figure 6. Plot of the first two discriminant functions from the cross-validated linear discriminant analysis. Group 1 is samples from both Akaishiyama summit and outcrop location; Group 2 is the Oketo source samples; Group 3 is the Tokachimitsumata source samples; Group 4 is the Tokachiishikawa source samples; and Group 5 is the Tokoro source samples.

further light on the origin of the obsidians and date the volcanic events from which they originated.

The four primary sources examined in this study are: Akaishiyama (both summit and outcrop), Oketo, Tokachimitsumata, and Tokoro. The fifth source group is the secondary deposit of Tokachiishikawa in the Shirataki valley. At this time, it is uncertain where the primary deposit forming the Tokachiishikawa deposit is located. Further collection and survey is needed in the Shirataki valley to resolve this issue.

Despite their very different physical appearances, the obsidian from the outcrop at and the summit of Akaishiyama have identical incompatible trace element geochemistries. The finding that Akaishiyama, Oketo and Tokachimitsumata are geochemically distinct is similar to the results of Osawa (1991) and Warashina (1998). Since the results presented here are quantitative, other scholars doing geochemical studies of Japanese obsidian can utilize them. Furthermore, information on the Ba and Th contents is also provided. These elements are usually not determined in most studies of Japanese obsidian. For the sources under study here, step-wise discriminant analysis identified Ba as a useful element in source discrimination.

While visual sourcing is a useful and valid method for distinguishing between obsidians from the summit and outcrop of Akaishiyama, red and black variegated obsidians were also found at Oketo. The caveat is that visual sourcing must be supplemented with chemical analyses.

Finally, it must be stressed that this study is only a preliminary one and in no way reflects the full complexity of the obsidian sources in Hokkaido.

Warashina (1998) lists over 10 primary deposits of obsidian in the northern half of Hokkaido alone. Furthermore, the issue of secondary deposits of obsidian in Hokkaido has yet to be addressed. Secondary deposition is an important area of study since obsidian could be moving naturally across the Hokkaido landscape without any involvement from human agency (Shackley, 1998). For documenting local and regional exchange patterns this is a necessary piece of information.

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Appendix 1

Detection limits and X-ray counting and least squares linear regression errors. The detection limits are the smallest amounts that can be quantitatively measured. These limits are defined as the signal that is six standard deviation units above the background, or as for the case with Fe and Ti, the lowest concentration in the standards available. All values are in parts per million (ppm)

	Ti	Fe	Ga	Th	Rb	Sr	Y	Zr	Nb	Ba	Ce
Detection limit	260	500	15	8	7	10	10	6	6	50	20
Error	300	1900	1	2	7	13	2	6	3	85	3

Appendix 2

Geological standards run with the unknowns. All values are in parts per million (ppm). The recommended values for JG3 are from the Geological Survey of Japan. The CV is calculated as: $(CV=100\% \times (\text{sample standard deviation}/\text{sample average}))$. The accuracy is calculated as: $\text{Accuracy}=100\% \times (|\text{standard value} - \text{average value}|/\text{standard value})$

Sample	Ti	Fe	Ga	Th	Rb	Sr	Y	Zr	Nb	Ba	Ce
JG2, this study ($n=35$)	375	7245	19	29	301	17	91	103	12	79	47
JG2, recommended (Hallet & Kyle, 1993)	360	6785	17	29.9	300	16	85	88	13.4	82	48.3
CV (%)	57	5.4	12	8.1	2.7	18	4	2.8	18	32	4
Accuracy (%)	4.3	6.8	9.6	2	0.5	7.5	7.3	16	14	4.1	3.6
JG3, this study ($n=18$)	2881	25,667	18	9	76	425	20	140	9	556	35
JG3, recommended	2900	25,800	17.1	8.28	67.3	379	17.3	144	7	466	40.3
CV (%)	6.4	4.6	10	2.7	4.8	5	10	4.4	55	3.6	3.7
Accuracy (%)	6.3	7.4	7.6	0.7	12	15	6.7	3.3	3.8	21	16