Quantitative and semi-quantitative analyses using a portable energy dispersive X-ray fluorescence spectrometer: Geochemical applications in fault rocks, lake sediments, and event deposits

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Quantitative and semi-quantitative procedures using a portable energy dispersive X-ray fluorescence spectrometer (portable XRF) were applied to geochemical studies in fault rocks, lake sediments, and soils, including paleotsunami deposits. The results obtained are as follows:

- 1) Correlation coefficients (r^2 ; measured values by portable XRF versus reported values) for working curves of major elements obtained using powdered reference standard materials were 0.70–0.99 with $p < 0.01$, except for Mg, and r^2 values for the trace elements were 0.72–0.99 with $p < 0.05$, except for Cl, Ba, and U.
- 2) In the fault rocks from Central Japan (e.g., Shiraki-Nyu fault, Atera faults; powdered and nonpowdered rock fragment samples), measured values of K, Ca, Ti, Mn, Fe, Rb, Sr, Zr, and Th contents obtained using portable XRF are consistent with the reported values ($r^2 = 0.47$ –0.90, with $p < 0.01$). Clear Fe and Mn enrichments and K and Rb depletions were observed within the gouges of the Shiraki-Nyu fault from Central Japan.
- 3) The depth profiles of chemical components in lake sediments (powdered) from the Noto Peninsula in Central Japan measured using portable XRF methods were similar to those measured using the stationary-type XRF ($r^2 = 0.61$ in Ti and $r^2 = 0.40$ in Zr contents, with $p < 0.05$).
- 4) For paleotsunami deposits on the Pacific coast of northeast Japan, the chemical components and titanium-normalized values (Si/Ti, Ca/Ti, Sr/Ti, and As/Ti) in powdered samples measured using portable XRF correlated well with those in a previous study measured using stationary-type XRF ($r^2 = 0.84$ –0.98, with $p < 0.01$). Cluster analyses of geochemical data conducted using portable XRF were useful to characterize event deposits on the north Sendai Plain.

In each kind of sample, the element concentration values (SiO_2 , TiO_2 , Fe_2O_3 , MnO, CaO, K_2O , S, V, Cr, Cu, Zn, As, Rb, Sr, Zr, Pb, and Th) obtained via quantitative analyses using portable XRF were consistent with the reported values obtained via other methods, such as stationary-type XRF and inductively coupled plasma-mass spectrometry.

Keywords: Portable XRF, Geochemistry, Fault rock, Lake sediments, Event deposits

INTRODUCTION

Quantification procedures for chemical elements in geo-

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logical samples have been developed by improving instrumental analyses, including atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES), and ICP-mass spectrometry (ICP-MS; Wood et al., 1997; Dick et al., 2008; Och et al., 2014; Schaffhauser et al., 2014). Although these ma-

chines provide high sensitivity analyses of trace elements (ppt-ppm level), the preparation procedures need skilled techniques, such as acid digestion, alkaline fusion, and separation by chelate resin, as well as clean facilities to avoid contamination during the procedures in many case (Eggins et al., 1997; Butler et al., 2009; Yamasaki et al., 2016; Watanabe et al., 2018). Furthermore, stationary-type energy dispersive X-ray fluorescence spectrometry (EDXRF) and wavelength dispersive XRF (WDXRF) conducted using fused glass beads and pressed powder pellets have been adopted for quantitative analyses of geological and environmental samples (Matsunami et al., 2010; Yamasaki et al., 2011, 2015; Niwa et al., 2019).

Recently, portable XRF has been used to measure chemical elements in geological and environmental samples (Kalnicky and Singhvi, 2001; Solum et al., 2010; Rowe et al., 2012; Rincheval et al., 2019; Tanikawa et al., 2019), International Ocean Discovery Program (IODP) drilled cores (Ryan et al., 2017), biological and agricultural samples (Turner et al., 2017; Afzal et al., 2018; Byers et al., 2019), and cultural property (Papadopoulou et al., 2006; Ogburn et al., 2013). Previous studies have also reported quantification procedures using igneous rocks, mudrocks, carbonates, soils, and other geological samples from North America and Europe (Young et al., 2016; Steiner et al., 2017; Caporale et al., 2018; Al-Musawi and Kaczmarek, 2020; Ravansari et al., 2020). Portable XRF has also been used for marine, lake, and land sediments, including event deposits (Turner and Taylor, 2018). Ryan et al. (2017) listed the instrument detection limit for portable XRF analysis (25–75 ppm for K, Ca, Ti, Mn, and Fe; and 2–25 ppm for V, Cr, Cu, Zn, Rb, and Sr). In previous studies of lake and wetland sediments, geochemical studies were also conducted to estimate global, local, and regional environmental changes because of recent human and industrial activities (De Vleeschouwer et al., 2007; Fagel et al., 2014; Ochiai et al., 2015). Portable XRF also has been applied to geochemical studies of mining areas in Chile and estuarine sediments in the UK (VanCott et al., 1999; Figueroa-Cisterna et al., 2011; Turner and Solman 2016; Turner and Taylor, 2018).

In addition, geochemical data and their statistical analyses are effective for estimating the behavior, distribution, and sources of materials regarding geological events, such as fault activities in Japan (Yoshida and Yamamoto, 2014; Niwa et al., 2015, 2019). Although data accumulation is required for further research to evaluate faults and other event deposits, simple and rapid analyses using portable XRF are limited (Solum et al., 2010). Therefore, this study confirmed working curves using geochemical standards (Supplementary Table S1; Supplementary Tables S1–S14 are available online from <https://doi.org/10.2465/>

jmps.201224). Subsequently, quantitative and semi-quantitative analyses were performed in this study using portable XRF in a) fault rocks, b) lake sediments from Central Japan, and c) soils with paleotsunami deposits from the Pacific coast of northeast Japan (Fig. 1). Moreover, we showed advantages and drawbacks of the portable XRF method for geochemical studies using these samples.

GEOLOGICAL SETTINGS AND SAMPLES

Fault rocks

Geological and geochemical characteristics for the faults with displacements in the Quaternary, such as the Shiraki-Nyu, Atera, Sakai-toge, Rokko, and Gosukebashi faults in Central Japan, have been well described in previous studies (Fig. 1A; Maruyama and Lin, 2000; Kano et al., 2002; Niwa et al., 2016, 2019; Manaka et al., 2020). The Shiraki-Nyu fault is in the western Tsuruga Peninsula in Central Japan (total length, ~ 15 km; Fig. 1; Niwa et al., 2016; 2019). Fault rocks of the Shiraki-Nyu fault comprising the fault core and an adjacent damage zone with high fracture density are well-exposed in the Cretaceous Kojaku Granite. The fault core contains incohesive cataclasite and a brownish gouge less than 6-cm thick. The Atera fault (total length, ~ 35 km) cuts the Cretaceous Naegi-Agematsu Granite and Nohi Rhyolite (Niwa et al., 2009, 2015). The Sakai-toge fault (total length, ~ 50 km) is developed in sedimentary rocks of the Jurassic Mino accretionary complex and Cretaceous granite (Kano et al., 2002). The Rokko fault (total length, ~ 10 km) separates the Cretaceous Rokko Granite from felsic volcanic rocks of the Arima Group (Tanaka et al., 2018; Manaka et al., 2020). The Gosukebashi fault (total length, ~ 14 km) is developed in the Rokko Granite (Maruyama and Lin, 2000; Tanaka et al., 2018). Fault rocks composed of cataclasite, gouge, and breccia frequently develop along these faults.

Major and trace elements in rock samples from the Shiraki-Nyu and Atera faults have been analyzed using WDXRF and ICP-MS in previous studies (Kato et al., 2015; Niwa et al., 2015, 2019; Fig. 1). Niwa et al. (2019) suggested that Mn and Fe oxide accumulations recorded in the gouges from the Shiraki-Nyu fault resulted from redox changes in fluids (Fig. 1). Mn enrichment in fault gouges has also been reported for Atera fault (Kato et al., 2015). Furthermore, differences were found in the chemical compositions of fault gouges between samples from outcrops and boring cores from the Shiraki-Nyu fault (Niwa et al., 2019). Therefore, geochemical studies of fault rocks are useful to understand gouge characteristics produced via water-rock interactions.

Figure 1. (A) Map showing the location of the study area in Japan, and (B) sampling site of the boring core (Core 1-c) at the Tsuruga Peninsula on the Wakasa Bay coast in Central Japan. (C) A photograph of half-cut boring core (Core 1-c, from 10.00 to 10.23 m in core depth), including fault gouge of the Shiraki-Nyu fault (Niwa et al., 2019). Filled circles denote the sampling sites of fault rocks. Filled triangle and diamond denote the sampling sites of the lake sediments and paleotsunami deposits, respectively. Color version is available online from <https://doi.org/10.2465/jmps.201224>.

For this study, we used fault rock samples from Central Japan (Shiraki-Nyu, Atera, Sakai-toge, Rokko, and Gosukebashi faults; Fig. 1A; Niwa et al., 2015, 2019; Japan Atomic Energy Agency and Central Research Institute of Electric Power Industry, 2020). Twenty-one powdered samples from these areas were used for quantitative and semi-quantitative analyses by portable XRF. For the Shiraki-Nyu fault in the Tsuruga Peninsula, hanging wall and footwall cataclasite and fault gouge samples were obtained from an outcrop (35°43'N, 135°59'E). Furthermore, nonpowdered rock fragment samples from a half-cut boring core (Core 1-c; polished rocks with resin) across the Shiraki-Nyu fault were used (Figs. 1B and 1C; Niwa et al., 2019). Nonpowdered rock fragment samples (polished rocks with resin) collected from an outcrop across the Atera fault, including fault breccia of welded tuff and light gray clayey gouge were also used in our study (35°36'N, 137°30'E; Niwa et al., 2015).

Lake sediments

Our study performed quantitative and semi-quantitative analyses of chemical components in lake sediments from the Noto Peninsula, Central Japan (on the Sea of Japan coast; Fig. 1A) using portable XRF with our working curves, and WDXRF was used for comparison. The study site is called the Bishaguso-ike artificial reservoir in the Noto Peninsula, Central Japan (Fig. 1A). The study site's

watershed area, including the river catchment system, reached $\sim 48800 \text{ m}^2$, and the lake surface area was $\sim 1500 \text{ m}^2$ in 2015 (Ochiai et al., 2015). The lake sediments have been well surveyed for recent environmental changes near the agricultural and forestry activities area. Chronological and paleoenvironmental studies were conducted using radiometric dating with ^{210}Pb and ^{137}Cs , physical properties (e.g., grain size distribution), bulk organic geochemistry, and stable carbon and nitrogen isotopes (Ochiai et al., 2015). These records show deforestation and erosion rate changes in the last half-century near the concerned area. However, inorganic geochemical analysis, such as heavy metal analyses, has not been conducted in these sediment cores.

Modern lake sediments were obtained in 2011 from the Bishaguso-ike artificial reservoir in the Noto Peninsula, Central Japan (B11-1 core; 37°07'N, 136°49'E; Japan Sea coast; Fig. 1A; Ochiai et al., 2015). The B11-1 core (63 cm-long) was subsampled at 1-cm intervals. In a previous study, ^{210}Pb and ^{137}Cs dating was performed for another sediment core (Core B; 26.5 cm-long) from the Bishaguso-ike that is close to the sampling site of the B11-1 core. The core B bottom age was estimated to be 1984 common era (CE) (Ochiai et al., 2015). Tentative ages of sediment layers in the B11-1 core can be estimated by comparison with lithology and physical properties across both cores. Fifteen dried and powdered samples (upper part of the core, 1–30 cm depth) were measured

using portable XRF and WDXRF.

Paleotsunami deposits

Chemical components of event deposits, such as tsunami deposits from the northeastern Japan coast, have also been measured using portable XRF (Chagué-Goff et al., 2012a, 2014). However, the measured elements were limited to Ti, Mn, Fe, S, Cl, Rb, Sr, and Ba in previous studies. Moreover, the geochemical signature of event deposits is effective for characterizing paleotsunami deposits from huge earthquakes in the area (Kuwatani et al., 2014a; Watanabe et al., 2020). Large datasets are needed for statistical analysis of chemical components in event deposits, such as machine learning techniques (Figuerola-Cisterna et al., 2011). Therefore, we evaluated rapid analytical procedures using portable XRF for deposits from northeast Japan (north Sendai Plain, Tohoku; Fig. 1A).

The sampling site of paleotsunami deposits from the north Sendai Plain is on the Pacific coast side of northeast Japan (Fig. 1A; Sawai et al., 2015; Watanabe et al., 2020). In this area, an earthquake with a moment magnitude (M_w) of 9.0 occurred on March 11, 2011, off the Pacific coast of the Tohoku District in northeast Japan (2011 Tohoku tsunami; Ministry of the Environment Government of Japan, 2013). Predecessors of the 2011 Tohoku tsunami, represented in paleotsunami deposits of ~ 1080 calibrated years before present (cal BP) based on radiocarbon dating have been reported in the Sendai Plain (so-called Jogan tsunami; Abe et al., 1990; Mino-ura and Nakaya, 1991; Sugawara et al., 2012; Sawai et al., 2012). In our study site, the Jogan tsunami deposits are found between a volcanic ash layer (Towada-a, 915 CE: ~ 1035 cal BP) and peaty clay layers. The Jogan tsunami deposits in the north Sendai Plain are distributed at least 1.5 km from the modern shoreline (Sawai et al., 2012). The minimum M_w value of the Jogan earthquake was estimated to be ~ 8.6 (Namegaya and Satake, 2014).

In addition, geochemical studies of the 2011 tsunami and Jogan tsunami deposits in the area have been well-documented in previous studies (Chagué-Goff et al., 2012a, 2012b; Watanabe et al., 2014, 2020).

A continuous soil sample (SND7), including paleo-tsunami deposits, was collected using a 4-m long rectangular geoslicer (Fukken Co. Ltd.; Nakata and Shimazaki, 1997) on the north Sendai Plain in the Pacific coast of northeast Japan (SND7; 38°13'N, 140°58'E; Fig. 1A, Sawai et al., 2015; Watanabe et al., 2020). The SND7 geoslicer sample included surface soils (2011 tsunami deposit and paddy soil before the 2011 event), peaty clay layers (soil deposits), and sandy layers (paleotsunami and beach deposits; Watanabe et al., 2020). The SND7 contained the Towada-a tephra (To-a, 915 CE) and a sandy event deposit. The event deposit was correlated with the Jogan tsunami based on radiocarbon ages in previous studies (~ 1080 cal BP; Sawai et al., 2015; Tamura et al., 2015). Thirty subsamples from SND7 were used for quantitative and semi-quantitative analyses using portable XRF. Previous studies have addressed the milling processes for powdered samples (Watanabe et al., 2020).

ANALYTICAL METHODS

A portable energy dispersive X-ray fluorescence spectrometer (portable XRF; Niton XL3t-950S, Thermo Fisher Scientific) was used for quantitative and semi-quantitative analyses of fault rocks and lake sediments from Central Japan and the paleotsunami deposits from the Pacific coast of northeast Japan (Tables 1 and 2). Portable XRF was equipped with X-ray filters for each element analysis (main filter for Mn, Fe, Cu, Zn, As, Rb, Sr, Zr, Nb, Pb, Th, and U; low filter for V, S, K, Ca, Ti, and Cr; high filter for Ba; light filter for Mg, Al, Si, P, and Cl). Matrix corrections were performed using the pre-installed fundamental parameter (FP) method on the portable XRF; subsequently, X-ray spectra and measured values

Table 1. Measurement conditions for major and trace elements

Configuration of Niton XL3t	
X ray tube	Ag anode
X ray tube voltage	50 kV, 200mA, 2.0W max
Detection window	8.0 mm diameter
Detector	Silicon drift detector
Resolution	<185eV, at 60000 cps for 4 msec shaping time
Matrix correction	Fundamental parameter method
Measured elements in this study	
Major elements	SiO ₂ , TiO ₂ , Al ₂ O ₃ , T-Fe ₂ O ₃ , MnO, MgO, CaO, K ₂ O, P ₂ O ₅
Trace elements	S, Cl, V, Cr, Cu, Zn, As, Rb, Sr, Zr, Nb, Ba, Pb, Th, U

Table 2. Parameters for the working curves obtained from powdered samples and fused glass beads

	SiO ₂	TiO ₂	Al ₂ O ₃	T-Fe ₂ O ₃	MnO	MgO (mass%)	CaO	K ₂ O	P ₂ O ₅	S	Cl	
Powder												
Range min	0.1	0.03	0.66	0.02	0.06	0.08	0.04	0.22	0.083	0.001	0.03	
Range max	97.8	1.44	17.2	14.4	0.27	8.14	9.82	5.38	1.26	1.32	0.09	
n	24	21	22	23	17	18	22	21	10	13	4	
Slope	1.07	0.93	0.64	0.98	1.13	0.31	1.08	1.23	0.90	1.04	0.76	
Intercept	-5.56	0.06	0.13	0.35	-0.04	0.21	0.08	-0.08	-0.02	0.04	0.005	
rmse	4.27	0.08	1.61	0.58	0.01	1.20	0.20	0.15	0.05	0.14	0.03	
r ²	0.97	0.98	0.70	0.99	0.98	0.58	0.98	0.98	0.77	0.90	1	
p *	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	≥0.05	
CI **	Lower	0.96	0.97	0.65	0.98	0.97	0.44	0.97	0.98	0.56	0.83	-
	Upper	0.99	1.00	0.93	1.00	1.00	0.91	1.00	1.00	0.97	0.98	-
Fused glass bead												
Range min	51.0	0.04	11.90	0.77	0.16	0.05	0.50	0.42	0.002	-	-	
Range max	76.8	1.44	17.2	14.3	0.22	8.14	9.82	5.38	0.294	-	-	
n	14	14	14	14	3	5	13	14	8	-	-	
Slope	0.40	0.44	0.11	0.43	0.77	0.03	0.47	0.43	0.30	-	-	
Intercept	-4.68	-0.01	0.16	0.03	-0.10	0.15	-0.05	0.00	0.01	-	-	
rmse	2.26	0.03	0.90	0.14	0.01	3.00	0.20	0.14	0.08	-	-	
r ²	0.97	0.98	0.62	0.99	1	0.49	0.92	0.99	0.59	-	-	
p *	<0.01	<0.01	<0.01	<0.01	≥0.05	≥0.05	<0.01	<0.01	<0.05	-	-	
CI **	Lower	0.95	0.98	0.44	0.99	-	-0.48	0.87	0.99	0.13	-	-
	Upper	0.99	1.00	0.93	1.00	-	0.98	0.99	1.00	0.96	-	-

	V	Cr	Cu	Zn	As	Rb	Sr (mg/kg)	Zr	Nb	Ba	Pb	Th	U
Powder													
Range min	4	2.83	1.67	13.6	16.3	7.37	4.20	5.92	12.40	6.1	19.20	7.79	0.86
Range max	575	439	1120	264	38.6	453	454	1494	510	1860	430	112	56.8
n	17	14	13	17	5	21	22	22	7	22	14	13	5
Slope	0.65	0.63	0.88	0.95	0.91	1.01	0.96	1.08	0.83	0.34	1.03	1.28	1.16
Intercept	29.6	29.4	15.9	0.50	-2.11	-1.92	6.77	-9.97	9.05	229	-3.79	-1.44	4.55
rmse	24.6	34.9	29.8	10.0	1.90	5.06	10.6	15.8	3.47	460	3.95	4.34	3.96
r ²	0.94	0.72	0.92	0.98	0.89	0.98	0.99	0.93	0.80	0.39	0.95	0.91	0.49
p *	<0.01	<0.01	<0.01	<0.01	<0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	≥0.05
CI **	Lower	0.91	0.58	0.87	0.97	0.56	0.98	0.91	0.44	0.28	0.92	0.86	-0.48
	Upper	0.99	0.95	0.99	1.00	0.99	1.00	0.99	0.98	0.83	0.99	0.99	0.98
Fused glass bead													
Range min	52	20.0	-	-	-	12.3	8.11	51.2	-	-	-	12.8	16.5
Range max	575	439	-	-	-	453	439	1494	-	-	-	112	56.8
n	8	6	-	-	-	13	14	13	-	-	-	7	5
Slope	0.52	0.45	-	-	-	0.39	0.36	0.43	-	-	-	0.47	0.45
Intercept	26.7	71.5	-	-	-	-2.38	1.48	-3.11	-	-	-	-0.30	2.58
rmse	39.8	71.7	-	-	-	4.83	6.08	10.2	-	-	-	2.78	1.97
r ²	0.91	0.09	-	-	-	0.97	1	0.79	-	-	-	0.93	0.81
p *	<0.01	≥0.05	-	-	-	<0.01	<0.01	<0.01	-	-	-	<0.01	≥0.05
CI **	Lower	0.75	-0.79	-	-	0.94	-	0.67	-	-	-	0.77	0.09
	Upper	0.99	0.93	-	-	1.00	-	0.97	-	-	-	0.99	0.99

n, number of data for the working curves; rmse, root mean square error, using data from the reported and calculated values from the working curves; r, Spearman nonparametric correlation coefficients; p, p-values for the Spearman nonparametric correlation test.

* p < 0.01, correlation coefficients are statistically different from zero at 1% significance level.

** CI, 95% compatibility intervals for correlation coefficients (lower and upper 95% CI limits for r values).

Figure 2. XRF spectra of the JG-1 reference material (powdered igneous rock, AIST) using the Niton XL 3t portable XRF. The 10-point centered running average values of the original XRF intensities are shown in (A) 0–10 keV and (B) 5–20 keV ranges. A possible peak of Ag from the X-ray tube anode was found at 2.98 keV.

of each element were obtained using the Niton NDT version 8.2 software (Fig. 2). In this study, working curves were obtained to calibrate the portable XRF measured values (Figs. 3 and 4). The measured values obtained using the portable XRF with FP methods were calibrated using reported values for standard reference materials from the Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology (GSJ, AIST; Imai et al., 1995, 1996, 1999; Terashima et al., 1998, 2002, <https://gbank.gsj.jp/geostandards/welcome.html>), United States Geological Survey (USGS; Wilson, 1998; Pretorius et al., 2006), and the International Atomic Energy Agency (IAEA; IAEA, 2000a, 2000b, 2000c) (geochemical standards including igneous rocks, sedimentary rocks, carbonate, ore, river sediments, and soils; Table 2 and Tables S1–S5).

The powdered samples (standard reference materials, fault rocks, lake sediments, and soils with tsunami deposits) were filled in polyethylene double open-ended sample cups (26-mm inner diameter; 24-mm height; Niton) and covered with polypropylene thin-film (4 μ m thickness; Niton) for portable XRF measurements. The fused glass beads of the standard reference materials were also measured using the portable XRF for comparison

(Table S5). Core 1-c across the Shiraki-Nyu fault and rock samples from the Atera fault (K4, K6, and K7) were consolidated in epoxy resin, and the surface was polished before inorganic analysis using the portable XRF (polished rock samples; Tables S6–S8). The detecting window (8-mm diameter) of the portable XRF was covered completely by analytical point on the polished rock surface to obtain stable XRF intensities during the measurement. Measurement time by the portable XRF was $\sim$ 120 seconds at each analytical point. For all geological samples, triplicate measurements were performed using the portable XRF at each analytical point.

Subsequently, statistical analyses including p-tests for significant difference, compatibility intervals, and principal component analysis (PCA) of geochemical data measured using portable XRF were performed using R version 3.5.2 (<http://cran.r-project.org/>). Before calculating the correlation matrix and PCA, the original compositional data were processed via the log-ratio transformation with the zero replacement to avoid the constant-sum constraint (Aitchison, 1982; Kucera and Malmgren, 1998; Arai and Ohta, 2006; Ohta and Arai, 2006). Cluster analysis was also performed using Euclidean distance and Ward's method in R software (R Core Team, 2018; Maechler et al., 2018) for normalized geochemical data in the paleotsunami deposits (SND7; north Sendai Plain) on the Pacific coast of northeast Japan.

Furthermore, fused glass beads of the lake sediment samples were also measured using WDXRF (ZSX Primus II, Rigaku) for comparison. The method for glass bead preparation generally followed Niwa et al. (2019).

RESULTS AND DISCUSSION

Geochemical standards and working curves

Representative XRF spectra of the standard reference materials (JG-1 geochemical standards; powdered igneous rock from AIST) are shown in Figure 2. The working curves for nine major elements (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , K_2O , and P_2O_5) in the standard reference materials revealed notable correlation coefficient (r^2) values of 0.58–0.99 ($p < 0.01$; correlation coefficients are statistically different from zero at 1% significance level; Fig. 3, Table 2, and Tables S2–S3). Correlation coefficients for the working curves of 15 trace elements (S, Cl, V, Cr, Cu, Zn, As, Rb, Sr, Zr, Nb, Ba, Pb, Th, and U) were from 0.72 to 0.99 ($p < 0.05$; correlation coefficients are statistically different from zero at 5% significance level), except for Cl, Ba, and U. Ryan et al. (2017) have also shown r^2 values of 0.84–1.00 for working curves using portable XRF. For

Figure 3. Relationships between the reported chemical component values and the values obtained using portable XRF in this study for powdered geochemical standard materials. Correlation coefficients (between the reported and measured values) and p-values for the Spearman nonparametric correlation test are shown in each plot. The $p < 0.05$ and < 0.01 indicate that correlation coefficients are statistically different from zero at 5 and 1% significance levels, respectively. The red dashed lines (bold) and gray dotted lines (narrow) denote regression curves with $p < 0.05$ and $p \geq 0.05$, respectively. Color version is available online from <https://doi.org/10.2465/jmps.201224>.

accurate quantification of Cl and U, additional reference materials with wider concentration range for these elements need to be used.

Conversely, Ba has a relatively low correlation coefficient ($r^2 = 0.39$) in this study (Table 1), probably owing to the mass interference from $TiK\alpha$, $ScK\beta$, and minor peaks of other elements. The P_2O_5 content in most of the

powdered reference materials was too low to be detected using portable XRF (down to 0.002 mass%; 0.17 mass% on average; Table S3). The correlation plots of MgO and Al_2O_3 were more scattered than those of other major elements (Si, Ti, Fe, Mn, Ca, and K; Fig. 3). In particular, the r^2 values of the MgO and Al_2O_3 working curves were relatively low 0.58 and 0.70 respectively, owing to their

Figure 4. Relationships between the reported chemical component values and the values obtained using portable XRF in this study for fused glass bead geochemical standard materials. Correlation coefficients (between the reported and measured values) and p-values for the Spearman nonparametric correlation test are shown in each plot. Color version is available online from <https://doi.org/10.2465/jmps.201224>.

low excitation energies (possibly affected by surface structure), interference of other light elements such as oxygen, and high Si peaks.

Stability tests of major and trace elements using the standard reference materials (igneous rocks; JA-2, JG-1, and JG-1a) were performed by analyses repeated ten times using portable XRF (Table S4, powdered samples). In JA-2 and JG-1, the coefficients of variation (CVs) of the repeated major element analyses were 2.4–8.9%, ex-

cept for MgO and P₂O₅. The CV values for JG-1a were 1.8–33.8% in our case. The CV value of Fe₂O₃ in JG-1a was relatively high (more than 30%), probably because of its low content (~2 mass%) in the sample. For Rb, Sr, Zr, and Pb in the three standard reference materials, the CV values were 1.9–4.9%. These CV values are comparable to the reported values (0.5–5.2%; Ryan et al., 2017).

In the fused glass beads of the reference materials, the correlation coefficients of the major elements working

Figure 5. Relationships between the reported values (Niwa et al., 2015, 2019; Japan Atomic Energy Agency and Central Research Institute of Electric Power Industry, 2020) and the portable XRF values in this study for chemical components in the fault rock samples (powdered, polished rock with resin, and unpolished rock samples). Correlation coefficients (r^2) and p-values for the Spearman nonparametric correlation test are shown in each plot. Lower and upper limits of 95% compatibility intervals for the r values are shown in parentheses. The $p < 0.05$ and < 0.01 indicate that correlation coefficients are statistically different from zero at 5 and 1% significance levels, respectively. Color version is available online from <https://doi.org/10.2465/jmps.201224>.

curves were higher than 0.62 ($p < 0.01$), except for MgO and P₂O₅ (Table 2, Fig. 4, and Table S5). In addition, some trace elements (V, Rb, Sr, Zr, and Th) had correlation coefficients higher than 0.79 ($p < 0.01$). However, portable XRF did not detect some trace elements, e.g., Cu, Zn, As, and Pb, probably due to dilution by the flux reagent (lithium tetraborate: sample dilution factor = 3), which was used to make the fused glass bead samples for each reference material. Therefore, in our study, portable XRF analyses of powdered and nonpowdered rock samples without alkali-fusion were performed for the following three geochemical studies.

Fault rocks from Central Japan

Geochemical data acquired from the fault rock samples in

Central Japan were obtained using portable XRF with our working curves (Figs. 5 and 6 and Tables S6–S8). Based on the relationships between the measured values using portable XRF and reported values of fault rock samples from Central Japan (Shiraki-Nyu, Atera, Sakai-toge, Rokko, and Gosukebashi faults; Figs. 1A and 5), the correlation coefficients (r^2) of the regression lines for the major elements were 0.47–0.90 with $p < 0.01$, except for SiO₂ (Fig. 5). Additionally, the slopes of the regression lines were 1.00–1.48, and the intercept values were close to 0 (from -0.1 to +0.1), except for SiO₂ and Al₂O₃ (Fig. 5). The correlation coefficients of the regression lines for the trace elements (Rb, Sr, Zr, and Th) were 0.48–0.88 ($p < 0.01$), and the slopes were 0.91–1.30. Sr has a relatively high correlation coefficient of 0.88 ($p < 0.01$). Other heavy metals such as Cu and Zn were not

Figure 6. Distribution of chemical components in and around the fault gouge of the Shiraki-Nyu fault at the Tsuruga Peninsula. Left plots show the data of chemical components for powdered samples collected from outcrops, and right plots show the data for nonpowdered samples of Core 1-c. Blue squares indicate the reported values (using WDXRF and ICP-MS, Niwa et al., 2019), and the red diamonds denote the measured values obtained using portable XRF. Gray bars denote layers with fault gouge. Color version is available online from <https://doi.org/10.2465/jmps.201224>.

detected in our case. In contrast, Al_2O_3 showed a low correlation coefficient ($r^2 = 0.55$), probably due to interference from water and organic material (H, C, and O) in the samples. The surface structure of these geological samples might have also affected the scatterplot of Al_2O_3 owing to the relatively low excitation energy for XRF analyses (Fig. 5). The contents of SiO_2 and Al_2O_3 varied slightly from 62.4 to 79.6 mass% and from 10.2 to 18.5 mass%, respectively, which may result in the relatively low correlation coefficients for these elements (Tables S6 and S7).

Data acquired from nonpowdered rock samples of the Shiraki-Nyu and Atera faults in Central Japan measured using the portable XRF were close to those of the

powdered samples using the traditional WDXRF and ICP-MS methods of previous studies (Fig. 5 and Tables S6 and S7). The measured values for CaO content of gouges from the Atera fault (open squares in Fig. 5) using portable XRF varied from 1.1 to 3.0 mass% because of the possible heterogeneity of Ca contents in the rock samples. For other fault rock samples from the Atera, Sakai-toge, Rokko, and Gosukebashi faults (Fig. 5 and Tables S6 and S7), Fe_2O_3 contents varied from 0.4 to 4.4 mass%, and MnO contents were low, up to 0.1 mass%, compared to those in the Shiraki-Nyu fault (Tables S6 and S7).

Distributions of chemical contents in fault rock samples from the Shiraki-Nyu fault at Tsuruga Peninsula in Central Japan (Fig. 1) measured using portable XRF (this study; Figs. 5 and 6 and Tables S6 and S7) were similar to the reported values estimated using WDXRF and ICP-MS (Niwa et al., 2019). For the boring core (Core 1-c, polished rocks with resin; Fig. 1C), triplicate analyses using portable XRF were performed at six points along the gouges (Fig. 6) owing to chemical inhomogeneity on the bulk rock surface for nonpowdered samples. Slight increases in Fe_2O_3 and MnO contents were observed for the polished gouge sample from the Shiraki-Nyu fault, up to 1.6 and 0.4 mass%, respectively. Furthermore, Fe_2O_3 and MnO contents in the fault rocks collected from an outcrop of Shiraki-Nyu fault (powdered samples) also exhibited elevated values in the gouges, up to 1.9 and 1.3 mass%, respectively (Fig. 6 and Table S7), compared to those of the hanging wall and footwall cataclasite. Decreases in K_2O and Rb contents were observed in the gouges, down to 2.4 mass% and 140 mg/kg, respectively. Sr contents were constant in the gouges and in both cataclasite samples at this sampling site (27–29 mg/kg).

Niwa et al. (2019) indicated that increases in Fe_2O_3 and MnO within the gouges of the Shiraki-Nyu fault could be caused by redox changes. In addition, differences in MnO contents between the fault gouges from the outcrop and borehole core were also observed in our study using portable XRF (Fig. 6 and Table S7). In the fault gouges from outcrop samples (130604-3), MnO contents were up to 1.3 mass% (CV, 1.7%; Tables S6 and S7). Based on triplicate measurements at six points within fault gouges from the borehole core (H24-06, 07; Fig. 6), a small MnO peak (0.2 to 0.4 mass%) was also observed, but it was less clear compared to those of the outcrop from the Shiraki-Nyu fault. Mn enrichment in outcrop samples from the Shiraki-Nyu fault indicated manganese oxide precipitation along the principal slip surface in the near-surface above the groundwater table (Niwa et al., 2019). K and Rb depletions were also observed both for powdered samples and nonpowdered polished samples analyzed using portable XRF (Fig. 6). Therefore, for the Shiraki-Nyu

Figure 7. (A)–(D) Depth profiles of geochemical data in the lake sediment samples (B11-1 core; 0–30 cm depth) from the Noto Peninsula. The blue squares and red diamonds denote the measured values using WDXRF and portable XRF, respectively. Light gray and gray bars mark the $\pm 2\sigma$ range of average concentrations in each element through the samples, using the portable XRF and EDXRF, respectively. (E)–(F) Correlation plots between the measured values using WDXRF (fused glass beads) and portable XRF in this study (powdered samples). The correlation coefficients and p-values for the Spearman nonparametric correlation test are shown in each plot. Lower and upper limits of 95% compatibility intervals for the r values are shown in parentheses. Color version is available online from <https://doi.org/10.2465/jmps.201224>.

fault, portable XRF analyses are useful in nonpowdered rock samples. In particular, the portable XRF will be effective for recognizing horizontal and vertical distributions of chemical elements around the research area.

Lake sediments from the Noto Peninsula in Central Japan

Depth profiles of chemical elements measured using portable XRF (powdered samples) and WDXRF (fused glass beads) in the B11-1 core from the Bishaguso-ike artificial reservoir on the Noto Peninsula, Central Japan (Fig. 1A) are shown in Figure 7, Tables 3 and 4, and Table S9. The average values for chemical components (SiO₂, TiO₂, Sr, and Zr) in the core (0–30 cm depth) obtained using portable XRF correlated well with those obtained using WDXRF within $\pm 2\sigma$ (Fig. 7). The CVs (relative standard deviations) for triplicate analyses of SiO₂ contents were within 5% (Table S9). Major and trace element distributions in the lake sediment core measured using portable XRF resemble the results from WDXRF (Tables 3 and 4). For TiO₂, Fe₂O₃, and Zr contents, the r^2 values between the values measured using portable XRF and WDXRF were 0.61 ($p < 0.01$), 0.53 ($p < 0.01$), and 0.40 ($p < 0.05$), respectively (Fig. 7). Although a relatively high r^2 value (0.53, $p < 0.01$) was observed for Fe₂O₃, the values of Fe₂O₃ contents measured using portable XRF were different (~ 1.2 times higher) from those measured using WDXRF in our case (Tables 3 and 4). The slight

differences observed between the WDXRF and portable XRF results may be due to chemical heterogeneity within the samples. Alternatively, they could be caused by the effects from different sample matrices and Compton scattering during XRF analyses (Ryan et al., 2017). The r^2 values for SiO₂ and Sr contents were lower than 0.2 ($p \geq 0.05$) owing to limited variation, ~ 43 –46 mass% and ~ 74 –80 mg/kg, respectively in these contents through the core. For the Al₂O₃ contents, significant differences were observed between the values from portable XRF and WDXRF (Tables 3 and 4). These results could be caused by interference from organic materials containing the light elements, H, C, and O in the core from the Noto Peninsula (up to ~ 8 mass % carbon, which is relatively high; Ochiai et al., 2015).

The SiO₂ contents measured using the portable XRF decreased slightly from the bottom to the top of the core (from 49 to 41 mass%; Fig. 7A and Table 4). TiO₂, Al₂O₃, and Zr contents are decreased slightly from the bottom upward in the core (Table 4). The Fe₂O₃ contents in the core from the Noto Peninsula measured using portable XRF varied from 7.7 to 9.5 mass%. Other elements (K₂O, Cu, Zn, Rb, and Sr) showed almost constant values across the samples in our case. In a study conducted by Ochiai et al. (2015), sedimentation rates and bulk density fluctuated in surface sediments (~ 40 –cm depth below the lake bottom) from the Noto Peninsula. In several cases, fresh sediments are compacted with depth after burial (Watanabe et al., 2009; 2010). Although our data showed

Table 3. Chemical components of lake sediment samples (B11-1 core, powdered samples) from the Noto Peninsula measured using WDXRF (non-portable)

Sample ID	Sample name	Average depth (cm)	SiO ₂	TiO ₂	Al ₂ O ₃	T-Fe ₂ O ₃	MnO	CaO	K ₂ O
			(mass%)						
B11-1 core (37°07'N, 136°49'E)			WDXRF (non-portable; fused glass beads)						
2-1	B11-1_1-2	1.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2-2	B11-1_3-4	3.5	43.1	0.91	18.0	6.77	0.04	0.28	0.62
2-3	B11-1_5-6	5.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2-4	B11-1_7-8	7.5	42.7	0.91	17.9	6.47	0.03	0.26	0.60
2-5	B11-1_9-10	9.5	45.0	1.00	18.7	6.39	0.04	0.24	0.64
2-6	B11-1_11-12	11.5	44.2	0.96	18.2	6.24	0.03	0.22	0.62
2-7	B11-1_13-14	13.5	44.8	0.97	18.5	6.27	0.03	0.21	0.64
2-8	B11-1_15-16	15.5	45.1	0.97	18.7	6.24	0.03	0.20	0.64
2-9	B11-1_17-18	17.5	45.0	0.96	18.5	6.20	0.03	0.19	0.64
2-10	B11-1_19-20	19.5	45.6	0.96	18.4	6.15	0.03	0.20	0.63
2-11	B11-1_21-22	21.5	43.9	1.00	18.0	6.62	0.03	0.20	0.62
2-12	B11-1_23-24	23.5	44.8	1.00	18.3	6.34	0.03	0.20	0.62
2-13	B11-1_25-26	25.5	43.6	1.03	18.1	7.02	0.03	0.19	0.60
2-14	B11-1_27-28	27.5	43.9	1.08	18.1	7.05	0.03	0.19	0.62
2-15	B11-1_29-30	29.5	46.1	1.04	18.4	6.93	0.03	0.18	0.67

Cu	Zn	Rb	Sr	Zr
(mg/kg)				
n.a.	n.a.	n.a.	n.a.	n.a.
16.0	104	38.6	78.5	177
n.a.	n.a.	n.a.	n.a.	n.a.
26.0	105	37.2	76.5	177
12.0	99.0	38.7	79.2	195
21.0	86.0	36.9	76.7	189
17.0	103	38.5	74.8	187
19.0	86.0	38.4	76.9	192
18.0	98.0	37.5	73.7	179
19.0	91.0	37.7	75.5	185
17.0	98.0	37.0	75.2	187
29.0	105	36.8	76.7	190
20.0	95.0	35.1	79.6	198
16.0	104	35.7	79.3	195
18.0	94.0	39.7	73.8	206

n.a., not analyzed.

almost constant values across the samples, mass accumulation rates of each chemical element (g/cm²/year) should be calculated after accurate dating of the core to evaluate environmental changes in the lake watershed.

Paleotsunami deposits from northeast Japan

Concentrations and titanium normalized values of chemical elements in SND7 from the north Sendai Plain on the Pacific coast of northeast Japan are shown in Figure 8

and Tables S10–S12. The depth profiles of chemical components in SND7 obtained using portable XRF correlated well with those in Watanabe et al. (2020) obtained using WDXRF, except for Al₂O₃ (Figs. 8A–8J). Some of the CaO contents obtained using portable XRF were relatively low (Fig. 8E) compared to the reported values in Watanabe et al. (2020), which could be caused by the distribution of shell fragments in the samples. Conversely, titanium-normalized element ratios from the portable XRF data (Si/Ti, Ca/Ti, and Sr/Ti; Figs. 8L–8N) for SND7 resemble those of the reported values. In our study, these titanium-normalized values using portable XRF showed clear peaks in the Jogan tsunami deposits. In addition, relationships between the titanium-normalized values for SND7 based on the measured portable XRF (this study) and reported values from WDXRF (Watanabe et al., 2020) had relatively high correlation coefficients (r^2), i.e., more than 0.84 with $p < 0.01$ (Fig. 9). Therefore, the element ratios measured using portable XRF might be suitable for identifying signatures of past marine incursions (e.g., tsunami in our case).

Based on portable XRF analyses, the SiO₂ contents varied from 13.5 to 86.6 mass% (Fig. 8A). The depletion of SiO₂ contents down to 13.5 mass% was observed below the Jogan tsunami deposits (~1080 calBP), and rapid enhancement occurred in the boundary between peaty clays and paleotsunami deposits (74–67 cm depth, from 13.5 to 76.7 mass%). Al₂O₃ contents were relatively constant (8.2 mass% on average; Fig. 8B) but undetected in the peaty clays (88–69 cm depth). TiO₂ contents in the

Table 4. Chemical components of lake sediment samples (B11-1 core, powdered samples) from the Noto Peninsula measured using portable XRF

Sample ID	Sample name	Average depth (cm)	SiO ₂	TiO ₂	Al ₂ O ₃	T-Fe ₂ O ₃	MnO	CaO	K ₂ O	Cu	Zn	Rb	Sr	Zr
			(mass%)							(mg/kg)				
B11-1 core (37°07'N, 136°49'E)			portable XRF (powdered samples)											
2-1	B11-1_1-2	1.5	41.4	1.07	9.73	8.68	n.d.	n.d.	0.82	33.9	138	46.9	86.2	188
2-2	B11-1_3-4	3.5	40.5	1.01	9.45	8.07	n.d.	n.d.	0.79	35.7	126	42.0	76.7	181
2-3	B11-1_5-6	5.5	43.0	1.11	10.4	8.63	n.d.	n.d.	0.83	27.4	150	46.1	79.1	193
2-4	B11-1_7-8	7.5	43.5	1.12	10.6	8.21	n.d.	n.d.	0.79	33.7	147	45.8	80.4	186
2-5	B11-1_9-10	9.5	43.6	1.12	10.6	7.68	n.d.	n.d.	0.82	30.6	132	42.4	77.1	200
2-6	B11-1_11-12	11.5	44.0	1.19	10.3	7.97	n.d.	n.d.	0.86	30.0	140	47.3	82.5	211
2-7	B11-1_13-14	13.5	44.5	1.08	10.5	7.68	n.d.	n.d.	0.79	30.6	124	44.8	79.3	212
2-8	B11-1_15-16	15.5	47.6	1.20	11.5	8.11	n.d.	n.d.	0.89	36.3	131	45.9	82.2	209
2-9	B11-1_17-18	17.5	47.5	1.17	11.3	7.73	n.d.	n.d.	0.85	33.7	120	45.4	80.4	204
2-10	B11-1_19-20	19.5	46.3	1.11	10.6	7.76	n.d.	n.d.	0.81	31.7	121	46.2	79.9	203
2-11	B11-1_21-22	21.5	49.1	1.19	11.7	8.14	n.d.	n.d.	0.81	36.0	139	45.2	79.5	215
2-12	B11-1_23-24	23.5	46.1	1.18	11.1	8.40	n.d.	n.d.	0.83	31.3	132	43.4	78.2	209
2-13	B11-1_25-26	25.5	46.3	1.21	11.2	8.70	n.d.	n.d.	0.81	29.6	137	41.2	83.1	214
2-14	B11-1_27-28	27.5	48.7	1.39	12.3	9.46	n.d.	n.d.	0.95	39.7	148	44.5	87.7	226
2-15	B11-1_29-30	29.5	47.0	1.22	11.0	8.55	n.d.	n.d.	0.88	36.6	123	47.4	74.7	218

n.d., not detected.

peaty clays were depleted to 0.2 mass%, and a small peak was observed within the paleotsunami deposits (up to 0.5 mass% at 58.5-cm depth; Fig. 8C). The variations of K₂O, CaO, Sr, and Rb contents (Figs. 8D–8G) resemble that of SiO₂ through the geoslicer sample. Moreover, clear peaks of Fe₂O₃, S, As, and Cl were found in the peaty clays just below the Jogan tsunami deposits (the highest peaks were found at 69.5-cm depth, with relatively smaller peaks at 81.5-cm depth; Figs. 8H–8K and Table S11). The As contents within the peaty clay layers were ~ 600 mg/kg. Obvious changes were observed in SiO₂, TiO₂, K₂O, CaO, Sr, and Rb contents across the boundary between the peaty clays and Jogan tsunami deposits (68-cm depth).

Correlation coefficients among the chemical components in SND7 from the north Sendai Plain in Tohoku are shown in Table S13. The nonparametric correlation coefficients (Spearman's rank correlation calculated using R) of the data revealed that Si showed either a positive or negative correlation, which is statistically different from zero at 1 or 5% significance levels ($p < 0.01$ or 0.05, Spearman's rank correlation tests) for the elements (Ti, Al, Ca, K, Cl, As, Rb, Sr, and Zr) measured using portable XRF in this study (Table S13). Ca had positive correlations with Sr ($p < 0.01$). In addition, positive correlations were observed between Ti and Zr, which could have originated from detrital materials (heavy minerals, such as ilmenite and zircon). In contrast, Fe had positive

correlations with S and As, which could be from sulfides, such as pyrite or arsenopyrite.

Traditionally, statistical analysis such as PCA has been applied in geology, mineralogy, and geochemistry to evaluate chemical characteristics, sources, material cycles, and chemical and physical weathering trends (Fagel et al., 2003; Kuwatani et al., 2014b; Chagué et al., 2018). PCA results for the chemical components in SND7 from Tohoku are shown in Figure 10, Table S14, and Figure S1 (Supplementary Figures S1–S3 are available online from <https://doi.org/10.2465/jmps.201224>). The cumulative proportions of the 1st, 2nd, and 3rd principal components accounted for ~ 80.3% of the variation (PC1, 55.5%; PC2, 14.4%; PC3, 10.4%; Table S14). The depth profile of PC1 scores in SND7 indicates positive values within the peaty clays (69–88 cm depth) below the Jogan tsunami deposits (Fig. 10A). Furthermore, this positive trend of PC1 well coincides with those previously obtained based on analyses by WDXRF and ICP-MS (Fig. 10; Watanabe et al., 2020). PC2 showed a positive trend within the layer containing the Jogan tsunami deposits. The causes of this PC2 trend are unclear; however, we speculate that PC2 indicates the layers with the paleotsunami deposit (relatively rich in Ca, Sr, and Mn) in our case. Although the PC1 and PC2 values can be used equally to evaluate chemical characteristics of the event deposits based on the portable XRF and EDXRF data, PC3 scores exhibit different trends between the data tak-

Figure 8. Depth profiles of geochemical data in the continuous geoslicer samples (SND7) from the north Sendai Plain. Photographs of sedimentary facies from the SND7 are also shown for comparison. Blue opened squares and red opened diamonds indicate reported values (Watanabe et al., 2020) and portable XRF values in this study, respectively. Gray bars denote the layers with paleotsunami deposits (Jogan tsunami deposits, ~ 1080 cal BP). Color version is available online from <https://doi.org/10.2465/jmps.201224>.

en by these two distinct methods (Fig. 10C). The differences in PC3 could be caused by the relatively low Ca contents found in the portable XRF data (Fig. 8E). On the biplot of PC1 and PC2, the peaty clays (69–88 cm depth) with relatively high Fe, S, As, and Cl contents are plotted on the right side (positive PC1). The layer with the Jogan tsunami deposits is plotted on the upper left part of the biplot (negative PC1 and positive PC2; Fig. S1).

A cluster analysis of chemical components in SND7 measured using portable XRF (Fig. S2) or stationary-

type EDXRF (Fig. S3) was performed based on Euclidean distance using Ward's method. First, the reported data from the Jogan tsunami deposits using stationary-type EDXRF (Watanabe et al., 2020) were distinguished from other layers via cluster analysis (Fig. S3). With respect to the portable XRF data, the cluster dendrogram of SND7 revealed four main clusters (Fig. S2). The first cluster is the upper peaty clay layer (30–41 cm depth), and the second one consists of Jogan tsunami deposits (~ 1080 cal BP; 52–68 cm depth). The third cluster includes beach

Figure 9. Correlation plots between the reported values (Watanabe et al., 2020) and portable XRF values for titanium-normalized element ratios in the paleotsunami deposits and other layers from SND7 (powdered samples). Correlation coefficients and p-values for the Spearman nonparametric correlation test are shown in each plot. Lower and upper limits of 95% compatibility intervals for the r values are shown in parentheses.

ridge deposits (90–118 cm depth), except for samples ID 7-43, 7-46, and 7-50 (43–51 cm depth) located on the uppermost part of the Jogan tsunami deposits, mixed with peaty clays. The last cluster includes the lower peaty clay layers (69–88 cm depth) in SND7. One sample with tsunami deposits (Sample ID 7-58; 58–59 cm depth; Fig. S2) was excluded from the above four clusters, probably because of Si enrichment compared to the other layers (86.6 mass% Si content; Tables S13–S14). The geochemical data acquired using portable XRF from typical Jogan tsunami deposits (~1080 cal BP; 52–68 cm depth) constitute one cluster, which was discriminated from other deposits, beach ridge deposits, and peaty clays in this

study. Therefore, cluster analyses of geochemical data using portable XRF were useful to characterize event deposits on the north Sendai Plain.

CONCLUSIONS

To evaluate the precision and reliability of a portable XRF, we compared quantification data from the portable XRF and reported values for a) fault rocks, b) lake sediments from Central Japan, and c) soils with paleotsunami deposits from the Pacific coast of northeast Japan. Measured portable XRF values were calibrated via our working curves determined using reference materials, such as igneous rocks and other geochemical standards distributed by national and international organizations (AIST, USGS, and IAEA). Subsequently, quantitative analyses of 24 elements (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , K_2O , P_2O_5 , S, Cl, V, Cr, Cu, Zn, As, Rb, Sr, Zr, Nb, Ba, Pb, Th, and U) in the samples were performed using portable XRF. Based on our study, the usefulness and weaknesses of portable XRF are summarized as follows:

Major elements

SiO_2 , TiO_2 , Fe_2O_3 , MnO , CaO , and K_2O . Working curves showed significant correlations between the measured portable XRF values and reported values for reference materials ($r^2 = 0.97\text{--}0.99$, $p < 0.01$). The contents of these elements in the powdered and nonpowdered fault rock samples coincide with reported values ($r^2 = 0.47\text{--}0.90$, $p < 0.01$; except for SiO_2 owing to limited variation in the samples). The depth profiles of SiO_2 and TiO_2 contents in powdered lake sediments of the Noto Peninsula measured using portable XRF were similar to those using the stationary-type XRF. Additionally, relationships between the Ti-normalized values for tsunami deposits measured using portable XRF and the reported values

Figure 10. Depth profiles of PC1, PC2, and PC3 scores using principal component analysis (PCA) in paleotsunami deposits and other layers from SND7. Geochemical data for the PCA were measured using portable XRF (red open diamonds) and EDXRF (blue open squares). Gray bars denote the layers with paleotsunami deposits (Jogan tsunami deposits, ~1080 cal BP). Color version is available online from <https://doi.org/10.2465/jmps.201224>.

had high correlation coefficients ($r^2 = 0.84\text{--}0.98$, $p < 0.01$).

Al₂O₃. The intensity of the Al peak measured using portable XRF was relatively small owing to its low excitation energy (affected by surface structure). Al contents determined using portable XRF had large differences from the reported values in our samples.

Na₂O and MgO. Light elements, such as Na, are not measurable owing to their low excitation energies and interference from other light elements (oxygen, nitrogen, and carbon). Similarly, the working curve of MgO was more scattered ($r^2 = 0.58$) relative to those of other major elements.

P₂O₅. Although the working curve of P₂O₅ has significant correlation ($r^2 = 0.77$, $p < 0.01$), most of the values in our geological samples were too low to evaluate the geochemical characteristics by portable XRF.

Trace elements

S, V, Cr, Cu, Zn, As, Rb, Sr, Zr, Pb, and Th. Working curves showed significant correlations with reference materials ($r^2 = 0.72\text{--}0.99$, $p < 0.01$). For Rb, Sr, Zr, and Th in the fault rock samples, the r^2 values of the regression lines between the measured portable XRF values and reported values were 0.48–0.88 ($p < 0.01$), and the slopes were 0.92–1.32. For the lake sediment and tsunami deposit samples, most of the trace element variations observed by portable XRF were consistent with the reported values.

Cl and U. Although positive regression lines were obtained between the portable XRF data and reported values, additional reference materials are needed with wider concentration ranges to improve the reliability of r^2 values for the regression lines.

Ba. Relatively scattered data were observed on the working curve for Ba, possibly due to mass interference from TiK α , ScK β , and minor peaks of other elements. In our study, the data were not useful in the range of Ba contents (less than ~ 0.2 mass%).

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SUPPLEMENTARY MATERIALS

Color version of Figures (1, 3–8, and 10), Supplementary Tables S1–S14, and Supplementary Figures S1–S3 are available online from <https://doi.org/10.2465/jmps.201224>.

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