

## Contamination from mortars and mills during laboratory crushing and pulverizing

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**Abstract:** Contamination of rock samples from laboratory equipment during crushing and pulverizing was investigated. Pulverization using iron and tungsten carbide mortars, and agate and tungsten carbide mills produced three suites of powders. Whole-rock data from the analyses of the three suites of samples enabled assessment of the degree of contamination of samples by coarse crushing and pulverization. The samples analyzed for major and trace elements compositionally represent basalt, basaltic andesite, dacite, and rhyolite. The results from the analyses of major elements exhibit insignificant contamination from the mortars and the mills. The heterogeneity of rock chips explains the compositional differences observed. The tungsten carbide mill contaminated samples with tungsten and cobalt. The significant scatter of other trace elements data is attributed to sample heterogeneity, with no systematic effect from contamination.

**Keywords:** contamination, pulverizing of rock samples, powdered rock samples, whole-rock major element, whole-rock trace element

### 1. Introduction

Whole-rock analysis of rock samples provides fundamental and important data for earth science studies. Advances in analytical methods and the expansion in the use of analytical instruments have facilitated the precise chemical compositional analysis of rock samples. The preparation of samples before analysis includes cutting, crushing, splitting, and pulverizing (e.g., Terashima *et al.*, 1990; Potts, 2003). Such processes generally include an iron jaw-crusher, iron mortar and tungsten carbide mortar for crushing, and an agate mill and tungsten carbide mill for pulverizing. In particular, equipment composed of tungsten carbide is commonly used for crushing and pulverizing because of its hardness; however, contact between samples and the equipment during preparation exposes the samples to contamination from different elements (e.g., Ando, 1986). Several authors (Myers and Barnett, 1953; Barnett *et al.*, 1955; Thompson and Bankston, 1970; Hickson and Juras, 1986; Roser *et al.*, 1998; Iwansson and Landström, 2000; Takamasa and Nakai, 2009) have documented the contamination of samples from preparation equipment. Analytical instruments currently determine trace element concentrations at sub-ppm (parts per million) levels in rock samples. Contamination by any element from pulverization poses the risk of geochemical data misinterpretation. Although contamination is inevitable, its impact on the data generated is dependent

on the content of contaminant elements in the samples. An appraisal of contamination is thus important for the interpretation and reliable discussion of whole-rock data.

This paper examines the contamination of rock samples by pulverization using laboratory crushing mortars and grinding mills. The data employed in this study included major elements and forty-five trace elements generated using X-ray fluorescence spectrometer (XRF) and a laser ablation-inductively coupled plasma-mass spectrometer (LA-ICP-MS).

### 2. Materials and methods

#### 2.1 Overview: combinations of crushing and grinding equipment

Three suites of pulverized samples provided data used for the evaluation of contamination by coarse crushing and milling (Fig. 1). Visibly homogeneous fine-grained rocks were split into two portions and coarsely crushed in an iron mortar and a tungsten carbide mortar, respectively. An agate ball mill was used to grind the samples crushed using the iron mortar. An agate ball mill and a tungsten carbide mill were used to grind a portion of each sample crushed in the tungsten carbide mortar. The prepared samples comprised basalt, basaltic andesite, dacite, and rhyolite, which amounted to twelve samples for comparison and evaluation. The sections below contain detailed descriptions of the procedures.

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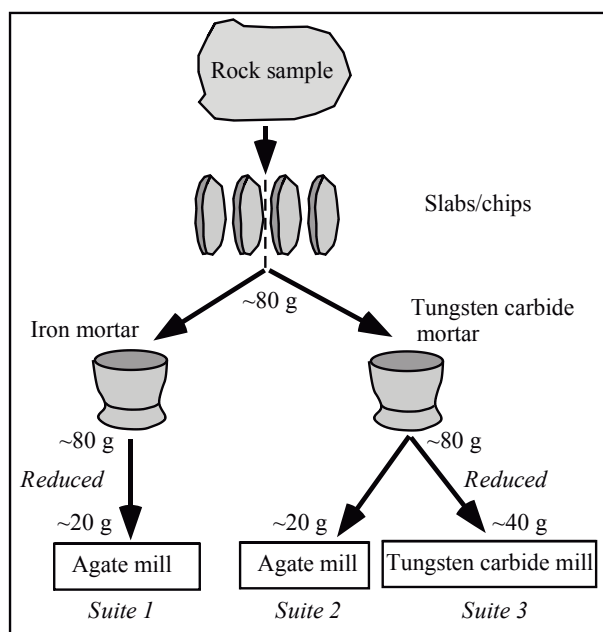


Fig. 1 Schematic illustration of the pulverizing process. The rock samples were split into two portions and crushed using iron or tungsten carbide mortars. Coarsely crushed sample from the iron mortar was ground using an agate mill (suite 1). Coarsely crushed sample from the tungsten carbide mortar was further split into two portions and ground using an agate mill (suite 2) and a tungsten carbide mill (suite 3).

## 2.2 Samples and sample pretreatment

The homogeneity of samples is important for the evaluation of contamination from equipment because pulverizing occurs after crushing. To evaluate the effect of contamination required samples of varying composition because the concentration of elements in igneous rocks is dependent on the degree of differentiation. Therefore, volcanic rocks of the Nikoro Group from the Tokoro Belt, in Hokkaido, with compositions ranging from primitive basalt to rhyolite were utilized (for details of the Nikoro Group, see Yamasaki and Nanayama, 2017, 2018 and references therein). The samples studied showed varying degrees of alteration; although a heterogeneous distribution of alteration veins is undesirable for any sample, a pervasive alteration had minimal impact on the comparison in this study. The scarcity of samples controlled the choice of samples and accounts for the collection of some altered samples.

The rock samples were cut into slabs (a few millimeters thick) or chips using a rock-cutting saw. Scraping of the surfaces of the chips with a diamond disk removed any contamination from the rock-cutting saw. Cleaning by ion-exchanged water was conducted for 30 min in an ultrasonic bath after the initial cleaning of the chip surfaces. The samples were then dried in an oven for over 24 h.

## 2.3 Crushing and milling

The slabs or chips of samples (~80 g) were crushed coarsely to <4 mm fragments using iron and tungsten carbide mortars (Fig. 2a). The sizes of the iron and tungsten carbide mortars were 14.5 cm in diameter and 12.5 cm, high and 10.0 cm in diameter and 11.0 cm high, respectively. The coarsely crushed fragments were then reduced to ~40 g and ~20 g for pulverizing with tungsten carbide and agate mills, respectively. Contamination of the samples during coarse crushing in the tungsten carbide mortar was unexpected due to the durability of the mortar material. However, trace elements such as nickel, cobalt, and tungsten, which are important in petrogenetic interpretation, are sensitive to minor contamination. The higher (a few to several wt%) content of FeO/Fe<sub>2</sub>O<sub>3</sub> in many igneous, metamorphic and sedimentary rocks minimizes the impact of contamination by iron from the iron mortar, even though the iron mortar is less durable than the tungsten carbide mortar.

An agate planetary ball mill (Fritsch – GmbH, MP-7; Fig. 2b, c) and a tungsten carbide automatic pulverizing mill (Herzog, HP-MA; Fig. 2d) in the laboratory of the Geological Survey of Japan (GSJ-Lab) served for pulverization of the samples. The agate planetary ball mill was used to pulverize approximately 20 g of samples at 800 rpm for 10 min, with the rotational direction switched every 2 min. The size of the vessel was 4 cm in diameter and 4 cm deep, and the balls were 1.5 cm in diameter. Six balls were used for pulverizing in each vessel. Cleaning of the agate vessel and balls was performed using quartz sand after each sample to avoid cross-contamination. Automatic features of the Herzog HP-MA pulverizing mill, such as emptying and cleaning with compressed air and ethanol, allowed sufficient removal of material after each sample. The mill consists of a 100 cm<sup>2</sup> vessel with an inner floating ring and cylinder set. The automatic pulverizing mill ground approximately 40 g of coarsely-crushed samples for 40 s. The final fineness of the powdered sample using both mills was 40–0.5 μm, which is comparable with the grain size distributions reported from another laboratory (Roser *et al.*, 1998).

## 2.4 Geochemical analyses

An XRF spectrometer (PANalytical Axios) in the GSJ-Lab was used to determine major element compositions following the procedure described by Yamasaki (2014). Glass beads were prepared by mixing 0.5 g of powdered rock sample and 5.0 g of a lithium tetraborate flux (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>; Merk Co. Ltd., Spectromelt A10, #10783; 10 times the amount of the standard powder sample). The glass beads were used for subsequent LA-ICP-MS analyses. An LA-ICP-MS system in the GSJ-Lab was used to measure the trace element compositions. The equipment consisted of an LA system (New Wave Research, NWR213) coupled to a quadrupole ICP-MS (Agilent, 7700x), and analysis employed procedures described by Yamasaki *et al.* (2015) and by Yamasaki and Yamashita (2016).

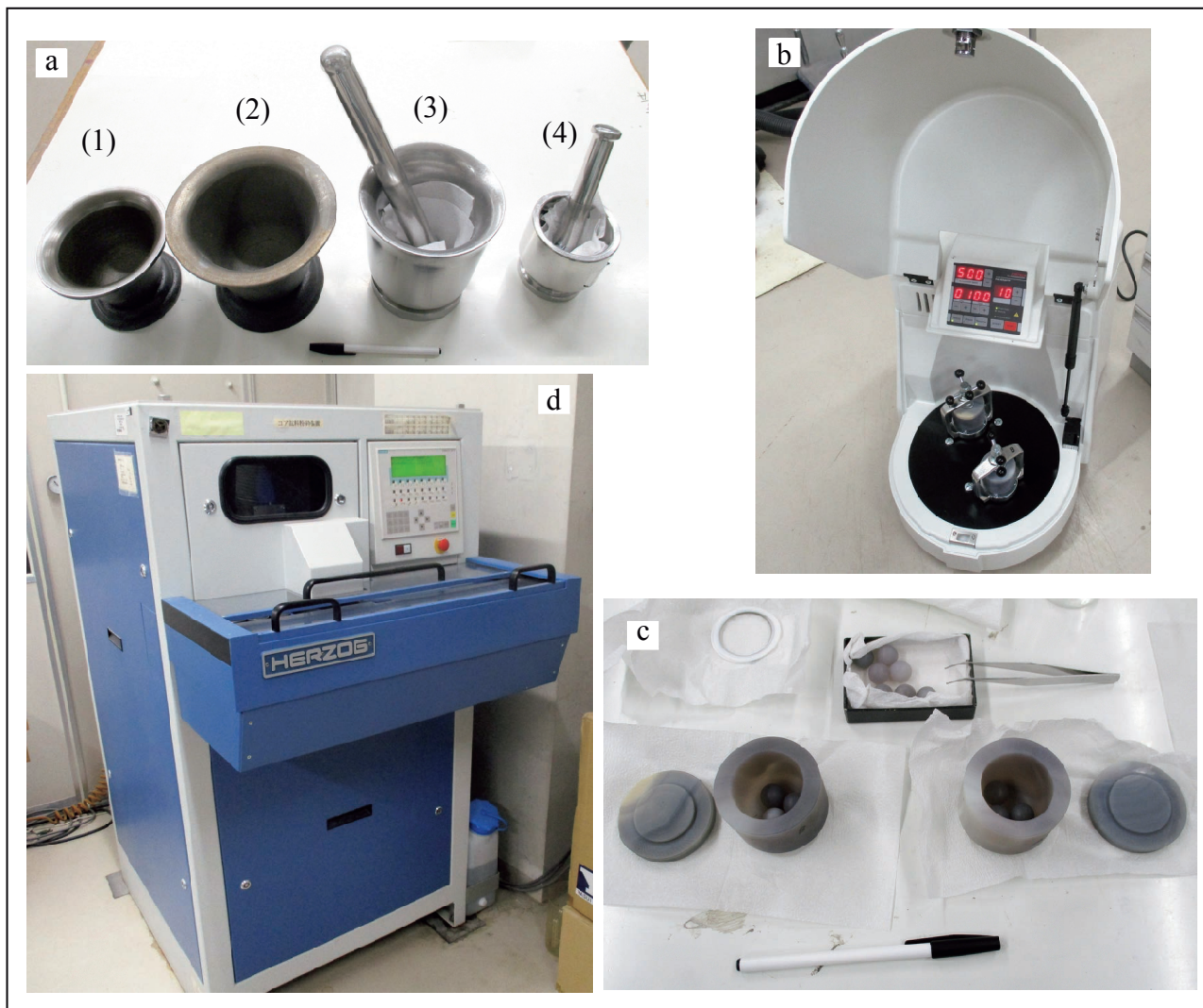


Fig. 2 Equipment for the crushing and pulverizing processes. a) Mortars: iron mortars (1 and 2), and tungsten carbide mortars (3 and 4). (1) and (4) were used for this study. b) Planetary mill (Planetary Micro Mill PULVERISETTE 7 classic line, Fritsch-GmbH). c) Agate grinding vessels and balls for the planetary mill, and d) Tungsten carbide mill (HP-MA: Automatic pulverizing mill, Herzog).

### 3. Results

The results for the geochemical analyses of the studied samples are listed in Table 1. The major elements data were normalized to 100% for the compensation of weighing errors, which enabled comparison of the various pulverizing suites (Table 2). Table 2 and Fig. 3 show the differences in the compositions of suites 2 and 3, relative to suite 1. The comparison shows significant differences between suite 1 and suites 2 or 3, but lower differences between suites 2 and 3 (Fig. 3). The differences observed exceed the precision of the XRF analysis (i.e., 0.04 wt%; Yamasaki, 2014). The smaller differences between the samples of suites 2 and 3 compared to samples of suite 1 (e.g., Fig. 3b and c) suggests slightly different compositions of the crushed rock chips. This difference is attributed to the heterogeneous distribution of alteration

veins in some samples.

Contamination of the samples from the crushing and milling equipment could result in iron enrichment from crushing in the iron mortar and silica enrichment from grinding in the agate mill. The  $\text{Fe}_2\text{O}_3^*$  (total Fe as  $\text{Fe}_2\text{O}_3$ ) content of the various suites of samples was used to assess the impact of the iron mortar during preparation. Comparison of data for samples pulverized in the agate ball mill showed no enrichment in iron for suite 1 samples crushed in the iron mortar, and suite 3 samples had silica contents comparable to those of samples pulverized in the agate mill (Table 2 and Fig. 3). Contamination from the iron mortar should be prominent in rhyolite due to its low iron content. The basaltic andesite and the dacite samples from suites 2 and 3 were depleted in iron relative to suite 1 samples; however, this was not observed for the basalt and rhyolite samples. The samples for suites 2 and 3, except

Table 1 Whole-rock major (wt%) and trace (ppm) element geochemistry for the studied samples.

	Basalt			Basaltic andesite			Dacite			Rhyolite		
	Suite 1	Suite 2	Suite 3	Suite 1	Suite 2	Suite 3	Suite 1	Suite 2	Suite 3	Suite 1	Suite 2	Suite 3
SiO <sub>2</sub>	48.18	48.32	48.49	53.13	54.13	54.98	63.48	63.59	63.54	78.61	78.42	78.45
TiO <sub>2</sub>	2.60	2.69	2.58	2.63	2.53	2.49	0.43	0.42	0.42	0.43	0.46	0.44
Al <sub>2</sub> O <sub>3</sub>	16.27	16.33	16.09	13.34	13.07	13.18	16.23	16.24	16.11	9.30	9.66	9.54
Fe <sub>2</sub> O <sub>3</sub> *	12.87	12.91	12.53	14.14	13.44	12.85	6.16	5.86	5.64	4.28	4.35	4.24
MnO	0.24	0.23	0.23	0.17	0.17	0.16	0.11	0.11	0.10	0.13	0.14	0.13
MgO	6.00	6.08	5.87	3.90	3.71	3.60	0.50	0.47	0.45	1.31	1.37	1.34
CaO	8.82	7.84	8.92	8.90	9.35	9.44	0.86	0.86	0.87	0.61	0.65	0.62
Na <sub>2</sub> O	4.30	4.31	4.31	3.61	3.42	3.55	2.43	2.33	2.34	1.30	1.35	1.33
K <sub>2</sub> O	0.88	0.95	0.89	0.55	0.38	0.31	9.97	10.19	10.19	3.10	3.23	3.20
P <sub>2</sub> O <sub>5</sub>	0.35	0.36	0.35	0.35	0.34	0.34	0.06	0.06	0.05	0.16	0.17	0.17
Total	100.50	100.02	100.27	100.72	100.53	100.89	100.24	100.13	99.72	99.24	99.80	99.45
LOI	7.69	7.18	7.91	2.94	2.98	2.87	1.35	1.28	1.55	2.07	2.19	2.13
Sc	27.5	38.5	21.7	37.5	37.4	36.7	19.3	14.6	12.8	18.6	16.3	13.9
V	288	315	291	329	335	329	4	2	3	84	81	85
Cr	74.87	77.02	68.68	36.86	63.36	35.00	10.49	9.71	5.99	23.15	41.25	23.11
Co	42.5	42.4	43.4	40.8	39.1	47.6	1.4	0.4	69.4	11.9	10.6	16.5
Ni	108.94	108.61	119.39	55.41	56.00	55.02	162.23	167.53	55.36	25.04	26.87	37.89
Cu	98	103	92	103	103	103	5	7	4	86	85	72
Zn	133.1	134.3	134.1	134.3	136.8	134.4	292.1	290.8	286.4	77.9	73.3	76.6
Ga	24.5	25.0	23.4	25.4	22.8	24.5	45.1	38.6	33.6	17.3	15.3	12.4
Ge	2.56	0.13	0.58	n.d.	n.d.	n.d.	1.15	1.38	1.02	0.81	0.59	0.72
As	n.d.	n.d.	n.d.	3.95	0.44	1.55	1.77	1.68	1.39	1.45	1.80	1.53
Rb	13.0	13.0	11.2	12.1	11.8	11.5	190.0	198.2	190.3	102.1	87.3	87.4
Sr	176	177	170	102	102	104	55	60	55	81	78	80
Y	28.3	29.4	27.4	41.0	36.5	38.5	92.0	88.3	92.2	16.7	15.8	13.4
Zr	186.0	194.0	185.7	187.4	184.5	188.9	1869.8	1745.5	1771.2	75.9	75.4	77.0
Nb	12.97	16.11	12.82	15.18	13.87	14.64	160.62	150.86	146.66	4.09	3.31	2.97
Mo	0.60	0.51	0.31	1.17	3.39	1.70	3.14	2.77	4.72	0.83	0.19	0.28
Cd	n.d.	n.d.	n.d.	0.25	0.22	0.20	0.31	0.37	0.10	0.01	0.00	0.05
Sn	1.56	2.08	1.38	2.53	1.83	1.23	7.02	6.56	4.45	0.91	0.56	0.58
Sb	n.d.	n.d.	n.d.	0.04	0.06	0.05	0.14	0.04	0.15	0.31	0.20	0.26
Cs	1.43	0.42	0.39	1.42	0.73	2.29	1.31	1.16	1.28	1.44	1.54	1.35
Ba	108	113	105	127	118	130	572	514	528	328	295	280
La	16.66	21.07	17.60	20.43	19.84	19.78	111.25	109.49	104.88	17.73	15.71	13.61
Ce	40.2	45.9	40.5	45.8	41.6	41.3	226.0	212.0	210.8	43.7	40.3	43.1
Pr	4.90	5.51	4.13	5.15	4.76	5.50	32.62	30.99	31.80	5.54	4.90	4.12
Nd	21.1	22.4	19.6	24.1	22.6	24.6	116.5	111.5	108.9	18.3	17.8	15.7
Sm	6.33	6.49	7.61	10.02	7.57	6.54	22.47	24.32	21.88	4.10	4.16	3.08
Eu	1.8	2.9	2.0	2.2	1.9	2.0	4.0	3.2	3.5	1.1	0.8	0.7
Gd	5.65	6.36	4.44	7.90	7.90	7.18	21.77	19.09	18.77	3.39	2.87	2.85
Tb	0.76	1.09	0.90	1.12	0.99	1.23	2.87	2.94	2.41	0.52	0.57	0.51
Dy	5.19	5.99	4.75	6.14	5.85	5.86	21.03	18.65	23.26	3.57	3.09	2.80
Ho	1.24	1.56	1.47	1.86	2.00	1.60	3.46	3.54	4.31	0.69	0.54	0.57
Er	2.89	2.93	2.93	3.22	3.82	3.32	9.86	8.97	11.10	1.84	1.61	1.39
Tm	0.32	0.60	0.46	0.58	0.54	0.46	1.57	1.63	1.68	0.31	0.29	0.20
Yb	2.05	3.63	1.85	2.88	3.58	3.18	9.65	9.00	8.82	1.56	1.58	1.38
Lu	0.54	0.35	0.41	0.55	0.72	0.71	1.52	1.55	1.50	0.27	0.25	0.22
Hf	3.63	4.20	3.10	3.89	3.87	3.73	34.18	34.17	33.59	2.01	1.86	1.59
Ta	1.83	2.13	1.80	2.41	2.16	2.08	15.72	16.37	14.69	0.49	0.48	0.36
W	0.30	0.97	25.37	1.15	1.33	119.63	1.46	1.13	163.55	0.39	0.81	43.62
Tl	0.05	0.08	0.09	0.08	0.08	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	0.76	1.29	1.18	1.42	1.21	1.24	5.50	5.45	6.90	9.26	9.12	7.34
Bi	0.032	0.030	0.032	0.030	0.031	0.027	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Th	1.49	1.85	1.51	1.99	1.65	1.73	12.56	11.61	12.99	4.33	3.82	3.47
U	0.45	0.47	0.30	0.55	0.54	1.50	3.48	3.31	3.80	0.80	0.75	0.58

Fe<sub>2</sub>O<sub>3</sub>\* denotes total Fe as Fe<sub>2</sub>O<sub>3</sub>.

Table 2 Differences in major element compositions (wt%) for suite 2 and 3 samples relative to suite 1 samples.

		SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> *	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Total
Basalt	Suite 1	47.94	2.59	16.19	12.81	0.24	5.97	8.78	4.27	0.88	0.35	100.00
	Suite 2	48.32	2.69	16.33	12.91	0.23	6.08	7.84	4.31	0.95	0.36	100.00
	Diff.	0.38	0.10	0.14	0.10	0.00	0.11	-0.94	0.03	0.07	0.01	–
	Suite 3	48.36	2.57	16.04	12.50	0.23	5.86	8.90	4.30	0.89	0.35	100.00
	Diff.	0.42	-0.02	-0.14	-0.31	0.00	-0.11	0.12	0.03	0.01	0.00	–
	Basaltic andesite	Suite 1	52.75	2.61	13.25	14.04	0.16	3.87	8.83	3.59	0.55	0.35
Suite 2		53.84	2.51	13.00	13.36	0.17	3.69	9.30	3.40	0.38	0.34	100.00
Diff.		1.09	-0.10	-0.24	-0.68	0.00	-0.18	0.47	-0.19	-0.17	-0.01	–
Suite 3		54.50	2.47	13.06	12.73	0.16	3.57	9.36	3.52	0.31	0.33	100.00
Diff.		1.74	-0.14	-0.18	-1.31	-0.01	-0.30	0.53	-0.07	-0.24	-0.02	–
Dacite		Suite 1	63.33	0.42	16.19	6.15	0.11	0.50	0.86	2.43	9.95	0.06
	Suite 2	63.51	0.42	16.21	5.85	0.11	0.47	0.85	2.33	10.18	0.06	100.00
	Diff.	0.18	0.00	0.02	-0.29	0.00	-0.03	0.00	-0.10	0.23	0.00	–
	Suite 3	63.72	0.42	16.15	5.66	0.10	0.45	0.87	2.34	10.22	0.05	100.00
	Diff.	0.39	0.00	-0.04	-0.49	-0.01	-0.04	0.02	-0.08	0.27	-0.01	–
	Rhyolite	Suite 1	79.22	0.43	9.37	4.31	0.13	1.32	0.62	1.31	3.13	0.16
Suite 2		78.58	0.46	9.68	4.36	0.14	1.37	0.65	1.35	3.23	0.17	100.00
Diff.		-0.64	0.03	0.31	0.05	0.01	0.05	0.04	0.04	0.10	0.01	–
Suite 3		78.88	0.44	9.59	4.27	0.13	1.35	0.62	1.33	3.22	0.17	100.00
Diff.		-0.33	0.01	0.22	-0.04	0.00	0.03	0.01	0.02	0.09	0.01	–

Fe<sub>2</sub>O<sub>3</sub>\* denotes total Fe as Fe<sub>2</sub>O<sub>3</sub>. Diff. denotes the difference in the composition of suite 2 or 3 samples from those of suite 1 samples.

the rhyolite, indicated an apparent enrichment in silica. The agate mill can enrich even rhyolite because of its high silica content. The variations observed are attributed to compositional differences between the batches used for coarse crushing (i.e., compositional differences from the crushed samples). The contamination of samples from the pulverizing equipment was thus low for the major elements. However, an appraisal of the degree of heterogeneity within a single sample by repetitious crushing and pulverization as different batches would be required for precise evaluation of the contamination extent.

For trace element analyses, the averaged Ca content for the three suites of samples for each rock (i.e., basalt, basaltic andesite, dacite, and rhyolite) were used as standards to compensate for the propagation of analytical errors from the XRF analyses. The differences in the trace element compositions for the suite 2 and 3 samples relative to suite 1 samples are shown in Table 3 and Fig. 4. The standard deviations from five replicate analyses of reference materials (Yamasaki and Yamashita, 2016; JB-2 for basalt and basaltic andesite samples, JA-1 for dacite sample, and JR-1 for rhyolite sample) are included as references for the analytical errors (precision) at any given composition. Differences beyond analytical errors were observed for major elements for the three suites of samples, and samples from suite 2 displayed similar

compositions to samples from suite 3 for several elements (Fig. 4). Several studies indicate that tungsten carbide mills produce significant Nb and possibly Ta, as well as substantial W and Co contamination (e.g., Miyake and Musashino, 1991; Condie, 1993; Ujike and Tsuchiya, 1993; Rollinson, 1993 and references therein). The W contents for suite 3 samples were higher than those of the suite 1 and 2 samples for all rock types, which confirms contamination from the tungsten carbide mill (Fig. 4). The elevated Co contents for suite 3 samples relative to suite 1 and 2 samples lack a clear trend. According to Roser *et al.* (1998), the tungsten carbide of a mill head contains 90% of W and 9.5% of Co. If this composition is standard for a tungsten-carbide alloy, then the increase of the Co content in suite 3 samples relative to suite 1 samples falls between 6–13% of the W content (i.e.,  $[\text{CCo, Suite 3} - \text{CCo, Suite 1}]/[\text{CW, Suite 3} - \text{CW, Suite 1}] \times 100$ , where C denotes the content of the elements). The increased ratio is consistent with the expected Co/W ratio for tungsten carbide, except for the dacite samples (Table 3). Therefore, Co contamination also results from use of the tungsten carbide mill. The cause of the high Co content for the dacite samples, reproduced by several re-analyses is unclear. If the high Co content originates from contamination due to the tungsten carbide mill, then the analytical data for W is expected to be ca. 658 ppm. The absence of such higher data for W suggests that the

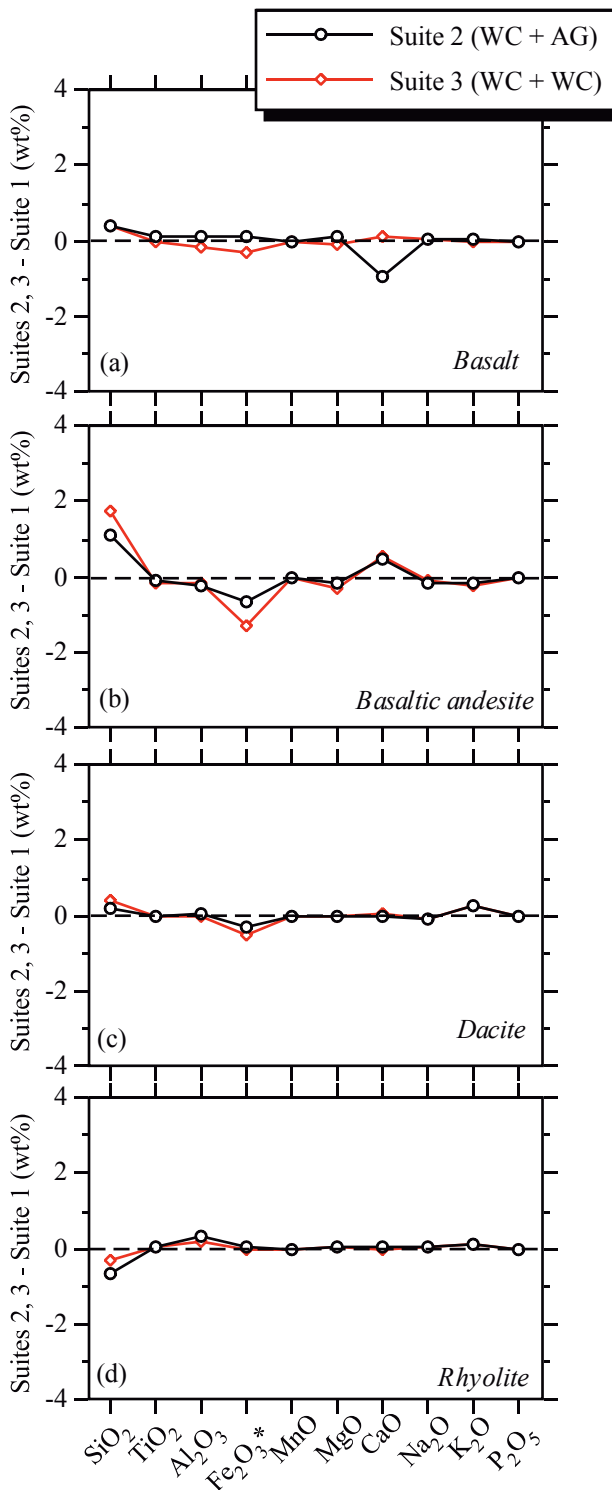


Fig. 3 Differences in major element compositions (wt%) for suite 2 and 3 samples relative to suite 1 samples. WC + AG and WC + WC denote the combination of a tungsten carbide mortar and agate mill, and a tungsten carbide mortar and tungsten carbide mill, respectively.

original sample contained Co-rich minerals.

The samples ground using the tungsten carbide mill exhibited no significant contamination by Nb and Ta, which is consistent with Roser *et al.* (1998, 2003). The V content for the basalt and Cr contents for the basaltic andesite and rhyolite of suite 2 samples were higher than those for suite 1 samples. The Ni content for the rhyolite is elevated for suite 3 relative to suite 1 samples. The differences observed for V, Cr, and Ni are not systematic for the various rock types. Therefore, contamination of the samples from sample preparation cannot account for the scatter of data for elements, including V, Cr, and Ni.

Depletion in some elements, particularly in the dacite and rhyolite samples is prominent, but such depletion is unrelated to contamination. Zn, Zr, Nb, Ba, and Ce have similar patterns in the suite 2 and 3 samples; therefore, the scatter in data is attributed to the heterogeneity of the slabs and the chips selected for crushing. Roser *et al.* (1998, 2003) reported the impact of the heterogeneity of subsamples on analytical data and that the minor effect of contamination from pulverizing equipment may be obscured by significant sample heterogeneity. The absence of a systematic increase in the sample concentrations of the expected contaminant elements, except for Co and W, suggests that contamination from pulverization does not significantly impact analytical data for other elements. The variations in the abundance of elements between the splits crushed using different mortars suggest that subsample heterogeneity is a major problem. The compositional differences due to sample heterogeneity are higher than those attributed to contamination from pulverizing, as suggested by Roser *et al.* (1998, 2003).

#### 4. Summary and conclusions

Three suites of pulverized samples were prepared using combinations of iron and tungsten carbide mortars, and agate and tungsten carbide mills. The results of major element analyses show no evidence of sample contamination from the mortars and mills. The compositional differences observed are attributed to the heterogeneity of the original rock chips. Trace elements analyses was affected by contamination of tungsten and cobalt from the tungsten carbide mill. Although other trends are discernible, without confirmation of contamination as the cause, the heterogeneity of the original samples explains the scatter observed in the compositional data.

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Table 3 Differences in the trace element compositions (ppm) for suite 2 and 3 samples relative to suite 1 samples.

	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Rb	Sr	Y	Zr	Nb	Mo	Cd	Sn	Sb	Cs	Ba		
Basalt	Suite 1	27.5	288	74.87	42.5	108.94	98	133.1	24.5	2.56	n.d.	13.0	176	28.3	186.0	12.97	0.60	1.56	n.d.	1.43	108		
	Suite 2	38.5	315	77.02	42.4	108.61	103	134.3	25.0	0.13	n.d.	13.0	177	29.4	194.0	16.11	0.51	2.08	n.d.	0.42	113		
	Diff.	11.0	27	2.16	-0.1	-0.33	5	1.2	0.5	-2.43	-	0.0	1	1.1	8.0	3.14	-0.10	-	0.52	-	-1.00	5	
	Suite 3	21.7	291	68.68	43.4	119.39	92	134.1	23.4	0.58	n.d.	11.2	170	27.4	185.7	12.82	0.31	1.38	n.d.	0.39	105		
	Diff.	-5.8	4	-6.19	0.9	10.45	-6	1.0	-1.1	-1.98	-	-1.9	-6	-0.9	-0.3	-0.15	-0.29	-	-0.17	-	-1.04	-3	
Basaltic andesite	Suite 1	37.5	329	36.86	40.8	55.41	103	134.3	25.4	n.d.	3.95	12.1	102	41.0	187.4	15.18	1.17	0.25	2.53	0.04	1.42	127	
	Suite 2	37.4	335	63.36	39.1	56.00	103	136.8	22.8	n.d.	0.44	11.8	102	36.5	184.5	13.87	3.39	0.22	1.83	0.06	0.73	118	
	Diff.	-0.1	6	26.50	-1.7	0.58	0	2.5	-2.5	-	-3.51	-0.3	0	-4.4	-2.9	-1.31	2.20	-0.03	-0.69	0.02	-0.69	-8	
	Suite 3	36.7	329	35.00	47.6	55.02	103	134.4	24.5	n.d.	1.55	11.5	104	38.5	188.9	14.64	1.70	0.20	1.23	0.05	2.29	130	
	Diff.	-0.7	0	-1.85	6.8	-0.39	0	0.1	-0.9	-	-2.40	-0.6	2	-2.5	1.5	-0.53	0.53	-0.06	-1.30	0.02	0.88	3	
Dacite	Suite 1	19.3	4	10.49	1.4	162.23	5	292.1	45.1	1.15	1.77	190.0	55	92.0	1869.8	160.62	3.14	0.31	7.02	0.14	1.31	572	
	Suite 2	14.6	2	9.71	0.4	167.53	7	290.8	38.6	1.38	1.68	198.2	60	88.3	1745.5	150.86	2.77	0.37	6.56	0.04	1.16	514	
	Diff.	-4.7	-2	-0.79	-1.0	5.30	2	-1.4	-6.5	0.23	-0.08	8.2	5	-3.8	-124.3	-9.76	-0.37	0.06	-0.46	-0.10	-0.15	-58	
	Suite 3	12.8	3	5.99	69.4	55.36	4	286.4	33.6	1.02	1.39	190.3	55	92.2	1771.2	146.66	4.72	0.10	4.45	0.15	1.28	528	
	Diff.	-6.5	-2	-4.50	68.0	-106.86	0	-5.8	-11.5	-0.13	-0.38	0.2	0	0.2	-98.7	-13.96	1.58	-0.20	-2.57	0.01	-0.03	-44	
Rhyolite	Suite 1	18.6	84	23.15	11.9	25.04	86	77.9	17.3	0.81	1.45	102.1	81	16.7	75.9	4.09	0.83	0.01	0.91	0.31	1.44	328	
	Suite 2	16.3	81	41.25	10.6	26.87	85	73.3	15.3	0.59	1.80	87.3	78	15.8	75.4	3.31	0.19	0.00	0.56	0.20	1.54	295	
	Diff.	-2.3	-3	18.11	-1.3	1.83	-1	-4.6	-2.0	-0.22	0.35	-14.9	-3	-1.0	-0.5	-0.79	-0.64	-0.01	-0.35	-0.11	0.10	-33	
	Suite 3	13.9	85	23.11	16.5	37.89	72	76.6	12.4	0.72	1.53	87.4	80	13.4	77.0	2.97	0.28	0.05	0.58	0.26	1.35	280	
	Diff.	-4.7	1	-0.04	4.6	12.84	-14	-1.3	-4.8	-0.09	0.08	-14.7	0	-3.3	1.1	-1.12	-0.55	0.04	-0.33	-0.06	-0.09	-48	
Basalt	Suite 1	16.66	40.2	4.90	21.1	6.33	1.8	5.65	0.76	5.19	1.24	2.89	0.32	2.05	0.54	3.63	1.83	0.30	0.05	0.76	0.032	1.49	0.45
	Suite 2	21.07	45.9	5.51	22.4	6.49	2.9	6.36	1.09	5.99	1.56	2.93	0.60	3.63	0.35	4.20	2.13	0.97	0.08	1.29	0.030	1.85	0.47
	Diff.	4.42	8.2	1.00	4.0	4.45	1.1	2.74	0.33	0.80	0.32	0.05	0.28	1.57	-0.19	0.56	0.30	0.67	0.02	0.53	-0.002	0.36	0.02
	Suite 3	17.60	40.5	4.13	19.6	7.61	2.0	4.44	0.90	4.75	1.47	2.93	0.46	1.85	0.41	3.10	1.80	25.37	0.09	1.18	0.032	1.51	0.30
	Diff.	0.94	0.3	-0.77	-1.4	1.28	0.2	-1.21	0.14	-0.44	0.23	0.04	0.13	-0.20	-0.13	-0.54	-0.04	25.07	0.03	0.42	0.000	0.02	-0.16
Basaltic andesite	Suite 1	20.43	45.8	5.15	24.1	10.02	2.2	7.90	1.12	6.14	1.86	3.22	0.58	2.88	0.55	3.89	2.41	1.15	0.08	1.42	0.030	1.99	0.55
	Suite 2	19.84	41.6	4.76	22.6	7.57	1.9	7.90	0.99	5.85	2.00	3.82	0.54	3.58	0.72	3.87	2.16	1.33	0.08	1.21	0.031	1.65	0.54
	Diff.	-0.59	-4.3	-0.39	-1.5	-2.45	-0.3	0.00	-0.13	-0.29	0.14	0.60	-0.05	0.70	0.17	-0.02	-0.25	0.18	0.00	-0.21	0.001	-0.34	-0.01
	Suite 3	19.78	41.3	5.50	24.6	6.54	2.0	7.18	1.23	5.86	1.60	3.32	0.46	3.18	0.71	3.73	2.08	119.63	0.07	1.24	0.027	1.73	1.50
	Diff.	-0.65	-4.5	0.34	1.2	-3.48	-0.2	-0.73	0.10	-0.28	-0.26	0.10	-0.12	0.31	0.16	-0.16	-0.33	118.48	-0.01	-0.18	-0.004	-0.26	0.95
Dacite	Suite 1	111.25	225.97	32.6	116.54	22.5	4.03	21.8	2.87	21.03	3.46	9.86	1.57	9.65	1.52	34.18	15.72	1.46	n.d.	5.50	n.d.	12.561	3.48
	Suite 2	109.49	212.0	30.99	111.5	24.32	3.2	19.09	2.94	18.65	3.54	8.97	1.63	9.00	1.55	34.17	16.37	1.13	n.d.	5.45	n.d.	11.61	3.31
	Diff.	-1.76	-14.0	-1.63	-5.1	1.85	-0.9	-2.68	0.08	-2.38	0.08	-0.88	0.06	-0.66	0.03	-0.01	0.65	-0.33	-	-0.05	-	-0.95	-0.17
	Suite 3	104.88	210.8	31.80	108.9	21.88	3.5	18.77	2.41	23.26	4.31	11.10	1.68	8.82	1.50	33.59	14.69	163.55	n.d.	6.90	n.d.	12.99	3.80
	Diff.	-6.37	-15.2	-7.48	-19.8	-0.59	-0.6	5.46	-0.45	2.23	0.85	1.25	0.11	-0.83	-0.02	-5.99	-1.03	162.09	-	1.40	-	0.43	0.32
Rhyolite	Suite 1	17.73	43.7	5.54	18.3	4.10	1.1	3.39	0.52	3.57	0.69	1.84	0.31	1.56	0.27	2.01	0.49	0.39	n.d.	9.26	n.d.	4.33	0.80
	Suite 2	15.71	40.3	4.90	17.8	4.16	0.8	2.87	0.57	3.09	0.54	1.61	0.29	1.58	0.25	1.86	0.48	0.81	n.d.	9.12	n.d.	3.82	0.75
	Diff.	-2.03	-3.4	-0.63	-0.5	0.06	-0.3	-0.52	0.04	-0.48	-0.15	-0.23	-0.02	0.02	-0.03	-0.15	-0.01	0.42	-	-0.14	-	-0.51	-0.05
	Suite 3	13.61	43.1	4.12	15.7	3.08	0.7	2.85	0.51	2.80	0.57	1.39	0.20	1.38	0.22	1.59	0.36	43.62	n.d.	7.34	n.d.	3.47	0.58
	Diff.	-4.13	-10.4	-1.42	-2.7	-1.02	-0.3	-0.54	-0.02	-0.77	-0.12	-0.45	-0.10	-0.18	-0.05	-0.42	-0.13	43.23	-	-1.91	-	-0.86	-0.22

Diff. denotes the difference in the composition of suite 2 or 3 samples from those of suite 1 samples.

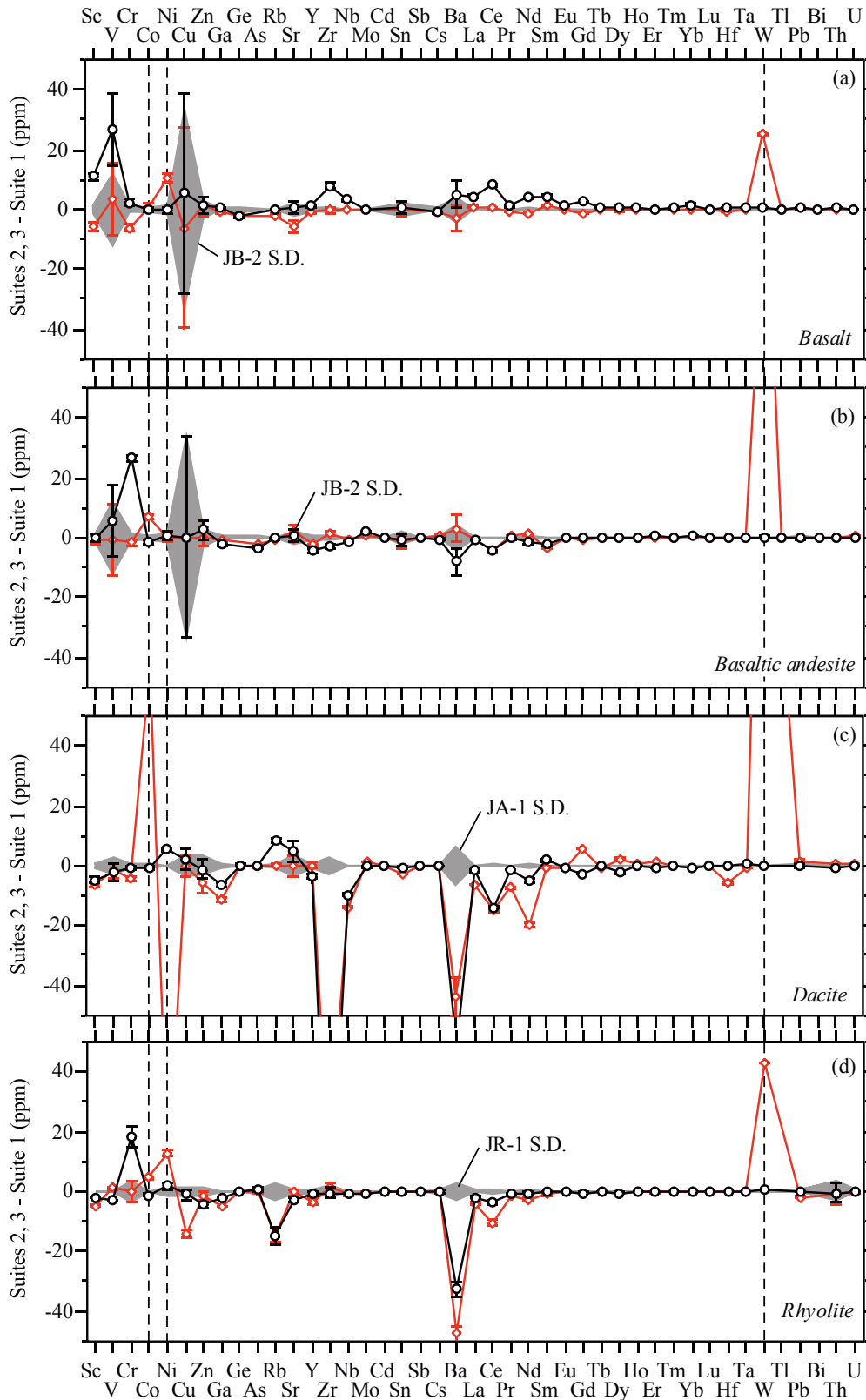


Fig. 4 Differences in trace element compositions (ppm) for suite 2 and 3 samples relative to suite 1 samples. The error bars and shaded areas showing the standard deviations (S.D.;  $n=5$ ) were extrapolated from the analytical results for reference materials (Yamasaki and Yamashita, 2016) with similar compositional ranges; JB-2 for the basalt and the basaltic andesite samples; JA-1 for the dacite samples; and JR-1 for the rhyolite samples. The symbols and colors are the same as in Fig. 3.



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## References

- Ando, A. (1986) Preparation method of rock samples. *Bull. Geol. Surv. Japan*, **37**, 347–348 (in Japanese).
- Barnett, P.R., Huleatt, W.P., Rader, L.F. and Myers, A.T. (1955) Spectrographic determination of contamination of rock samples after grinding with alumina ceramic. *Am. J. Sci.*, **253**, 121–124.
- Condie, K.C. (1993) Chemical composition and evolution of the upper continental crust: Contrasting results from surface samples and shales. *Chem. Geol.*, **104**, 1–37.
- Hickson, C.J. and Juras, S.J. (1986) Sample contamination by grinding. *Canad. Mineral.*, **24**, 585–589.
- Iwansson, J.K. and Landström, O. (2000) Contamination of rock samples by laboratory grinding mills. *J. Radioanal. Nucl. Chem.*, **244**, 609–614.
- Miyake, Y. and Musashino, M. (1991) Evaluation of contamination effects during crushing powder samples for neutron activation analysis. *Geosci. Rep. Shimane Univ.*, **10**, 31–34 (in Japanese with English abstract).
- Myers, A.T. and Barnett, P.R. (1953) Contamination of rock samples during grinding as determined spectrographically. *Am. J. Sci.*, **251**, 814–830.
- Potts, P.J. (2003) Concepts in analytical chemistry. *Handbook of Rock Analysis*, 1–46, Viridian Publishing.
- Rollinson, H.R. (1993) *Using Geochemical Data: Evaluation, Presentation, Interpretation*. Harlow, Longman Group, 352 p.
- Roser, B., Sawada, Y. and Kabeto, K. (1998) Crushing performance and contamination trials of a tungsten carbide ring mill compared to agate grinding. *Geosci. Rep. Shimane Univ.*, **17**, 1–9.
- Roser, B., Kimura, J.-I. and Sifeta, K. (2003) Tantalum and niobium contamination from tungsten carbide ring mills: much ado about nothing. *Geosci. Rep. Shimane Univ.*, **22**, 107–110.
- Takamasa, A. and Nakai, S. (2009) Contamination introduced during rock sample powdering: Effects from different mill materials on trace element contamination. *Geochem. J.*, **43**, 389–394.
- Terashima, S., Okai, T., Ando, A. and Itoh, S. (1990) Homogeneity tests for twenty-four GSJ rock reference samples. *Bull. Geol. Surv. Japan*, **41**, 129–138.
- Thompson, G. and Bankston, D.C. (1970) Sample contamination from grinding and sieving determined by emission spectrometry. *Appl. Spectrosc.*, **24**, 210–219.
- Ujike, O. and Tsuchiya, N. (1993) Geochemistry of Miocene basaltic rocks temporally straddling the rifting of lithosphere at the Akita-Yamagata area, northeast Japan. *Chem. Geol.*, **104**, 61–74.
- Yamasaki, T. (2014) XRF major element analyses of silicate rocks using 1:10 dilution ratio glass bead and a synthetically extended calibration curve method. *Bull. Geol. Surv. Japan*, **65**, 97–103.
- Yamasaki, T. and Nanayama, F. (2017) Enriched mid-ocean ridge basalt-type chemistry of basalts and gabbros from the Nikoro Group, Tokoro belt, Hokkaido, Japan. *J. Min. Petrol. Sci.*, **112**, 311–323.
- Yamasaki, T. and Nanayama, F. (2018) Immature intra-oceanic arc-type volcanism on the Izanagi Plate revealed by the geochemistry of the Daimaruyama greenstones in the Hiroo Complex, southern Hidaka Belt, central Hokkaido, Japan. *Lithos*, **302–303**, 224–241.
- Yamasaki, T. and Yamashita, K. (2016) Whole rock multiple trace element analyses using fused glass bead by laser ablation-ICP-MS. *Bull. Geol. Surv. Japan*, **67**, 27–40.
- Yamasaki, T., Yamashita, K., Ogasawara, M. and Saito, G. (2015) Multiple trace element analyses for silicate minerals and glasses by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). *Bull. Geol. Surv. Japan*, **66**, 179–197.

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## 岩石粉末試料作成過程における乳鉢及びミルからのコンタミネーション

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### 要 旨

全岩化学組成分析用の粉末岩石試料作成プロセスにおける、粉碎器具及び機器からのコンタミネーションの程度を検討した。鉄乳鉢とタングステンカーバイド乳鉢、めのうボールミルとタングステンカーバイドミルを用いて3通りの組みあわせて岩石粉末試料を作成し、粗粉碎及び微粉碎のそれぞれの過程でのコンタミネーションの程度を調べた。検討試料には玄武岩、玄武岩質安山岩、デイサイト及び流紋岩を用い、主成分組成と微量成分組成に対する影響を検討した。3通りの組合せの粉碎方法で作成した4つの組成の試料の分析結果は、粗粉碎に用いた試料の組成の違いに起因すると思われる差が認められたものの、主成分元素においてはコンタミネーションの影響は検出されなかった。微量元素組成においても、試料間の初生的な組成差と思われる分散が大きいものの、タングステンカーバイドミルを用いた粉末試料に対する明らかなタングステンと若干のコバルトのコンタミネーション以外は、系統的な組成差は認められなかった。