島根大学地球資源環境学研究報告　17, 1～9ページ（1998年12月）
Geoscience Rept. Shimane Univ., 17, p.1～9（1998）

Crushing performance and contamination trials of a tungsten carbide ring mill compared to agate grinding

Barry Roser*, Yoshihiro Sawada** and Kurkura Kabeto***

Abstract

Crushing and contamination trials have been carried out on a new tungsten carbide ring mill, compared to material ground in a automated agate pestle and mortar grinding system. Granite and reagent grade quartz sand were crushed in the ring mill for times ranging between 30 and 120 seconds per sample. Agate-system samples were ground for 60 minutes. Grain size analysis of the resulting pulps shows that grain size distributions of the material crushed in the ring mill compare very favourably with those from the agate mortar. Mill times of only 60 seconds produce pulp with grain size distributions equivalent to 60 minutes grinding in the agate system. Extending the crushing time to 90 seconds lowers median grain size to 4 microns, compared to 6-10 microns in the agate ground samples. Increasing the mill time to 120 seconds does not significantly reduce median grain size, and 90 second mill time is thus optimal for the sample weights used.

Granite and quartz sand pulps were analysed by XRF to test for contamination from the ring mill. Results show that crushing times of 60-120 seconds produce only 15-20 ppm Co, and inferred W contamination of 190-200 ppm. No other contaminants can be identified from the XRF data. Estimation of maximum contamination by proportion between measured Co contents and assayed abundances in the ring mill tungsten carbide show that contamination of all other elements is trivial. This suggests that powders crushed with equipment such as that utilised here can be safely used for analysis of low-level trace elements (e.g. Nb, Ta) by more precise methods such as ICP/MS, without materially affecting geologic interpretations. Variations in element abundances between the splits crushed for different times, and between beads prepared from the same split, indicate that chemical variability introduced by subsample heterogeneity is a far more serious problem, being several orders of magnitude greater than possible contamination from the mill.

key words: XRF analysis, tungsten-carbide ring mill, automatic agate mortar, contamination

Introduction

In October 1996 the Dept of Geoscience at Shimane University took delivery of a ROCKLABS (model RC) ring mill equipped with a 100 g capacity tungsten carbide head. The equipment was purchased with the assistance of a Monbusho Science Foundation grant in aid. The purpose of the purchase was to provide an additional and more rapid method for crushing geologic materials to grain sizes sufficient for chemical analysis by techniques such as XRF and mass spectrometry.

Two Ishikawa Manufacturing Co. AGA automatic agate pestle and mortar grinding mixers were available in the department for this purpose, but required grinding times of up to 60 minutes, after reduction of sample to <1 mm in size by elective use of a combination of jaw crushers, ball mills and manual disintegration in a tungsten carbide pestle and mortar. Increasing pressure on this equipment due to steadily rising numbers of samples for analysis, and the commencement of several projects which required the processing of large numbers of samples made the purchase of a ring mill desirable.

Ring mills are not common in geological institutions in Japan, due in part to tradition and concerns over trace element contamination and inferior crushing performance compared to agate systems. Although contamination from tungsten carbide mills has been alluded to in the literature, hard data demonstrating this is rare. One of the few recent studies which addresses contamination is that of Miyake and Musashino (1991). They examined contamination from steel, agate, and tungsten carbide equipment, by crushing clear quartz crystals. The tungsten carbide

---

* Department of Geoscience, Shimane University, Matsue 690–8504, Japan. Present address : Department of Earth and Planetary Science, Graduate School of Science, Hokkaido University, Sapporo 060–0810, Japan
** Department of Geoscience, Shimane University, Matsue 690–8504, Japan
***United Graduate School of Agriculture Sciences, Tottori University, Tottori 680–0945, Japan

equipment used was a ball mill, with crushing times of up to one hour. This produced extreme tungsten contamination in the worst case (up to 35320 ppm), significant Co (>1597 ppm), Ta (>147 ppm), and detectable Cr (>15.5 ppm) and Sc (>17 ppm). Such gross contamination has not been reported from tungsten carbide ring mills, and is not likely. This is due to the far shorter mill times used (usually <120 seconds), and the rotary crushing action of ring mills verses random impact crushing in ball mills. However, concerns over ring mill contamination persist. During compilation of data to derive average values of upper continental lithotypes, Condie (1993) excluded Nb data from rocks crushed in tungsten carbide mills because of concern over possible Nb contamination. Ujike and Tsuchiya (1993) also suspected Ta contamination in suites of Japanese arc volcanics. Anecdotally, other possible contaminants include Cr, V, and Ni.

To establish how ring mills perform in respect to crushing efficiency and contamination, and to determine optimal crushing times, we have carried out crushing and contamination trials with the ring mill, using two different materials (quartz sand and granite) and differing crushing times, compared with the same materials prepared in the existing agate system using standard techniques. This paper reports the results of these trials. Nb is of particular interest, given exclusion of such data by Condie (1993), and the low levels of Nb present in arc volcanics, which form part of the normal workload for the XRF at Shimane.

Methods

Materials

Crushing trials were conducted using well sorted reagent grade quartz sand and a sample of fresh quartz-bearing granite. The quartz sand was taken from a single 500 g bottle of "Chameleon Reagent" 30-50 mesh sand (Kishida Chemical Co.). Although no analytical data were available for this product, visually it is of high purity.

The granite consisted of approximately 1-3 mm grains of quartz (35%), plagioclase (30%) and K-feldspar (25%), with granular texture. Quartz typically shows undulose extinction, and contains inclusions of biotite, hornblende and titanite. Plagioclase displays oscillatory zoning, and with K-feldspar, is typically dusted with sericite. Biotite (5%) and hornblende (2 %) are minor phases, and sericite, titanite, apatite, epidote, actinolite and orthite (allanite) occur as accessories. Biotite grains are frequently bent, display pleochroic haloes, are altered to epidote, and contain inclusions of apatite and orthite. Hornblende is altered to actinolite, biotite and epidote.

The sample was split with a manual rock splitter, and chip 3-4 cm in diameter put through a manganese steel-faced jaw crusher in single passes. This produced material <5 mm maximum diameter. One kilogram of this material was then split by coning and quartering down to 70 g portions for the ring mill trials. As a secondary test for contamination from the jaw crusher, 100 g of clean <10 mm chip were prepared using the manual rock splitter, and retained for crushing in the ring mill.

Crushing and grinding times

Previous experience using ring mills suggests that mill times of 60 seconds or less are usually adequate for most rock types, so individual samples were milled for only 30, 60, 90 or 120 seconds to exceed the range of times expected in routine use. For the granite 70 g portions were milled, verses 50 g portions of the quartz sand. After crushing and removal of the sample, any material adhering to the walls of the mill head was discarded, and the mill cleaned with compressed air and ethanol. No other cleaning was necessary. The 30 second granite sample was not adequately crushed for glass bead manufacture, and was not proceeded with. The separate sample of chip from the manual splitter was crushed in two loads, each for 60 seconds, and the loads combined as a single sample.

As the control, two standard 20 g portions of both the quartz sand and the granite were ground in the agate system. Tanaka and Kamioka (1994) demonstrate d that impurities in agate used in grinding equipment are trivial, and generally cause no contam-ination except in exceptional samples where levels in agate exceed those in samples. In this study, no prior grain size reduction of the quartz sand was necessary before agate grinding. For the granite sample, a full 70 g portion was manually pounded in a tungsten carbide pestle and mortar until all grains were <1 mm in diameter. This material was then split down to 20 g for grinding. Both materials were ground for 60 minutes, which is standard procedure for quartz-bearing samples.

Grain size distribution

Grain size distributions of the crushed samples were determined using a multi channel SK Laser micron sizer (Shinsei PRO-7000), using standard measuring conditions and water as the medium. Statistical parameters were calculated by the equipment software, using graphical methods after Folk and Ward (1957). Samples were washed through a 2 phi (192 µm) sieve to check for coarser particles. None were seen, except for a few (3-4) biotite flakes in the granites. These occurred in all samples from the ring mill, and also those from the agate system, indicating that neither method adequately crushes biotite adequately in the times used.

XRF analyses

The crushed granite samples were analysed for 22 elements using the Rigaku RIX 2000 XRF at Shimane University, using standard procedures. Both major elements and trace elements (Cr, Ni, Nb, Zr, Y, Sr, Rb, V, Co, Zn, Cu and Ba) were determined using single glass beads prepared with MERCK Spectromelt® A10 lithium tetraborate flux using a flux:sample ratio of 5:1. Duplicate beads were prepared for all granite samples, using a NT-2000 automatic bead sampler, with preheat, fusion and agitation times of 120, 120 and 180 seconds, respectively. To accommodate long-term drift typical of normal analytical conditions, each bead was analysed five times, at least 12 hours apart. Sample batches were separated by analyses of the GSJ reference standards JB-1a and JG-1a to monitor drift. These monitors showed no systematic drift over the course of the analysis. Average results for the samples were normalised to 100% anhydrous. The same normalising factors were also applied to the trace elements. Single beads were also prepared of quartz sand from agate grinding, and from 30, 60 and 120 second ring mill crushes. These were analysed only for Co.

Table 1 Grain size parameters for the pulps. X_{50}=median (50th percentile) ;X_{10} and X_{90} are the 10th and 90th percentiles, respectively.

	Microns		
	X_{50}	X_{90}	X_{10}
Quartz sand			
Agate (60 mins)	6.3	41.0	0.8
Ring Mill			
30 secs	5.1	34.9	2.6
60 secs	4.9	33.1	1.2
90 secs	3.9	27.9	1.1
120 secs	3.7	26.7	1.1
Granite			
Agate (60 mins)	12.4	72.2	1.6
Ring Mill (ex-jaw crusher)			
60 secs	11.1	68.2	1.6
90 secs	4.1	29.5	1.1
120 secs	3.9	28.6	1.1
Ring Mill (chip ex-trimmer)			
60 secs	6.5	47.5	1.3

Results & Discussion

Grain size distributions

Results of the grain size analysis are given in Table 1 and Figs 1 and 2. These show that the ring mill actually produces material with finer median grain size (X_{50}) than the agate system at all crushing times. For the quartz sand, however, the sample milled for only 30 seconds is not well crushed, with slightly coarser

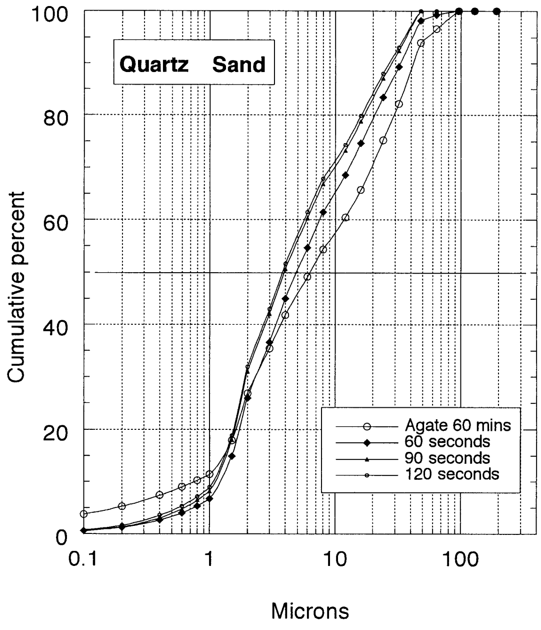

Fig. 1 Grain size distributions of quartz sand pulps produced from agate pestle and mortar grinding (60 minutes), and by the tungsten carbide ring mill (60, 90 and 120 seconds).

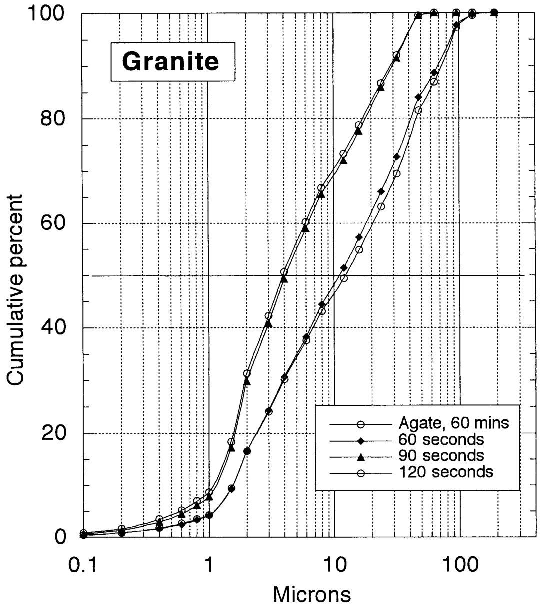

Fig. 2 Grain size distributions of granite pulps produced from agate pestle and mortar grinding (60 minutes), and by the tungsten carbide ring mill (60, 90 and 120 seconds).

Table 2 Composition of tungsten carbide used in the manufacture of the ring mill head. The analysis excludes carbon in the carbide. Source: ROCKLABS ring mill operation manual.

	%		
W	90		
Co	9.5		
Mo	0.005	Cu	0.002
Fe	0.10	Zn	0.002
Si	0.005	Pb	0.002
Al	0.003	As	n.d.
Cr	0.003	Sb	n.d.
P	n.d.	Ta	0.001
S	n.d.	Nb	0.001
Ni	0.005	Ti	0.001
Mn	0.005	B	n.d.
Mg	0.001	V	0.001
Ca	0.003	Ba	n.d.
Na	0.005	Zr	n.d.
K	0.002		

n.d. - not detected
Source: Rocklabs manual

X_{10} and X_{90} values than the 60, 90 and 120 second samples (Table 1). Crushing time of at least 60 seconds is therefore desirable for highly quartzose samples. The granite at 60 seconds shows a very similar distribution to that ground in agate, but the 90 seconds the product is significantly finer. Increasing the crushing time to 120 seconds, however, had little effect (Fig. 2). The sample that was prepared from < 1 cm chip from the manual splitter was milled for 60 seconds, but shows similar grain size distribution and median to the equivalent sample from the jaw crusher.

The results show that for the ring mill times of 60-90 seconds are adequate for most samples of this size, and produce powders as fine or finer than 60 minutes grinding in the agate system. Little is gained by grinding for longer than 90 seconds in the ring mill.

Contamination trials

The manufacturer's indicative analysis of the tungsten carbide used for the ring mill head is given in Table 2. Tungsten and cobalt contamination can be expected, since these two metals together comprise 99.5 wt%. Fe is the next most significant component at 0.10%, while all other elements listed are 0.005% (50 ppm) or less. Nb and Ta, which have been cited as contaminants from tungsten carbide equipment (e.g. Condie 1993; Ujike and Tsuchiya 1993) are present only at the 0.001% (10 ppm) level. Ni (0.005%), Cr (0.003%) and V (0.001%), which anecdotally are suspect, are also present at very low levels.

Much of the wear of ring mill heads occurs in the first 10-20 secs after start-up while the largest grains are being crushed, and levels off after 60-120 secs (I. Devereux, pers. comm, 1998). Contamination (if any) should therefore be curvilinear for a given sample when aliquots are milled for differing times, flattening off and reaching a plateau as mill time increases.

Major element results in the granite samples show no consistent patterns which can be attributed to contamination (Table 3), which is understandable given the low concentrations of these elements in the tungsten carbide analysis listed in Table 2. Fe, the only major element present in any quantity (0.10%), shows no linear or curvilinear relation to mill time compared to the agate ground sample (Fig. 3a). Considerable variation is seen for some elements, however, both between and within duplicate pairs of beads. These differences are outside the precision of the measurements. This suggests that the sample splits crushed are heterogeneous, and the differences are caused by variation in the proportion of individual minerals. The differences are most marked for K_2O (3.91-4.31 wt%; Fig. 3b), CaO (1.40-1.54%), Al_2O_3 (13.22-13.76%), Na_2O (3.75-4.00%) and SiO_2 (73.64-

Table 3 Average compositions and population standard deviations of the analysed granite. Each bead was analysed 5 times. A and B are duplicates. All data is normalised to 100% anhydrous. Decimals in the trace element data are retained for comparative purposes, and that level of precision is not implied. Cr, V and Cu were sought, but not detected (<3–5 ppm) in any bead.

	AGATE 60 minutes				RING MILL 60 seconds				RING MILL 90 seconds				RING MILL 90 seconds				Trim-Ring 60	
	A		**B**		**A**		**B**		**A**		**B**		**A**		**B**		**A**	
	X	SDp	X	SDp	X	SDp	X	SDp	X	SDp	X	SDp	X	SDp	X	SDp	X	SDp
Major elements (wt.%)																		
SiO_2	73.64	0.02	73.69	0.02	74.17	0.01	74.00	0.02	74.46	0.01	74.55	0.01	74.19	0.01	74.35	0.02	73.90	0.02
TiO_2	0.19	0.00	0.19	0.00	0.18	0.00	0.19	0.00	0.19	0.00	0.19	0.00	0.18	0.00	0.18	0.00	0.19	0.00
Al_2O_3	13.74	0.01	13.76	0.01	13.40	0.01	13.56	0.01	13.24	0.01	13.22	0.01	13.43	0.01	13.43	0.01	13.53	0.01
Fe_2O_3	2.52	0.00	2.53	0.00	2.41	0.00	2.59	0.01	2.56	0.00	2.58	0.01	2.47	0.00	2.46	0.01	2.59	0.01
MnO	0.08	0.00	0.08	0.00	0.07	0.00	0.08	0.00	0.08	0.00	0.08	0.00	0.08	0.00	0.08	0.00	0.08	0.00
MgO	0.20	0.00	0.19	0.00	0.19	0.01	0.20	0.01	0.21	0.01	0.20	0.01	0.21	0.01	0.19	0.00	0.20	0.01
CaO	1.54	0.01	1.54	0.00	1.40	0.01	1.49	0.00	1.48	0.00	1.48	0.00	1.49	0.00	1.48	0.00	1.49	0.00
Na_2O	4.00	0.02	3.93	0.02	3.82	0.01	3.78	0.01	3.83	0.01	3.73	0.01	3.87	0.01	3.75	0.02	3.90	0.01
K_2O	4.04	0.00	4.05	0.00	4.31	0.01	4.07	0.00	3.91	0.00	3.92	0.00	4.03	0.00	4.03	0.00	4.06	0.00
P_2O_5	0.05	0.00	0.04	0.00	0.05	0.00	0.04	0.01	0.05	0.00	0.04	0.00	0.05	0.00	0.04	0.00	0.05	0.00
Trace elements (ppm)																		
Ni	3.9	0.9	4.4	1.1	4.0	1.0	3.4	1.1	4.0	0.9	3.5	0.6	4.2	0.7	11.8	0.8	3.8	1.0
Nb	12.0	1.0	12.2	0.6	11.6	0.7	12.6	0.8	12.3	0.4	12.5	0.7	11.9	0.7	11.0	0.4	13.0	0.6
Zr	179.1	1.1	188.5	0.8	172.8	0.9	182.6	0.9	186.0	0.6	185.2	1.1	174.9	0.9	173.4	0.7	187.5	1.3
Y	41.5	0.6	41.7	0.8	39.7	0.5	43.0	0.6	43.8	0.5	44.1	0.8	41.8	0.6	42.0	0.9	43.7	0.9
Sr	115.0	0.6	114.6	0.5	103.9	0.3	109.0	0.4	104.6	0.3	105.5	0.5	109.0	1.0	108.8	0.6	109.4	0.6
Rb	170.5	0.4	172.0	0.5	173.6	0.7	172.3	0.2	167.3	0.5	168.0	0.2	169.0	0.5	168.4	0.5	172.4	0.3
Co	3.9	0.3	4.2	0.2	16.1	0.2	14.4	0.2	21.4	0.4	21.6	0.3	20.0	0.2	19.3	0.4	14.5	0.2
Zn	86.2	0.9	87.2	1.0	78.8	1.3	90.3	1.0	87.4	1.4	90.1	1.8	86.8	0.8	85.8	1.2	89.4	1.7
Ba	564.6	7.8	567.2	14.0	607.4	6.3	568.6	5.4	546.1	6.6	543.5	11.4	568.4	9.6	570.5	10.9	572.1	7.8

X=average of five analyses. SDp=population standard deviation. A,B are duplicate beads.

Data listed normalised anhydrous to 100%. Decimals retained in trace element data for comparitive purposes; that level of precision is not implied.

Note: Cr, V and Cu were sought but not detected (<3 ppm).

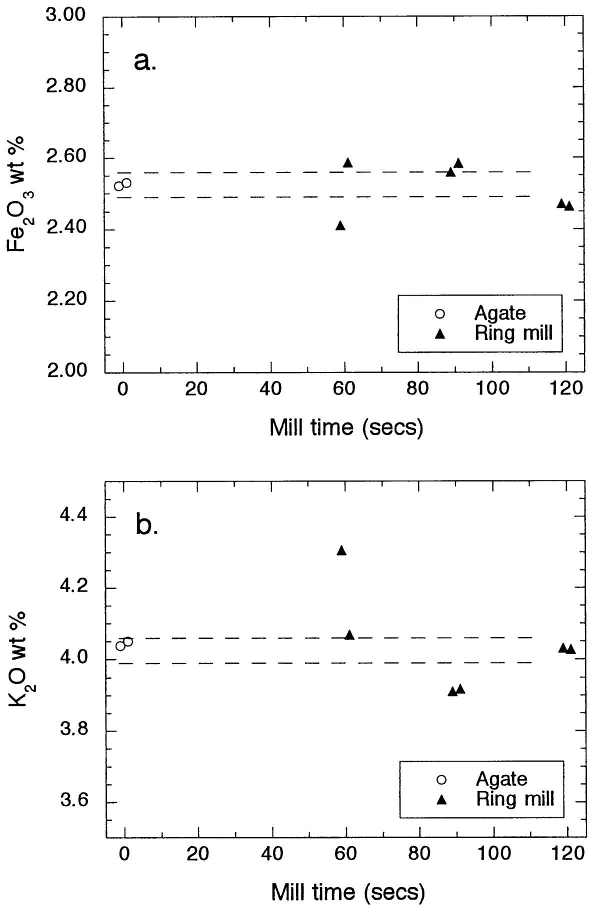

Fig. 3 Averaged XRF analyses of (A) Fe_2O_3 and (B) K_2O in the granite pulps. Dashed horizontal lines are the total range shown by the control agate duplicates. Confidence intervals are not plotted as in Fig. 4 because the errors are generally <0.01 wt%.

74.55%). The association of elements suggests that variation in the ratios of quartz, plagioclase and K-feldspar are largely responsible.

As expected, cobalt shows clear evidence of contamination (Fig. 4a). In the agate ground control beads the average content is 4.0 ppm. This increases to 15 ppm at 60 seconds grinding in the ring mill, and peaks at 21.5 ppm at 90 seconds, and is ~20 ppm in the 120 second sample. The levelling off at 120 seconds may represent the plateau at longer mill times, as noted above. Nevertheless, Co contamination is significant. The level of contamination seen here, however, may be higher than in a mill in routine use. The tests carried out here were the first samples crushed in a new mill. With new mills, Co contamination will be at maximum initially, as Co metal at the mill surfaces is abraded, and the carbide particles which subsequently do the bulk of the grinding are exposed (I. Devereux, pers. comm., 1998).

Analysis of Co in single beads of the quartz sand shows similar results. Five analyses of agate crushed sample give a value of 0.9±0.1 ppm. Average values in the material crushed in the ring mill for 30, 60 and 120 seconds are 12, 15 and 16 ppm, respectively. This suggests that Co contamination of approx-imately 12-16 ppm can be expected in quartzose samples. Variation in the granite splits, and differences in contamination between the granite chip and quartz sand, however, suggest that the level of contamination will vary according to mill load, sample hardness, initial chip size, mineralogy, and crushing time. The level of contamination in any given sample for given crushing time is thus not predictable.

Because all elements added through contamination can be expected to be contributed in direct proportion to their abundance in the mill, Co abundances in the samples can be used to infer maximum contamination levels of all other elements. A similar approach was taken by Miyake & Musashino in their study of ball mill contamination. The 9.5% (95,000 ppm) Co present in the mill tungsten carbide in this case produced ~20 ppm Co in the granites, a ratio of 1: 4750. In the case of Nb, simple proportions dictate that possible contamination is thus restricted to 1/4750 of the 0.001% (10 ppm) Nb present in the mill tungsten carbide. This equals 0.002 ppm, an amount clearly not detectable by XRF, as shown by Fig. 4b. Although detection of these levels is possible by more precise techniques such as ICP/MS, in most cases such contamination is unlikely to be of geological significance. Similar proportional calculations could be carried out for the other trace elements analysed here, but the maximum level of contamination expected would be for Ni, which is 5 times more abundant in the tungsten carbide according to the ROCKLABS analysis. This, however, could still only produce contamination of 0.01 ppm Ni, which is again insignificant and cannot be detected (Fig. 4c). Simple proportions thus show that no detectable contamination is possible for the elements analysed here apart from Co. Level of tungsten contamination can be inferred by simple ratio to cobalt from the ROCKLABS analysis (Table 2). This suggests maximum W contamination here is 190-200 ppm.

It is clear, however, that considerable variation

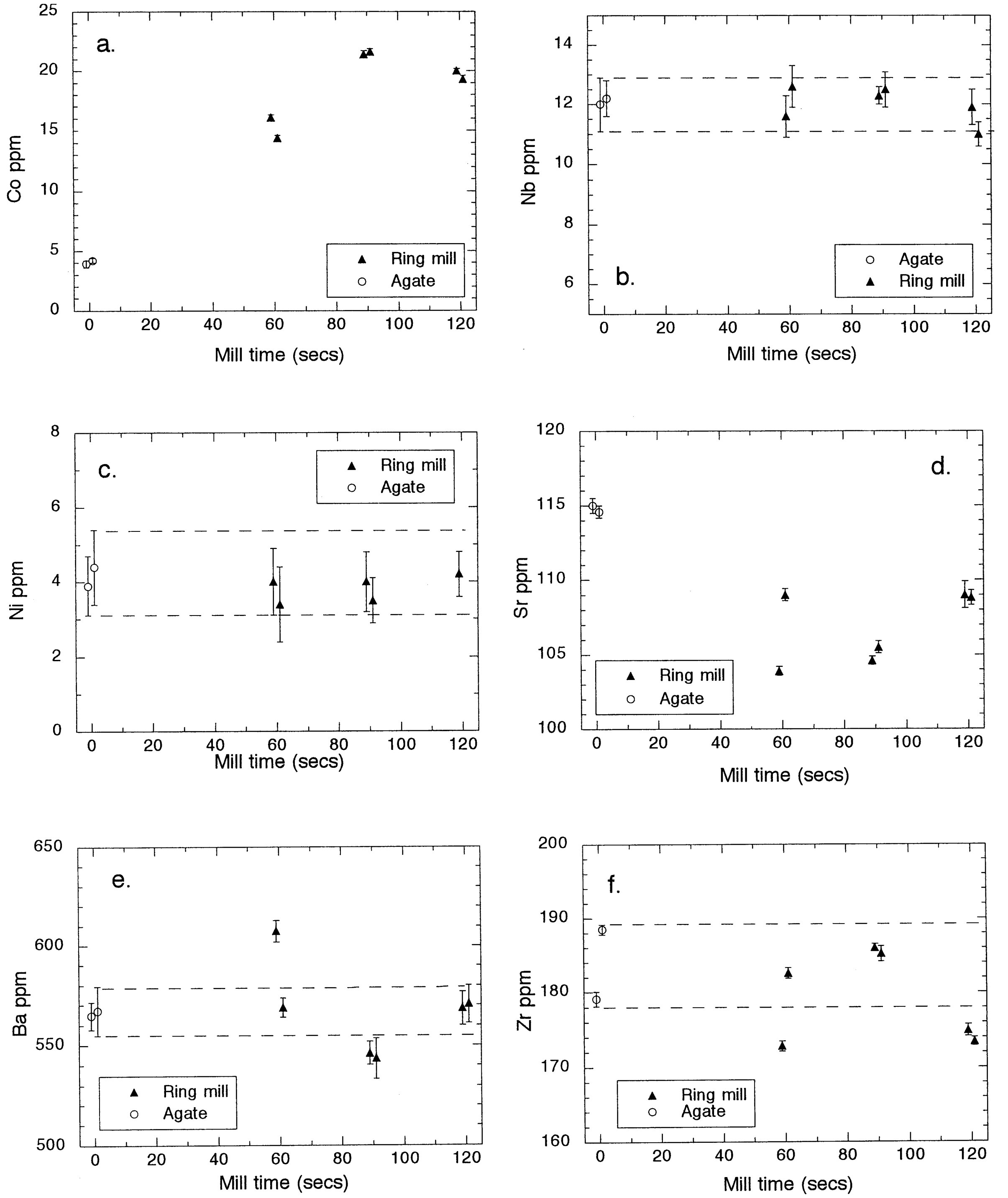

Fig. 4 Representative trace element analyses of the granite pulps. Analyses are duplicates, error bars are 95% confidence intervals about the mean of five replicate analyses. Dashed horizontal lines are the total range shown by the control agate duplicates.

occurs in some elements. Ba, Rb, Sr, Y, and Zr show significant contrasts (higher or lower) in some of the ring mill samples compared to the agate-ground sample. In the case of Sr (Fig. 4d), all ring mill analyses are 6-10 ppm (5-10% relative) lower than in the agate ground sample, well outside the agate range. Rb and Ba (Fig. 4e) in ring mill samples may be higher or lower than the agate range at differing mill times. The non-systematic nature of these variations suggest that these, like the major element contrasts, reflect subsample heterogeneity. The association of elements suggests unequal contents of feldspar, mica, and accessory phases in the sample splits. Largest disparity between duplicate beads in the ring mill suites is found in the 60 second sample for Ba, Zr (Fig. 4e and 4f), Y and Sr. Although mean grain size in this sample is comparable with the agate ground split, it may be that 60 seconds mill time is not sufficient to fully homogenise the powder. It is also possible that some grain-size and mineralogical stratification may have occurred within the 10 ml vial subsamples from which the 60 sec beads were prepared, producing heterogeneity. Duplication in the 90 and 120 second splits is, in general, at least as good as in the agate sample (Fig. 4). For Zr (Fig. 4f) duplication in the agate sample is clearly worse, indicating that agate ground samples are also not immune to subsampling problems.

The low levels of Ta in most rocks precludes analysis of this element by XRF. However, some estimate of the potential Ta contamination can again be made by simple proportion. Assuming the ROCKLABS analysis is correct, typical Ta contamination from the ring mill is the same as for Nb, only 0.002 ppm under the conditions used here. Ta contents of suspected contaminated basalts in the study of Ujike and Tsuchiya (1993) are not listed that paper or in the source reference (Ujike, 1989). However, Ta content in the MORB normaliser of Pearce (1983) is 0.18 ppm. The possible Ta contamination expected from the ROCKLABS mill is thus only 1.1% of the amount present in the normaliser. MORB-normalised spidergrams of the possibly contaminated basalts in Ujike (1989) have sample/N-MORB ratios of ~3-20, suggesting Ta contents of about 0.5-3.6 ppm. Although the Ta contents of the basalts analysed by Ujike (1989) may well have resulted by contamination of the equipment he used, such levels of contamination are not possible with the mill used here. In fact, the inferred low level of contamination suggests that samples crushed here could safely be used for Ta analysis in highly precise techniques such as ICP/MS. The small error introduced relative to MORB is of no significance in normal petrologic interpretation.

The granite sample which was only chipped with a manual splitter, rather than passed through the jaw crusher, was also crushed in the ring mill for 60 seconds. Five replicate analyses of a single bead of this sample were also made (Trim-Ring 60; Table 3). Concentrations of all elements generally lie within the range of all other samples, whether agate or ring mill ground. Co content is also comparable with the 60 second sample prepared using the jaw crusher, although the chip from the manual splitter contained no fines, in contrast to the product from the jaw crusher. This suggests that the chip size distribution of material crushed in the ring mill does not greatly influence contamination, at least in this case. Comparability of the results ex-jaw crusher and from the trimmer also suggests that the jaw crusher produces no significant metallic element contamination.

Conclusions

Grain size distributions of the quartz sand and granite samples crushed in the ring mill compare favourably with those ground in an automatic agate mortar. Mill times of only 60 seconds produce powder with equivalent grain size distributions to the same material ground for 60 minutes in the agate system. Extending the crushing time to 90 seconds lowers median grain size to 4 microns, compared to 6-10 microns in the agate ground samples. Increasing the mill time to 120 seconds does not significantly reduce median grain size, and 90 second mill time is optimal for the sample weights used.

Contamination trials show that crushing times of 60-120 seconds produce only 15-20 ppm Co, and inferred W contamination of 190-200 ppm. No other contaminants can be identified from the XRF data. Simple proportions between measured Co contamination and assayed contents of the ring mill tungsten carbide show that contamination of all other elements is trivial. This suggests that powders crushed with equipment such as that used here can be safely used for analysis of low-abundance trace elements (e.g. Nb, Ta) by more precise methods such as ICP/MS. Geologic interpretations cannot, in the majority of cases, be materially affected by the contamination from this ring mill. Variations in element abundances between the splits crushed for different times, and between beads prepared from the same split, indicate that chemical variability introduced by subsample heterogeneity is a far more serious problem, being several orders of magnitude greater than possible contamination from the mill.

Ring mills offer a clear advantage over agate grinding in terms of speed, and the volume of sample that can be crushed. The results also clearly show that sample contamination is not a problem with this equipment.

Acknowledgements

We thank K. Nakayama for his help with the grain size analysis, and J. Kimura and I. Devereux for helpful comments on the manuscript. This work was funded by Monbusho grant-in-aid 08640571 (to B.P. Roser).

References

Condie, K.C. 1993. Chemical composition and evolution of the upper continental crust: Contrasting results from surface samples and shales. *Chemical Geology,* 104, 1-37.

Folk, R.L. and Ward, W.C. 1957. Brazons river bar: a study in the significance of grain size parameters. *Journal of Sedimentary Petrology*, 27, 3-26.

Miyake. Y. and Musashino, M. 1991. Evaluation of contamination effects during crushing powder samples for neutron activation analysis. *Geol. Rept. Shimane Univ.*,10, 31-34 (in Japanese; English abstract).

Pearce, J.A. 1983. Role of the sub-continental lithosphere in magma genesis at active continental margins. In: Hawkesworth, C.J. and Norry M.J. (eds), *Continental basalts and mantle xenoliths.* Shive, Nantwich, 230-249.

Tanaka, T. and Kamioka, H. 1994. Trace element abundance in agate. *Geochemical Journal,* 28, 359-362.

Ujike, O. 1989. Geochemical magma-type discrimination diagrams: A case study on Miocene basaltic rocks from northeastern Japan. *Bulletin of the Volcanological Society of Japan, Special Issue,* 34, 157-168 (in Japanese).

Ujike, O. and Tsuchiya, N. 1993. Geochemistry of Miocene basaltic rocks temporally straddling the rifting of lithosphere at the Akita-Yamagata area, northeast Japan. *Chemical Geology,* 104, 61-74.

(Received: 1 Sep. 1998, Accepted: 30 Sep. 1998)

（要　旨）

Barry Roser・澤田順弘・Kurkura Kabeto,1998, 自動メノウ乳鉢と比較したタングステン・カーバイド・リング・ミルによる粉砕の性能と汚染試験, 島根大学地球資源環境学研究報告, 17, 1-9

タングステン・カーバイド・リング・ミルを用いて岩石の粉末試料作成の性能と汚染試験を行い，その結果を自動メノウ乳鉢によるものと比較した．試験試料は花崗岩と試薬グレードの石英砂で，リング・ミルにより30–120秒／試料，自動メノウ乳鉢では60分間／試料で粉末化された．リング・ミルによる粉末試料の粒度分析の結果は自動メノウ乳鉢による結果と比較して，非常に良い結果であった．ミルによる60秒の粉砕時間で自動メノウ乳鉢での60分に相当する粒度分布をもつ粉末試料を作成できる．粉砕時間を90秒に延ばすと中央粒径は，自動メノウ乳鉢では6–10ミクロンに対し，4ミクロンと小さくなる．粉砕時間を120秒にしても中央粒径は顕著には低くはならず，90秒が最適であるといえる．

リング・ミルで作成したこれらの粉末試料をXRFによって汚染試験を行った．粉砕時間が60–120秒のもので15–20 ppmのCoの汚染，推定190–200 ppmのWの汚染があるのみである．他の汚染元素はXRFでは確認できず，最大汚染量はごく少量であるといえ，ICP/MSのようなより精密な方法での低レベル微量元素（例えばNb,Ta）の分析においても安全に使用できる．むしろ，岩石試料の異なったスプリットや同じスプリットから作成したビードの間に見られる元素濃度の違いの方がはるかにより厳しく，ミルによる汚染の数オーダーの違いとなっている．