

Trace element contamination from tungsten carbide rod mill

Shusaku YAMAZAKI*

Abstract

The grinding of rock sample by tungsten carbide (WC) mill provides higher efficiency and performance than other mill materials such as agate. However, it has disadvantage of contamination of the sample with the grinding unit material. In order to evaluate the contamination effect from WC mill, we analyzed 31 trace elements of the quartz sand that was ground by WC rod mill and agate ball mill.

The results of the quartz sand analysis demonstrate that the grinding by WC rod mill leads to the significant high contamination of W (1963 ppm) and Co (482 ppm). Their abundances were more than 1000 times higher than those by agate ball mill. The contaminations of Ta (0.6 ppm) and Nb (0.15 ppm) were also detected in the quartz sand ground by WC rod mill. The contaminations of Fe and Ti were also estimated to be in sub-ppm levels as well as the Ta contamination. The contamination of Fe and Ti can be considered as negligible for typical igneous rock samples containing over hundreds of ppm in these elements. In order to investigate the effect of the contamination for natural igneous rock, the plagiogranites from the Oman ophiolite were ground by the WC and agate mills and were measured for their trace element compositions. The WC ground plagiogranites demonstrate the compositional correlations of SiO₂ with Co and Ta concentrations. These correlations indicate that the contamination is controlled by the amount of quartz in the sample. The regression analyses of these correlations indicate that the contamination in the quartz-free rock, such as basalt and gabbro, is equivalent to 30% of the effect by the quartz sand.

Collectively, these trace element analyses suggest that the grinding by the WC rod mill leads to the contaminations of W, Co, Ta and Nb in the sample. The contaminations of W and Co seriously affect on discussion of their geochemical characteristics. The contamination of Ta also affects on the plot on some discrimination diagrams. The contamination of Nb does not seem to affect so much if the original Nb concentration is sufficiently high (more than a

* Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan
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few ppm) or analytical detection and error are significantly larger than the extent of contamination. These indicate that if the analyses of W and Co are not needed, the grinding by the WC mill is applicable for the rock sample with more than a few ppm in Nb and tens of ppm in Ta.

Key words: agate, contamination, grinding, ICP-MS, plagiogranite, tungsten carbide.

Introduction

The contamination from grinding media is unavoidable and considerable problem for whole rock trace element analysis. In order to avoid significant contamination, it is required to select pod material appropriate for analyzing sample and method. Basically, the pod material should not contain the element to be analyzed. Although it contains such elements, the contamination should be negligibly lower for the analyzing sample. For example, Fe contamination in ppm level is not significant for the sample with Fe in wt% level.

Tungsten carbide (WC) rod mill and agate ball mill are placed at Department of Geology, Faculty of Science, Niigata University. WC material has higher hardness and density than the agate. The grinding by WC mill provides high performance for reduction of particle size and grinding time. However it is also known that WC mill causes the contaminations of W, Co, Fe, Ti, Nb and Ta to the crushed material (e.g. Roser et al., 2003). Agate ball mill is almost free from contamination of trace elements, although it requires longer grinding time. Therefore, agate ball mill is normally recommended for trace element analysis using inductively coupled plasma mass spectrometry (ICP-MS). In order to evaluate the applicability of WC rod mill to the grinding of typical igneous rock, we investigated the contamination effect on quartz sand and plagiogranites from WC rod mill.

Method

Reagent-grade quartz sand (Wako Pure Chemical Industries, Ltd.; CAS No. 14808-60-7) was ground by a WC rod mill and an agate ball mill. The grinding with WC rod mill used the Hi-speed Vibration Sample Mill Model TI-100 of Hirako Mechanical Technology Co. Ltd. (now Cosmic Mechanical Technology Co. Ltd.) installed at the Department of Geology, Faculty of Science, Niigata University. The grinding with agate ball mill used the Planetary Mill PULVERISETTE 5 of Fritsch Co. installed at the Graduate School of Science and Technology, Niigata University. The agate pod was 250 cc-size with ϕ 10 mm and ϕ 20 mm agate balls. The reference composition of typical WC mill is WC 93.5%, Co ca. 6.0%, Ti 0.5%, Ta 0.5% and Fe 0.3%, and the agate composition is SiO₂ 99.9%, Al₂O₃ <0.02%, Na₂O <0.02%, Fe₂O₃ <0.01%, MnO <0.01%, CaO <0.01%, MgO <0.01% (values after FRITSCH JAPAN Co. Ltd. Catalog;

Table 1. Analytical results of ICP-MS analysis for prepared samples.

	Quartz sand		Detection limit (3 σ)	Standard		Relative difference (%)
	WC lod mill	Agate ball mill		W-2a	W-2 GeoReM prefered value	
Sc	b.d.	b.d.	2.1	35.3	35.9	1.7%
V	b.d.	b.d.	22.7	256.6	268	4.3%
Co	482.46	0.05	0.03	43.69	45	2.9%
Zn	b.d.	b.d.	0.36	71.82	77	6.7%
Ga	b.d.	0.023	0.015	17.28	18	4.0%
Rb	0.118	0.06	0.002	19.79	21	5.7%
Sr	b.d.	0.16	0.14	186.77	196	4.7%
Y	b.d.	b.d.	0.006	22.63	22	2.9%
Zr	0.032	b.d.	0.022	96.35	92	4.7%
Nb	0.146	b.d.	0.001	7.47	7.5	0.4%
Cs	0.012	0.009	0.006	0.9	0.92	2.2%
Ba	0.204	b.d.	0.046	170.33	172	1.0%
La	0.003	b.d.	0.002	10.53	10.8	2.5%
Ce	b.d.	b.d.	0.002	22.51	23.4	3.8%
Pr	0.003	b.d.	0.002	2.98	3	0.7%
Nd	b.d.	0.005	0.005	12.90	13	0.7%
Sm	0.006	b.d.	0.005	3.23	3.3	2.1%
Eu	b.d.	b.d.	0.001	1.09	1.08	0.7%
Gd	b.d.	0.003	0.002	3.78	3.66	3.1%
Tb	b.d.	0.001	0.001	0.63	0.62	1.0%
Dy	b.d.	b.d.	0.001	3.69	3.79	2.8%
Ho	b.d.	b.d.	0.001	0.79	0.79	0.1%
Er	b.d.	b.d.	0.002	2.26	2.22	1.8%
Yb	b.d.	b.d.	0.003	2.06	2.05	0.3%
Lu	b.d.	b.d.	0.001	0.31	0.31	0.0%
Hf	0.003	b.d.	0.001	2.43	2.45	0.8%
Ta	0.626	0.004	0.001	0.48	0.47	1.5%
W	1963.2	0.9	0.3	0.7	0.3	133.3%
Pb	0.23	0.08	0.01	7.99	7.7	3.8%
Th	b.d.	0.001	0.001	2.23	2.17	2.7%
U	0.006	0.004	0.001	0.49	0.51	4.1%

Unit in ppm. Relative difference is percentage of difference between the analytical result in this study and the GeoReM preferred value. Abbreviation; b.d.: below detection limit

<http://www.fritsch.co.jp>). The grinding of the quartz sand was performed under the following conditions. In order to reduce cross-contamination, before the main grinding, the mills were cleaned by grinding of the quartz sand and rinsed with deionized water. About 20 g of the

quartz sand was ground for 6 minutes in the WC rod mill and for 20 minutes in the agate ball mill. Finally, the powders were stored in polystyrene bottles.

Abundances of 31 elements, Sc, V, Co, Zn, Ga, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Hf, Ta, W, Pb, Th and U, were determined using an inductively coupled plasma mass spectrometer (ICP-MS; Agilent 7500a) at the Graduate School of Science and Technology, Niigata University. The fusion method employed in this study was followed the procedure of Neo et al. (2009). The ground powders were burned at 900 °C for 6 hours in a muffle oven. The baked powders were weighed to 100 mg and then were dissolved with 50% HF in a Pt-Au crucible. After evaporation at 150 °C for 1 hour, the residue was fused with 500 mg Na₂CO₃ for 10 minutes at 1050 °C in a muffle oven. The residue was further dissolved in a mixed acid of HNO₃, HF and ultrapure water at 150 °C for 20 minutes in twice. The residue was finally diluted by 50 µg/mL with 5% HNO₃. Internal standard materials of In, Tm, Re and Tm were added to the solution. BHVO-1 (Hawaiian basalt) in the USGS Reference Materials was used an external calibration standard with reference values from Eddins et al. (1997). In order to evaluate measurement accuracy, W-2a (diabase) in the USGS Reference Materials was also analyzed.

Table 1 lists the detection limits determined by four measurements of blank. Most elements have detection limits of sub-ppm level, except Sc (3.2 ppm) and V (31.7 ppm). Abundances of most elements in W-2a are consistent with the GeoReM preferred values for W-2 (Jochum et al., 2005) within 5% relative difference (RD), except for Zn (6.7% RD), Rb (5.7% RD) and W (133% RD). The exceptional large difference in W was resulted from W content in the W-2 standard (0.3 ppm) that is equivalent to the detection limit (0.3 ppm). The other major components of WC material, Co, Nb and Ta, have small relative differences of 2.9%, 0.4% and 1.5%, respectively.

Results and discussion

Abundances of 31 elements in the ground quartz sand are listed in Table 1 and illustrated in Fig. 1a. The quartz sand ground by WC rod mill shows distinctly higher concentrations of W (1963 ppm), Co (482 ppm), Ta (0.63 ppm) and Nb (0.15 ppm) than those by the agate ball mill. Abundances of Sc, V, Zn, Y, Ce, Eu, Dy, Ho, Er, Yb and Lu are below their detection limits for the both grinding methods. Abundances of Ga, Sr, Zr, Cs, La, Pr, Nd, Sm, Gd, Tb, Hf, Th and U are comparable with their detection limits. In the WC ground quartz sand, abundance of Ba shows slightly higher (0.2 ppm) than its detection limit (0.05 ppm) and Rb and Pb are also significantly higher (0.12 ppm and 0.23 ppm) than those by the agate grinding (0.06 ppm and 0.08 ppm) and their detection limits (0.002 ppm and 0.01 ppm).

In the both grinding methods, the contamination of the quartz sand with the grinding unit material was not detected for the 24 elements of Sc, V, Zn, Ga, Sr, Y, Zr, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Hf, Th and U (Table 1). In the quartz sand ground by WC

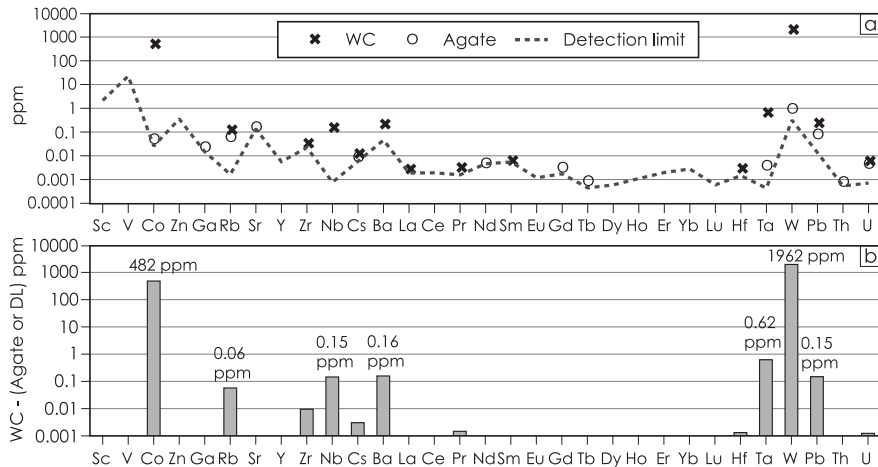


Fig. 1. The comparison of analytical results for the quartz sand ground by WC rod mill and agate ball mill. (a) The concentrations of 31 trace elements in the quartz sand ground by WC mill and by agate ball mill with the detection limits. (b) The difference between by WC rod mill and either by agate ball mill or their detection limits. Abbreviation; DL: detection limit.

rod mill, abundances of W and Co are over 1000 times higher than those by the agate ball mill (Fig. 1a). Abundances of Ta and Nb in the quartz sand ground by WC rod mill are also over 100 times higher than those by the agate ball mill. Abundances of these four elements, W, Co, Ta and Nb, certainly indicate the contamination from the WC rod mill.

Abundance ratio among W, Co and Ta in the WC ground quartz sand is 80.3:19.7:0.03 which has higher Co and lower Ta than the catalog value of 93:6.5:0.5. WC material consists of ultrahard WC micro grains with some trace carbide such as TaC and TiC, and interstitial cementing material of Co-alloy. This high Co ratio can be explained as the selective abrasion of the interstitial cementing material.

Fe and Ti are other possible elements introduced from WC grinding material. However, the contributions of Ti and Fe are estimated to be less than a few ppm, given their low contents in WC material (0.3-0.5%) that are similar to Ta content (0.5%). This indicates that Ti and Fe contaminations can be considered negligible for typical igneous rocks containing these elements over hundreds of ppm.

The quartz sand ground by WC rod mill introduced Rb (0.12 ppm) and Pb (0.23 ppm) in the quartz sand that are two to three times higher than those of the agate grinding (0.06 ppm and 0.08 ppm, respectively). The contributions of Rb and Pb from agate ball mill are significantly higher than the detection limits for these elements (0.002 ppm and 0.01 ppm, respectively). Because these elements are detected in the both grinding methods, the origin of Rb and Pb do not appear to be the contamination from the WC rod mill. This is probably due to the cross

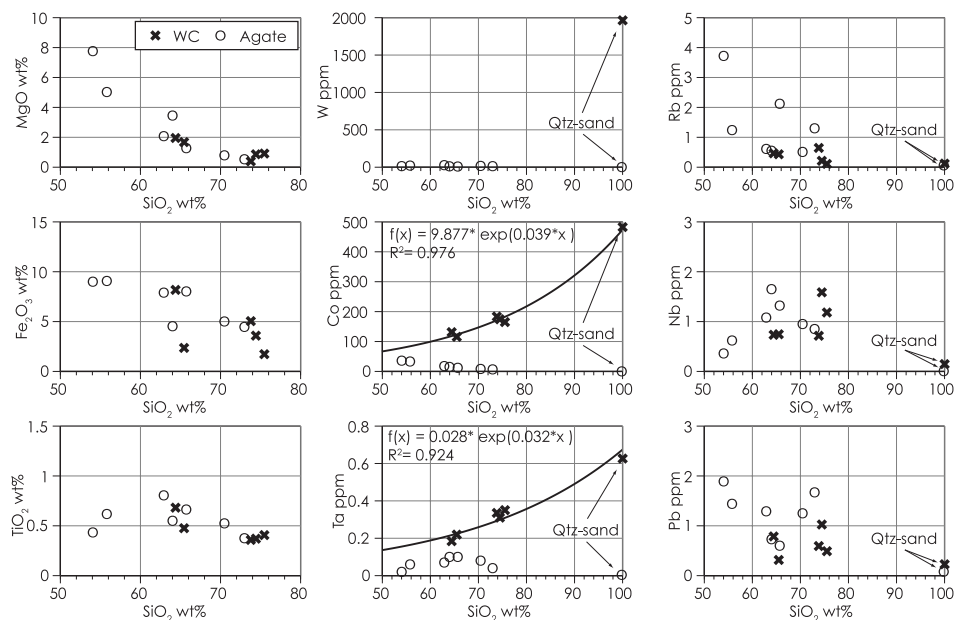


Fig. 2. SiO₂ versus major and trace elements in the whole rock powders for the quartz sand and for the Oman HFS-depleted type plagiogranites after grinding by WC rod mill and by agate ball mill. Abundance of W in the WC ground plagiogranite powders was not analyzed. MgO, Fe₂O₃ and TiO₂ contents for quartz sand were not determined.

contamination from previous grinding sample and/or the inherent component of the quartz sand. In the WC ground quartz sand, Ba is also detected (0.2 ppm), which has about four times higher concentration than the detection limit (0.05 ppm). The origin of Ba is also not identified either by cross contamination, by contamination from the WC rod mill or by analytical error. This problem can be solved with multiple analyses of analytical-grade quartz sand.

In order to estimate the contamination from WC rod mill on whole rock compositions of natural rock samples, we investigated the Oman HFS-deplete plagiogranites (S. Yamazaki, unpublished data), ground by WC rod mill and by agate ball mill.

The Oman plagiogranites decrease in MgO content with increasing SiO₂ content from 52 to 78 wt% (Fig. 2). This trend is consistent with fractional crystallization. In the SiO₂ versus MgO, TiO₂ and Fe₂O₃ diagrams, both WC and agate ground plagiogranite powders form uniform trends. Abundances of Co and Ta for the WC ground powders increase with increase of SiO₂, while those for the agate ground powders do not show such variation (Fig. 2). Contaminations of Rb, Pb and Nb are negligible in plagiogranites considering their lower contents in the quartz sand ground by both methods.

The increase in W, Co and Ta contamination associated with increasing SiO₂ content appears to be controlled by the amount of quartz, which has Mohs hardness of 7. The total amount of

contamination from WC rod mill to the quartz sand can be calculated 2445 ppm based on the sum of W, Co and Ta contents. In order to estimate the amount of contamination, we used the exponential regression for Co and Ta as a function of SiO_2 content. The regression equations are as follows:

$$\text{Co (ppm)} = 9.877 * \exp [0.039 * \text{SiO}_2 \text{ (wt\%)}]; (R^2 = 0.976) \quad (1)$$

$$\text{Ta (ppm)} = 0.028 * \exp [0.032 * \text{SiO}_2 \text{ (wt\%)}]; (R^2 = 0.924) \quad (2)$$

The calculated amount of Co contamination by the regression equation at SiO_2 60 wt% and 80 wt% are 103 ppm (21% of the quartz sand) and 224 ppm (45.8%), respectively. In the same way, those of Ta contamination are 0.19 ppm (27.8%) and 0.36 ppm (52.7%), respectively. This suggests that the Ta contamination for the quartz-free rock, such as basalt and gabbro ($\text{SiO}_2 < 60$ wt%), is estimated up to 0.2 ppm, and for typical granite ($\text{SiO}_2 < 80$ wt%) is estimated up to 0.4 ppm. On the other hand, it is known that the amount of contamination is also correlated with grinding time (e.g. Iwansson et al., 2000). Therefore, these regression curves are applicable for the grinding time of 6 minutes by the WC rod mill.

The trace element contamination from the WC grinding may affect on geochemical discrimination in terms of tectonic setting. In order to evaluate this influence, we plot the

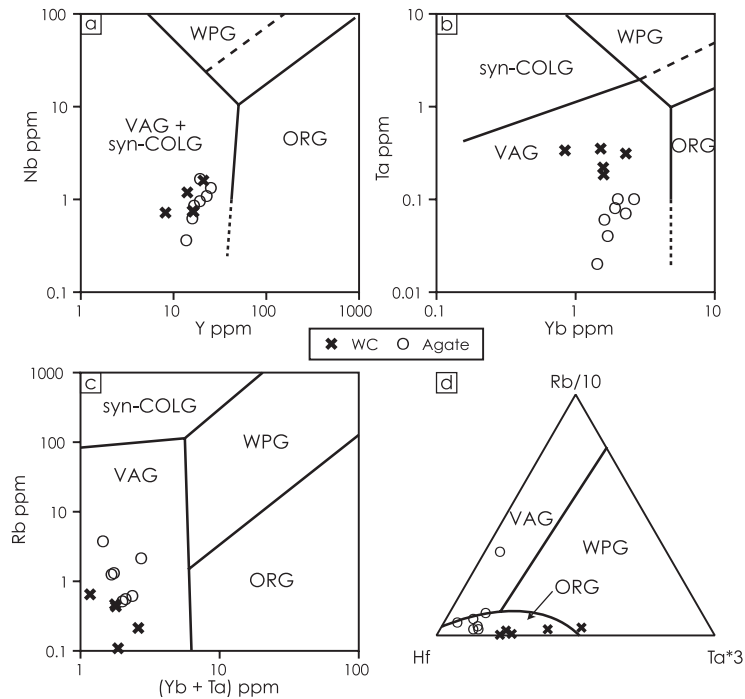


Fig. 3. The discrimination diagrams for granites. (a) Y versus Nb, (b) Yb versus Ta and (c) (Yb+Ta) versus Rb after Pearce et al. (1984). (d) HF-Rb/10-Ta*3 after Harris et al. (1986). The plotting data are Oman HFS-depleted plagiogranites same as in Fig 2. Abbreviations: ORG: ocean-ridge granites; syn-COLG: syn-collisional granites; VAG: volcanic-arc granites; WPG: within-plate granites.

Oman HFS-depleted plagiogranites on discrimination diagrams for granites (Fig. 3). These plagiogranites have depleted compositions in Nb (0.5-2 ppm) and Ta (<0.1 ppm). On the Y-Nb discrimination diagram, abundance of Nb cannot be distinguished by grinding methods (Fig. 3a), implying that the Nb contamination in sub-ppm level is negligible for typical granite with Nb in a few to several tens of ppm. On the other hand, the plots for the WC ground plagiogranites on the Yb-Ta discrimination diagram are shifted from those for the agate ground powders (Fig. 3b). Although the contamination of Ta is estimated up to 0.4 ppm, it does not shift their plots across the boundary between the volcanic-arc granites (VAG) and syn-collisional granites fields. In the diagram of (Yb+Ta)-Rb, the influence of the Ta contamination is negligible compared to the high Yb content (Fig. 3c). In the diagram of Hf-Rb-Ta, the agate ground plagiogranites are mostly plotted in the ocean-ridge granites (ORG) field. However, the plots for the WC ground plagiogranites shift toward Ta corner across the boundary between ORG and within-plate granites (WPG) fields. On the basis of evaluation using the discrimination diagrams, the Nb contamination from the WC rod mill has little impact on the igneous rocks with high Nb concentration (>1 ppm). However, the Ta contamination has a serious influence on the geochemical discrimination for granitic rocks.

Conclusions

The high precision trace element analysis of the quartz sand ground by WC rod mill demonstrates the significant amount of W and Co and the less amount of Ta and Nb contaminations. Furthermore, the analyses of Oman plagiogranites demonstrate that the extent of contamination is correlated with the amount of quartz. The effect of contamination is significantly large for the sample with Ta and Nb in sub-ppm level. Thus, agate ball mill should be used for the low-concentrated sample. If the sample contains Ta and Nb more than several-ppm, the contamination is negligible. In this case, the high performance WC rod mill is appropriate for reducing grinding time.

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