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Article

Tantalum and niobium contamination from tungsten carbide ring mills: much ado about nothing

Barry Roser*, Jun-Ichi Kimura* and Kibret Sifeta*

Abstract

Modern analytical methods such as ICP-MS permit accurate determination of sub-ppm levels of ultra trace elements, and contamination during crushing samples is therefore a potential problem. Nb and Ta are frequently cited as possible contaminants from tungsten carbide crushing equipment. To test this, we analyzed quartz sands pulps prepared both by agate grinding (60 minutes) and crushing separate splits in a tungsten carbide ring mill for varying times (30, 60, 90 and 120 seconds). Solution ICP-MS analyses showed that no significant Nb or Ta contamination was present in the ring mill pulps, compared to that ground in agate. This was also the case for the REE, Rb, Y, Zr, Sb, Hf, Th, and U. Combined with a previous test, the results show that Co and W are the only significant contaminants. Rocks powders prepared using tungsten carbide equipment can therefore be used for any geochemical studies with confidence, even when elemental abundances are <1 ppm. The possibility of contamination must assessed by each laboratory, however.

Introduction

Tantalum and niobium are key high field strength elements (HFSE) which are often used as petrogenetic indicators in volcanic suites. Nb and Ta exhibit similar geochemical behaviour, and along with the other HFSE (Hf, Zr, and Ti) are characteristically depleted in calcalkaline convergent margin igneous rocks compared to those erupted at divergent margins (Salter, 1999). These characteristics and the resistance of the HFSE to postmagmatic redistribution have led to their use in several discrimination diagrams aimed at determining the tectonic setting of eruption of volcanic suites (e.g. Pearce and Cann, 1973; Floyd and Winchester, 1975; Wood, 1980).

Average upper crustal abundances of Nb, Ta, and Hf are 12, 1.0 and 5.8 ppm, respectively; those for Zr and Ti are considerably greater at 190 ppm and 0.41 wt.% (McLennan, 2001). Although it is not an issue for Ti and Zr, one potential problem with determining Nb, Ta and Hf abundances accurately is the possibility of contamination during sample preparation for whole-rock analysis, particularly if tungsten carbide equipment is used. Several studies have shown or suggested that tungsten carbide ball mills or ring mills can produce significant Nb contamination (e.g. Miyake and Musashino, 1991; Condie, 1993), and possible Ta contamination has also been reported (e.g. Ujike and Tsuchiya, 1993; Rollinson, 1993 and references therein).

A tungsten carbide ring mill is part of the rock crushing equipment available at Shimane University. This mill has been used to crush over 2000 rock samples since 1996. An earlier report (Roser *et al*., 1998) described crushing trials with this mill, assessed the Co contamination produced during crushing of quartz sand and granite, and estimated the level of W contamination. No clear evidence could be found for Nb contamination, based on X-ray fluorescence (XRF) analysis. To further assess the possibility of contamination, we have analyzed the quartz sand pulps produced in that study by inductively-coupled plasma mass spectrometry (ICP-MS), which gives far more accurate Nb determinations than by XRF. This also permits assessment of potential contamination of Ta, Hf and the REE from our tungsten carbide mill relative to agate grinding.

Materials and Methods

Crushing

Details of the material used and the crushing methods employed are given in Roser *et al.* (1998). The ring mill used was a Rocklabs (model RC) machine with a 100 g tungsten carbide head. A single 500 g bottle of "Chameleon Reagent" 30–50 mesh quartz sand (Kishida Chemical Co.) was split into 50 g portions. Individual splits were then ground in the ring mill for periods of 30, 60, 90, and 120 seconds. A separate 20 g split of quartz sand was also ground in an automatic agate pestle and mortar system for 60 minutes to act as the control, assuming it produced no contamination other than silica. Laser micron sizer measurements showed the pulp produced by agate grinding had a median grain size of 6.3 μm, slightly coarser than those from the ring mill, which ranged from 5.1 μm (30 s) to 3.7 μm at 120 seconds (Roser *et al*., 1998).

ICP-MS analysis

Solution ICP-MS analyses of the quartz pulps were made using the VG Elemental PQ 3 instrument at Shimane University, operated in normal nebulization mode. The analytical methods used follow those described by Kimura *et al.* (1995). Solutions were prepared using a combined

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*Department of Geoscience, Shimane University, Matsue 690-8504

Table 1. Solution ICP-MS analyses of quartz sand crushed agate and tungsten carbide (WC).

Element (ppm)	Agate 60m	WC 30s	WC 60s	WC 90s	WC 120s
Rb	0.44	0.24	0.26	0.19	0.41
Y	0.02	0.04	0.01	0.01	0.01
Zr	0.11	0.45	0.08	0.05	0.09
Nb	0.00	0.06	0.06	0.06	0.07
Sb	0.02	0.09	0.03	0.01	0.01
La	0.05	0.05	0.04	0.06	0.06
Ce	0.09	0.13	0.10	0.10	0.11
Pr	0.01	0.01	0.01	0.01	0.01
Nd	0.02	0.04	0.02	0.03	0.20
Sm	0.01	0.00	0.00	0.00	0.00
Eu	0.00	0.00	0.00	0.00	0.00
Gd	0.01	0.01	0.00	0.00	0.00
Tb	0.00	0.00	0.01	0.00	0.00
Dy	0.00	0.01	0.01	0.01	0.00
Ho	0.00	0.00	0.00	0.00	0.00
Er	0.00	0.00	0.00	0.00	0.00
Tm	0.00	0.00	0.00	0.00	0.00
Yb	0.00	0.01	0.00	0.00	0.00
Lu	0.00	0.00	0.00	0.00	0.00
Hf	0.00	0.01	0.00	0.00	0.00
Ta	0.34	0.28	0.34	0.30	0.31
Th	0.02	0.04	0.00	0.00	0.00
U	0.02	0.01	0.00	0.00	0.00

alkali fusion and acid digestion procedure (AFAD), which will be described in detail by Kimura *et al*. (*in prep*.), but is outlined in Roser *et al.* (2000). Briefly, AFAD consists of digestion of 0.1000 g oven-dried sample with 1.0 ml $HClO_4$ and 1.0 ml 40% HF, in Pt crucibles heated to 200℃, followed by evaporation to dryness over 3 h. Anhydrous Na_2CO_3 alkali flux (0.5 g) is then added, and the samples are fluxed in the crucibles by heating for 10 minutes at >900℃. The fluxed samples are then partly dissolved by addition of 5 ml HNO_3^+ several drops of HF, heated on a 100℃ hot plate for 10 minutes, followed by addition of 10 mls deionized distilled water and 20 minutes further heating. The solutions are then transferred quantitatively to weighed 100 ml polyethylene bottles, retaining any residue (if present) in the crucibles. A third digestion is then carried out, with addition of 10 mls HCl, several drops of HF, and 5 mls deionized water, and heating at 150℃ for 30 minutes to dissolve any residue. This step ensures complete recovery of the HFSE. This digest solution is then quantitatively added to the polyethylene bottles, and the solutions made up to 100 ml by addition of deionized water. These stock solutions are subsequently diluted 50,000 x for the solution ICP-MS analysis. Elemental concentrations in the unknowns are determined by standard addition. Procedural blanks for the elements analyzed are typically <1 ppt (Kimura *et al. in prep*.)

Results and Discussion

Analyses of the quartz sand pulps from the ring mill and agate grinding are given in Table 1. The results show that Nb and Hf were not detected in the quartz sand ground in agate, whereas Ta content was significant (0.34 ppm). Among the REE, only La (0.05 ppm) and Ce (0.09 ppm) were present in quantities >0.02 ppm. Trace quantities of Zr (0.11 ppm) and Rb (0.44) suggest slight impurities for these elements, but Y, Sb, Th and U were essentially undetected (<0.02 ppm).

Results were similar for the splits crushed in the ring mill (Table 1). Although low levels of Nb (0.06-0.07 ppm) were recorded in all four samples, this is not attributable to contamination, since values are virtually identical, irrespective of crushing time. The zero value recorded in the single analysis of quartz sand may simply reflect noise at the lower limit of detection. Hf was also not detected in the ring mill pulps, but Ta contents ranged from 0.28 to 0.34 ppm, levels similar to or less than those seen in the agate-ground sample. Again there is no systematic increase with mill time, so the Ta present does not originate from the ring mill. The similar level seen in the agate-ground sample suggests the Ta present is an impurity in the sand itself. Contamination during the preparation of the solutions using AFAD is precluded by the characteristically low levels in the procedural blanks which are prepared with each set of samples.

Zirconium was detectable (0.45 ppm) in the sample crushed in the ring mill for 30 seconds, but values in the other three splits (0.05-0.09 ppm) are lower than that for the agate-ground sample (0.11 ppm). This precludes contamination, and suggests the presence of a trace heavy mineral impurity in the quartz sand which varies between splits. Fractionally higher levels of Y, Sb, Ce and Th in the 30 second ring mill sample compared to the other splits are also probably associated with this impurity. With the exception of an anomalous Nd value (0.20 ppm) in the 120 second sample, all REE are present at the same levels as in the agate sample or were not detected.

The results clearly show that no contamination of HFSE or REE occurs from crushing samples in the tungsten carbide equipment used here. Consequently, data from precise techniques such as solution ICP-MS can safely be applied to petrogenetic studies even when elements are present in samples at the sub-ppm level. An example of this is given by data for Upper Proterozoic porphyritic and pyroclastic metavolcanic rocks from the Werri district (Tsaliet Group) of Ethiopia (Sifeta, 2003). These rocks were analyzed by ICP-MS at Shimane University, after being crushed for 30-60 seconds in the same ring mill as that used here.

Based on a variety of geochemical characteristics, including discrimination diagrams using a variety of elements, REE patterns, and MORB-normalized multielement diagrams, Sifeta (2003) concluded that the metavolcanics represented sub-alkaline basalts erupted in a developed arc island setting. Nb contents of these rocks are moderate (average 5.74 ppm; range 2.28-10.80 ppm), as are La (17.04; 9.2-26.9 ppm) and Y (20.46; 14.02-35.55 ppm). Hf (2.38 average; 1.06-4.70 ppm), Ta (0.40; 0.14-0.82 ppm) and Th (1.69; 0.53-3.37 ppm) contents are much lower, and at the levels where contamination could pose a problem, if present. The elements above are combined in two discriminants aimed at differentiating the tectonic setting of eruption of basalts, the Th-Hf-Ta diagram of Wood (1980), and the La-Y-Nb diagram of Cabanis and Lecolle (1989). On both diagrams (Fig. 1), the Werri volcanics fall clearly within the field of calcalkaline volcanic arc basalts, confirming the conclusions of Sifeta (2003). More importantly, on neither diagram is any systematic shift observed toward Ta or Nb, as could be expected if contamination was an issue. The low Ta contents of the Werri metavolcanics also suggest that the Ta observed in the quartz sand pulps was present as an impurity in the sand itself, and did not result from contamination during AFAD.

The results overall show that no significant contamination of the elements analyzed results from crushing rock samples in the ring mill used here. Combined with the results of Roser *et al.* (1998), Co and W are the only significant contaminants. These are expected from the nature of the mill material. The speed of using tungsten carbide mills compared to agate grinding is an obvious advantage if large numbers of samples are being handled, as the pulps are of equivalent size grade and quality. Data from our samples crushed in tungsten carbide can safely be used for any geochemical purpose, even when elemental abundances are <1 ppm. However, this may not be the case with other tungsten carbide equipment, as reported in the literature, and it is desirable for any laboratory to test their own sample preparation methods for possible contamination.

Conclusions

Quartz sand pulps prepared by agate grinding (one hour) and crushing in a tungsten carbide ring mill (30 to 120 seconds) were analyzed by solution ICP-MS to test for Nb, Ta and Hf contamination from the ring mill. The REE, Rb, Y, Zr, Sb, Th, and U were also determined. Comparable results were obtained from both preparation techniques, with most elements not detected. Where elements were detected, similar levels were observed in both the agate-ground and ring mill samples, suggesting they were original impurities in the quartz sand. No elements increased systematically with ring mill crushing time. The results show that no significant contamination of the elements analyzed occurs during crushing in tungsten carbide, and data from such pulps can be used confidently even when abundances are low.

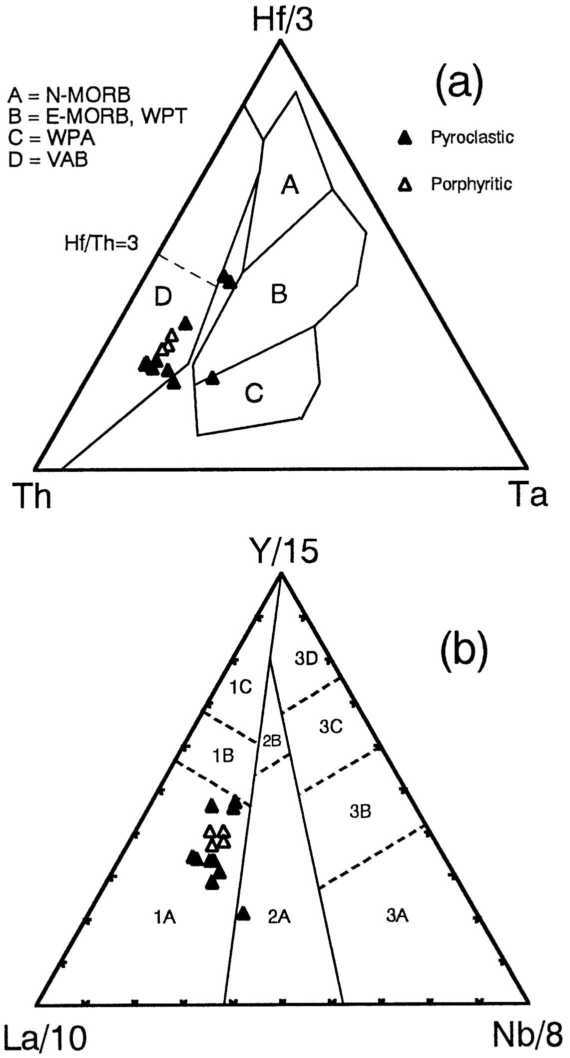

Fig. 1. Basalt discrimination diagrams for metavolcanic rocks from the Tsaliet Group, Werri district, Ethiopia. Data from Sifeta (2003). (a) Th-Sc-Ta diagram of Wood (1980). WPT = within-plate tholeiite; WPA = within-plate alkaline basalts; VAB = volcanic arc basalts. Calcalkaline VAB plot below Hf/Th=3, and tholeiitic VAB above. (b) La-Y-Nb diagram of Cabanis & Lecolle (1989). Fields: 1A, calcalkali basalts; 1B, overlap zone with 1C, volcanic-arc tholeiites; 2A, continental basalts; 2B, back-arc basalts; 3A, intercontinental rift alkali basalts; 3B & 3C enriched and weakly enriched E-type MORB, respectively; 3D N-type MORB.

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（要　旨）

バリー・ロザー，木村純一，キブレット・シフィータ，2003，タングステンカーバイトリングミルからのタンタラムとニオビウムの混染：空騒ぎ，島根大学地球資源環境学研究報告，22, 107-110.

Nb と Ta は，タングステンカーバイト粉砕装置からの混染元素として，数多くの報告がある．このことをテストするため，メノウ乳鉢で 60 分と，タングステンカーバイトリングミルによる 30, 60, 90，120 秒粉砕した石英砂について ICP-MS で分析を行った．その結果，Nb や Ta，さらに REE，Rb，Y，Zr，Sb，Hf，Th，U については混染は検出されなかった．過去の研究と併せるてみると，Co と W が唯一の混染元素であることがわかった．混染については個々のラボにおいて検討されるべきであるのは論を待たないが，本ラボのタングステンカーバイトリングミルは，全ての地質学的試料に関して 1 ppm 以下の濃度の元素についても問題なく用いることができる．