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SAMPLE CONTAMINATION BY GRINDING

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ABSTRACT

The extent of contamination resulting from the use of hardened high-carbon steel grinding plates, a chrome-steel shatterbox, a tungsten carbide shatterbox, an agate mortar and a corundum–ceramic handmill was evaluated on samples of Ottawa Sand Standard (>99% SiO_2). These samples, after preparation in each of the different types of equipment, were analyzed for twenty-one major, minor and trace elements by X-ray-fluorescence methods and for five rare-earth elements by flameless atomic absorption. Semiquantitative results show that the agate mortar produced no measurable contamination. Other materials contributed the following: corundum–ceramic contaminated the samples with Al, Mg, Ba, Cu, Zn and Cr; tungsten carbide, with Co, Nb and W; chrome steel, with Fe, Cr and Mn; and hardened high-carbon steel, with Fe, Cr, Zn, Mn, Cu and Ni.

Keywords: contamination by grinding, sample preparation, Ottawa Sand Standard.

SOMMAIRE

On a évalué la contamination d'un sable (Ottawa Sand Standard, 99% + SiO_2) que produisent différents moyens de pulvérisation, à savoir: plaques de broyage en acier durci, à haute teneur en carbone, deux boîtes de broyage, l'une en acier chromé, l'autre en carbure de tungstène, un mortier d'agate, et un moulin-à-bras en céramique de corindon. Après préparation dans chacun de ces différents instruments, les échantillons de sable ont été analysés; on y a dosé, par fluorescence X, vingt-et-un éléments (majeur, mineur ou en traces) et cinq terres rares, par absorption atomique (sans flamme). Les résultats, semi-quantitatifs, établissent que l'agate du mortier ne produit pas de contamination appréciable. Quant aux éléments introduits par les autres compositions, la céramique de corindon produit une contamination en Al, Mg, Ba, Cu, Zn et Cr, le carbure de tungstène, en Co, Nb et W, l'acier chromé, en Fe, Cr et Mn, l'acier durci à haute teneur en carbone, en Fe, Cr, Zn, Mn, Cu et Ni.

(Traduit par la Rédaction)

Mots-clés: contamination au broyage, méthodes de broyage, sable (Ottawa Sand Standard).

INTRODUCTION

For modern instrumental techniques the limiting factor in terms of time for geochemical analysis is now sample preparation. It is also during sample preparation that contamination can result in large, difficult-to-detect errors. This study examines the contamination contributed by five types of sample-preparation apparatus commonly used in geological laboratories.

METHOD

Table 1 lists the specifications of the five grinding apparatus used: tungsten carbide and chrome steel shatterboxes, an agate mortar, a corundum–ceramic handmill, and hardened steel-disk grinding plates. Fifty grams of Ottawa Sand Standard (Fisher Scientific, >99% SiO_2, 20 to 30 mesh) were ground to less than 200 mesh in each apparatus after cleaning by (1) grinding a discard sample of sand to reduce cross contamination (Thompson & Bankston 1970), (2) compressed air, and (3) scrubbing with a clean dry nylon brush. Minimum grinding times required to reduce the samples to less than 200 mesh were used (Table 2), as determined by test-sieving samples after sequential grinding periods of 10 seconds; these samples were then discarded. Samples used for analysis were not sieved owing to the possibility of contamination from the steel or brass sieves that were available (Thompson & Bankston 1970, Lavergne 1965).

After grinding the samples were kept in 5-dram polyvinyl chloride (PVC) vials (PVC is a potential source of Ti, Zn, Na and Cd; Scott & Ure 1972). The powders were then made into 3-g pellets for X-ray-fluorescence (XRF) analysis. The pellet press uses a tungsten carbide piston and has a stainless-steel housing; polyvinyl alcohol was used as a binder. Two XRF units were used: a Philips PW 1400 with a Rh tube for the major elements and most of the minor and trace elements, and a Philips PW 1410 with a Mo tube for La, Ce and Nd (Table 3). Tungsten concentrations could not be determined because of the lack of standards of known concentrations; however, the W$L\alpha_1$ and $L\alpha_2$ peaks were scanned to determine the presence of this element (Fig. 1). The Ta$L\alpha_1$ peak was also scanned, but no Ta could be detected owing to the poor detection-limit inherent in the XRF method.

Five rare-earth elements were determined by using a graphite furnace and flameless atomic absorption

TABLE 1. APPARATUS USED FOR SAMPLE PROCESSING

SURFACE[1]	FORM	MANUFACTURER
Brazilian agate: SiO_2 99.91%, Al_2O_3 0.02% Na_2O 0.02%, Fe_2O_3 .01%, K_2O 0.01%, MnO 0.01%,CaO 0.01%, MgO 0.01%	mortar and pestle; outer diameter 18 cm, inner diameter 13.5 cm, pestle 7 cm.	Fitsh "pulverisette-2", type 02.001
Corundum-ceramic[2]: αAl_2O_3 with possible trace amounts of K, Na, Si, Ca, Cu, Fe, Mg, Pb, B, Cr, Li, Mn, and Ni	handmill (buckboard) with 30 cm square plate and manual anvil-shaped rocker	unknown
Tungsten Carbide: C 6%, Co 6%, W 88%.	shatterbox/ring grinder, outer diameter 17 cm X 8 cm, puck and 1 ring	Spex Industries shatterbox No. 8500
Chrome steel: High Cr, high C steel type AISI.03; C 1.93%, Cr 13.21%, Cu 0.03%, Mn 0.46%, Mo 0.02%, Ni 0.08%, P 0.019%, Si 0.38%, S 0.005%, W 0.01%, other metals <0.01%.	shatterbox/ring grinder: outer diameter 21.5 cm X 6 cm, puck and two rings.	Rocklab ring grinder #137
High Carbon Steel: Special iron alloy, class 30/35; Si 2.30%, Fe 93.4%, Mn 0.70%, P 0.12%, C 3.45%	disc grinder 20 cm diameter with one stationary and one rotating disc.	Bico-Braun UA Pulverizer equipped with UA 51 and UA 52 standard grinding plates.

[1] The compositions of the surfaces are those reported by the manufacturer, except as noted.
[2] The exact composition of this apparatus is not known.

(AA) (Table 3) after dissolution of the rock powder in hydrofluoric and perchloric acids (Horsky & Fletcher 1981, Horsky, Juras & Hickson, in prep.).

RESULTS

Analytical results are given for each of the grinding techniques (Table 3). The results are semiquantitative and, because of the highly abrasive properties of the Ottawa Sand, reflect maximum contamination from the grinding apparatus. The relative values for W are shown in Figure 1.

In a study using neutron-activation techniques, St. Louis (1984) found that W contamination from a tungsten carbide shatterbox was high enough that counting could not be undertaken for more than five

TABLE 2. SAMPLE PREPARATION

SAMPLE	APPARATUS	TIME TO <200 mesh
OS-Ag	agate mortar	10 min.
OS-MUL	corundum-ceramic handmill	15 min.
OS-W2	tungsten carbide shatterbox	120 s
OS-CR	chrome steel shatterbox	45 s
OS-DSK	steel-disk mill	two passes with plates touching

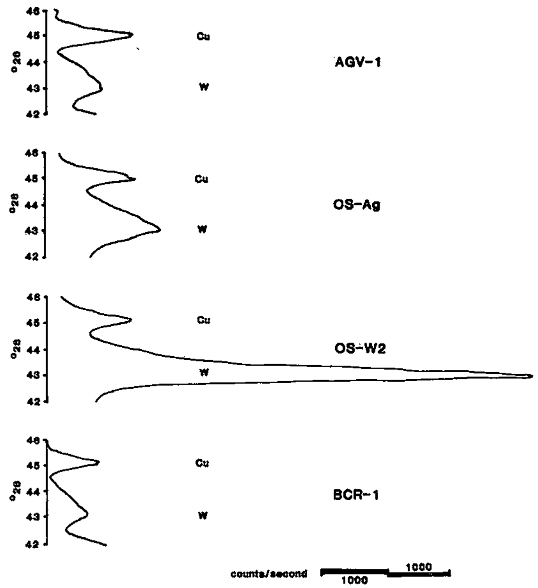

FIG. 1. XRF peak scan between 42° and 46° 2θ for W and Ta $L\alpha$ peaks. AGV-1 and BCR-1 are USGS standard rock samples with 0.55 ppm and 0.4 ppm W, respectively. Sample OS-Ag was prepared using an agate mortar and OS-W2 prepared using a tungsten carbide shatterbox. Analytical conditions for the Philips PW 1410: 40 mA, 60 kV, LiF200 analyzing crystal.

days following irradiation of the sample. Joron *et al.* (1980) showed evidence of W contamination on the order of hundreds of ppm; they found Nb and Ta contamination of 3–5 ppm as a result of the use of the tungsten carbide shatterbox. Nisbet *et al.* (1979) also indicated W, Co and Ta contamination from the use of tungsten carbide equipment. At UBC, P.J. Michael (oral comm.) found consistent contamination of approximately 0.5 ppm Nb after grinding basaltic rock for 50 seconds in a tungsten carbide shatterbox. St. Louis (1984) found Sc contamination at a level of 0.05 ppm when grinding quartz sand in a tungsten carbide shatterbox. Joron *et al.* (1980) also analyzed for Sc but found no contamination when rocks of basaltic composition were ground. The results of these studies are combined with our work in Table 4; elements are listed alphabetically with the relative degree of contamination indicated.

CONCLUSIONS

The agate mortar introduced no measurable contamination of the thirty-one elements studied. Similar results were achieved by Thompson & Bankston (1970); thus we would recommend the agate mortar for precise work. However, the expense of this equipment, the small amount of sample that can be processed and the longer time for sample processing should be taken into consideration.

The tungsten carbide shatterbox introduces less contamination than the chrome-steel shatterbox, and samples require similar grinding times for mills of comparable diameters. However, because of the high cost of tungsten carbide shatterboxes, chrome-steel shatterboxes are usually more readily available and can be of a larger size. Samples for a study of major elements and most minor and trace elements may be adequately processed in the chrome-steel shatterbox unless Fe and Cr contaminants are of concern. Although this contamination would be minimal for soft samples processed for a short period of time, it might be a significant problem for samples with naturally low Fe and Cr contents.

The number of steps undertaken in sample preparation should be minimized. A jaw crusher can be used to reduce samples directly to a size suitable for the shatterbox. The disk mill, although rapid, should

TABLE 3. ANALYTICAL RESULTS FOR PREPARED SAMPLES

SAMPLE (wt.%)	OS–Ag	OS–MUL	OS–W2	OS–CR	OS–DSK	SAND[1]	DET. LIMIT[2] (wt.%)	MACH PREC[3] (e %)
SiO_2	99.8 ± .1%	99.8 ± .1%	99.7 ± .1%	99.5 ± .1%	97.8 ± .1%	99.8	0.60	3
TiO_2	≤ Det.	0.01 ± 4%	0.01 ± 4%	0.01 ± 5%	0.01 ± 4%	.01	0.01	5
Al_2O_3	≤ Det.	0.96 ± 1%	≤ Det.	≤ Det.	≤ Det.	≤ Det.	0.20	6
Fe_2O_3T	0.03 ± 1%	0.05 ± 1%	0.04 ± 1%	0.24 ± .4%	1.93 ± .1%	0.04	0.01	3
MgO	0.02 ±14%	0.07 ± 5%	0.03 ±11%	0.03 ± 9%	0.01 ±18%	0.02	0.05	4
CaO	0.03 ± 3%	0.05 ± 2%	0.03 ± 3%	0.04 ± 3%	0.03 ± 3%	0.03	0.015	3
Na_2O	0.04 ±17%	0.05 ±16%	0.05 ±17%	0.06 ±12%	0.04 ±22%	0.05	0.11	1
K_2O	0.01 ± 4%	0.02 ± 3%	0.01 ± 4%	0.02 ± 3%	0.01 ± 5%	0.01	0.015	3
P_2O_5	0.01 ±11%	0.01 ± 7%	0.01 ±12%	0.01 ±11%	0.01 ± 9%	0.01	0.01	4
(ppm)							(ppm)	
Ba	22 ±30%	81 ± 6%	18 ±20%	19 ±30%	19 ±30%	18	15	5
Rb	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	3	8
Sr	≤ Det.	≤ Det.	≤ Det.	5 ±22%	≤ Det.	≤ Det.	4	1
Nb	≤ Det.	≤ Det.	4 ± 79%	≤ Det.	≤ Det.	≤ Det.	5	5
Y	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	3	7
Zr	33 ± 5%	33 ± 7%	33 ± 5%	33 ± 5%	31 ± 6%	33	3	2
Cr	9 ± 1%	14 ± 2%	9 ± 1%	340 ± 5%	76 ± 5%	9	4	4
Ni	9 ±10%	10 ± 9%	11 ± 9%	10 ± 9%	13 ± 9%	9	8	4
Co	≤ Det.	≤ Det.	270 ± 1%	≤ Det.	≤ Det.	≤ Det.	9	8
Cu	≤ Det.	≤ Det.	≤ Det.	≤ Det.	22 ±30%	≤ Det.	10	7
Pb	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	7	76
Zn	≤ Det.	≤ Det.	≤ Det.	≤ Det.	8 ± 7%	≤ Det.	6	5
Mn	≤ Det.	≤ Det.	≤ Det.	17 ± 2%	130 ± 1%	≤ Det.	3	5
V	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	4	7
La	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	4	5†
Ce	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	13	4†
Nd	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	4	5†
Sm	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	0.6‡	
Eu	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	0.1‡	
Dy	≤ Det.	0.3	0.3	≤ Det.	≤ Det.	≤ Det.	0.2‡	
Er	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	0.3‡	
Yb	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	≤ Det.	0.1‡	

[1]) **SAND** is the best estimate for the concentration of elements in the Ottawa Sand Standard based on the results of all of our analyses.

[2] The detection limit is set at 2 σ of the counting error.

[3]) The ±% errors given for each element are based on counting statistics of peak and background counts and counting times. Close to the detection limit the precision is very low owing to the low numbers of counts/second on the peak. As the peak counts increase away from the detection limit, this error becomes very low and the error from the reproducibility of the analyses becomes significant. This error (given as e%) is listed below and is based on 16 replicate analyses of a homogenized internal-laboratory standard.

† e % for La, Ce, and Nd is based on 6 replicate analyses.

‡ .0044 absorbance units was set as the detection limit for AA analyses.

TABLE 4. ELEMENTAL CONTAMINATION

Surface	Ag•	Al‡	B•	Ba‡	Bi•	Ca†	Cd•	Ce†	Co‡	Cr‡	Cu‡	Dy†	Er†	Eu†
Agate				tr										
Corundum-ceramic†		S		M						tr	M	tr		
Mullite•		•								•				
Alumina-ceramic•		•	•	•					•		•			
Tungsten Carbide									S					
Chrome Steel†										S		tr		
High Carbon Steel†										M	M			

Surface	Fe‡	Ga•	K†	La†	Li•	Mg†	Mn‡	Mo‡	Na†	Nb‡	Nd†	Ni‡	P†
Agate													
Corundum-ceramic†						M							
Mullite•	•	•											
Alumina-ceramic•	•				•		•						
Tungsten Carbide										tr			
Chrome Steel†	S						M						
High Carbon Steel†	S						M					tr	

Surface	Pb‡	Rb†	Sc•	Sm†	Sn•	Sr‡	Ta•	Ti‡	V†	W‡	Y‡	Yb†	Zn‡	Zr‡
Agate														
Corundum-ceramic†													M	
Mullite•														•
Alumina-ceramic•								•					•	•
Tungsten Carbide			•				•			S				
Chrome Steel†														
High Carbon Steel†													M	

S = significant contamination that would affect most analyses.
M = moderate contamination that may affect only those rock samples with naturally low concentrations.
tr = trace quantities that may not be above analytical uncertainties.
• Denotes the elements, the grinding surfaces used, and the results of studies by Thompson and Bankston (1970), Joron *et al.* 1980 or St. Louis (1984). No attempt has been made to rank these results.
Mullite• and *Alumina-ceramic•* were analyzed by Thompson and Bankston. Applicable elemental contamination are those elements marked with a • or ‡.
† Grinding surfaces analyzed in this study only, with applicable possible elemental contamination marked with a † or ‡ the grinding surfaces so marked.
‡ Denotes elements studied in this and at least one other work, contamination results are applicable to all of the grinding surfaces listed.

be avoided. From this work and that of Thompson & Bankston (1970), corundum, mullite, and other forms of ceramic should be avoided; they introduce a wide variety of elements, and samples must typically undergo further processing. This extra step increases the potential for cross contamination and, as well, introduces further direct contamination. Sieving increases the time needed for sample preparation and is a source of considerable elemental contamination (Thompson & Bankston 1970, Lavergne 1965) as well as of potential cross-contamination. Other precautions must be taken if the ratio of ferrous to ferric iron or the amount of CO_2 is to be determined (Whipple *et al.* 1984, Reay 1981).

Cross contamination remains one of the largest sources of contamination. Equipment should be cleaned by grinding SiO_2 sand for about one half the sample grinding time then using compressed air and nylon brushes to clean the grinding surfaces. Procedures involving acid washing, as outlined by Thompson & Bankston (1970), may be necessary for the most precise work.

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