Trace element contamination of sand samples by grinding

Olivier Pourret
UniLaSalle, AGHYLE, 19 rue Pierre Waguet, 60000 Beauvais, France
Corresponding author: olivier.pourret@unilasalle.fr

ABSTRACT

Blanks during powdering processes were examined for major and trace elements using inductively coupled plasma mass spectrometry (ICP-MS). Quartz sand (reference CV32.2) was used as a test substrate for powdering with grinding mills of several kinds: an agate mortar grinder, a stainless steel mortar grinder, a hard porcelain mortar grinder, an agate hand mill, and a hard porcelain hand mill. The stainless steel mortar grinder introduced significant contamination in Fe_2O_3, Mo, Cu, and Ni. The agate mortar grinder introduced minor W contamination. The hard porcelain mortar grinder introduced minor Cs contamination. The agate hand mill and hard porcelain hand mill showed minimal contamination for most elements examined. These results emphasize the importance of careful selection of grinding mills for sample pulverization prior to ICP-MS trace element analysis.

Keywords: grinding mill; contamination; trace elements; ICP-MS; sample preparation

1 INTRODUCTION

Sample preparation of rocks and sediments, prior to wet chemical analysis, includes crushing, splitting, and powdering (Potts, 1992). These processes homogenize samples and facilitate subsequent chemical decomposition. During powdering, both cross-sample contamination and contamination from grinding equipment can occur. Although the former can be minimized by pre-cleaning and sequential powdering of blank material before the sample, contamination from the grinding facility itself is unavoidable. For the sake of effective use of high-sensitivity analytical instruments such as ICP-MS, contamination introduced during pulverization must be kept at an acceptably low level.

Several previous studies have described the influence of contamination from grinding facilities (Myers and Barnett, 1953; Barnett et al., 1955; Thompson and Bankston, 1970; Ando, 1986; Hickson and Juras, 1986; Iwansson and Landström, 2000; Takamasa and Nakai, 2009; Yamasaki, 2018). Using DC arc excitation and a photoelectric spectrometer, Thompson and Bankston (1970) examined contamination from twelve elements during powdering and sieving, showing that tungsten carbide, alumina, and alumina-ceramic mills introduced contamination, while boron carbide mortar and agate mortar did not, except for boron from the boron carbide mortar. Hickson and Juras (1986) examined contamination from high-carbon steel, chrome-steel, tungsten carbide, agate mortar, and corundum-ceramic equipment using X-ray fluorescence spectrometry and flameless atomic absorption spectrometry, reporting that the agate mortar produced no measurable contamination. Ando (1986) similarly recommended agate mortar for sample powdering.

Iwansson and Landström (2000) examined contamination during powdering of various rock types in steel and cemented carbide grinding mills using neutron activation analysis and ICP emission spectrometry. Their results showed that contamination is proportional to the free quartz content of the sample and to powdering time. Takamasa and Nakai (2009) examined contamination from an agate hand mill, agate ball mill, Fe hand mill, alumina ceramic hand mill, and artificial crystalline quartz hand mill using ICP-MS, concluding that the artificial crystalline quartz hand mill introduced the least contamination. Yamasaki (2018) investigated contamination from iron and tungsten carbide mortars and agate and tungsten carbide mills, finding that the tungsten carbide mill significantly contaminated samples with tungsten and cobalt. More recently, Balaram and Subramanyam (2022) reviewed modern strategies for sample preparation in geochemical analysis with ICP-MS, reiterating the critical importance of appropriate mill selection for minimizing blank contributions.

With the continuing improvement in ICP-MS sensitivity now routinely achieving sub-ppb detection limits, even minor contamination introduced during grinding can significantly affect analytical results for trace elements, particularly for elements used as geochemical tracers such as Mo, W, Co, and REE. The present study investigates contamination levels introduced by five common laboratory grinding devices using a well-characterized quartz sand standard as test substrate. The objective is to provide practical guidance for selection of appropriate grinding equipment when preparing sand and soft rock samples for ICP-MS analysis.

2 MATERIALS AND METHODS

2.1 Sample splitting

Samples were split prior to grinding using the coning and quartering method. Samples were carefully poured into a cone on a flat paper surface. A thin, flat piece of cardboard was driven through the apex of the pile and dragged perpendicularly for a few centimeters to divide the pile in half. The cardboard was then rotated 90° and driven through the center to create four quadrants (Gerlach et al., 2002). Opposing quadrants were systematically combined and re-split, following standard protocols, always retaining the first and third quadrants.

2.2 Quartz sand standard

The quartz sand used as the test substrate (reference CV32.2, Sibelco) was characterized without grinding to establish baseline elemental abundances. Prior to analysis, this unground sand was ultrasonically washed with Milli-Q water for 30 minutes, dried, and analyzed as the blank reference. The results are reported as “CV32.2 Raw” in the data tables. All contamination values reported represent the difference between abundances measured in the powdered sample and those in the unpowdered reference sand.

2.3 Grinding equipment and procedures

Five grinding facilities were investigated in this study: (1) an agate mortar grinder (Retsch® RM200); (2) a hard porcelain mortar grinder (Retsch® RM200); (3) a stainless steel mortar grinder (Retsch® RM200); (4) an agate hand mill; and (5) a hard porcelain hand mill. Table 1 presents the major element compositions of the grinding media as reported by Retsch (2004).

All mortar grinders (Retsch® RM200) were cleaned with an ultrasonic cleaner using Milli-Q water for 15 minutes, repeated three times, followed by five pre-grinding passes of quartz sand at 300 rpm for 5 minutes each before grinding the analyzed sample. All hand mills were cleaned ultrasonically with Milli-Q water (15 min, three times) and pre-ground with quartz sand three times for 5 minutes each before use. Target grain size for all pulverized samples was approximately 100 µm.

The agate mortar grinder was additionally pre-cleaned by grinding Fontainebleau quartz sand (reference material) before processing the analyzed CV32.2 sand. All grinding equipment is located in the rock preparation room at UniLaSalle, Beauvais.

2.4 Chemical analysis

Major oxide abundances were determined on 0.2 g samples by ICP Optical Emission Spectrometry (ICP-OES) following lithium metaborate/tetraborate fusion and dilute nitric acid digestion. Loss on ignition (LOI) was determined by weight difference after ignition at 1000°C. Rare earth elements (REE) and refractory trace elements were determined by ICP-MS following lithium metaborate/tetraborate fusion and dilute nitric acid digestion of 0.2 g samples. Base and precious metals were determined by ICP-MS following hot (95°C) aqua regia digestion of a separate 0.5 g split. All analyses were performed in triplicate. Values reported in Tables 2 and 3 represent the mean of three replicates.

Table 1: Major element composition (wt.%) of grinding media used in this study (data from Retsch, 2004). SS = stainless steel.

Component	Agate	Hard Porcelain	SS
SiO_2 (wt.%)	99.91	61	1
Al_2O_3 (wt.%)	0.02	34	—
Na_2O (wt.%)	0.02	—	—
Fe_2O_3 (wt.%)	0.01	—	84.5 (Fe)
K_2O (wt.%)	0.01	3	—
MgO (wt.%)	0.01	1	—
CaO (wt.%)	0.01	1	—
Cr (wt.%)	—	—	13
Mo (wt.%)	—	—	0.42

3 RESULTS AND DISCUSSION

3.1 Major element contamination

Major element compositions of the CV32.2 quartz sand before and after grinding in the five different mills are presented in Table 2. The raw sand is dominated by SiO_2 (∼98.4 wt.%), with minor Al_2O_3, K_2O and trace Fe_2O_3. Overall, major element compositions show limited variation across grinding methods. The most notable exception is Fe_2O_3, which increases from 0.07 wt.% in the raw sand to 0.20 wt.% after grinding in the stainless steel mortar grinder, an increase of approximately 0.13 wt.%, reflecting the high Fe content of the stainless steel grinding medium (Table 1). All other grinding media produced Fe_2O_3 values indistinguishable from or lower than the raw sand. Cr_2O_3 also shows a slight increase to 0.02 wt.% after stainless steel grinding, consistent with the Cr content (∼13 wt.%) of the stainless steel medium. These results are broadly consistent with earlier findings on steel grinding equipment (Iwansson and Landström, 2000; Yamasaki, 2018).

Table 2: Major element oxide compositions (wt.%) and LOI of CV32.2 quartz sand before and after grinding. SS = stainless steel mortar grinder.

	CV32.2 Raw	Agate mill	SS mill	Porcelain mill	Agate mortar	Porcelain mortar
SiO_2	98.43	98.31	98.10	98.25	98.25	98.05
Al_2O_3	0.62	0.55	0.55	0.65	0.63	0.74
Fe_2O_3	0.07	0.06	0.20	0.05	0.05	0.04
MgO	0.01	0.01	0.01	0.01	0.01	0.01
CaO	0.02	0.01	0.01	0.01	0.02	0.01
Na_2O	0.03	0.04	0.03	0.03	0.03	0.04
K_2O	0.45	0.40	0.39	0.40	0.46	0.42
TiO_2	0.02	0.02	0.02	0.02	0.02	0.03
P_2O_5	0.01	0.01	0.01	0.01	0.01	0.01
MnO	0.01	0.01	0.01	0.01	0.01	0.01
Cr_2O_3	0.01	0.00	0.02	0.00	0.00	0.00
LOI	0.40	0.63	0.70	0.63	0.60	0.70
Sum	100.04	100.05	100.05	100.05	100.04	100.05

3.2 Trace element contamination

Trace element compositions are presented in Table 3. The stainless steel mortar grinder introduced the most significant contamination, with notably elevated Mo (0.80 vs. 0.10 ppm in raw sand), Cu (1.17 vs. 0.13 ppm), and Ni (2.20 vs. 0.10 ppm). These elevated values are consistent with the elemental composition of stainless steel (Fe, Cr, Mo, Ni; Table 1) and confirm findings from earlier studies on steel grinding equipment (Iwansson and Landström, 2000; Takamasa and Nakai, 2009; Yamasaki, 2018). In particular, Mo and Ni contamination from steel equipment is a well-documented issue that can seriously compromise geochemical interpretations when these elements are used as petrogenetic or environmental tracers (Takamasa and Nakai, 2009).

The agate mortar grinder (Retsch® RM200) introduced minor but detectable W contamination (1.10 ppm vs. 0.60 ppm in the raw sand; +0.50 ppm). This is a somewhat unexpected result, as agate equipment is generally considered one of the cleanest options for sample preparation. However, it is consistent with observations by Takamasa and Nakai (2009) who noted W contamination from alumina ceramic mills. The origin of W in agate grinding equipment may reflect trace W impurities or contamination from manufacturing processes, as also reported by Takamasa and Nakai (2009). The hard porcelain mortar grinder and hard porcelain hand mill showed minor elevation in Cs (0.30 ppm vs. 0.17 ppm in the raw sand), which may reflect the K_2O-rich composition of hard porcelain (Table 1) since Cs is geochemically coherent with K.

REE patterns across all grinding media are broadly similar and closely match the raw sand (Table 3). No systematic enrichment or depletion in any REE was observed for any grinding device. This is an important result given the increasing use of REE patterns in environmental and pedogenic studies, suggesting that agate, hard porcelain, and stainless steel grinding equipment all preserve REE compositions well, notwithstanding the broader contamination issues discussed above.

Table 3: Trace element compositions (ppm unless indicated) of CV32.2 quartz sand before and after grinding. SS = stainless steel mortar grinder.

Element (ppm)	CV32.2 Raw	Agate mill	SS mill	Porcelain mill	Agate mortar	Porcelain mortar
Ba	86.67	73.67	74.67	80.33	86.67	76.00
Co	0.83	0.20	0.40	0.23	0.27	0.20
Cs	0.17	0.23	0.20	0.30	0.27	0.30
Cu	0.13	0.30	1.17	0.33	0.20	0.30
Ga	1.20	0.90	0.83	0.50	0.80	0.80
Hf	0.83	0.60	0.60	0.57	0.73	0.60
Mo	0.10	0.10	0.80	0.10	0.10	0.10
Nb	0.57	0.43	0.50	0.53	0.33	0.60
Ni	0.10	0.10	2.20	0.10	0.10	0.10
Pb	0.57	0.60	0.70	0.63	0.47	0.40
Rb	9.37	7.87	7.87	8.70	8.50	10.10
Sr	14.07	11.93	11.63	12.97	13.17	11.70
Th	0.63	0.40	0.40	0.63	0.47	0.50
U	0.20	0.13	0.23	0.17	0.13	0.20
V	8.00	8.00	8.00	8.00	8.00	8.00
W	0.60	0.50	0.50	0.50	1.10	0.50
Y	1.20	0.87	1.13	1.07	0.97	1.00
Zr	28.50	18.97	20.50	20.53	21.20	20.80
La	2.03	1.53	1.57	1.93	1.73	1.60
Ce	3.87	2.87	2.83	3.27	3.10	2.90
Pr	0.42	0.32	0.31	0.39	0.37	0.35
Nd	1.60	1.13	1.23	1.37	1.43	1.50
Sm	0.26	0.22	0.23	0.28	0.26	0.27
Eu	0.06	0.05	0.04	0.05	0.05	0.05
Gd	0.17	0.19	0.16	0.24	0.21	0.24
Tb	0.04	0.03	0.03	0.03	0.03	0.03
Dy	0.21	0.18	0.20	0.19	0.19	0.18
Ho	0.04	0.04	0.04	0.04	0.03	0.05
Er	0.13	0.10	0.12	0.12	0.12	0.14
Tm	0.02	0.02	0.02	0.02	0.02	0.02
Yb	0.12	0.10	0.12	0.12	0.12	0.13
Lu	0.03	0.02	0.02	0.02	0.02	0.02

Gold (Au) showed anomalously elevated values after grinding with the porcelain mortar grinder (1.33 ppb vs. 0.50–0.60 ppb in other preparations). This single elevated value may reflect nugget effects or analytical heterogeneity rather than systematic mill contamination, and further investigation with larger sample sets would be warranted. V, Be, Sn, As, Cd, Sb, Bi, Ag, Zn, and Hg showed no systematic variation attributable to grinding across any of the five mills.

Overall, the hard porcelain hand mill and agate hand mill performed comparably and introduced the least contamination across the suite of elements analyzed. The stainless steel mortar grinder is not recommended when Mo, Cu, Ni, or Fe determinations are analytically relevant, as previously emphasized by multiple studies (Hickson and Juras, 1986; Takamasa and Nakai, 2009; Yamasaki, 2018; Balaram and Subramanyam, 2022). For soft-rock samples such as limestone or sand, agate and hard porcelain hand mills remain the most suitable options.

4 CONCLUDING REMARKS

This study evaluated the trace element contamination introduced by five common laboratory grinding devices during pulverization of quartz sand, using ICP-MS analysis. The main conclusions are:

(1) The stainless steel mortar grinder introduces significant contamination in Fe_2O_3, Mo, Cu, and Ni, consistent with the elemental composition of stainless steel. This device should not be used when these elements are analytically critical.

(2) The agate mortar grinder (Retsch® RM200) introduces minor W contamination, despite agate being widely regarded as a low-contamination grinding material. This result should prompt additional investigation.

(3) Hard porcelain grinding equipment introduces minor Cs contamination, likely related to its K_2O-rich composition.

(4) The agate hand mill and hard porcelain hand mill introduced the least contamination overall and are recommended as the most appropriate devices for preparing soft-rock samples (such as sand and limestone) for multi-element ICP-MS analysis.

(5) REE patterns are preserved faithfully by all five grinding devices, which is an important practical observation for environmental geochemistry and pedogenic studies employing REE as tracers.

These results contribute to an evolving body of knowledge on grinding-induced contamination (Takamasa and Nakai, 2009; Yamasaki, 2018; Balaram and Subramanyam, 2022) and reinforce the need for systematic blank testing of grinding equipment at the commencement of any ICP-MS analytical campaign.

Acknowledgments

The author thanks Montupet SA and Sibelco for providing the sand samples, and colleagues from UniLaSalle: Sébastien Laurent-Charvet and Sébastien Potel. Thanks are also extended to former students Pierre Louis Junot, Robin Pelletier, Karine Charbonnier, Adrien Moreau, Maximilien Guillot, and Christophe Marin who contributed to sample preparation and data collection.

Funding

This research is part of the Ecosable project and was funded by Région Picardie, the European Regional Development Fund (ERDF), and UniLaSalle.

Authors' contributions

O.P.: Conceptualization, data curation, formal analysis, writing – original draft, writing – review and editing.

Conflicts of interest

The author declares no conflicts of interest.

REFERENCES

Ando, A., 1986. Recommended sample preparation procedure for GSJ reference samples. In: Imai, N. et al. (Eds.), *A compilation of analytical data for major and trace elements in seventeen GSJ geochemical reference samples.* Geological Survey of Japan, pp. 7–12.

Balaram, V. and Subramanyam, K.S.V., 2022. Sample preparation for geochemical analysis: strategies and significance. *Advances in Sample Preparation*, 2, 100010. `https://doi.org/10.1016/j.sampre.2022.100010`

Barnett, P.R., Huleatt, W.P. and Myers, A.T., 1955. Spectrographic determination of contamination of rock samples after grinding with alumina ceramic. *American Journal of Science*, 253, 121–124.

Gerlach, R.W., Dobb, D.E., Raab, G.A. and Nocerino, J.M., 2002. Gy sampling theory in environmental studies. 1. Assessing soil splitting protocols. *Journal of Chemometrics*, 16, 321–328. `https://doi.org/10.1002/cem.705`

Götze, J., Tichomirowa, M., Fuchs, H., Pilot, J. and Sharp, Z.D., 2001. Geochemistry of agates: a trace element and stable isotope study. *Chemical Geology*, 175, 523–541. `https://doi.org/10.1016/S0009-2541(00)00356-9`

Hickson, C.J. and Juras, S.J., 1986. Sample contamination by grinding. *Canadian Mineralogist*, 24, 585–589.

Imai, N., Terashima, S., Itoh, S. and Ando, A., 1995. 1994 compilation values for GSJ reference samples, "Igneous rock series". *Geochemical Journal*, 29, 91–95. `https://doi.org/10.2343/geochemj.29.91`

Iwansson, K. and Landström, O., 2000. Contamination of rock samples by laboratory grinding mills. *Journal of Radioanalytical and Nuclear Chemistry*, 244, 609–614. `https://doi.org/10.1023/A:1006769401251`

Myers, A.T. and Barnett, P.R., 1953. Contamination of rock samples during grinding as determined spectrographically. *American Journal of Science*, 251, 814–830. `https://doi.org/10.3133/TEI179`

Potts, P.J., 1992. *A Handbook of Silicate Rock Analysis.* Blackie, Glasgow, 622 pp.

Retsch, 2004. *Materials and Material Analyses.* Retsch GmbH, Haan, 60 pp.

Robertson, I.D.M., Dyson, M., Hudson, E.G., Crabb, J.F., Willing, M.J. and Hart, M.K.W., 1996. A case-hardened, low contamination ring mill for multi-element geochemistry. *Journal of Geochemical Exploration*, 57, 153–158. `https://doi.org/10.1016/S0375-6742(96)00031-3`

Takamasa, A. and Nakai, S., 2009. Contamination introduced during rock sample powdering: effects from different mill materials on trace element contamination. *Geochemical Journal*, 43, 389–394. `https://doi.org/10.2343/geochemj.1.0032`

Thompson, G. and Bankston, D.C., 1970. Sample contamination from grinding and sieving determined by emission spectrography. *Applied Spectroscopy*, 24, 210–219. `https://doi.org/10.1366/000370270774371886`

Yamasaki, T., 2018. Contamination from mortars and mills during laboratory crushing and pulverizing. *Bulletin of the Geological Survey of Japan*, 69, 201–210. `https://doi.org/10.9795/bullgsj.69.201`