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CONTAMINATION OF ROCK SAMPLES DURING GRINDING AS DETERMINED SPECTROGRAPHICALLY

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# GEOLOGY AND MINERALOGY

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# CONTAMINATION OF ROCK SAMPLES DURING GRINDING AS DETERMINED SPECTROGRAPHICALLY

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## A. T. Myers and Paul R. Barnett

#### ABSTRACT

Spectrographic analysis was used by the Geological Survey to investigate the kind and degree of contamination resulting from the pulverizing in heavy grinding machinery of three different groups of rock samples: (1) six hard rocks, (2) six unconsoligated sediments, and (3) one massive quartz and one quartzite. It was found that iron can be increased as much as 1.5 percent, nickel 0.006 percent, molybdenum 0.002 percent, chromium 0.001 percent, cobalt 0.002 percent, vanadium 0.001 percent, copper 0.003 percent, and manganese 0.1 percent. The data presented also show there is danger of contamination of samples from grinding on a bucking board.

#### INTRODUCTION

It has been known for some time that spectrographic analysis of rocks and ores is complicated by contamination introduced during grinding. 1/
Whenever grinding machinery made of steel is used to pulverize rocks, some of the steel from the mill plates or crushers will be added to the finely

<sup>1/</sup> For the purpose of this report, the word grinding will include both the crushing and grinding processes.

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ground sample. Furthermore, when the sample is sieved through brass screens, it may pick up additional contaminants such as copper and zinc. If the rock samples come in contact with utensils containing galvanized material or solder, contamination by zinc, lead, and tin is likely to occur. This contamination is not serious when the rock is analyzed only for the major components, but when minor elements are to be determined spectrographically or chemically, the error introduced may be very serious.

According to Lundell, Hoffman, and Bright (1931), the ordinary constituents of steel are iron, carbon, manganese, phosphorus, sulfur, and silicon. The common alloying constituents are copper, nickel, chromium, vanadium, molybdenum, tungsten, and cobalt. The less common constituents are aluminum, titanium, zirconium, niobium, tantalum, uranium, rare earths, arsenic, tin, antimony, zinc, and boron. Furnace refractories, scrap steel, and iron ore, as well as limestone and other fluxes, all may contribute minor-element impurities to the final steel.

Washington (1930, pp. 79-83) and Ahrens (1950, p. 38) discuss contamination of the rock sample by steel mortars and screens. Ahrens also gives a useful bibliography which includes the subject of sample preparation for spectrochemical analysis.

Sandell (1947, p. 652) gives some data on the amount of contamination by iron when quartz and feldspar are crushed in a Plattner mortar. He found that after crushing the samples contained the following contamination in parts per million: Fe 280, Mn 1.8, Cr. 0.4, V 0.1, Ni 0.25, Co 0.1, Cu 0.35. During this crushing reasonable care was taken that undue contamination did not occur. A decrease in contamination was noted when the collar

of the mortar was not used.

The present investigation was undertaken in the Trace Elements

Denver Laboratory of the Geological Survey to find out whether pulverized rock samples are contaminated by metal grinders of the Braun
or McCool type to a degree significant in spectrographic analysis. No
attempt has been made nor was there any intention to investigate systematically the contamination due to separate types of crushing or pulverizing
machinery.

In an attempt to determine the extent of contamination for the routine grinding procedure several experiments were conducted and particular attention has been given to elements that are frequently studied by users of our spectrographic analyses.

#### Acknowledgments

The authors wish to thank their associates in the U. S. Geological Survey, especially M. K. Carron, Michael Fleischer, A. W. Helz, W. P. Huleatt, R. U. King, L. R. Page, L. F. Rader, L. B. Riley, and R. E. Stevens for their valuable suggestions in reviewing the manuscript. This work is part of a program undertaken by the Geological Survey on behalf of the U. S. Atomic Energy Commission.

# PREPARATION AND TREATMENT OF SAMPLES

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The investigation can be roughly divided into three experiments. In the first experiment two sets of rock samples (six hard rocks and aix unconsolidated sediments) were handled so that each kind of sample was ground by two methods: the first method (Huleatt, 1950) was by heavy grinding machinery (routine grinding) and the second method was by bucking board (only when necessary) and agate mortar (control grinding 2/) as shown in the flow diagrams, figures 1 through 4. An effort was made in the control grinding to keep steel or metal contamination at the lowest possible level. In the flow diagrams the six hard-rock samples are referred to as group 1 and the six unconsolidated sedimentary samples are labelled group 2. These two sets of rock samples are later used to demonstrate contamination by making quantitative spectrographic analyses on them.

In the second experiment a massive quartz sample and a quartzite sample were collected in large amounts for this study. From all outward appearances each sample was quite uniform. These samples were prepared for routine and control grinding so that, in contrast to the first experiment, they were ground by an improved control grinding method that added very little, if any, metal to the sample. The ground massive rock was heated to 600 C and dropped into cold distilled H<sub>2</sub>O. The shattered fragments then needed very little crushing in a Plattner mortar before the final grinding in an agate mortar. Figure 3 (group 3 samples) illustrates how the samples were handled in this experiment.

<sup>2/</sup> In the control grinding the bucking board was used as a crushing machine. Some grinding inevitably took place in the crushing process, but the spectrographic data for some of the steel elements clearly indicate that a significant control of contamination was effected.

In the third experiment two carefully selected perthite samples and one silica-sand sample 3/ were used to collect iron or steel impurity from the heavy grinding machinery and the bucking board. In the flow diagrams the sample treatments are shown as groups 4 and 5. Chemical determinations for iron were made on the two samples of perthite and one sample of silica sand from the grinding machinery, as well as on a second silica-sand sample that had been thoroughly ground on the bucking board. The photographs in figure 6 show what grinding machinery does to a sample of white perthite.

In the fourth experiment iron filings were separated from the two perthite samples and one silica-sand sample with a magnet, and some of the steel elements (Ni, Mo, Cr, V, Co, Cu, Mn, and Sn) were determined spectrographically. Steel filings were not removed from any of the samples before analysis.

# DISCUSSION OF RESULTS

Inasmuch as there is a demand for both quantitative and semiquantitative spectrographic determinations of trace elements, the contamination data obtained are here discussed on the basis of those two methods of determination.

# Quantitative analysis

(One significant figure)

After pulverizing the samples by the two methods of grinding (control and routine), quantitative spectrographic analyses of the samples in the

This should not be confused with the grinding of a rock samples for the only purpose was to grind and collect steel filings (see special grinding).

#### Group 1

Six hard-rock samples Mixture of quartz, pyrite, and altered igneous rock

Reduced to 1/4 inch using the bucking board as a jaw crusher, and divided into two equal parts with Jones splitter.

# Routine grinding

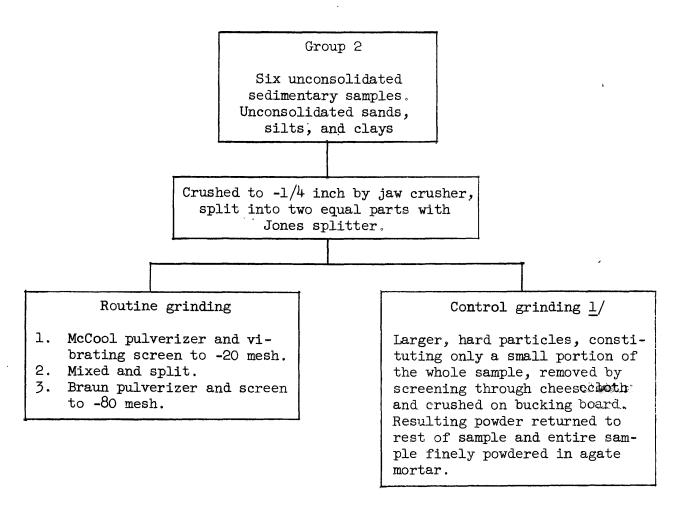
- 1. Crushed in jaw crusher to -1/4 inch.
- 2. Split.
- 3. Pulverized with McCool 6-1/2-inch disk, screened through -20-mesh vibrating screen, and over-sized particles sent back through McCool. Process repeated until all passed through screen.
- 4. Mixed.
- 5. Split.
- 6. Pulverized in Braun pulverizer and screened through -80 mesh.

Control grinding 1/

Samples further crushed on the bucking board; pulverizing action completed in the agate mortar.

1/ The process of control grinding probably added more steel filings to these samples than was added to the samples of group 2 by the same process (see control grinding fig. 2). These rocks were so hard in comparison that more abrasive action on the bucking board was unavoidable.

Figure 1.--Flow diagram of treatment of hard-rock samples, group 1



 $\underline{1}/$  Control grinding for the softer sedimentary samples probably added less bucking-board steel because less abrasive action was necessary to reduce the samples to size for finishing in the agate mortar. Therefore the group 1 samples seem less contaminated.

Figure 2.--Flow diagram of treatment of sedimentary samples, group 2

Group 3

One quartzite sample

One quartz sample

# Routine grinding

- 1. Crushed in jaw crusher to -1/4 inch.
- 2. Split.
- 3. Pulverized with McCool 6-1/2-inch disk, screened through -20-mesh vibrating screen, and over-sized particles sent back through McCool. Process repeated until all passed through screen.
- 4. Mixed.
- 5. Split.
- 6. Pulverized in Braun pulverizer and screened through -80 mesh.

# Control grinding

Samples heated to 600 C. Crushing effected by quenching in cold distilled water. The shattered fragments were further crushed in a Plattner mortar (without the collar) and the final grinding or pulverizing action completed in the agate mortar.

Figure 3.--Flow diagram of treatment of quartz and quartzite samples, group 3.

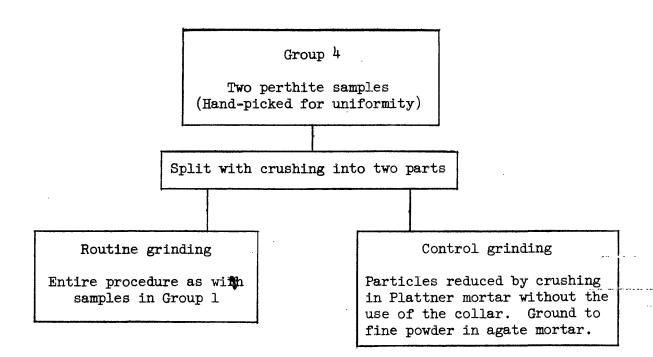
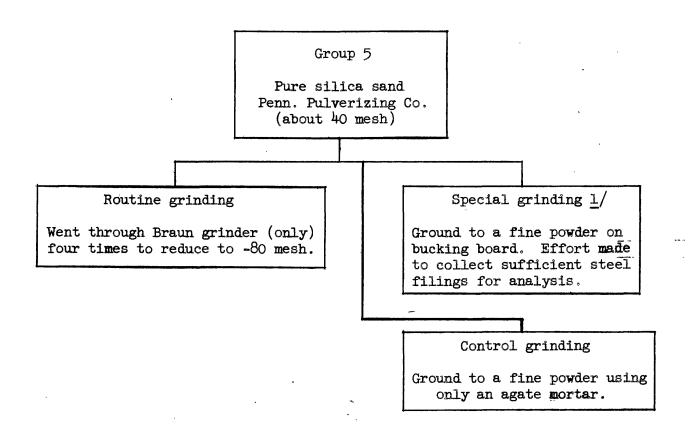


Figure 4.--Flow diagram of treatment of perthite samples, group 4



1/ As mentioned in the text "Special grinding" means only that an effort was made to grind off sufficient bucking-board steel for spectrographic analysis.

Figure 5.--Flow diagram of treatment of pure silica sand, group 5

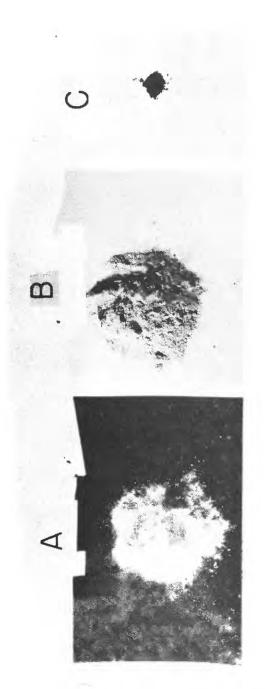


Figure 6. -- Differences in contamination as a result of grinding a perthite sample by two methods.

- shows the white powder (perthite) crushed in a diamond mortar, then ground in an agate mortar. ۷I
- shows the dark-gray powder (perthite) resulting from grinding in heavy machinery. <sub>α</sub>
- This represents only the amount of steel from grinding that was not shows iron filings separated by a magnet from a sample similar to B. tightly attached to the finely powdered sample. Ol

(The powder in A was too white to show against a white background.)

two groups (groups 1 and 2) were compared to determine whether there were any differences in the elements that occur in steels between routine grinding and control grinding.

The quantitative data, given to one significant figure, are presented in tables 1, 2 and 3. A densitometer was employed in obtaining these data. In tables 1 and 2, sample 1A is compared with sample 1B; sample 2A is compared with 2B, 3A with 3B, etc., through 12A compared with 12B. As explained in these tables, the  $\underline{A}$  sample numbers all represent routine grinding and the  $\underline{B}$  numbers represent control grinding. Differences found, if any, between the two methods of grinding are used as a criterion of sample contamination.

In table 3 quantitative results are shown on a massive quartz sample and a quartzite sample that were subjected to a routine and a control grinding. As previously indicated an improved technique was used for the control grinding of these samples. (See figure 3.) In table 3 sample 13A is compared with sample 13C and 14A is compared with 14C. As explained in this table, the A sample numbers will represent routine grinding and the C numbers represent control grinding.

As tables 1 and 2 illustrate, seven elements were determined quantitatively for the six sample comparisons for each table. If all the elements for all six comparisons showed contamination due to routine-grinding procedures, there would be a total of 42 comparisons in each table where contamination could be demonstrated by the quantitative data. Actually our data show that contamination due to routine grinding occurs in 19 comparisons for the six hard-rock samples and 29 comparisons for the six unconsolidated sediments. There were only four comparisons showing greater contamination by control grinding, one for molybdenum and three for copper.

All of these occurred in the first group of samples (table 1). The increases in metal content due to routine grinding shown in tables 1 and 2 are summarized in table 4.

The quantitative data presented in table 3 show further evidence of sample contamination by heavy grinding machinery as illustrated in tables 1 and 2. The data of tables 1 and 2 when compared to the data in table 3 shows the contamination to be roughly of the same order of magnitude (except for Mn in the hard rocks) even though control grinding was not under perfect control for the rock samples of tables 1 and 2.

It must be emphasized that each of the three groups of samples--group 1, group 2, and group 3--were ground at different times (weeks and months apart) by the heavy grinding machinery (routine grinding) so that different grinding plates varying in composition were undoubtedly involved. No direct analysis was made of the different grinding plates. However, the data in table 6 indicate there are differences in composition of the "tramp iron or steel filings" that were separated from the sample by the Alnico magnet. Sample numbers 4 and 5 in table 6 were ground by the same steel plate (Braun) and the analysis of their filings shows an indentical composition.

Table 1.--Quantitative spectrographic analysis to determine contamination of group 1 samples by routine grinding.

of quartz, pyrite, and altered rock. Samples collected by Frank Moore and Douglas Sheridan of the U. S. Geological Survey.) (Hard-rock material from veins in a monzonite stock from the Front Range, Colo. A mixture

| Sample description  | Sample no.                                   | Cr     | Mo              | Cu                                    | Percent<br>Co   | ŊŢ                     | Mn         | Λ              |
|---|--|--------|-----------------|---------------------------------------|-----------------|------------------------|------------|----------------|
|   |  |        |                 |                                       |                 |                        |            |                |
| Lead-silver vein with<br>quartz and carbonate<br>minerals | 1A<br>1B 2/                                  | 0.002  | 0.005           | 0.002 0.004<br>0.003 <u>3</u> / 0.004 | ,00.00<br>400.0 | 0.001                  | 0<br>4 ど。  | 0.003          |
| Altered monzonite<br>wall rock                            | 2A<br>2B                                     | 0.0003 | 9000°0          | 0.003                                 | 0.003           | 0.0007                 | ٥,0<br>د.٥ | 0.003          |
| Altered monzonite<br>wall rock                            | 7. A. S. | 0.0003 | 9000.0          | 0.0001 0.001<br>0.0002 <u>5</u> /0.03 | 0.001           | 0.0005<br>0.000¢       | ٠.<br>١٠٥  | 0.002<br>0.003 |
| Altered monzonite<br>wall rock                            | . <b>У</b> †                                 | †000°0 | 0.001           | 0.001 0.003<br>0.003 <u>3</u> / 0.002 | 0.003           | 0.001                  | ٥ o<br>۵ d | 0.003          |
| Lead-silver vein with<br>quartz and carbonate<br>minerals | 5.A<br>57B                                   | 0.0004 | 0.002           | 0.1<br>0.1                            | 0.002           | 0.00 <sup>4</sup> 00.0 | 0.09       | 0.003          |
| Altered monzonite<br>wall rock                            | 6A<br>6B                                     | 0.001  | 0.002<br>0.0004 | 0.1                                   | 0.002           | 0.002                  | 00<br>ون   | 0.005          |

 $\frac{1}{2}$  A samples were subjected to routine grinding.  $\frac{2}{2}$  B samples were subjected to control grinding.  $\frac{2}{2}$  The only increases shown by control grinding.

Table 2. -- Quantitative spectrographic analysis to determine contamination of group 2 samples by routine grinding.

Split samples supplied by Frank Moore and Douglas Sheridan of (Auger-drill samples of unconsolidated Tertiary sediments containing fluorescent material from Sweetwater County, Wyo. the U. S. Geological Survey.)

| Sample description                      | Sample no.                    | Cr              | Mo                   | Cu              | Percent<br>Co | ľN              | Mn    | Λ      |
|---|-------------------------------|-----------------|----------------------|-----------------|---------------|-----------------|-------|--------|
| Gray-green clayey sand                  | 7A <u>1/</u><br>7B <u>1</u> / | 0.002           | 0.001                | 900.0           | 0.01          | 0.003           | 0.01  | 0.003  |
| Brown clayey sand                       | 8A<br>8B                      | 0.003           | 0.0007               | 0.007           | 0.015         | 0.003           | 0.01  | 0.003  |
| Green-gray silty<br>arkosic sand        | 9A<br>9B                      | 0.002           | 0.001                | 0.005           | 0.01          | 0.003           | 0.009 | 0.002  |
| Gray-green silty<br>pebbly sand         | 10A<br>10B                    | 0.001           | 0.0005               | 0.005           | 0.004         | 0.002<br>0.0002 | 0.006 | 0.002  |
| Gray-green silt and<br>brown sandy clay | 11 <b>A</b><br>11B            | 0.003           | Trace $-\frac{5}{4}$ | 0.004           | 900°0         | 0.0005          | 0.006 | 0.005  |
| Dark-gray to brown-<br>gray sandy silt  | 12 <b>A</b><br>12B            | 0.0004<br>Trace | 0.0003               | 0.002<br>0.0001 | 0.001         | 0.002<br>Trace  | 0.005 | 0.0008 |
|   | •                             |                 |                      |                 |               |                 |       |        |

 $\frac{1}{2}$  A samples were subjected to routine grinding.  $\frac{2}{2}$  B samples were subjected to control grinding.  $\frac{2}{3}$  Looked for but not found.

Table 3. -- Quantitative spectrographic analysis to determine contamination of group 3 samples by routine grinding.

ģ Collected in Coal Creek Canyon, Colo., Route 119, (A massive quartz and a quartzite of high uniformity and low minor-element content collected Frank Moore and Douglas Sheridan of the 10 5. Geological Survey. specifically to test grinding equipment.

| •  |                                  |              |        |        |                  |                 |                  |             |
|--|----------------------------------|--------------|--------|--------|------------------|-----------------|------------------|-------------|
| Sample description                           | Sample no.                       | Cr.          | Mo     | Cu     | Percent<br>Co Ni | Mn              | Λ                | 다.<br>9     |
| Coal Creek quartzite<br>Coal Creek quartzite | 13A <u>1</u> /<br>13C <u>2</u> / | 0.0010       | 0.0013 | 0.0015 | 0.0002 0.0028    | 42.00°0 8:      | 0.0009<br>0.0004 | 1.3         |
| Contamination                                |                                  | 0.0009 0.001 | 0.001  | 0.002  | 0.0002 0.003     | 900.0           | 0.0005 0.9       | 6.0         |
| Massive quartz<br>Massive q <b>uar</b> tz    | 14 <b>A</b><br>14C               | 0.0013       | 0,002  | 0.0016 | 0.0005 0.0055    | 0.012<br>0.0023 | 0.0007           | 1.5<br>0.04 |
| Contamination                                |                                  | 0.001        | 0.002  | 0.001  | 900°0 €000°0     | 0.010           | 0.0007 1.5       | 1.5         |

grinding, using a new and better technique. A samples were subjected to routine grinding. samples were subjected to control Looked for but not found HIGIM

Table 4.--Number of sample comparisons by the quantitative method that show increased metal content due to routine grinding.

| Element | Group 1<br>(Six hard-rock<br>samples) | Group 2<br>(Six unconsolidated sedimentary samples) |
|---------|---------------------------------------|---|
| Ni      | 5                                     | 6   |
| Мо      | J+ <u>T</u> /                         | 6   |
| Cr      | 3                                     | 3   |
| Co      | 1                                     | ц   |
| V       | 2                                     | 0   |
| Cu      | o <u>1</u> /                          | 6   |
| Mn      | 4                                     | 4   |
| Total   | 19                                    | 29*   |

<sup>1/</sup> Preparation by control grinding caused an increase in Mo content for one other sample comparison and an increase in Cu for three sample comparisons.

Note: A densitometer was used to obtain quantitative data to show differences, if any, in the actual metal content between the two methods of pulverizing the rock sample. The actual metal content is shown to one significant figure in tables 1 and 2.

# Semiquantitative analysis

# (Powers of 10)

In semiquantitative determinations (table 5) on the six sample comparisons of group 1, it is clear that the increased metal content was due to routine grinding with the exception that preparation by control grinding an increase in Mo content for one comparison. The number of comparisons showing specific metal increases are as follows: three for Ni; two for Mo; one for Cr; and one for Mn. Thus a total of seven comparisons show an increased metal content due to routine grinding.

Comparisons of the six samples of group 2 also show an increase in metal content that is due to routine grinding. The number of comparisons showing specific metal increases are as follows: four for Ni; six for Mo; two for Cr; two for Co; two for Cu; and one for Mn. A total of 17 comparisons show an increased metal content due to routine grinding (see table 5).

#### Chemical and radiometric analysis for uranium

Radiometric and chemical determinations were made on all the samples of groups 1, 2, and 3 to determine whether uranium was added to the sample as a contaminant. The results in table 6 show that under the conditions of grinding of the above samples no uranium was added in the routine grinding.

Table 5.--Number of sample comparisons by the semiquantitative method that show increased metal content due to routine grinding.

| Element | Group 1<br>(Six hard-rock<br>samples) | Group 2<br>(Six unconsolidated<br>sedimentary samples) |
|---------|---------------------------------------|--|
| Ni      | 3                                     | 4  |
| Мо      | 2 <u>1</u> /                          | 6  |
| Cr      | 1                                     | 2  |
| Co      | 0                                     | 2  |
| Ÿ       | 0                                     | 0  |
| Cu      | 0                                     | 2  |
| Mn.     | 1.                                    | 1  |
| Total   | 7                                     | 17   |

Note: The quantitative data of tables 1 and 2 are here converted to a semiquantitative or order-of-magnitude basis. The order of magnitude is expressed by x.o, o.x, or o.oox, etc. The number 3 in column one opposite Ni means that of six sample comparisons for Ni three comparisons showed an increase in the order of magnitude due to routine grinding.

<sup>1/</sup> Preparation by control grinding caused an increase in the Mo content for one other sample comparison.

Table 6.--Radiometric and chemical analyses for uranium to determine contamination of samples by routine grinding.

|            | 1 Samples d rocks) | ,             |            | 2 Samples<br>ated sedimer | its)          |
|------------|--------------------|---------------|------------|---------------------------|---------------|
| Sample no. | <u>% eU 1</u> /    | <u>% U 2/</u> | Sample no. | <u>% eU</u> <u>l</u> /    | <u>% U 2/</u> |
| 1A         | 0.004              | 0.0011        | ` 7A       | 0.007                     | 0.004         |
| 1B         | 0.005              | 0.0011        | 7в         | 0.006                     | 0.004         |
| 2A         | 0.004              | .0.0008       | 8 <b>a</b> | 0.021                     | 0.044         |
| <b>\$B</b> | 0.003              | 0.0007        | 8в         | 0.023                     | 0.047         |
| 3A         | 0.006              | 0.0008        | 9 <b>A</b> | 0.005                     | 0.006         |
| 3B         | 0.006              | 0.0009        | 9в         | 0.005                     | 0.004         |
| 14A        | 0.005              | 0.0009        | lOA        | 0.906                     | 0.005         |
| $_{ m 4B}$ | 0.004              | 0.0008        | 10B        | 0.007                     | 0.006         |
| 5 <b>A</b> | 0.001              | 0.0010        | 11A        | 0.037                     | 0.080         |
| 5B         | 0.001              | 0.0010        | 11B        | 0.037                     | 0.081         |
| 6 <b>A</b> | 0.004              | 0.0015        | 12A        | 0.003                     | 0.000         |
| 6в         | 0.004              | 0.0016        | 12B        | 0.004                     | 0.000         |

Group 3 Samples (one quartzite; one quartz)

| Sample no.                | % eU 1/ | 10 2/          |
|---------------------------|---------|----------------|
| 13A                       | 0.001   |                |
| 13C                       | 0.000   |                |
| 1 <sup>1</sup> 4 <b>A</b> | 0.000   | <b>***</b> C23 |
| 14C                       | 0.000   | · ·            |

 $<sup>\</sup>underline{1}/$  Radiometric determinations by Sylvia Furman of the Trace Elements Section Denver Laboratory.

 $<sup>\</sup>underline{2}/$  Chemical U determinations by George Boyes and Wayne Mountjoy of the same laboratory.

#### CONCLUSIONS

When Braun and McCool pulverizers are used to grind rock and ore samples, contact with steel may result in contamination. Although the idea of sample contamination involved in this processs is not new, no significant quantitative data have been presented to show the relative importance of the minor-element increase under routine working conditions. Contamination may occur, at least for the elements Co, Cu, Cr, Fe, Mn, Mo, Ni, and V, when samples are subjected to the usual mechanical grinding. The steel plates of the machinery are the main source of these elements as contaminants, and the element Fe may be added to the sample in even larger amounts.

The results suggest that a "bucking board" could also introduce many of the same minor elements that contaminate rock samples pulverized in Braun and McCool grinders. The nature and quantity of contaminating elements, however, may vary widely depending upon the composition of the steels in the grinding machinery which are in contact with the rock sample during the pulverizing action. Other factors governing the amount of contamination are the extent of the abrasive action and the hardness of the rock, as well as the length of time of contact between steel and rock particles.

When a feldspar (perthite) and silica sand were used as a test material on the heavy grinding machinery, the amount of iron accumulated as a contaminant was 1.2 percent for silica sand and varied from 0.5 to 0.6 percent for perthite.

Great care should be exercised in handling samples to prevent contamination when the samples are intended for spectrographic analyses

for the minor or trace elements.

The use of a Braun grinder with one set of grinding plates added certain elements as contaminants to samples of quartz and quartzite in the following amounts: Quartz sample - Cr 10 ppm, Mo 20 ppm, Cu 10 ppm, Co 3 ppm, Ni 60 ppm, Mn 100 ppm, V 7 ppm, and Fe 15,000 ppm; Quartzite sample - Cr 9 ppm, Mo 10 ppm, Cu 20 ppm, Co 20 ppm, Ni 30 ppm, Mn 60 ppm, V 5 ppm, and Fe 9,000 ppm.

There are other ways in which steel or metals may have been added to rock samples during collection in the field (from chisels, hammers, and galvanized containers), and they should be avoided as much as possible. When using samples from drill cores, one should recognize that metal from the drills is probably added to the exterior surface of the sample.

#### REFERENCES

- Ahrens, L. H., 1950, Spectrochemical analysis, Addison-Wesley Press, p. 38.
- Huleatt, W. P., 1950, Automatic sample preparation saves time and money for U. S. Geological Survey: Eng. and Min. Jour., vol. 151, no. 6, pp. 62-67.
- Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., 1931, Chemical analysis of iron and steel, John Wiley and Sons, New York.
- Sandell, E. B., 1947, Contamination of silicate samples crushed in steel mortars: Ind. and Eng. Chemistry, Anal. Ed. 19, p. 652.
- Washington, H. S., 1930, The chemical analysis of rocks, John Wiley and Sons, pp. 79-83.

#### APPENDIX

# Spectrographic method

### Apparatus

Excitation source

Applied Research Laboratories, multisource interrupted d-c arc.

Spectrograph

Jarrell-Ash, 21-foot, Wadsworth-mounted grating.

Intensity control

Applied Research Laboratories neutral filters.

Densitometers

Applied Research Laboratories and Jarrell-Ash.

Development equipment

G.E. X-ray Corporation one-gallon tank; Applied Research Laboratories plate washer and drier.

Electrode cutters

A. Tool designed (A. T. Myers) to cut 1/4-inch lower electrodes (outside diameter 0.24 inch; inside diameter 0.22 inch; depth of crater 0.16 inch; depth of shoulder 0.40 inch; bottom of cavity is an inverted, flattened, truncated cone.)

B. Tool designed (ARL no. 2380A) to cut hemispherically tipped upper electrode.

# Procedure

The following multisource and plate-processing conditions were used:

| Capacitance                     | 60 microfarads                      |
|---------------------------------|-------------------------------------|
| Inductance                      | 400 microhenries                    |
| Resistance                      | 15 ohms                             |
| Initiator                       | Low                                 |
| Phase                           | 90°                                 |
| Strike                          | Strike position                     |
| Amperes                         | 12                                  |
| Spectrograph                    | Jarrell-Ash                         |
| Distance from electrode to slit | 72.2 cm                             |
| Slit                            | 25 microns                          |
| Optics                          | Arc image focused on grating        |
| Emulsion                        | III-O (Eastman)                     |
| Development                     | 4 minutes at 20°C $\pm$ 1/2°C, DK50 |
| Gap                             | 5-6 mm                              |
| Transmission                    | 50 percent                          |

A 10-mg charge of each unknown sample was weighed on a Roller-Smith torsion balance, mixed thoroughly with two parts of pure graphite in the weighing pan, and transferred to the electrode cavity. The samples were arced for 120 seconds and the spectra recorded on III-O Eastman plates.

Standards containing six or eight elements in concentrations of 1.0, 0.32, 0.1, 0.032, 0.01, 0.0032, 0.001, and 0.00032 percent were prepared in a powdered matrix of pegmatite-like composition consisting of

A 10-mg charge of each standard was weighed out and treated like the above unknown samples. The spectra of these standards were recorded on plates--referred to as standard plates--under exactly the same conditions as used on the unknown samples.

The spectra of the unknown samples were analyzed by two methods found useful in trace-elements work. In the semiquantitative method visual matches are made between a given line of the unknown sample and the same line on the standard plate. The results are expressed in powers of 10. In the quantitative method analytical curves are drawn from the standard plates and from standards exposed on plates with the samples by plotting the densitometer reading of light transmission for a given element line against element concentration. The densitometer values of light transmission for the same element line in the unknown sample are obtained and the concentration of that element determined from the analytical curve. The result is expressed to one significant figure. The rock samples of groups 1 and 2 were analyzed by both methods for Ni, Mo, Cr, Co, V, Cu, and Mn. The quantitative results are given in tables 1 and 2.

The iron filings taken from the two perthite samples of group 4 and the silica sample of group 5 and the quartz and quartzite samples of group 3 were diluted, 1 to 4, in a quartz perthite-hematite mixture and analyzed for Mn, Cr, Ni, Mo, V, Co, Sn, and Cu, using the abovementioned standards. These data are shown in table 7. The analysis was refereed by the inclusion of a sample of a Bureau of Standards analyzed steel (B.S.-807) diluted in like manner in a quartz-perthite-hematite mixture.

<sup>4/</sup> The preparation of the standards is patterned after a method in use by K. J. Murata, U. S. Geological Survey.

Table 7.--Partial spectragraphic analysis of steel filings removed from samples with an Alnico magnet.

| 1   | Sample                       |      |      |       | Per   | Percent |             |       |      |
|-----|------------------------------|------|------|-------|-------|---------|-------------|-------|------|
| No. |                              | Mn   | Cr   | Ni    | Mo    | Λ       | င့          | Sn    | Cu   |
|     |                              |      |      |       |       |         |             |       |      |
| Н   | Perthite (Routine grinding)  | 1.0  | 0.27 | 0.071 | 0.035 | 0.018   | 0.018 0.021 | 0.018 | 0*15 |
|     |                              |      |      |       |       |         |             |       |      |
| α   | Perthite (Routine grinding)  | 0.63 | 24.0 | 760.0 | 0.035 | 0.030   | 0.050 0.014 | 0.023 | 0.09 |
| 8   | Silica sand (Bucking board)  | 0.65 | 64.0 | 0.045 | 0.012 | 0.020   | 0.018       | 0.016 | 0.17 |
| 4   | Quartz                       | 0,40 | 800  | 0.14  | 0.08  | 40.0    | 0.01        | 0.005 | 90.0 |
|     | (Routine gringing)           |      |      |       |       |         |             |       |      |
| 7   | Quartzite (Routine grinding) | 0,40 | 0.05 | 0.14  | 0.08  | 40.0    | 0.01        | 0.005 | 0.08 |

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Total iron was determined chemically on two samples of perthrite that had been ground in the heavy grinding machinery and two samples of silica sand, one ground in the grinding machinery, the other ground on the bucking board. These results are given in table 8.

Table 8.--Chemical analyses for iron in samples ground by hand, by bucking board, and by routine grinding

Analyst: C. A. Horr

| No. | Sample | Material                      | Routine<br>grinding<br>(percent Fe) | Bucking board<br>grinding only 1/<br>(percent Fe) | Hand grinding in agate mortar (percent Fe) |
|-----|--------|-------------------------------|-------------------------------------|---|--|
| 1   |        | Perthrite                     | 0.61                                |   | 0.03                                       |
| 5   |        | Perthrite<br>(Eugo)           | 0.53                                |   | 0.03                                       |
| 3   |        | Silica sand (Fenn. Pulv. Co.) |                                     | 1.03  | 0.01                                       |
| 4   |        | Silica sand (Penn. Pulv. Co.) | 1.24                                |   | 0.01                                       |

<sup>1/</sup> This does not represent what is meant by control grinding in this paper; it is referred to in fig. 5 as "Special grinding" to collect steel filings from the bucking board.