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Errors in FeO determinations caused by tungsten carbide grinding apparatus

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Recently, Reay (1981) reported on the effects of disc mill grinding on the grain size, carbon dioxide and ferrous oxide contents of rocks and minerals. An additional effect not mentioned is tungsten carbide contamination on ferrous iron determinations. Tungsten carbide acts as a reducing agent during the chemical procedure, producing a false titre of ferrous iron. This problem was found by Ritchie (1968).

In the present study, the ferrous iron procedure used was that of Whipple (1974) using pentavalent vanadium as an oxidizing agent. The tungsten carbide shatterbox was manufactured by Spex Industries (#8504).

Ritchie's result was confirmed when quartz sand was ground in the tungsten carbide shatterbox. Table 1 shows that a large amount of false ferrous iron content was produced, 0.69% FeO at five minutes and 0.77% FeO at twenty minutes shatterboxing. This is a large interference in comparison with typical total FeO contents of many rocks, especially granites, which have an average Fe content of 1.67% (Nockolds, 1954). Ritchie obtained results of 0.42–0.73% FeO with quartz, using chemical procedures with an oxidizing agent. Using Pratt's procedure, which uses no oxidizing agent, he found no interference (but see below).

Another test of the tungsten carbide shatterbox was with the granite WIN-1 (987) (Winnsboro pluton, South Carolina). A second shatterboxing of this rock nearly doubled the apparent FeO content (Table 1). When the strongly acidic vanadium reagent of the Whipple procedure was pipetted into this sample, crackling sounds were heard, and an odor was produced similar to acetylene produced from calcium carbide indicative of tungsten carbide reactivity. The solution contained unreacted tungsten carbide powder.

Fitton and Gill (1970) did not discuss the reactivity of the tungsten carbide powder even though they quote Ritchie's paper. The decreasing curves of FeO content of their samples, ground for increasing periods of time, are partly due to compensation of loss of FeO, due to oxidation, by introduction of reactive tungsten carbide powder from their apparatus. The oxidation loss is greater than is measured. The effects, summarized are: (1) oxidation on grinding in air (low FeO); (2) introduction of varying amounts of tungsten carbide, which is a reducing agent and gives a false titre of ferrous iron (high FeO); (3) varying degrees of 1 and 2;

Effect 3 (above) could produce curves different from those of Fitton and Gill; at times oxidation will prevail over tungsten carbide contamination (low FeO) and at other times the reverse will occur. This is shown by analyses of granites WIN-1 (290) and WIN-1 (620) in Table 1. For the first, oxidation prevails; in the second, tungsten carbide contamination prevails relative to samples handground in an alumina mortar. The greater relative errors (in duplicate samples with three blanks) in the handground samples are caused by inhomogeneity as a result of the less thorough pulverization. They are far more accurate, however, because of lack of systematic error due to oxidation and tungsten carbide contamination.

Any chemical procedure measuring FeO is potentially susceptible to tungsten carbide contamination. Even if the reagents contain no oxidizing agent (pentavalent vanadium in the Whipple procedure), ferric iron from the mineral samples *is* an oxidizing agent which can react with the tungsten carbide, produce ferrous iron in the solution and a false titre. The same can be said for mortars or any other apparatus of carbides, nitrides or borides (i.e., reducing agents) and these should not be employed in the ferrous iron sample preparation. Apparatus of oxidized (unreactive) materials such as agate, quartz, porcelain, mullite or alumina should be used to eliminate the possibility of reduction of ferric iron, pentavalent vanadium, etc., in the procedure. Similarly, rod mills, ball mills, and metal mortars introduce pieces of steel into the sample which are reducing agents and give a

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Table 1. Effects of grinding in a Tungsten Carbide Shatterbox.

	Grinding Time (Min)	Apparent % FeO
quartz sand	0	0.010±0.002
	5	0.690±0.020
	20	0.770±0.000
WIN-1(987)	0	unknown
	20	0.826±0.004
	40	1.428±0.021
WIN-1(290)	hand-ground	1.30±0.005
	20	1.094±0.005
WIN-1(620)	hand-ground	1.12±0.04
	20	1.20±0.004

false titre of ferrous iron (Ritchie, 1968). Also, oxidation on grinding in air can be facilitated by the high temperature of sliding contacts (Bowden and Thomas, 1954). Although Ritchie obtained no titre with quartz using Pratt's procedure (no oxidizing agent), a definite risk is still entailed because of varying amounts of ferric iron and tungsten carbide powder, differing compositions of the tungsten carbide due to batch or brand, and variation in the conditions of the chemical procedure. The loss due to oxidation will still occur. Also, Pratt's procedure does not easily dissolve magnetite and ilmenite, as the Whipple procedure does, Other recommendations for sample preparation are:

1. Never grind more finely than the procedure requires. Hillebrand (1919) recommends no finer than 70 mesh for silicate rocks, which is perhaps a bit coarse. Magnetite and ilmenite, difficult to dissolve in Pratt's procedure, are easily dissolved in Whipple's procedure in one day when 200+ mesh in grain size. Granites need not be ground excessively fine for the Whipple procedure because the common minerals are easily soluble.
2. For samples that are to be mechanically ground, the procedure requires planning depending on the elements to be analyzed. Alumina shatterboxes, for example, will not allow an accurate value for aluminum (Thompson and Bankston, 1970). For ferrous iron, preliminary results indicate that four minutes grinding or less is satisfactory in an alumina shatterbox (Spex Industries, #8505). Alumina contamination was 0.44 wt.% for one trial of quartz ground in an alumina shatterbox for four minutes. The admonition of Fitton and Gill to grind ferrous iron samples by hand is wise.
3. If one desires to grind under a solvent to avoid oxidation, acetone (Fitton and Gill) is better than alcohol. Traces of alcohol left in the powder can function as a reducing agent and produce a false titre. Acetone is far more inert and volatile.
4. Sulfides cause a false ferrous iron titre because they are reducing agents. Hand grinding of rocks containing sulfides produces the least interference, but grinding for long periods of time oxidizes both the sulfides and silicates (present authors, unpublished data).

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References

Bowden, E. P. and Thomas, P. H. (1954) The surface temperature of sliding solids. Royal Society of London Proceedings Series A, 223, 29–40.

Fitton, J. C. and Gill, R. C. O. (1970) The oxidation of ferrous iron in rocks during mechanical grinding. Geochimica et Cosmochimica Acta, 34, 518–524.

Hillebrand, W. R. (1919) The analysis of silicate and carbonate rocks. U.S. Geological Survey Bulletin 700, 285 p.

Nockolds, S. R. (1954) Average chemical compositions of some igneous rocks. Bulletin of the Geological Society of America, 65, 1007–1032.

Reay, A. (1981) The effect of disc mill grinding on some rock-forming minerals. Mineralogical Magazine 44, 179–182.

Ritchie, J. A. (1968) Effect of metallic iron from grinding on ferrous iron determinations. Geochimica et Cosmochimica Acta, 32, 1363–1366.

Thompson, G. and Bankston, D.C. (1970) Sample contamination from grinding and sieving determined by emission spectroscopy. Applied Spectroscopy, 24, 210–219.

Whipple, E. R. (1974) A study of Wilson's determination of ferrous iron silicates. Chemical Geology, 14, 223–238.

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