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# Using Powder X-ray Diffraction in the Undergraduate Curriculum to Determine Total Iron in Rocks and Minerals

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## ABSTRACT

We developed a simple X-ray diffraction (XRD) method to measure the iron content of rocks and minerals up to 10 weight percent Fe (total iron as Fe) which can be used routinely in undergraduate mineralogy and petrology courses. The method is based on the linear relationship between powder X-ray fluorescence intensity background and the wt% Fe in the sample. Using analytical rock standards with known total iron contents G-2, GSP-1, AGV-1, BCR-1, W-1 and Or-1, we established a calibration curve by plotting the X-ray fluorescence intensity background against wt% total Fe. We tested the method using several rock samples with known total Fe contents and found that it predicts the iron content of samples with an accuracy of  $\pm 10$  wt% of the amount present. It is very easy to teach undergraduate students how to use this technique and to develop lab exercises where they can test different hypotheses based on iron content of rock samples.

**Keywords:** Apparatus; geochemistry; education – undergraduate; petrology – general; mineralogy and crystallography.

## Introduction

In most geology departments, undergraduate students are introduced to XRD methods early in mineralogy or petrology courses (Brady and Boardman, 1995; Horton, 1994). In undergraduate mineralogy and petrology classes, students learn to identify minerals in rock powders using the powder X-ray diffraction method. They can also use XRD to measure sizes of atoms, determine chemical compositions

of minerals in solid solutions, and monitor phase transformations (Brady, Newton and Boardman, 1995). In this paper, we describe a new method for determining the total iron content of mineral and rock samples using an X-ray diffractometer. The method expands the utility of XRD by undergraduate students and allows them to combine chemical and mineralogical data to test hypotheses.

Although there are a number of well known methods for determining the total iron content of rocks and minerals, the methods either require specialized research equipment or extensive analytical experience. These analytical methods include, but are not limited to, wet-chemical analysis, X-ray fluorescence, Mossbauer spectroscopy, ICP, INAA, SEM, AAS and electron microprobe (Wilson, 1960; Carmichael and others, 1968; Mysen and Virgo, 1985; Virgo and others, 1983).

X-ray diffraction has primarily been used to identify minerals in powdered rock samples and to obtain crystallographic data from single crystals. Its use as a tool for analyzing the iron content of samples has not been developed extensively. The purpose of this paper is to discuss the determination of total iron content of rocks and minerals by the powder X-ray diffraction method.

## Analytical Method

It is well known that when Cu-K $\alpha$  radiation is used to bombard a sample with significant amounts of iron, the incident radiation gives rise to fluorescent X-rays which in turn results in a high background in the diffraction pattern (Klug and Alexander, 1954). In this paper we show that the X-ray fluorescence intensity background is linearly proportional to the total iron content of a

sample and that this relationship can be calibrated to quantitatively determine the iron content of rocks. Figure 1 shows the powdered rock diffraction patterns of Or-1 (0.02 wt% Fe), GSP-1 (2.95 wt% Fe) and BCR-1 (9.28 wt% Fe). This figure shows that in the  $2\theta$  interval from  $4^\circ$  to  $60^\circ$ , X-ray fluorescence intensity background increases with increasing total iron content of the sample.

We measured X-ray fluorescence intensities using a Siemens D-500 XRD unit with a copper tube and 0.05 detector slit. The XRD unit was operated at 40 KeV and 30 mA. After removing the filter and the monochromator, we X-rayed the samples at a rate of  $0.05^\circ 2\theta$  per second ( $3^\circ/\text{minute}$ ). We first scanned the analytical rock standards G-2 (1.90 wt% Fe), GSP-1 (2.95 wt% Fe), AGV-1 (4.80 wt% Fe), BCR-1 (9.28 wt% Fe), W-1 (7.73 wt% Fe) and Or-1 (0.02 wt% Fe) from  $4^\circ$  to  $60^\circ 2\theta$  to obtain their diffraction patterns and from each diffraction pattern we selected six points. These points were arbitrarily selected from the part of the diffraction pattern where the X-ray fluorescence intensity background is approximately constant and at some distance away from the immediate vicinity of peaks where intensity is rising or falling. At each of these six points, we collected single-point data for 30 seconds using a scan range of 0.002 degree  $2\theta$  with 0.002 step. We then divided by 30 to convert the intensity to counts per second (Table 1).

## Discussion

When the average X-ray fluorescence intensity background of G-2 (1.90 wt% Fe), GSP-1 (2.95 wt% Fe), AGV-1 (4.80 wt% Fe), BCR-1 (9.28 wt% Fe), W-1 (7.73 wt% Fe), and Or-1 (0.02 wt% Fe) are plotted against their wt% Fe, a straight line is obtained between

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zero and 10 wt% Fe (Figure 2). The linear regression equation for the line is:

$$\text{Wt\% Fe} = 0.0098 * I - 4.1511,$$

where "I" is the average of six readings of the X-ray fluorescence intensity background (in cps).

To determine how accurately this regression equation can predict the total iron content on unknown samples, we used four silicate rock samples with known iron concentrations as unknowns [JB-5 (0.33 wt% Fe), GSP-1 (2.95 wt% Fe), 1921 basalt from Hawaii (8.38 wt% Fe), and a tholeiitic basalt from Hawaii (9.83 wt% Fe)]. Figure 3 shows a plot of actual versus predicted total iron of the four unknowns. Horizontal error bars represent 10% of the amount of iron present in the sample, and the solid line represents the 1:1 line. Figure 3 shows that there is no statistical difference between the predicted and actual iron content of samples which have total iron concentrations ranging from less than one weight percent to about 10 wt%.

The method described has the advantage of being simple and accurate within 10% of the amount present. Since most geology departments are equipped with a x-ray diffraction unit and have access to few analytical rock standards, the method can be easily used by geology undergraduate students in courses such as analytical methods, mineralogy, petrology and geochemistry.

Undergraduate students can utilize the method to solve petrologic problems and to learn about testing hypotheses. For example, students can compare the total iron content of several olivine crystals from a single flow and interpret their data in terms of possible origins of the olivine crystals. Another application of the method is teaching undergraduate students how to test hypotheses.

For these exercises, students must first develop a calibration curve similar to that shown in Figure 2, using at least three (preferably more) analytical rock standards. Once the calibration curve is established, students can obtain powder X-ray diffraction

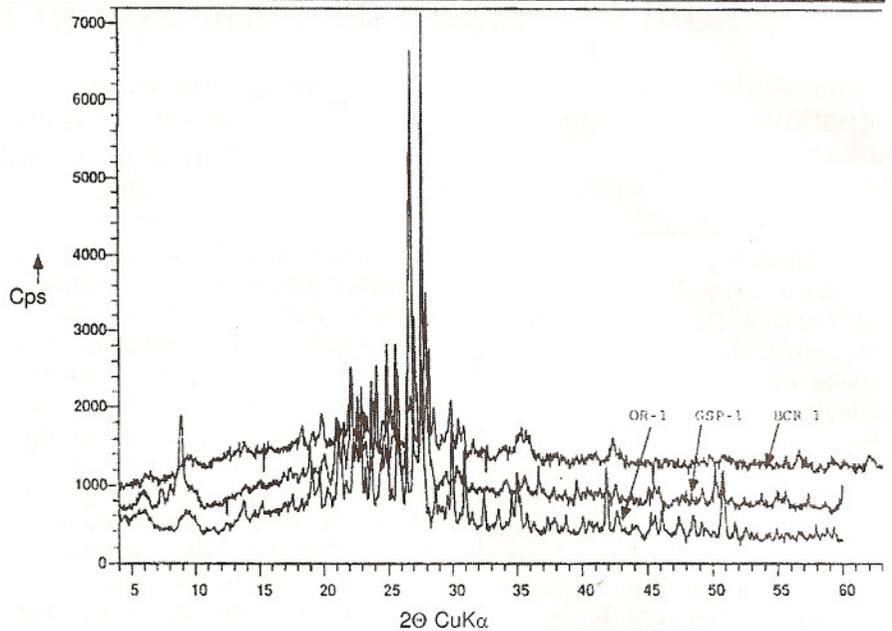


Figure 1. XRD patterns of analytical rock standards showing increasing X-ray fluorescence intensity background with increasing total iron in the samples. Lowermost pattern is for standard Or-1 (0.02 wt% Fe), middle pattern is for standard GSP-1 (2.95 wt% Fe), and the top pattern is for standard BCR-1 (9.28 wt% Fe).

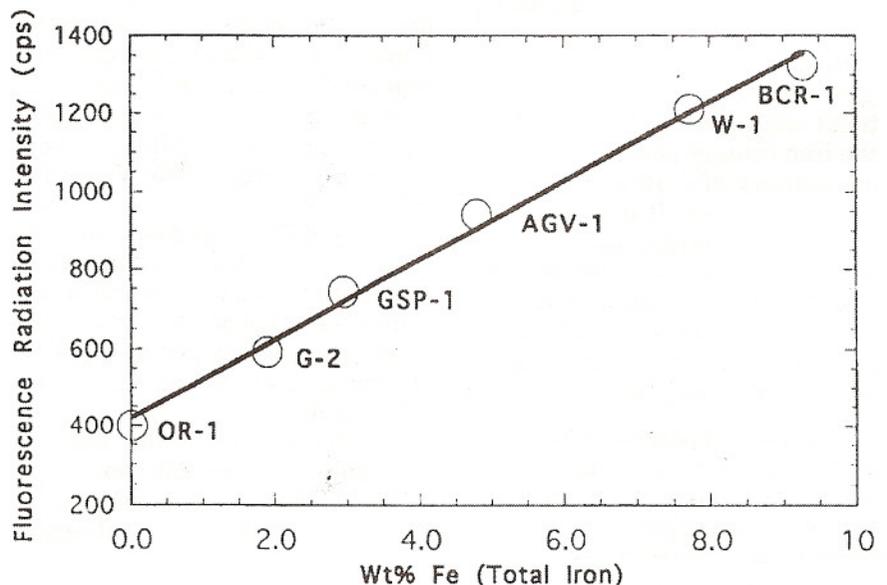
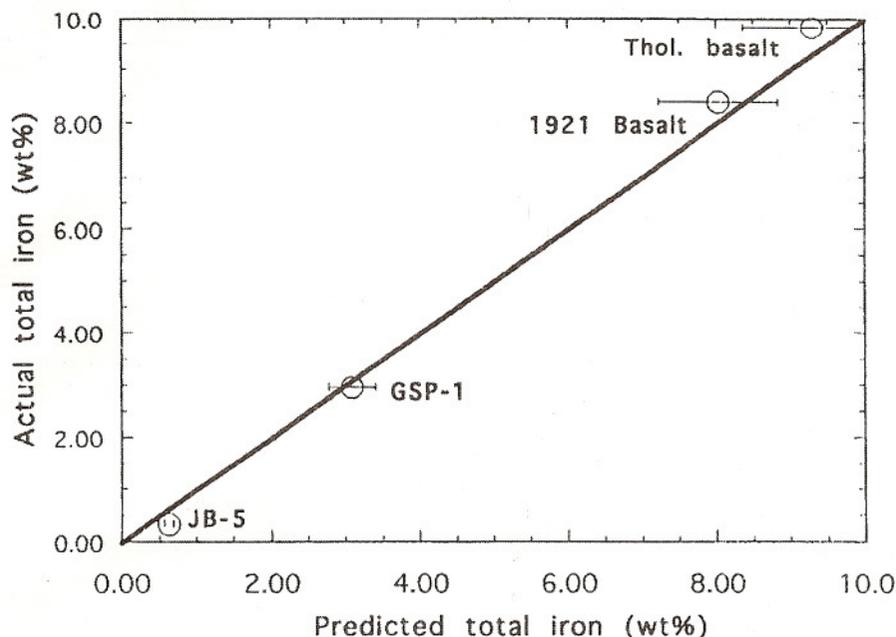


Figure 2. Total iron (as wt% Fe) versus X-ray fluorescence intensity background for the rock standards used in the calibration. The straight line fitted to the data predicts the iron content of unknown samples within  $\pm 10\%$  of the amount present.

	Or-1	G-2	GSP-1	AGV-1	W-1	BCR-1
Average of 6 counts	400	592	742	943	1210	1326
Total Iron (Wt% Fe)	0.02	1.90	2.95	4.80	7.73	9.28

Table 1. Average X-ray fluorescence intensity background for standards (cps) and their total iron content expressed as wt% Fe.



**Figure 3.** Total iron present in the unknowns versus the predicted iron using the calibration curve in Figure 3. Along the solid 1:1 line predicted and actual total wt% Fe are the same. The unknowns from lowest to highest total iron content are JB-5 (0.33 wt% Fe), GSP-1 (2.95 wt% Fe), 1921 basalt from Kilauea volcano, Hawaii (8.38 wt% Fe), #20 basalt from Hawaii (9.83 wt% Fe), and  $\pm 10\%$  of the amount present in each sample is shown by the horizontal lines.

patterns of the olivine crystals and can read the total iron content of each olivine from the calibration curve. If there is more than one generation of olivine in a lava sample, students can be asked to discuss whether their data are due to magma mixing, xenocryst origin of olivines, disequilibrium between olivine and melt, and so forth. Another exercise for students in an elementary petrology course might be the following. In the field, older lava flows from a volcano usually are more oxidized than younger flows, despite the fact that the total iron content of older and younger flows may be the same. The instructor in an elementary petrology course can provide a series of more oxidized and less oxidized basalt samples with similar total iron contents and ask undergraduate students to determine their total iron content by the XRD method described in this paper. Students can visually and analytically see the effect of oxidation on basaltic rocks.

Hypothesis testing is an important aspect of scientific research, and the method we describe in this paper can be used to teach hypothesis testing to undergraduate students. As an example, consider testing the diffusion hypothesis. If iron diffuses from a hydrothermal magnetite or hematite vein into the adjacent wall rock, we would expect the iron content of the wall rock to decrease with increasing distance from the vein. To test this hypothesis students are given a number of rock samples collected with increasing distance from an iron oxide vein and asked to determine the total iron content of the rocks using the XRD method described in this paper. In addition, the instructor can help students to calculate, using the diffusion equation, iron content of host rocks as a function of distance to the vein. Finally, students plot their analytical data (wt% Fe) on the diffusion profile and accept or reject the diffusion hypothesis.

## References Cited

- Brady, J.B., and Boardman, S.J., 1995, Introducing mineralogy students to x-ray diffraction through optical diffraction experiments using lasers: *Journal of Geological Education*, v. 43, p. 471-476.
- Brady, J.B., Newton, R.M., and Boardman, S.J., 1995, New uses for powder x-ray diffraction experiments in the undergraduate curriculum: *Journal of Geological Education*, v. 43, p. 466-470.
- Carmichael, I.S.E., Hample, J., and Jack, R.N., 1968, Analytical data on the U.S.G.S. standard rocks: *Chemical Geology*, v. 3, p. 59-64.
- Flanagan, F.J., 1969, U.S. Geological Survey standards II. First compilation of data for the new U.S.G.S. rocks, *Geochimica et Cosmochimica Acta*, v. 33, p. 81-120.
- Horton, R.A., 1994, X-ray diffraction as an instructional tool at all levels of the geology curriculum: *Journal of Geological Education*, v. 42, p. 452-454.
- Klug, H.P., and Alexander, L.E., 1954, X-ray diffraction procedures for polycrystalline and amorphous materials: Wiley-Interscience Publishers, 966 p.
- Mysen, B.O., and Virgo, D., 1985, Iron-bearing silicate melts: Relation between pressure and redox equilibria: *Phys. Chem. Minerals*, v. 12, p. 191-200.
- Virgo, D., Mysen, B.O., Dankwerth, P.D., 1983, The coordination of Fe<sup>3+</sup> in oxidized vs. reduced aluminosilicate glasses: A <sup>57</sup>Fe Mossbauer study: *Carnegie Institute Washington yearbook*, v. 82, p. 309-313.
- Wilson, A.D., 1960, The micro-determination of ferrous iron in silicate minerals by a volumetric and colorimetric method: *Analyst*, v. 85, p. 823-827.

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