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HANFORD AND COLUMBIA RIVER BASIN BASALTS:
X-RAY CHARACTERIZATION BEFORE AND AFTER
HYDROTHERMAL TREATMENT

Mary Barnes

June 30, 1978

Prepared for Rockwell Hanford Operations
A Prime Contractor to U. S. Department of Energy
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MATERIALS RESEARCH LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY

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1.0 INTRODUCTION

This topical report on basalts is part of the overall project at The Pennsylvania State University on the interactions between basalt and simulated nuclear waste. The objective of the project is to obtain quantitative data to assist in the evaluation of basalts as a nuclear repository host rock, in particular those basalts underlying the Hanford reservation. Knowledge of the characteristics of the basalt and its behavior in the presence of ground water at pressures and temperatures possible in the repository is necessary for the understanding of the system: Basalt Plus Waste Plus Water. This report describes X-ray diffraction data on basalts from the Hanford area.

The interactions between basalt and water at the temperatures which would occur in the immediate vicinity of the waste during the thermal period were the first object of the investigation. These conditions simulate the case in which the canister is not breached, but water has entered the repository.

Secondly, finding the species which control or monitor oxidation-reduction in the system is important, particularly for their effect on uranium and plutonium whose hexavalent species are so much more soluble than the tetravalent ones. Because basalt is present in such excess and because it contains both ferrous and ferric iron, it is likely to act as the oxidation-reduction buffer.

2.0 BASALTS

The two basalts studied are the U. S. Geological Survey's standard Basalt Columbia River-1 (BCR-1) and a section of core from Hanford Drill Hole DDH-3 (A2120/3320). Bulk powder diffractograms were made on the General Electric XRD-7 and the Picker-Siemens #5147. Both have constant potential generators, Cu targets, graphite diffracted-beam monochromaters, scintillation detectors, solid state electronics, and strip chart recorders. Samples were mounted with collodion or Vaseline; some were separated magnetically. National Bureau of Standards' Si was used both as an external and as an internal standard.

2.1 THE MINERALS IDENTIFIED

The minerals identified in these basalts were the plagioclase feldspar, labradorite (and/or andesine), augite, glass, and a solid solution of magnetite and ulvöspinel.

2.1.1 Labradorite

The dominant constituent of the bulk basalt in the X-ray diffractogram is labradorite. Figure 1 shows a portion of a powder pattern of BCR-1. Most of the peaks are due to the triclinic plagioclase feldspar labradorite, or possibly andesine. The particular plagioclase present can be identified by a technique originated by Smith and Yoder⁽¹⁾ and amplified by Smith and Gay⁽²⁾ and Bambauer, *et al.*⁽³⁾ In this method, the difference in position between two peaks in a plagioclase is shown to be a function of the proportion of anorthite in the feldspar. In basalt, the presence of augite masks the peaks enough to obscure the exact composition of the plagioclase; nonetheless, the latter is identifiable as labradorite, or possibly andesine, of composition nearly 50 percent anorthite. (By definition, labradorite contains 50-70 percent anorthite, and andesine 30-50 percent.) This result agrees with the data supplied by Mr. L. L. Ames, Battelle Pacific Northwest Laboratory, in 1976, who found mostly labradorite and some andesine in Basalt DDH-3. Table I shows the assignments of relevant lines for BCR-1; Table II shows the estimated anorthite content of the plagioclase in BCR-1.

2.1.2 Pyroxenes

Six peaks of the pyroxene-augite are identified from the Powder Diffraction File. Mr. Ames gives augite compositions from probe analyses of DDH-3; with the exception of one pigeonite, the compositions he reports are augites and ferroaugites near the center of the pyroxene composition ternary. Powder Diffraction File standards nearest in composition are 24-203, augite, and 24-201, called augite, but really a ferroaugite by the definition that ferroaugite has an iron to magnesium ratio greater than one. The augites have a wide range of substitution, so that some variation in peak position is to be expected. Also, pigeonite may co-exist with augite and some was identified by Mr. Ames in DDH-3. The X-ray diffraction patterns fit the two augites better than pigeonite, so it was deduced that augite dominates.

FIGURE 1

A PORTION OF THE X-RAY DIFFRACTOGRAM OF BCR-1

TABLE I

ASSIGNMENTS FOR LABRADORITE IN BCR-1

<u>hkl</u>	<u>Degrees 2θ</u>
220	28.35
1 $\bar{3}$ 1	29.55
131	31.43
2 $\bar{4}$ 1	35.38
2 $\bar{4}$ 1	35.77

TABLE II

ESTIMATED ANORTHITE CONTENT OF PLAGIOCLASE IN BCR-1

<u>Reference</u>	<u>Calculation</u>	<u>% Anorthite</u>
1	$2\theta_{131} - 2\theta_{1\bar{3}1} = 1.88$	50 - 60
3	$2\theta_{131} - 2\theta_{1\bar{3}1} = 1.88$	58 ± 10
3	$2\theta_{2\bar{4}1} - 2\theta_{2\bar{4}1} = 0.39$	58
2	$2\theta_{220} + 2\theta_{131} - 4\theta_{1\bar{3}1} = 0.68$	50 - 55

2.1.3 Glass

A glassy band is present with a maximum 2θ of 22 - 24°.

2.1.4 Magnetite and Related Phases

Mr. Ames obtained microprobe analyses of the opaque minerals in the Hanford basalt. In many cases, he found that the amount of titanium equalled the amount of iron. This occurs only in pure ilmenite. In other cases, there was an excess of iron. He assigned these compositions to magnetite-ilmenite because of the known presence of ilmenite in the other samples, while pointing out that magnetite-ulvöspinel is also possible. In fact, in the high-barium flows, exsolution lamellae of magnetite and ilmenite were seen.

The phase diagram, Haggarty,⁽⁴⁾ shows that in the $Ti^{+4} - Fe^{+2} - Fe^{+3}$ oxide system a solid solution of magnetite-ulvöspinel may occur in equilibrium with a solid solution of ilmenite-hematite. If both solid solutions are present and identifiable, this system is of particular interest because determination of the composition of both solid solutions allows the determination of both temperature and oxidation state of the basalt. Because the basalt is in such excess, it should buffer the oxidation state of the basalt + waste + water system.

The mineral magnetite-ulvöspinel has been positively identified. Four peaks midway between those of magnetite and ulvöspinel are observed in bulk powder patterns of the basalt. Two of these, at $2\theta = 35.1^\circ$ and 42.6° , appear in the part of the powder pattern of basalt shown in Figure 1. When the 2θ values of these peaks were converted to d-spacings and then to cell constants, a_0 , it was found that the cell constants were consistent from peak to peak. The cell constant was then used to calculate the fraction of magnetite in the solid solution, assuming a linear relation between cell constant and composition.

In order to better measure these peak positions, the magnetic fraction of the basalt was separated from the bulk. The ground sample was placed in a petri dish and covered with 2-3 millimeters H_2O . Aluminum foil was crimped over the pole of a large hand magnet and the pole of the magnet was passed over the water so that the foil skimmed the surface. The magnetic particles then moved toward the magnet. The magnet was then held over an evaporating dish, the foil removed, and the magnetized fraction rinsed off into the dish. After evaporation, the sample was weighed, 10 percent by weight of the National Bureau of Standards' Si was added, and the mixture was reground to make the final X-ray sample. One basalt was sieved after grinding and the various fractions were separated magnetically. Every size was satisfactory, except the one with particles greater than $150 \mu m$ (100-mesh). Sieving was not considered necessary thereafter.

The central portion of the X-ray diffractogram of the magnetically separated fraction of BCR-1 is shown in Figure 2. Five strong spinel peaks are present. The cell constant, a_0 , calculated from these data is $8.486\text{\AA} \pm 0.004$. The cell constants of magnetite and ulvöspinel from the Powder Data File are $8.396\text{\AA}$ and $8.538\text{\AA}$ respectively. Assuming a linear relationship between cell constant and composition in the solid solution range, the calculated fraction of magnetite in the solid solution is 0.37 ± 0.03 . Correspondingly, for basalt DDH-3, $a_0 = 8.481 \pm 0.004$ and the fraction magnetite = 0.40 ± 0.03 .

2.2 MINERALS AT THE LIMIT OF DETECTION

An ilmenite-hematite solid solution should, according to phase equilibria, be in equilibrium with the magnetite-ulvöspinel solid solution found above (see Section 2.1.4). Mr. Ames found the ilmenite composition in many Hanford basalts. However, a diligent search for ilmenite-hematite in the present samples has been inconclusive.

To be in equilibrium with the magnetite-ulvöspinel found, the ilmenite-hematite solid solution must be 90-100 percent ilmenite. The predicted peaks with 100 percent relative intensity are between 32.7° and 32.9° , and between 53.2° and 53.4° . The fact that there are possible, but inconclusive, peaks in that region leads to the conclusion that ilmenite-hematite is probably there, but in considerably smaller concentration than the magnetite-ulvöspinel. It would be instructive, in order to understand the oxidation state of the system, to separate out the ilmenite-hematite.

Cristobalite and montmorillonite may also be present at the limit of detection.

2.3 MINERALS NOT FOUND

The following minerals were looked for and not found:

Sulfides	Pyrite, pyrrhotite, troilite, chalcopyrite, chalcocite;
Clays	Nontronite;
Zeolites	Mordenite, heulandite;
Apatites	Chlor-, fluor-, hydroxyapatite.

FIGURE 2

A PORTION OF THE X-RAY DIFFRACTOGRAM OF A MAGNETICALLY SEPARATED FRACTION OF BCR-1

The region below $2\theta = 20^\circ$ has no peaks rising more than 10 percent above background. There is a small (<10 percent), but consistent peak at 2θ about 13.50° attributable to labradorite. Most clays and zeolites diffract strongly in this region. The conclusion is that neither is present in anything but a very low concentration.

3.0 BASALTS AFTER HYDROTHERMAL TREATMENT

X-ray powder diffractograms were made of Basalts BCR-1 and DDH-3 after treatment with 50 percent by weight of Hanford water at 300 bars. Table III shows the run designations, temperatures, times, and reports in which the runs were described.

TABLE III

RUN CONDITIONS FOR HYDROTHERMAL TREATMENT OF BASALTS

<u>Run Designation</u>	<u>Basalt</u>	<u>Temperature (Degrees C)</u>	<u>Time (Days)</u>
58D	BCR-1	100 (94)*	30
56D	BCR-1	300 (280)	28
55D	BCR-1	300 (280)	56
58I	DDH-3	100 (94)	30
11RI	DDH-3	200 (189)	30
56I	DDH-3	300 (280)	28
10RI	DDH-3	400 (368)	30
55I	DDH-3	300 (280)	56

*When the measured temperature varies very much from the nominal temperature, the nominal temperature is reported first and the experimentally observed temperature afterwards in parentheses.

3.1 BASALT MINERALS

Figure 3 shows bar graphs of X-ray diffraction patterns of Basalt DDH-3 before and after hydrothermal treatment. There are no major changes. All the principal labradorite, augite, and magnetite-ulvöspinel lines are still there. Also, the broad glassy band is still present. Some changes in shape and size of shoulders are attributable to sample-to-sample variation.

FIGURE 3

DIAGRAM OF X-RAY DIFFRACTOGRAMS OF BASALT DDH-3 BEFORE AND AFTER HYDROTHERMAL TREATMENT
WITH 50 PERCENT HANFORD GROUND WATER AT 300 BARS FOR 300 DAYS

3.2 SPINELS

There are compositional changes in the ratios of magnetite to ulvöspinel in some cases. These are not large, but are of interest because they reflect a change in oxidation state of the system. The error (standard deviation) in fraction of magnetite due to the error in measurement of the peak positions is only about 0.03 to 0.40. The error due to the presence of other metals substituted for the iron in the spinel is likely to be considerably larger; however, the relative change due to the change in oxidation state during hydrothermal treatment is of much more interest. Increase in proportion of magnetite corresponds to an increase in oxidation state. Figure 4 shows the fraction of magnetite as a function of time of treatment. Basalt DDH-3 shows little change, but BCR-1 is somewhat reduced (less magnetite) after treatment. This may be an experimental artifact owing to the use of steel autoclaves, and the fact that the gold tubes are somewhat permeable to hydrogen at these temperatures and pressures. Figure 5 shows the data for DDH-3 heated at 4 different temperatures. Here again, 2 runs were lower in magnetite; that is, they show a lower oxidation state. There is no demonstrated trend with temperature, so this variation may well also be experimental.

3.3 POSSIBLE NEW PHASES

A new phase was observed in BCR-1 treated with 50 percent Hanford water at 300° and 300 bars for 56 days (Run 55D). The only new peak in the the corresponding X-ray diffractogram is a low angle one, $I/I_0 = 10$ percent, at $2\theta = 11.5^\circ$. It has not been observed before with the possible exception of BCR-1, 50 percent H_2O , 300 bars, 28 days, where there is a low noisy peak between 10.5° and 12° . Clays and zeolites show peaks in this region, and both minerals are expected alteration products of basalts, but no positive identification is possible.

No other new phases are observed in the diffractograms of treated basalts.

4.0 SUMMARY AND CONCLUSIONS

The principal minerals of Basalts BCR-1 and DDH-3 are still present after hydrothermal treatment up to 400°C. No new phases have been observed,

FIGURE 4

FRACTION OF MAGNETITE IN SOLID SOLUTION WITH ULVÖSPINEL IN BASALTS
BEFORE AND AFTER HYDROTHERMAL TREATMENT AT 300°, 300 BARS WITH
50 PERCENT HANFORD GROUND WATER

FIGURE 5

FRACTION OF MAGNETITE IN SOLID SOLUTION WITH ULVÖSPINEL IN BASALT DDH-3 BEFORE AND AFTER HYDROTHERMAL TREATMENT WITH 50 PERCENT HANFORD GROUND WATER FOR 30 DAYS AT 300 BARS AND THE TEMPERATURE INDICATED

with the exception of one in the longest run, 300°C for 56 days. There is not enough of this phase present to give positive identification in the bulk powder diffractogram.

The spinel magnetite-ulvöspinel was observed to change oxidation state under some conditions. Because uranium and plutonium are both far more soluble in the +6 state than in the +4 state, the oxidation state of the system basalt + waste + water is important. The basalt is in enormous excess and contains both ferrous and ferric iron in its spinels and in augite. Together they should be the principal influence on the oxidation state of the system.

Several further X-ray measurements would be useful: first, examination of spinels in runs already made with 2 percent water and with 10x by weight water; second, examination of runs made in an all-stainless system; third examination of the Umtanum Basalt from Umtanum Ridge; fourth, search for ilmenite after further magnetic separation; and; fifth, look for possible changes in both spinels in order to follow the oxidation state in basalt + waste + water.

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