

**Mineral Abundances For Samples from Instrumentation Boreholes
in the Access Drift Scale Test Area (DST) Of The ESF**

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Introduction

Seventeen sub-samples from cores collected from instrumentation boreholes in the Drift Scale Test Area were x-rayed to estimate relative mineral abundances. Because other sub-samples from these cores are being used for thermal expansion measurements, the abundance of minerals that could affect the thermo-mechanical behavior of the rock at elevated temperature is of particular interest. Cristobalite, in particular, undergoes a phase transition and volume change at temperatures (200-250 °C) that could be encountered in the potential repository.

Previous x-ray diffraction analyses of samples from the Exploratory Studies Facility (ESF) (Roberts and Viani, 1997, Viani and Roberts, 1996) utilized the matrix flushing method of Chung (1974) and an internal intensity standard (corundum) to quantify the phases present. Although the method is adequate for obtaining relative abundances, its accuracy and precision is limited by the inherent differences between the external standards used to compute the reference intensity ratio and the phases in the samples. The mineral abundances reported here (Table 1) were estimated using the Rietveld method of whole x-ray pattern fitting (Snyder and Bish, 1989; Young, 1993). The Rietveld method of quantification avoids the use of external standards. This method is based on fitting a calculated x-ray diffraction pattern to the observed pattern over the entire angular range over which data is collected. The calculated pattern is refined by adjusting the quantity of the phases included in the calculation, as well as their crystallographic properties. The method requires identification of all the phases in the sample, as the refined abundances are normalized to 100%. In order to assess the overall accuracy of the method, a known quantity of corundum was added to each sample analyzed.

Mineral quantification involved two steps. First, the phases present in each sample were identified using an XRD pattern processing software program (Jade version 3.0, Materials Data, Inc., Livermore, CA), which utilizes data from the Joint Committee on Powder Diffraction Standards Powder Diffraction File (JCPDS-PDF). After the mineral phases were identified, then the Rietveld method of quantification was employed. A least squares refinement is carried out until the best fit is obtained between the entire observed powder diffraction pattern and the entire calculated pattern based on the crystal structures and lattice parameters of phases determined to be present. The Rietveld analyses were performed using a quantitative XRD software (Siroquant, version 2.0, Sietronics, Australia).

Sample and standard preparation

The samples received were the annular region of cores of approximately 3 inches in length (the center sections were used for thermal expansion tests at Sandia). Each sample was crushed using a hydraulic press to < 1/4 inch, then processed through a flat-plate pulverizer until the entire sample passed a 250- μm sieve. After crushing, the samples were placed in an homogenizer for a period of at least 8 hours. A sub-sample of each was then further ground in a vibratory micro-mill (Fritsch) with a sintered corundum mortar and ball for 30 minutes at $\sim 1/3$ full power using an intermittent power cycle. Particle sizes determined optically by this method were approximately 10 μm or less. The corundum internal standard used in the quantitative analyses (Buchler, 1.0- μm Al_2O_3) was not ground because of its small size. The ground samples were mixed with corundum in a 4:1 ratio, and again placed in the micro-mill for 30 minutes using the power cycles described above. Samples were packed into stainless steel side-mount holders having a sample length of 18 mm and width of 13 mm.

Xray diffractometer instrumental parameters

Xray scans were collected using a Scintag PAD-V generator equipped with a Cu xray tube operated at 45 kV and 35 mA, and a Sieffert goniometer with a solid state detector.

Diffraction patterns were collected in step scan mode at 2 seconds per $0.02^\circ 2\theta$.

Collimation was provide by a 1° divergence and 2° scatter slit on the xray tube and a 0.3

mm scatter and 0.2 mm registration slit on the detector. Samples were scanned from 2-72° 2θ.

Analysis of sample: corundum xray diffraction patterns

Internal calibration

Prior to mineral phase identification and Rietveld analysis, the observed diffraction pattern was corrected for instrumental error based on a calibration curve determined using standard phases. The calibration correction used to correct data from this report was derived by scanning two standards; a fluorophlogopite mica for the low angle peaks (NBS traceable), and a mixture of silicon (NBS traceable)-tungsten-silver metals (SiWA_g) for the high angle peaks. Both standards were scanned with the same instrumental parameters listed in the above section, the mica from 2-72° 2θ; and the SiWA_g from 20-110° 2θ. The two scans were merged into one and a calibration curve built on observed versus NBS and PDF 2θ angles.

Identification of mineral phases present

The Jade pattern processing program was used to identify major and minor mineral phases present in each sample. The Jade program searches located peaks only, and compares them with the strongest lines of a potential phase in the PDF database. The selected peaks are checked visually to confirm realistic phase identification.

Results

Mineral abundances for 17 samples (plus duplicate scans) are shown in Table 1. In most samples, albite, sanidine, and cristobalite are the dominant phases, with lesser amounts of quartz. Tridymite is significant in 3 samples; with cristobalite being less abundant in these samples. Zeolite phases were observed in 3 samples; clinoptilolite in two samples, and stilbite in one sample. Compared to results of previous analyses of ESF samples (Roberts and Viani, 1997, Viani and Roberts, 1996), these samples show similar composition with regard to total silica polymorph content (between 33 and 41 weight %). The quartz and cristobalite contents appear to be inversely related. No samples contained detectable mica

phases. Duplicate scans show excellent reproducibility; the method appears to yield better precision than the matrix flushing method of Chung (1974).

As mentioned above, the total abundance of the silica polymorphs is quite uniform. However, the cristobalite component varies from 4 to 31%. Hence, the thermo-mechanical properties of these samples might be expected to differ significantly at the temperatures over which cristobalite undergoes a phase change.

Discussion

The data in Table I were derived from the quantitative analysis results by subtracting out the estimated abundance of corundum, and normalizing the other phases to the remainder. The estimated abundance of corundum varied between 21.0 and 24.8 percent with a mean of 23.1 ± 1.0 percent. This suggests that there is a systematic overestimate of the corundum abundances by ~3%. A potential explanation is that there is an unidentified crystalline or amorphous phase in the samples with an abundance of ~ 13 percent. Because the fit between the calculated and observed patterns was good, the potential for an unidentified crystalline phase present in this quantity is unlikely. The presence of a small quantity of x-ray amorphous constituent cannot be discounted, but the baseline and background fits to these patterns are very flat and linear over the angular region where a volcanic glass would scatter and it is unlikely that 13 percent amorphous material would be present. An alternative explanation is that the estimates for the feldspar phases are still not accurate, and that there is a systematic underestimation of these phases. In performing the analysis it was observed that the goodness-of-fit statistics for the feldspar phases were always poorer than those for the silica polymorphs. Future work will attempt to obtain better feldspar refinements by allowing the site occupancies and the compositions of the feldspars to vary during the quantification analysis.

References

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Table 1. Mineral abundances⁽¹⁾ for samples from the Drift Scale Test Area of the Exploratory Studies Facility.

Sample #	quartz	crystalite	albite	sanidine	tridymite	zeolite phase	Data file ⁽²⁾
SDM-MPBX1-1.0-1.2-D	12	23	34	32	nd ⁽³⁾	nd	YMP070A
SDM-MPBX1-21.0-21.2-D	10	17	25	35	3	nd	YMP072A
SDM-MPBX1-21.0-21.2-D dup	9	27	25	35	4	nd	YMP072B
SDM-MPBX1-31.9-32.1-D	4	31	32	33	nd	nd	YMP071A
SDM-MPBX1-40.4-40.6-D	20	14	31	29	7	nd	YMP073A
SDM-MP3X1-62.0-D	11	26	27	36	nd	nd	YMP074A
SDM-MPBX1-80.7-80.9-D	12	24	31	33	nd	nd	YMP075A
SDM-MP3X2-29.0-29.2-D	4	31	33	32	nd	nd	YMP076A
SDM-MPBX2-29.0-29.2-D dup	4	29	34	33	nd	nd	YMP076B
SDM-MPBX2-48.6-D	18	18	30	34	nd	nd	YMP077A
SDM-MPBX2-72.0-D	6	28	34	32	nd	nd	YMP078A
SDM-MPBX2-85.0-D	7	26	34	33	nd	nd	YMP080A
SDM-MPBX3-17.5-17.7-D	8	25	33	34	nd	nd	YMP079A
SDM-MPBX3-38.5-38.7-D	5	31	24	40	nd	nd	YMP081A
SDM-MPBX3-85.6-D	11	22	30	34	nd	3 - stilbite	YMP082A
AOD-HDFR#1-9.0-D	13	20	32	34	nd	2 - clinoptilolite	YMP083A
AOD-HDFR#1-9.0-D dup	15	20	31	35	nd	trace - clinoptilolite	YMP083C
AOD-HDFR#1-48.5-D	12	25	26	37	nd	nd	YMP085A
AOD-HDFR#1-68.6-D	12	25	24	39	nd	nd	YMP086A
AOD-HDFR#1-98.0-D	37	4	29	30	nd	nd	YMP084A

(1) Mineral abundances were normalized to 100% after subtracting out the estimated abundance of the corundum standard. Sums may differ from 100% due to roundoff error.

(2) The identification YMP### refers to computer filenames associated with the diffraction pattern data.

(3) nd - not detected