1992

Analysis of Crystalline Phasesby X-Ray Diffraction Effect of Sample Grinding

Jeffrey K. Snyder

Recommended Citation

Snyder, Jeffrey K., "Analysis of Crystalline Phasesby X-Ray Diffraction Effect of Sample Grinding" (1992). *Undergraduate Theses and Senior Projects*. 79.
https://commons.und.edu/senior-projects/79

ANALYSIS OF CRYSTALLINE PHASES BY X-RAY DIFFRACTION: EFFECTS OF SAMPLE GRINDING

by

Jeffrey K. Snyder

A senior thesis
submitted to the faculty of the
Geology Department at the
University of North Dakota
in partial fulfillment of the requirements
for the Bachelor of Science in Geology Degree.

Grand Forks, North Dakota
May, 1992

This Thesis submitted by Jeffrey K. Snyder in partial fulfillment of the requirements for the Degree of Bachelor of Science in Geology from the University of North Dakota is hereby approved by the Faculty Advisor under whom the work has been done.

Frank Karner

(Advisor)

TABLE OF CONTENTS

Page

LIST OF TABLES

Table Page

LIST OF FIGURES

ABSTRACT

Longer sample grinding time results in reduced variation in peak intensities, allowing for precise semi-quantitative X-ray diffraction (XRD) analysis of abundance of crystalline phases; but also creates difficulties by reducing peak intensities and broadening peaks. Grinding samples for an extended period is known to reduce preferred orientation and the particle size in sample mounts. Grinding also increases the number of particles in a sample, which increases the probability of equal representation for all crystal orientations during XRD analyses and reduces the variation of integrated intensities.

Three separate samples of a dolomite-rich dolostone, a quartzose sandstone, and plagioclase-rich gabbro were ground with a tungsten carbide mortar and pestle until each passed through a 230 mesh (63 micron) sieve. The samples were ground in a Spex Mixer Mill from 5 to 60 minutes, packed into side drift plates, and analyzed using a Philips x-ray diffractometer. The computer software programs, Jade and Micro-ID, were used to analyze the XRD data.

The highest intensity peak of dolomite was examined in ten samples with grinding times of 5, 15, 30, and 60 minutes. The coefficient of variation for the mean integrated intensities decreased from 14% at 5 minutes to 5% at 60 minutes; the mean integrated intensity decreased from 1.47×10^5 to 1.03×10^5 counts; and the peak width at half-maximum increased from 0.179 degrees 2-theta to 0.210 degrees 2-theta.

The highest intensity peak of calcic plagioclase was studied in three samples at 0, 15, and 30 minutes of grinding time. The mean integrated intensity decreased from 4.67×10^4 to 3.33×10^4 counts and the peak width at half maximum increased from 0.127 to 0.136 2-theta.

The highest intensity peak of the quartz in the sandstone was examined in 3 samples at 0, 15, and 30 minutes of grinding time. The mean integrated intensity of the quartz samples decreased from 3.48×10^4 to 2.98×10^4 counts and the peak width at half maximum increased from 0.180 to 0.199 2-theta.

Increased grinding time in a Spex Mixer Mill reduced the observed integrated intensities (peak area) and the coefficient of variation of these intensities for all three materials. Increased grinding time also resulted in an increase in peak width. Higher integrated intensities and narrower peaks of more coarsely ground samples aid in qualitative identification of phases present in a sample, but the accompanying highly variable intensities decrease precision in semi-quantitative analysis. Variation in integrated intensities can be minimized by longer grinding. For consistent semi-quantitative results each sample should be prepared in a similar manner to ensure similar particle sizes. For mixtures of minerals with different resistances to grinding, sample preparation must be designed based on project objectives.

INTRODUCTION

X-ray diffraction (XRD) is a widely used analytical technique for obtaining qualitative and semi-quantitative information on crystalline materials (Klug and Alexander, 1974). Mineral identification from X-ray diffraction analysis is possible because each crystalline phase produces its own characteristic pattern of peak intensities and location, independent of the other phases present. While qualitative analysis by x-ray diffraction is well established, semi-quantitative analysis of all but the simplest mixtures of phases is difficult. The eventual goal of semi-quantitative analysis is to decode the compositional information about a mixture that is stored in the XRD pattern (Chung, 1974).

According to the American Geological Institute Glossary of Geology, third edition (1987), "X-ray diffraction is the diffraction of a beam of x-rays, usually by the three dimensional periodic array of atoms in a crystal that has periodic repeat distances (lattice dimensions) of the same order of magnitude as the wavelength of the x-rays." The interplanar spacing of the series (hkl) in a space lattice is the d-spacing (Klug and Alexander, 1974).

The necessary conditions for detecting a crystal lattice is given by Bragg's Law, n lambda = 2 d sin theta, where n is an integer, lambda is the wavelength of the x-ray radiation, d is the lattice spacing, and theta is the angle between the planes of the crystal and the incident beam. This law states that for reflection to occur, the distance travelled by an x-ray through a crystal must equal an integral multiple of the wavelength, therefore diffracted waves are in phase (Klug and Alexander, 1974).

In XRD analysis, sample is placed in the direct path of a beam of x-rays. The direction of this beam is constant, but the sample is rotated about an axis perpendicular to the incident radiation. The angle through which the sample moves is defined as theta, and the scintillation counter on the goniometer moves through an angle of 2-theta. This relationship insures that only one set of oriented crystals will be analyzed (Klug and Alexander, 1974).

In XRD analysis, the peak intensity of a particular phase is proportional to the amount of the phase present in a mixture. The internal standard method using reference intensity ratios (RIR) is the most common method for semi-quantitative x-ray analysis because it essentially eliminates matrix effects. The RIR is the ratio of the highest intensity peak of a single phase analyte to that of an internal standard in a 1 to 1 mix by weight (McCarthy and Thedchanamoorthy, 1989). The RIR method generally uses corundum (Al_2O_3) as an internal standard.

With a mixture of the multi-phase analyte and an internal standard proportioned to be 10 weight percent of the total mixture, the relationship is weight percent of a single phase analyte equals 10 divided by the RIR of that single phase analyte multiplied by the highest intensity peak of the analyte divided by the highest intensity of the internal standard multiplied by 1.11 (McCarthy and Thedchanamoorthy, 1989). The 1.11 converts the results to weight percent in a sample free of internal standard. This equation would have to be applied to each component of interest in a multi-phase mixture.

Chung (1974) detailed this method, which he described as "the adiabatic principle of x-ray diffraction analysis of mixtures", meaning that the intensity to concentration relationship of one phase is not affected by the presence or absence of another phase in the mixture.

The 100 peak of a mineral is the peak of highest intensity. A peak represents the x-ray diffraction of a specific orientation of atomic layers. The Miller indices (hkl) represent the intercept of crystal faces with the crystal axes (Klein and Hurlbut, Jr., 1985).

Several factors make precise and accurate semi-quantitative analysis of XRD results difficult, and these factors include preferred orientation of crystals in samples, particle statistics, primary extinction, microabsorption, and overlapping peaks. The effects of these factors are well understood, but it is not practical to account for all of these effects in XRD analysis.

Preferred orientation in the specimen, which is the tendency of plate-like or needle-like crystals to align in a non-random orientation due to the shape of the crystal, is the most important factor that affects XRD semi-quantitative analysis

(Cline and Snyder, 1983). Reducing the size of the particles is known to reduce preferred orientation. The effects of particle size larger than 5 microns has been clearly demonstrated (Klug and Alexander, 1974), but it is still relatively common for 325 mesh (45 micron) powders to be used for XRD analysis (Davis, 1987).

The powder XRD method depends on all possible orientations of crystals being randomly present in the sample and thus involves particle statistics. If the particles are too large, all orientations in a sample can not be represented. Thus, size has a great effect on diffracted intensities. In addition, the intensities of the same reflection from different specimens may vary depending on the size of crystallites. Large numbers of particles result in equal probability of x-ray diffraction for all sample orientations, thus the variation of the intensities is lowered. When the particle size is in the 5 micron range or smaller, the variation of the integrated intensities is minimized (Klug and Alexander, 1974). Sample rotation improves particle statistics, but does not compensate for preferred orientation (Parrish and Haung, 1983).

Extinction effects cause the reductions in intensities due to secondary reflection of the diffracted beam back into the sample. Primary extinction occurs when atoms are too perfectly ordered in perfect crystals, such as quartz and calcite. In an ideally imperfect crystal, each particle is composed of smaller crystallites, all slightly disoriented with respect to one another. Smaller particle size reduces the effects of primary extinction.

The absorption of x-rays within particles is microabsorption. A significant amount of the x-rays are absorbed when the particle size is large, and thus, the path length of the x-rays within the particles is longer. Reducing particle size by grinding minimizes the need to account for this factor, which arises when materials of different mass absorption coefficient are mixed (Klug and Alexander, 1974). Significant error may result based on particle size and large differences in mass absorption coefficients of the phases in a mixture (Brindley, 1972).

The maximum intensity peaks used in the internal standard method of semi-quantitative analysis must be examined for overlap with other peaks of the same phase, other phases present in the mixture, and the internal standard being used, commonly rutile or corundum (Schreiner and Jenkins, 1983). When key peaks overlap, alternate peaks may be used for analysis. If the alternate peak has a much lower intensity value, this could raise the detection limit. In such a situation, it might be necessary to examine an expanded analytical region. The integrated intensity is the only reliable measure of the reflection intensity (Klug and Alexander, 1974). The use of peak heights rather than the less variable integrated intensity would compound the problems of overlapping and broad peaks in semi-quantitative XRD analysis.

METHODS

A Philips x-ray diffractometer located in the Natural Materials Analytical Lab (NMAL) of the Energy and Environmental Research Center was used for this study, and Cu K alpha radiation of wavelength 1.54178 angstroms was utilized for all XRD analyses. The diffractometer was set at an accelerating voltage of 45 Kv and a current of 40 mA. The machine was allowed to equilibrate for at least one hour before any analysis were started. The machine was set at a step size of .02 degrees 2-theta and a counting time of 1 second, due to time considerations.

A pure dolomite-rich dolostone, a quartzose sandstone, and a plagioclase-rich gabbro were obtained from the Geology 101 sample collection, and ground with a tungsten carbide mortar and pestle until all of the sample passed through a 230 mesh (63 micron) sieve. Approximately 2 grams of each material was ground in a Spex Mixing Mill for times ranging from 5 to 60 minutes. The resulting powders were mounted in aluminum plates using the NBS side drift method (McMurdie et al., 1986). In this method the powder is poured into a cavity in an aluminum plate. The top of the cavity is covered by a glass slide, that is later removed, to give a flat sample surface. The sample is tapped to increase packing density.

The highest intensity peak of dolomite was studied in ten samples each at 5, 15, 30, and 60 minutes of grinding time. This peak is the 100 peak, located at 30.934 2-theta, or at 2.888 d-spacing, and the Miller index for this crystal face is (104). The samples were scanned from 29 to 33 degrees 2-theta. The highest intensity peaks of the calcic plagioclase and of the quartz in the sandstone sample were studied in three experiments each at 0, 15, and 30 minutes of grinding time. The 100 peak was studied for both minerals. The plagioclase peak was located at 28.034 2-theta, or 3.18 d-space, and the Miller index was (002). The quartz peak was located at 26.650 2-theta, or 3.342 d-space, the Miller index was (101). Each of these samples were scanned from 3 to 75 degrees 2-theta. The integrated intensities and peak width at half maximum intensity were determined for all scans using the computer software Jade Plus and Micro-ID.

The mean of the integrated intensities and of the peak width were calculated for each grinding time of each material. The standard deviation and coefficient of variation, which is standard deviation divided by the mean and expressed as a percentage, were also found for the integrated intensity and peak width for each run of the dolomite. These calculations were not performed for the plagioclase and quartz because of the smaller sample size.

RESULTS

The integrated intensities of dolomite exhibited a reduction in the mean, standard deviation and coefficient of variation with increased grinding time (Tables 1 and 2). The peak width of dolomite exhibited an increase in the mean, but the standard deviation and coefficient of variation did not seem to have a clear trend with increased grinding time. The decreasing coefficient of variation for the integrated intensities means that the standard deviation is decreasing more rapidly than the mean of the integrated intensities. The effects of the grinding on the integrated intensities of dolomite seemed most pronounced between 30 and 60 minutes (Figure 1). This change in slope may indicate that there is more than one important factor affecting integrated intensities, and perhaps there is a shift in the importance of the factors between 30 and 60 minutes. The mean peak width shows a definite increasing trend (Figure 2). The coefficient of variation for the integrated intensities of dolomite seems to have a linear relationship with grinding time (Figure 3).

The plagioclase and quartz both showed a reduction in mean integrated intensity and an increase in mean peak width (Tables 3 and 4). Due to the small sample size, standard deviation values were not calculated for plagioclase and quartz. The plagioclase and quartz both showed decreased mean integrated intensity and increased mean peak width (Figures 4-9). The grinding seems to have the least effect on mean integrated intensities for the

Table 1. Integrated intensity, peak width, and calculated mean, standard deviation, and coefficient of variation of the highest intensity peak for ten samples of dolomite (104) with grinding times of 5, 15, 30, and 60 minutes.

SAMPLE:	**D-05**		**D-15**	
	Integrated Intensity (counts)	Peak Width (degrees)	Integrated Intensity (counts)	Peak Width (degrees)
	180567	0.178	168572	0.183
	171865	0.172	162175	0.183
	116886	0.184	150329	0.184
	140679	0.178	138604	0.180
	144725	0.182	137757	0.180
	115663	0.182	110428	0.195
	161319	0.179	138812	0.182
	156880	0.178	139342	0.182
	152552	0.176	175579	0.187
	133406	0.179	147829	0.182
Mean	147454	0.179	146943	0.184
Std. Dev.	20482	0.003	17729	0.004
C. of Var.	13.9	1.800	12.1	2.280

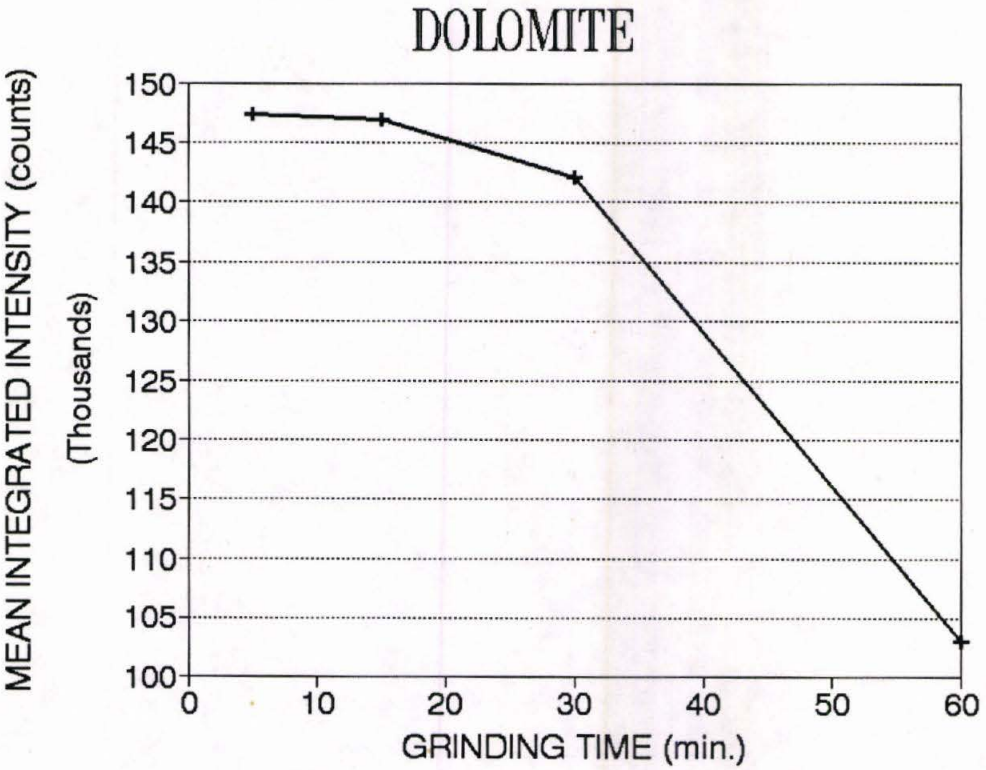
SAMPLE:	**D-30**		**D-60**	
	Integrated Intensity (counts)	Peak Width (degrees)	Integrated Intensity (counts)	Peak Width (degrees)
	167823	0.184	104912	0.213
	140152	0.180	101950	0.212
	144538	0.183	107391	0.211
	155165	0.180	97144	0.208
	135300	0.181	101481	0.211
	138388	0.179	102670	0.210
	140030	0.181	113418	0.207
	137568	0.184	99220	0.210
	115183	0.183	107319	0.210
	146463	0.184	94807	0.207
Mean	142061	0.182	103031	0.210
Std. Dev.	12925	0.002	5190	0.002
C. of Var.	9.1	0.997	5.0	0.915

Table 2. Mean, standard deviation, and coefficient of variation of integrated intensities and peak width of highest intensity peak for dolomite (104) with grinding times of 5, 15, 30, and 60 minutes.

Sample	Mean Integrated Intensity	Mean Peak Width	Std. Dev. Integrated Intensities	Std. Dev. of Peak Width	Coefficient of Variation Integ. Intens.	Coefficient of Variation Peak Width
Dolomite	(counts)	(degrees)			(%)	(%)
5 min.	147454	0.179	20482	0.003	13.9	1.8
15 min.	146943	0.184	17729	0.004	12.1	2.28
30 min.	142061	0.182	12925	0.002	9.1	0.997
60 min.	103031	0.210	5190	0.002	5.0	0.915

Figure 1. Decrease in mean integrated intensity with increase in grinding time for dolomite (104).

Figure 2. Increase in mean peak width with increase in grinding time for dolomite (104).


DOLOMITE
MEAN INTEGRATED INTENSITY (counts)
(Thousands)
150
145
140
135
130
125
120
115
110
105
100
0
10
20
30
40
50
60
GRINDING TIME (min.)

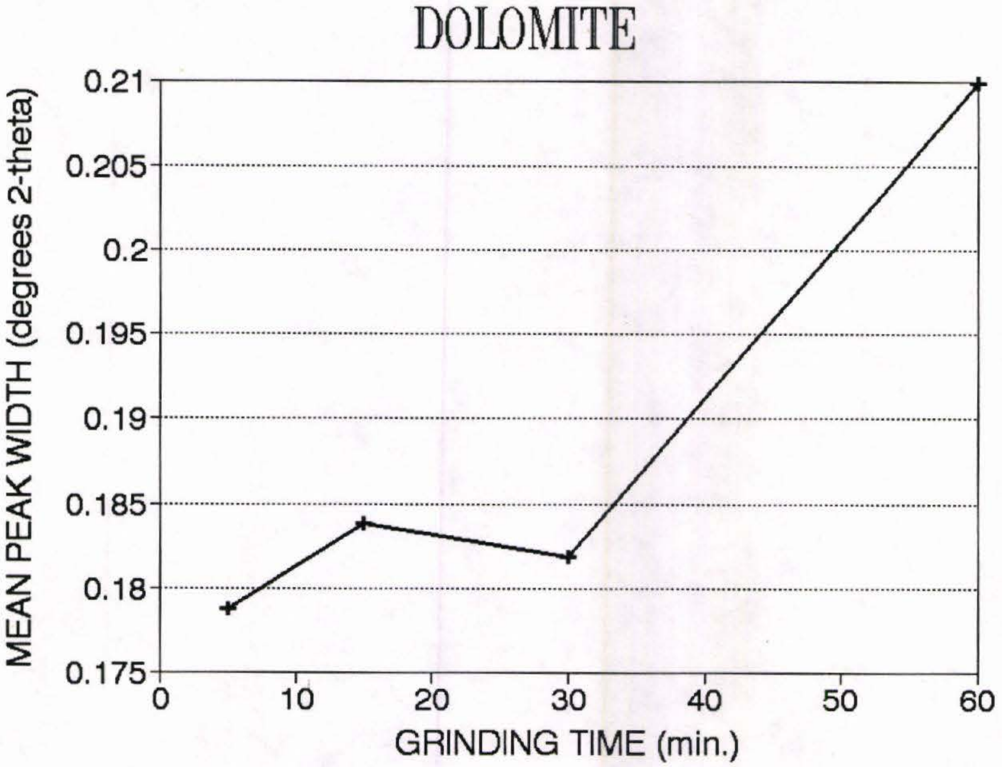

DOLOMITE
MEAN PEAK WIDTH (degrees 2-theta)
0.21
0.205
0.2
0.195
0.19
0.185
0.18
0.175
0
10
20
30
40
50
60
GRINDING TIME (min.)

Figure 3. Decrease in coefficient of variation of integrated intensity with increase in grinding time for dolomite (104).

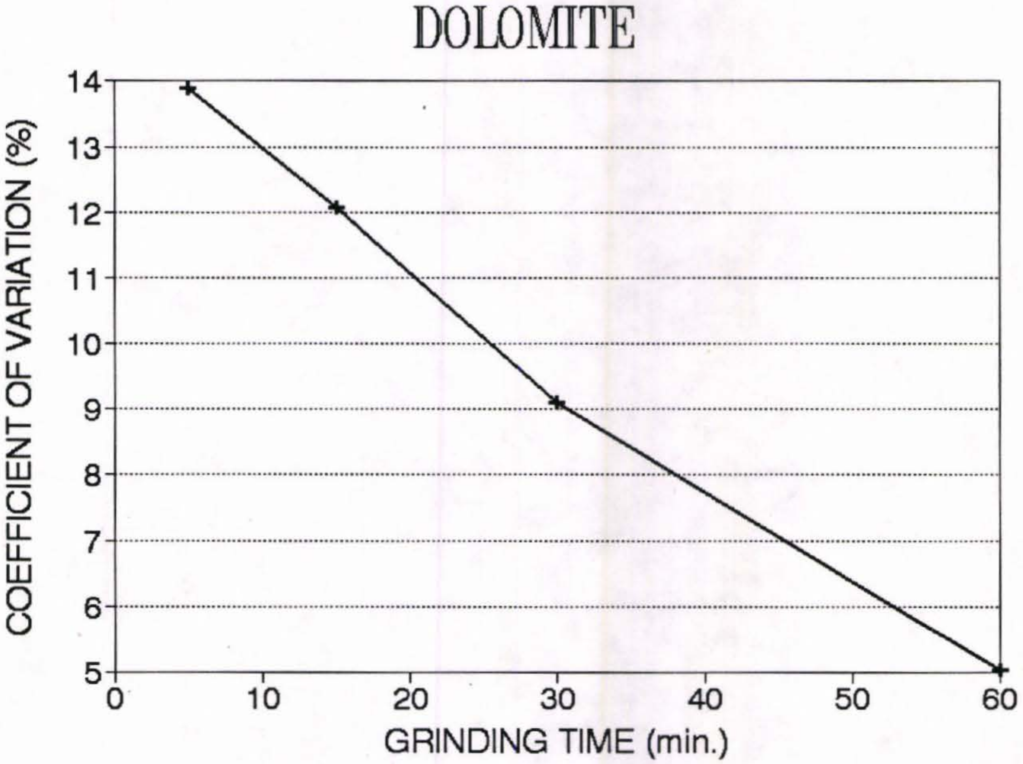

DOLOMITE
COEFFICIENT OF VARIATION (%)
14
13
12
11
10
9
8
7
6
5
0
10
20
30
40
50
60
GRINDING TIME (min.)

Table 3. Integrated intensity and peak width and calculated mean of the highest intensity peak for 3 samples of calcic plagioclase (002) and quartz (101) for grinding times of 0, 15, and 30 minutes

SAMPLE:	**Plagioclase-00**		**Plagioclase-15**	
	Integrated Intensity (counts)	Peak Width (degrees)	Integrated Intensity (counts)	Peak Width (degrees)
	23689	0.129	48816	0.136
	62906	0.124	57907	0.126
	55671	0.128	25651	0.135
Mean	47422	0.127	44124	0.132

SAMPLE	**Plagioclase-30**		**Quartz-00**	
	Integrated Intensity (counts)	Peak Width (degrees)	Integrated Intensity (counts)	Peak Width (degrees)
	51642	0.118	32633	0.179
	21766	0.139	39478	0.165
	26479	0.150	32429	0.197
Mean	33296	0.136	34847	0.180

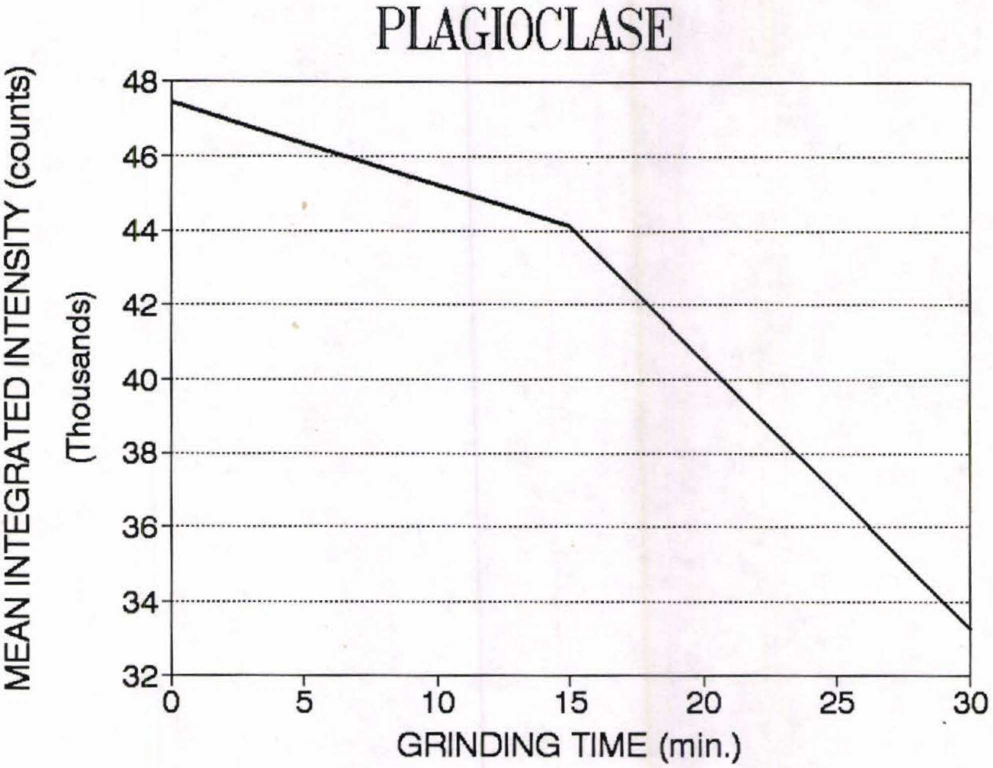
SAMPLE	**Quartz-15**		**Quartz-30**	
	Integrated Intensity (counts)	Peak Width (degrees)	Integrated Intensity (counts)	Peak Width (degrees)
	33820	0.190	31442	0.188
	31076	0.198	27630	0.213
	26747	0.191	30334	0.198
Mean	30548	0.193	29802	0.199

Table 4. Mean of integrated intensity and peak width for the highest intensity peak of calcic plagioclase (002) and quartz (101) for grinding times of 0, 15, and 30, minutes

Sample	Mean Integrated Intensity (counts)	Mean Peak Width (degrees)
Plagioclase		
0 min	47422	0.127
15 min	44124	0.132
30 min	33296	0.136
Quartz		
0 min	34847	0.180
15 min	30548	0.193
30 min	29802	0.199

Figure 4. Decrease in mean integrated intensity with increase in grinding time for plagioclase (002).

Figure 5. Increase in mean peak width with increase in grinding time for plagioclase (002).


PLAGIOCLASE
MEAN INTEGRATED INTENSITY (counts)
(Thousands)
48
46
44
42
40
38
36
34
32
0
5
10
15
20
25
30
GRINDING TIME (min.)

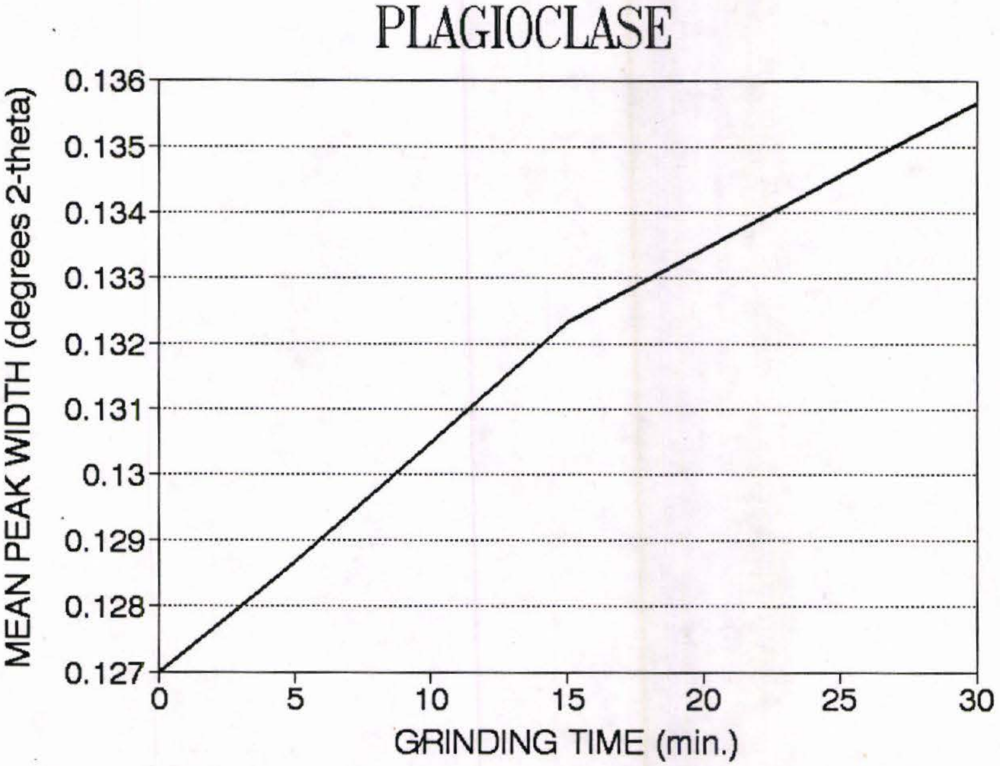
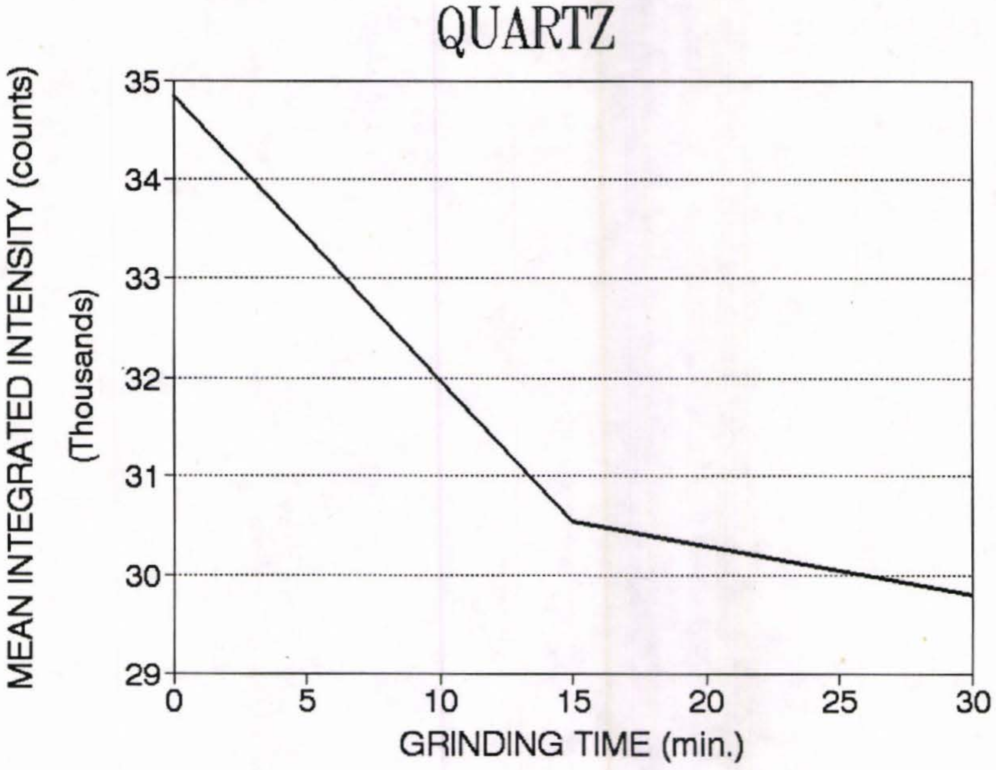

PLAGIOCLASE
MEAN PEAK WIDTH (degrees 2-theta)
0.136
0.135
0.134
0.133
0.132
0.131
0.13
0.129
0.128
0.127
0
5
10
15
20
25
30
GRINDING TIME (min.)

Figure 6. Decrease in mean integrated intensity with increase in grinding time for quartz (101).

Figure 7. Increase in mean peak width with increase in grinding time for quartz (101).


QUARTZ
MEAN INTEGRATED INTENSITY (counts)
(Thousands)
35
34
33
32
31
30
29
0
5
10
15
20
25
30
GRINDING TIME (min.)

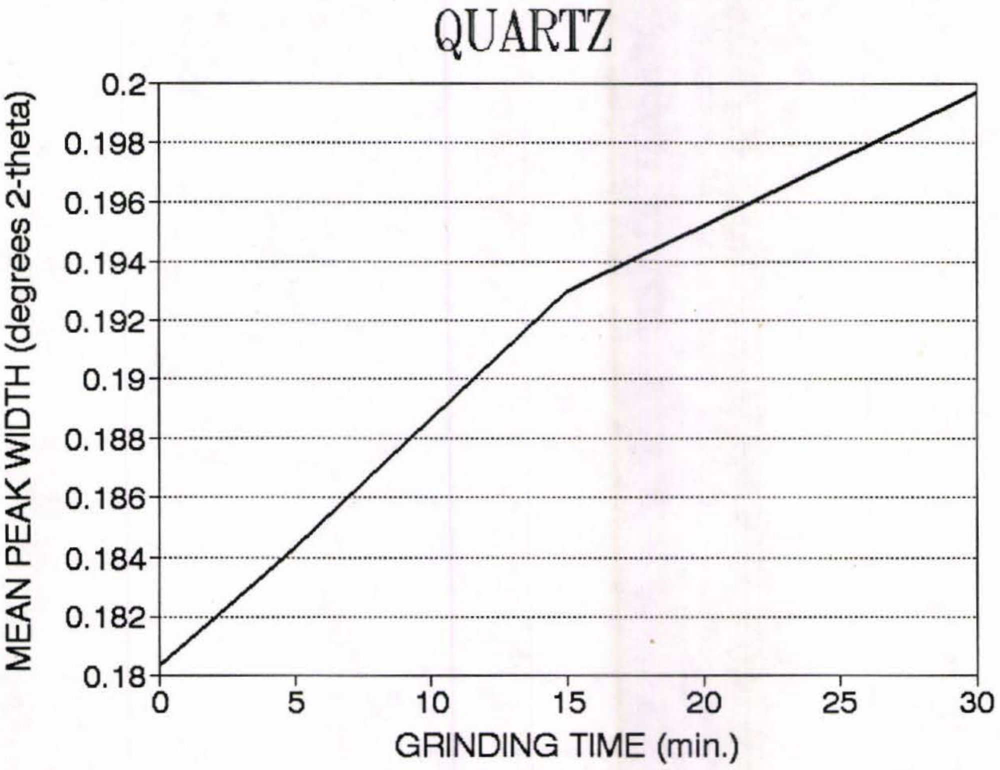
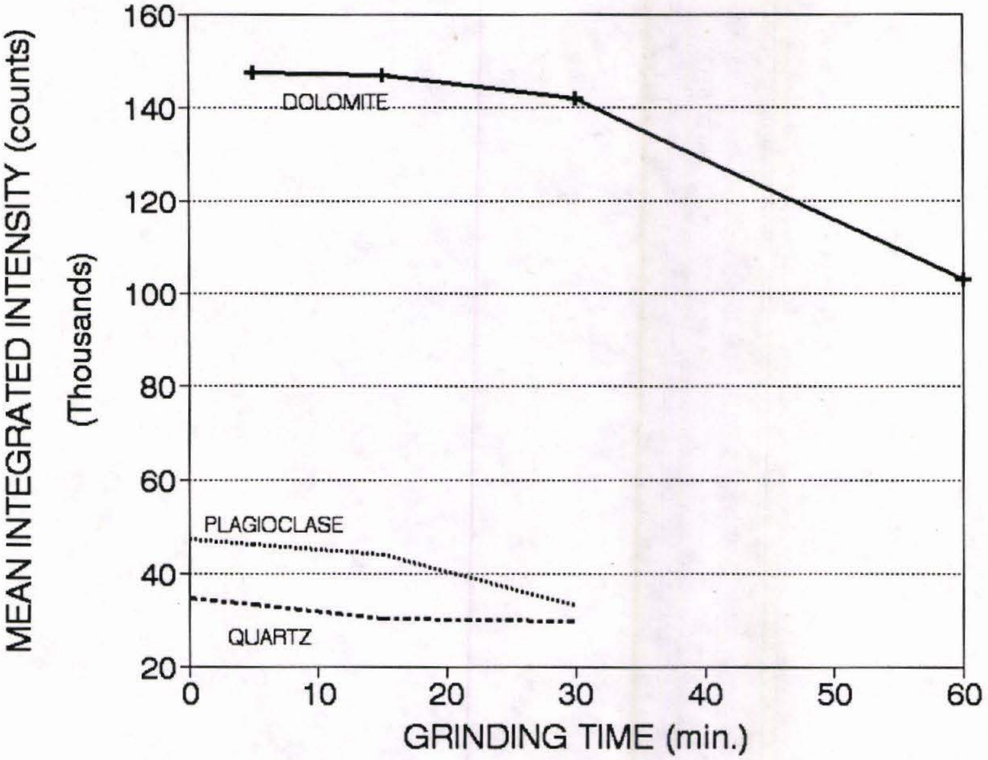
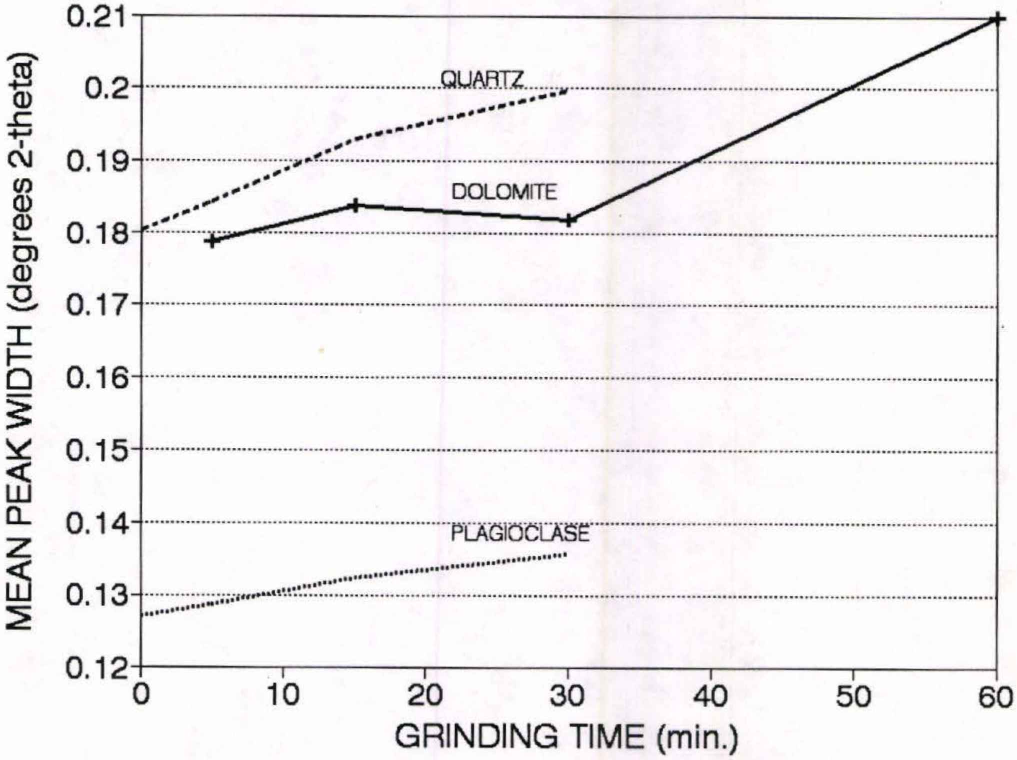

QUARTZ
MEAN PEAK WIDTH (degrees 2-theta)
0.2
0.198
0.196
0.194
0.192
0.19
0.188
0.186
0.184
0.182
0.18
0
5
10
15
20
25
30
GRINDING TIME (min.)

Figure 8. Decrease in mean integrated intensity with increase in grinding time for dolomite (104), plagioclase (002), and quartz (101).

Figure 9. Increase in mean peak width with increase in grinding time for dolomite (104), plagioclase (002), and quartz (101).


MEAN INTEGRATED INTENSITY (counts)
(Thousands)
160
140
120
100
80
60
40
20
DOLOMITE
PLAGIOCLASE
QUARTZ
0
10
20
30
40
50
60
GRINDING TIME (min.)


MEAN PEAK WIDTH (degrees 2-theta)
0.21
0.2
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
QUARTZ
DOLOMITE
PLAGIOCLASE
0
10
20
30
40
50
60
GRINDING TIME (min.)

quartz (Figure 8). The characteristic of quartz may be due to a combination of hardness and lack of cleavage.

DISCUSSION

The observed decrease in integrated intensities and in coefficient of variation, as well as the increase in peak width can be explained by the effects of grinding. The grinding reduced preferred orientation, primary extinction, and the size of the particles, which improves factors involving particle statistics. The width of XRD peaks is increased by small particle size and lattice distortion, both of which are effects of grinding (Lipson and Steeple, 1970). Because of small particle size, the XRD reflections appear over a range of angles, and are therefore broadened.

The increase in peak width and decrease in integrated intensities may be due to a possible reduction of crystallinity in the materials studied. This is a logical explanation, but no microscopic study of the particles was undertaken. Perhaps, other factors are involved in the increased peak width and decreased integrated intensities. It seems likely that the edges of the particle in a sample would become abraded and less crystalline. Klug and Alexander (1974) noted that a similar intensity loss occurs in quartz particles of much less than 5 microns and interpreted it as due to development of an amorphous surface layer, which has no lattice structure to diffract x-rays. The spaces between particles might also contain increasing amounts of amorphous material. Each would have an effect on XRD analysis, as significant amounts of amorphous material will drastically increase the background noise of scans.

The ideal characteristics for qualitative analysis would be narrow peaks with large integrated intensities. The variation in intensities would not be as important as for semi-quantitative analysis.

For semi-quantitative analysis, the variation in integrated intensities needs to be minimized, but the peaks must be narrow and have high enough intensities to still be identifiable. For semi-quantitative results from comparable samples, the sample preparation methods should be similar. It is very important that the internal standard is of the same particle size as the material being analyzed so that factors such as crystallinity and microabsorption are the same for both. For mixtures of minerals with differential resistances to grinding, a compromise in sample preparation procedure would have to be reached, based on the information desired from the XRD analysis. Quartz may act as a grinding agent on softer materials in some sample mixtures. If the particle size of the softer material was reduced more quickly than that of the other materials within the mixture, misleading results would be obtained from semi-quantitative analysis.

Although digital XRD results can be quickly and easily obtained, the analysis of complex mixtures is not routine. High quality work requires great care in sample preparation and data reduction and manipulation. A general sample preparation procedure would not work for all samples, so each sample would need to be evaluated separately. It would be necessary to determine and account for the factors, such as particle size, that determine the quality of the information obtained. It is very important that the sample preparation optimize the accuracy of the information desired.

A detailed scanning electron microscope (SEM) microprobe study of sample particles might suggest eliminating or changing certain steps in the sample preparation protocol. A study involving known mixtures that contain quartz would be very useful as a follow-up project.

ACKNOWLEDGEMENTS

I would like to thank Kurt Eylands and Tina Strobel for allowing me almost unlimited access to the equipment of the NMAL, and for taking the time to review the thesis. I would also like to thank Dr. Frank Karner for giving freely of his time and for offering invaluable advice, suggestions, and able guidance.

REFERENCES

Bates, R. L., and Jackson, J. A., (eds.), 1987, Glossary of Geology, Third Edition, American Geological Institute, Alexandria, Virginia.

Brindley, G. W., 1945, The Effects of Grain or Particle Size on X-Ray Reflections from Mixed Powders and Alloys Considered in Relation to the Quantitative Determination of Crystalline Substances, Philosophical Magazine, 36:347-369.

Chung, F. H., 1974, Adiabatic Principle of X-ray Diffraction Analysis of Mixtures, Journal of Applied Crystallography, 7:526-531.

Cline, J. P., and Snyder, R. L., 1983, The Dramatic Effect of Crystallite Size on X-Ray Intensities, in: "Advances in X-Ray Analysis," Plenum Press, New York, 26:111-117.

Davis, B. L., 1987, Quantitative Determination of Mineral Content of Geological Samples by X-Ray Diffraction, American Mineralogist., 72:438-440.

Klein, C., and Hurlbut, Jr., C. S., 1985, Manual of Mineralogy, Twentieth Edition, John Wiley and Sons, New York.

Klug, H. P., and Alexander, L. E., 1974, X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley, New York.

Lipson, H., and Steeple, H., 1970, Interpretation of X-Ray Powder Diffraction Patterns, Macmillan, London.

McCarthy, G. J., and Thedchanamoorthy A., 1989, Semi-Quantitative X-ray Diffraction Analysis of Fly Ash by the Reference Intensity Ratio Method, in: "Fly Ash and Coal By-Products: Characterization, Utilization and Disposal V," Materials Research Society, Pittsburgh, 136:1-10.

McMurdie, H. F., Morris, M. C., Evans, E. H., Paretzkin, B. and Wong, W., 1986, Methods of Producing Standard X-Ray Diffraction Powder Patterns, Powder Diffraction, 1:40-43.

Parrish, W., and Huang, T. C., 1983, Accuracy and Precision of Intensities in X-Ray Polycrystalline Diffraction, in: "Advances in X-Ray Analysis," Plenum Press, New York, 26:35.

Schreiner, W. N., and Jenkins, R., 1983, Profile Fitting for Quantitative Analysis in X-Ray Powder Diffraction, in: "Advances in X-Ray Analysis," Plenum Press, New York, 26:141.