

CHARACTERIZATION OF THE PARTICLE SIZE AND THE CRYSTALLINITY OF CERTAIN MINERALS BY IR SPECTROPHOTOMETRY AND OTHER INSTRUMENTAL METHODS—II. INVESTIGATIONS ON QUARTZ AND FELDSPAR

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Abstract—Infrared spectra of two minerals; Urkut quartz (Hungary) and a Swedish feldspar, of different origin with different physical characteristics and crystallinity were studied. Samples were taken after appropriate grinding, and infrared spectra, X-ray powder diffraction and water vapor absorption measurements were made along with electronmicrographs. Quantitative conclusions were drawn from changes of particle size and the ratio of bands of the Si—O groups and also the degree of crystallinity and changes of the particle size, respectively.

Key Words—Crystallinity, Feldspar, Grinding, Orthoclase, Quartz.

INTRODUCTION

Some problems of the quantitative analysis of minerals by infrared spectrophotometry were reported in Part I. It was stated that the intensity of the characteristic absorption bands of the kaolinites depends considerably on the shape and crystalline state of the particles, as well as on their actual chemical composition.

Quantitative determination of quartz, by infrared spectrophotometry, in dust, soil, other silicates and powdered coal was reported by Larsen (1972), Smallwood (1963), Hlavay (1976) and Tuddenham (1960). It was established that accurate and reproducible determinations can be carried out only on samples of strictly identical particle size and crystallinity. No literature data was found relating to a quantitative infrared analysis of feldspar.

In the present work infrared and X-ray spectra were recorded, as well as water vapor absorption and scanning electron microscopic measurements of the original samples and of those subjected to grinding, in order to reduce the particle size and the degree of crystallinity.

EXPERIMENTAL

Two minerals were examined: Urkut quartz (Hungary) and a Swedish feldspar (orthoclase). The Urkut quartz contains about 0.5–1% w/w amorphous material and the Swedish feldspar contains about 2% w/w quartz and other clay minerals as previously determined by X-ray powder diffraction. All measurements were carried out as described in Part I.

RESULTS AND DISCUSSION

The infrared spectra of Urkut quartz and Swedish feldspar are shown in Figures 1 and 2. Band assignments are listed in Table 1. Band intensities were determined by the baseline method and the characteristic absorption values were calculated. No internal refer-

ence band was found in the infrared spectra of quartz and feldspar because all band intensities were changed by the action of grinding. Moreover, we cannot investigate the irregularities of the lattices along selected crystal axes, because quartz and feldspar are not layered minerals. Changes of the band intensity taken at 802 cm^{-1} as a function of the grinding time is shown in Figure 3.

At the beginning, the absorption values considerably increase. After a certain grinding time (in our case 4 days) they pass a maximum, then decrease again. The explanation of this phenomenon was summarized in Part I.

It is well known that in the infrared spectra of amorphous silica the symmetrical bending vibration of the Si—O group taken at 695 cm^{-1} is missing. As in the infrared spectra of crystalline quartz, the symmetrical stretching vibration of the Si—O group at 800 cm^{-1} can be observed and the absorption ratio at $A_{800\text{ cm}^{-1}}/A_{695\text{ cm}^{-1}}$ can supply valuable information on the degree of crystallinity of quartz (Nemecz, 1960). The ratio of the above-mentioned absorption bands as a function of the grinding time is shown in Figure 4.

The ratio of these absorption bands increases considerably at first. Then after a certain grinding time only a slight increase is observed. This is explained as follows: at the beginning of the grinding the main process is the decrease of the particle size (band intensities increase). Later, because of the crystallinity decrease the 695 cm^{-1} band intensity decreases considerably and the $802/695\text{ cm}^{-1}$ ratio increases. During the grinding period the completely amorphous silica state could not be reached. After 10 days of grinding the intensity of the absorption band at 695 cm^{-1} could still be measured. When the aggregation began, the grinding was not so efficient and the ratio did not change appreciably. Other analytical measurements confirm the conclusions

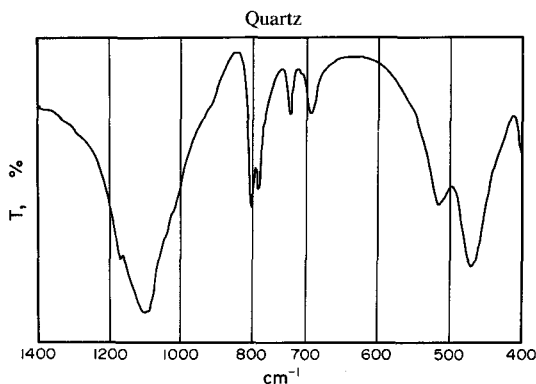


Fig. 1. Infrared spectra of Urkut quartz.

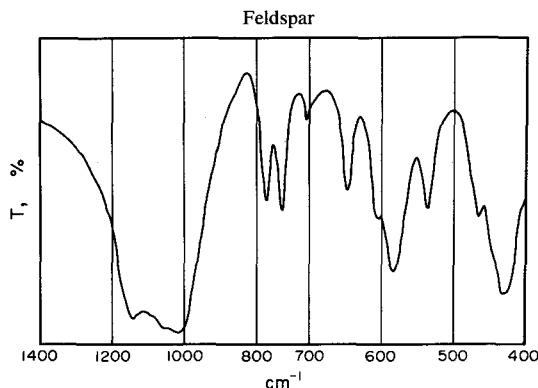


Fig. 2. Infrared spectra of Swedish feldspar.

drawn from the infrared spectra. The amorphitization of the Urkut quartz was followed by observing the decrease in intensity of the X-ray powder diffraction peak at 3.346 Å. Changes of this peak area as a function of the grinding time are shown in Figure 5.

At the beginning of the grinding there is a large change, later followed by a slighter decrease in the curve, i.e. the amorphitization of the quartz is continuous. When quartz is ground, the aggregation only can be observed later, compared to the grinding of clay minerals (that is, the efficiency of the grinding and the decrease of particle size is more pronounced with the later clay). In this period of grinding the specific surface area of quartz considerably increases. After 4 days of grinding only a small increase can be observed (Figure 6). The reason behind this may be that quartz is a very hard and brittle mineral and grinding breaks it into smaller pieces, resulting in large changes in the infrared and X-ray spectra as well as in the specific surface area measurements.

Similar curves were obtained on the Swedish feldspar. Changes of the two most characteristic absorption bands of the infrared spectra, at 735 and 570 cm^{-1} , in the characteristic reflection peak area of the X-ray spectra, as well as changes of the specific surface area as functions of the grinding time can be seen in Figure 7. No characteristic absorption ratio characterizing the

change of the crystallinity was found in the infrared spectra of the feldspar studied.

The explanation of the forms of the curves may be the same as that of the quartz. The decrease of the particle size and the agglomeratization of the Swedish feldspar was followed by stereoscanning electron microscopic (SEM) measurements. The SEM photograph of the original Swedish feldspar, and that of feldspar ground for 10 days, are shown in Figures 8 and 9. Some

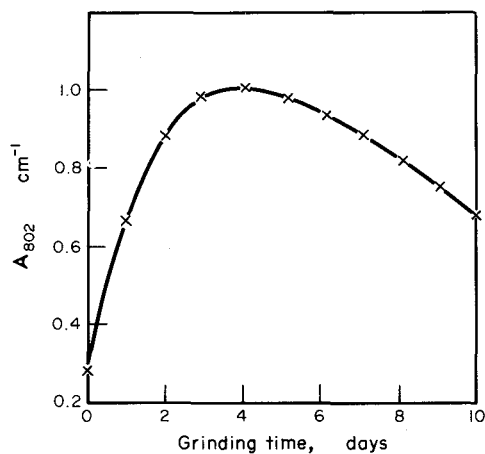
Fig. 3. Changes of the band intensity at 802 cm^{-1} (Urkut quartz).

Table 1. Band assignments of Urkut quartz and Swedish feldspar.

Samples	Wavenumber (cm^{-1})	Assignments
Quartz	1175, 1100	Si—O asymmetrical stretching vibrations
	802, 785	Si—O symmetrical stretching vibrations
	695	Si—O symmetrical bending vibrations
	516, 470	Si—O asymmetrical bending vibrations
Feldspar	1200–950	Si—O asymmetrical stretching vibrations
	775, 735	Si—O—Al compounded vibrations
	570	Si—O symmetrical bending vibration
	538	Si—O asymmetrical bending vibration
	648	Al—O co-ordination vibration

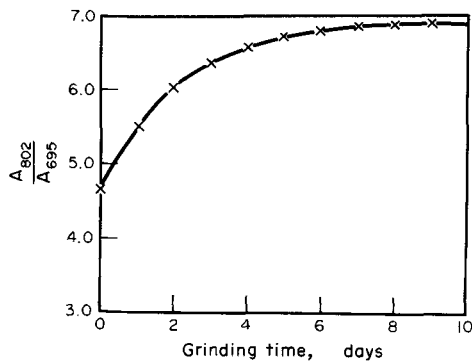


Fig. 4. Changes of the absorbance ratio taken at $A\ 800\ \text{cm}^{-1}/A\ 695\ \text{cm}^{-1}$ (Urkut quartz).

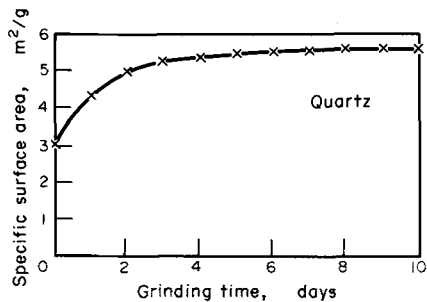


Fig. 6. Specific surface area of Urkut quartz.

large and irregular unground feldspar particles bearing the characteristic forms can be recognized in Figure 8.

At the beginning of the grinding period these large particles were broken and the small primary particles adhered to the larger, original particles thereby decreasing the effect of grinding. Then the aggregation and the degree of crystallinity become more pronounced, as can be seen in Figure 9.

Similar to the kaolins mentioned in Part I, we have attempted to establish correlations describing the particle size, the absorption ratio calculated from the infrared spectra and the loss in crystallinity calculated from the X-ray spectra as functions of the grinding time,

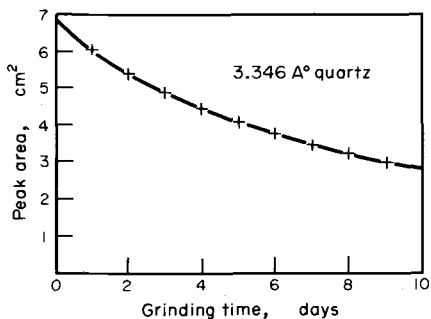


Fig. 5. Changes of the reflection peak area ($3.346\ \text{Å}$) as a function of the grinding time.

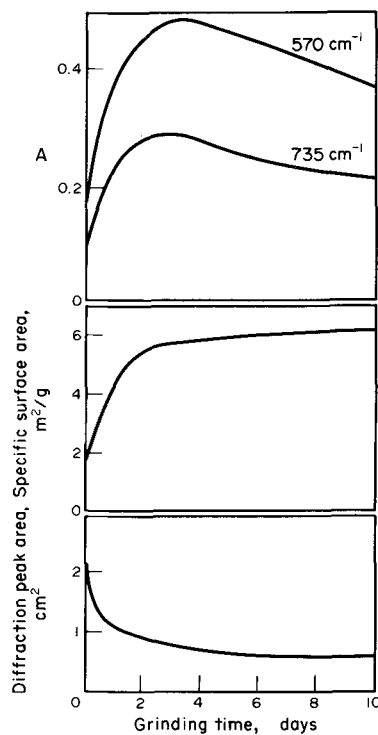


Fig. 7. Changes of the absorption bands of the infrared spectra (735 and $570\ \text{cm}^{-1}$); the reflection peak of the X-ray spectra and the specific surface area of the Swedish feldspar.

Table 2. The correlation functions of quartz and feldspar.

Samples	d vs t	y vs d	x vs d	y vs x
Urkut quartz	$d = d_0 e^{-0.237t}$ $a = 0.237$ $d_0 = 3.2\ \mu\text{m}$	$y = 0.228 d^2 + 7.0$	$x = 0.20 d + 0.37$	$y = -2.54 x^2 + 7.53$
Swedish feldspar	$d = d_0 e^{-0.147t}$ $a = 0.147$ $d_0 = 2.60\ \mu\text{m}$		$x = 0.03 d^{2.5} + 0.22$	

y , absorbance ratio calculated from infrared spectra ($A\ 802\ \text{cm}^{-1}/A\ 695\ \text{cm}^{-1}$).

x , degree of amorphism calculated from X-ray spectra.

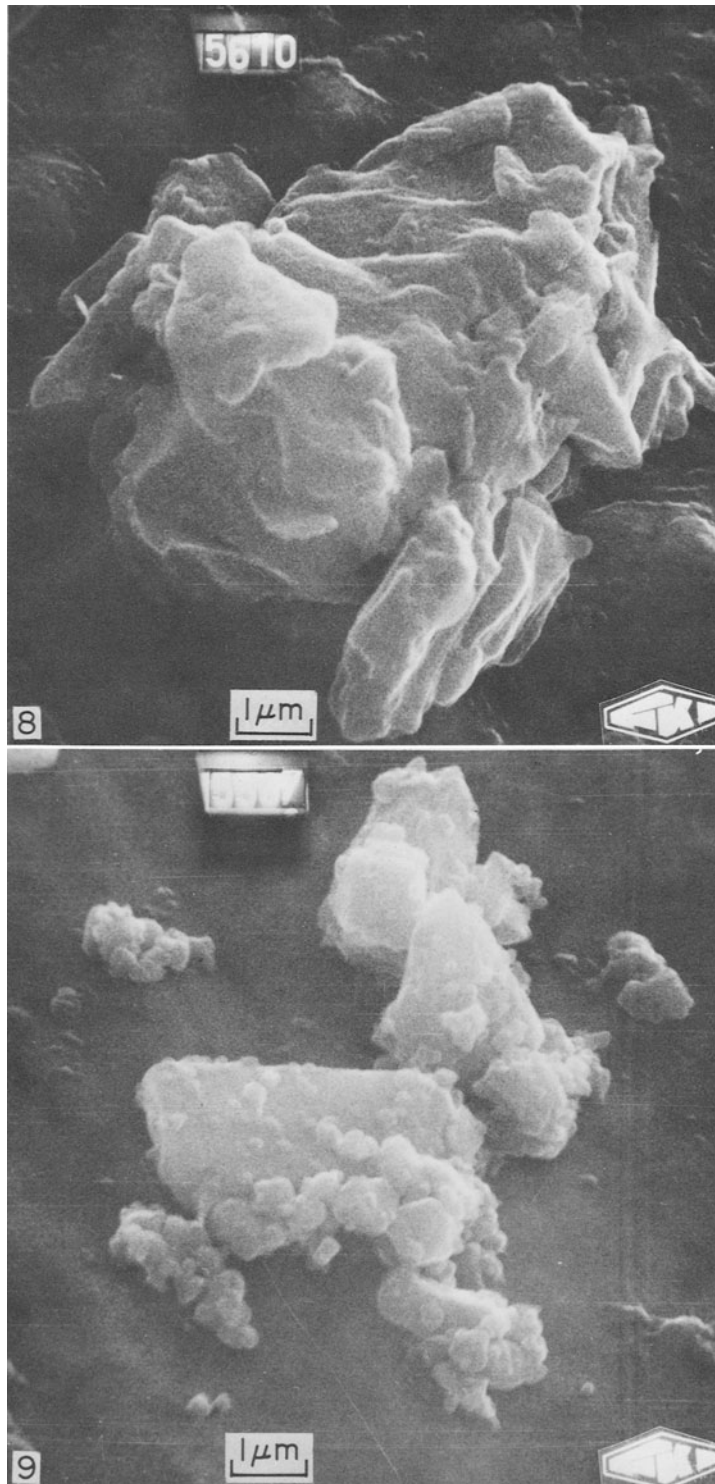


Fig. 8. SEM photograph of the original Swedish feldspar.

Fig. 9. SEM photograph of the Swedish feldspar after 10 days of grinding.

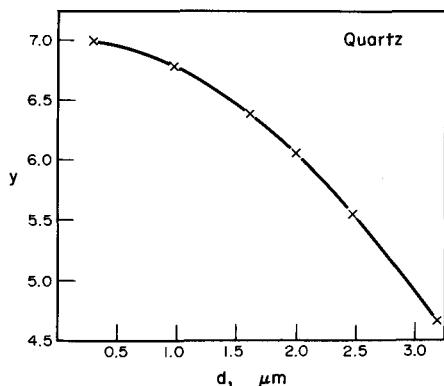


Fig. 10. Absorption ratio, y , vs. particle size, d , function.

as well as to determine the absorption ratio vs. amorphism. The appropriate equation was described in Part I. The particle size of the original and the ground samples was determined in Part I.

The peak area at 3.346 \AA (101), the characteristic reflection of the quartz and the peak area at 6.463 \AA of the feldspar, were measured. The ratio of the peak areas of the original and the ground samples serve as a measure of the loss of crystallinity. The correlation functions are listed in Table 2. No correlation was found for the absorption bands of the infrared spectra of the feldspar. Therefore characteristic absorbance ratios could not be calculated.

The y vs. d (average particle size) function of the Urkut quartz is shown in Figure 10. It can be seen that changes of the particle size result in considerable change of the absorption ratio of the quartz. The correlation function is a parabolic one with an asymptote at 7.0. This means that the values of y calculated from the infrared spectra may not be larger than 7.0 if the particle size of the sample is below the $0.3 \mu\text{m}$ limit.

The relationship between the degree of amorphism (x) calculated from the X-ray spectra and the particle

size (d) of the quartz is a linear function. The reason for this is that the quartz breaks into smaller pieces, decreasing the state of its crystallinity during the whole grinding period. These changes are proportional to the decrease of the particle size.

A parabolic function was found to exist between the y and x values of quartz. From the shape of the function it can be concluded that the changes in crystallinity of the quartz can result in a considerable change of the absorption ratio taken at $A 802 \text{ cm}^{-1}/A 695 \text{ cm}^{-1}$.

The x vs. d function of feldspar was calculated as a polynomial function. From this function the particle size of the samples can be determined if the x values are known.

In conclusion, we can state (similar to our earlier observations made in connection with kaolins, Part I), that if the particles are below the two micron size limit, the infrared bands intensities of quartz and feldspar depend on the average particle size of the primary particles, on the crystalline state of the particles and on the mechanochemical activation.

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Резюме- Изучались инфракрасные спектры двух минералов: кварца Уркут /Венгрия/ и Шведского полевого шпата, различного происхождения с различными физическими свойствами и кристалличностью. Образцы были отобраны после надлежащего измельчения, и затем проведены измерения инфракрасных спектров, рентгеновских спектров, полученных порошковым методом дифракции, и измерения абсорбции водяного пара, одновременно с изучением методом электронной микрографии. Были получены количественные данные благодаря изучению изменений размеров частиц и отношения связей групп Si-O, а также степени кристалличности и соответствующих изменений размера частиц.

Kurzreferat- Infrarotspektren zweier Mineralien, Urkutquartz (Ungarn) und ein schwedischer Feldspat, von verschiedener Abstammung mit unterschiedlichen physikalischen Eigenschaften und Kristallformen wurden untersucht. Nach angemessenem Mahlen, wurden Proben genommen und Infrarotspektren, Röntgenpulverdiagramme, und Elektronenmikrographien aufgenommen und Wasserdampfabsorptionen gemessen. Von der Veränderung der Teilchengröße, dem Verhältnis der Schwingungen von den Si-O Gruppen und auch dem Grad der Kristallinität, bzw. der Veränderung der Teilchengröße, wurden quantitative Schlüsse gezogen.