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QUANTITATIVE X-RAY DIFFRACTION ANALYSIS OF ALKALI FELDSPARS

RIASSUNTO. — È stato messo a punto un metodo, in diffrattometria di polveri a raggi X, per la determinazione quantitativa dei feldspati alcalini contenuti in una roccia o in una miscela artificiale di polveri cristalline. Il metodo permette un'analisi mineralogica di tipo quantitativo solo quando il feldspato alcalino è preventivamente scaldato a 1000° C per 4 ore e quindi rapidamente raffreddato in aria. I dati presentati mostrano, per i feldspati sodici, che le intensità del riflesso $\overline{2}01$ variano in funzione del loro contenuto in Or. In contrasto, nel range di composizione Or_{75}-Or_{90}, le intensità dei feldspati potassici non sono correlate al loro contenuto in Or ed inoltre sono indipendenti dallo stato strutturale.

La deviazione standard, in un'analisi quantitativa dei feldspati sodici e potassici, è risultata rispettivamente del $\sim 7\%$ e del $\sim 12\%$.

ABSTRACT. — A X-ray method has been developed for the quantitative determination of the percentage of alkali feldspars in a crystalline mixture or in a rock. The method enables quantitative diffraction analysis to be made when the alkali feldspar are previously heated. The data presented for Na-feldspar, show that the intensity of the $\overline{2}01$ reflection varies markedly as a function of solid-solution. In contrast, the intensity of the K-feldspar, in the composition range Or_{75}-Or_{90}, are not correlated to the Or composition and are practically independent of the structural state.

The estimated standard deviation in a quantitative analysis of Na-feldspar and K-feldspar is approximately 7% and 12% respectively.

Introduction

The problem of a quantitative mineralogical analysis of alkali feldspars, by the X-ray powder diffraction method, is very important both for a petrological classification of the rock and for its applied features.

The quantitative diffraction analysis, restricted to alkali feldspars with a composition and structural state of an orthoclase, has been studied in the past by BARBERI et al. (1963).

We have therefore considered it useful to investigate and extend the study of some aspect of that analysis. It is certain that factors such as isomorphous substitution and structural state, limit the accuracy of a quantitative X-ray analysis.

In this paper, these factors are examined in detail so as to reveal the difficulties involved in the quantitative determination of the alkali feldspar with powder X-ray diffractometry.

Accuracy limits for this type of analysis are presented.

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Methods of study

Samples analyzed

Twelve alkali feldspar specimens were selected for the investigation. They include one albite (Ab), five anorthoclases (A1, A2, A3, A4, A5), one maximum microcline (MM), three orthoclases (Or 1, Or 2, Or 3) and two sanidines: a high sanidine (HS) and a low sanidine (LS); the Or 1 sample is an international standard (Pennsylvania State University. Orthoclase, Or 1).

The feldspars used were separated by conventional techniques in the case of the specimens A1, A2, A3, A4, A5, Or 2, Or 3, LS· HS, while the samples Ab and MM were large (to 2 cm) crystals. Their purities were established by a powder X-ray examination and chemical analysis (see later). The nomenclature of the alkali feldspars suggested by WRIGHT and STEWART (1968) is used throughout this paper.

Sample preparation

A quantity of crystal fragments of the feldspar minerals to be analyzed was placed in the agate mortar and ground by hand with an agate pestle until final traces of grittiness had disappeared. Tre granulometry of the powders obtained by grinding, was in accordance with that suggested by KLUG and ALEXANDER (the powders used passed through a 325-mesh screen).

Cell parameters and structural state of the samples

Lattice parameters were computed by a least square refinement of X-ray powder records following the procedure suggested by WRIGHT and STEWART (1968) (Computer program with a « Variable-indexing »).

The spectra were calibrated against an external standard of quartz. Cell parameters are listed in table 1. Information on the structural state of the feldspar specimens can be drawn from the lattice parameters (*b-c* plot of WRIGHT and STEWART (1968), whose terminology has been adopted here, or by the method of JONES (1966) using the ratio c^*/b^* as a direct measure of the degree of order, see table 1).

The latter procedures indicate of high temperature structural state for all the anorthoclases and a sanidine, a low temperature structural state for the sample of albite and a structural state intermediate between high sanidine and maximum microcline for all the other samples. The *b-c* plot was also employed to recognize anomalus cell dimensions in same alkali feldspars (samples MM, LS, Or 1, Or 3).

Chemical composition

The analysis of all the samples are presented in table 2 in order of increasing potassium content together with the percentage of Or, Ab, An weight. Chemical analyses were performed using X-ray fluorescence following the analytical procedure developed by FRANZINI et al. (1975) for SiO_2· Al_2O_3, Fe_2O_3, CaO, K_2O and using atomic absorption for Na_2O.

X-ray intensity measurements

Before performing the diffraction intensity measurements we examined the more intense reflections of the alkali feldspars, in order to choose the most useful reflection for a quantitative X-ray diffraction analysis. This research has revealed that the only intense reflection common to potash-soda feldspars, suitable for a quantitative X-ray diffraction analysis, is the $\bar{2}01$ reflection.

TABLE 1

Unit cell dimensions*, degree of Al/Si order (JONES, 1966) and X-ray intensity measurements of the $\bar{2}01$ reflection for alkali feldspars

SAMPLE	a(Å)	b(Å)	c(Å)	α(° ')	β(° ')	γ(° ')	V(Å³)	Order Al/Si%	$I_{\bar{2}01,FeK_\alpha}$	$I_{\bar{2}01,CuK_{ir}}$
Ab	8.121(6)	12.781(7)	7.148(3)	94 17(3)	116 39(3)	87 43(3)	661.3(5)	62.0	3490[+] 4953[++]	11298[++]
A1	8.227(2)	12.927(1)	7.135(1)	92 43(1)	116 14(1)	90 14(1)	678.9(2)	5.8	2067 3891	9105
A2	8.252(1)	12.941(1)	7.139(1)	91 39(1)	116 22(1)	90 15(1)	682.7(1)	3.3	2448 3695	8957
A3	8.267(1)	12.937(2)	7.143(1)	91 39(1)	116 19(1)	90 11(1)	684.4(1)	5.0	2352 3609	8032
A4	8.282(2)	12.953(1)	7.157(1)	91 5 (1)	116 18(1)	90 13(1)	688.2(1)	7.7	1693 2903	6825
A5	8.326(1)	12.973(1)	7.163(1)	90	116 17(1)	90	693.8(1)	6.5	2133 2980	6703
HS	8.510(2)	13.018(2)	7.166(1)	90	115 56(1)	90	714.0(1)	6.4	2038 3080	7200
MM	8.559(8)	12.929(8)	7.198(4)	90 31(3)	115 56(3)	87 59(4)	715.9(6)	80.0	2159 3152	7357
Or1	8.539(6)	12.954(6)	7.199(3)	90	115 56(3)	90	716.1(5)	53.7	2259 2980	6886
L.S.	8.556(5)	12.988(5)	7.173(2)	90	115 59(2)	90	716.6(4)	13.3	2162 3020	7050
Or2	8.578(3)	12.974(3)	7.201(2)	90	116 1 (1)	90	720.1(3)	35.5	2375 2875	6750
Or3	8.574(3)	12.986(3)	7.200(1)	90	115 59(1)	90	720.6(3)	32.3	2277 2949	6890

* Parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left.
[+] Diffracted intensities from natural specimens.
[++] Diffracted intensities from heated specimens.

The position of the $\bar{2}01$ spacing is also proportional to the composition for homogeneous alkali feldspars (TUTTLE and BOWEN, 1958). Therefore the use of the $\bar{2}01$ reflection permits the evaluation of the eventual variation of diffracted intensity for different composition of the alkali feldspars, although other factors such as symmetry change and structural state can influence the $\bar{2}01$ intensity. In the composition range Or_{100}-Or_{70}, the disadvantage of using the $\bar{2}01$ reflection for a quantitative analysis is a result of its interference with the 100 reflection of the quartz, which is often present with the alkali feldspars in rocks. The intensity of the $\bar{2}01$ reflection, however, can be corrected for this interference by measuring on a sample of pure quartz the intensity ratio of the 100 reflection to another intense enough reflection of the quartz, free of interference from peaks of the K-feldspar. For example, the use of the 102 reflection is suitable for this correction. For those reasons, the intensity measurements were carried out only on the $\bar{2}01$ reflection. The measurements were obtained by integrating the peak-area and by rotation of the sample holder in order to obtain a better approximation to an ideal powder. X-ray diffraction measurements were determined on all the specimens both

in their natural state and after heating to 1000° C for about 4 hours. The specimens after the period of heating were rapidly cooled in air.

This procedure is necessary in order to assure a complete homogenization of all the unmixed feldspars, because many of the specimens studied showed considerable variation in the structural state and in the chemical composition. Mind that the experimental conditions for a complete homogenization differ from feldspar to feldspar as a consequence of the structural state, unmixing grade, and perthitic intergrowth dimensions of the alkali feldspar (SPENCER, 1937). After this heat--treatment· the powder diffraction spectra showed the presence of only one phase. For macroperthite and microperthite feldspars we suggest that the specimens be

TABLE 2

Chemistry of the alkali feldspars and weight percent of the feldspars components computed using the chemical composition

SAMPLE	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O▲	K_2O	Or	Ab	An
Ab	67.83	19.89	–	0.58	11.48	0.22	1.30	97.12	2.88
A1	65.28	20.92	0.53	2.09	9.08	2.10	12.40	76.80	10.40
A2	67.11	19.15	0.57	0.44	8.54	4.19	24.80	72.30	2.20
A3	66.92	19.14	0.66	0.41	8.44	4.43	26.20	71.40	2.00
A4	67.09	18.52	0.98	0.09	8.03	5.29	31.30	67.90	0.40
A5	66.39	18.96	0.93	0.12	7.07	6.53	38.60	59.80	0.60
L.S.	65.49	18.74	–	0.34	2.53	12.90	76.20	21.40	1.80
H.S.	64.77	19.08	–	0.59	2.07	13.49	79.73	17.51	2.93
Or3	65.38	18.56	–	0.36	1.98	13.72	81.10	16.80	1.80
Or2	65.72	18.40	–	0.40	1.72	13.76	81.30	14.60	2.00
MM	65.34	18.50	–	0.08	2.03	14.05	83.04	17.17	0.40
Or1	64.95	18.74	0.03	–	1.15	15.05	88.90	9.70	–

▲ Determination perferomed by the atomic absorption.

ground after homogenization to avoid a considerable broadening of the diffraction peaks due to the formation of a heterogeneous population of grains during the grinding (GIUSTI and LEONI, 1973).

The Philips X-ray diffractometer during the measurements was operated at 40 KV and 16 mA, using Mn-filtered iron radiation, 1° divergence and scatter slits, 0,2 mm receiving slit, scanning spread 1/2° 2 θ per minute and a time constant of 4 seconds. The diffraction intensities are listed in table 1.

For the heated specimens, the intensity measurements were also collected using Ni-filtered Cu radiation 38 KV, 18 mA and with the same strumental conditions as used for the iron radiation. These intensity measurements are also reported in table 1. The intensity measurements were corrected for background and calibrated against the external standard of Or 1 (peak-area intensity of 6886 counts). To check the reproducibility of the slides, the intensities of some feldspar specimens were measured several times, repacking the powder each time.

The standard deviation of the $\overline{2}01$ intensity for replicate slides was about 5.5 %. On the other hand, some sets of measurements repeated on the same slide showed that the statistical counting error is the only instrumental error. This error is of ± 2 %.
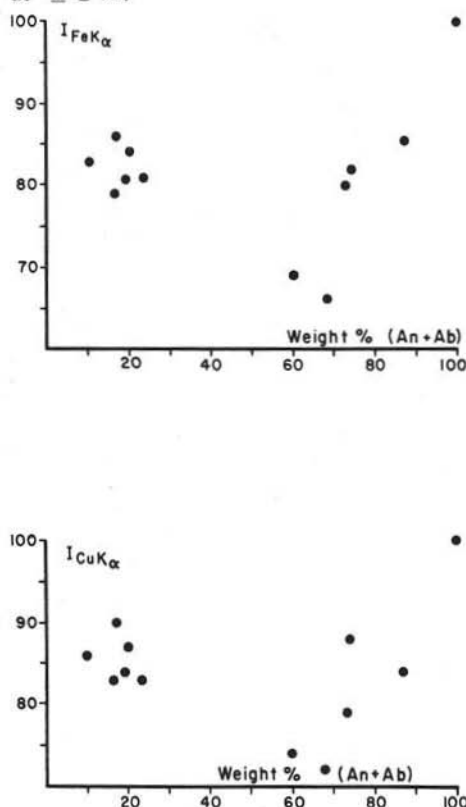

Fig. 1. — (An+Ab) content plotted against intensity measurements of the $\overline{2}01$ reflection for alkali heated feldspars. Intensity measurements are corrected by the absorption factor and scaled to the maximum observed which was set at 100.
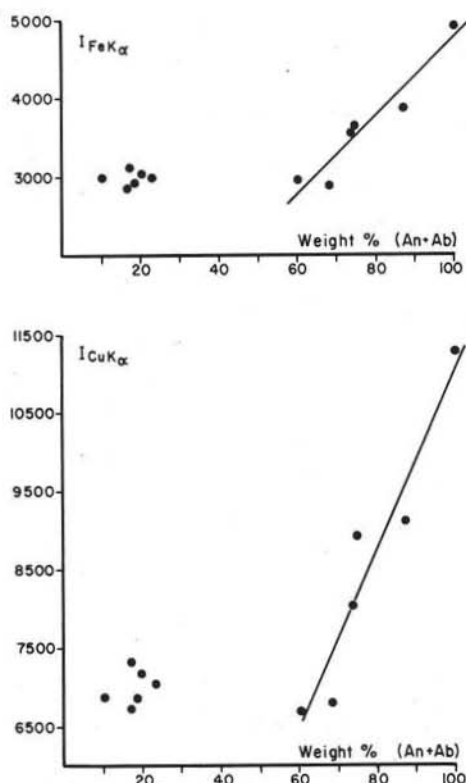
Fig. 2. — Measured $\overline{2}01$ intensities plotted against (An + Ab) content for alkali heated feldspars.

Discussion

The intensities of the $\overline{2}01$ reflection, listed in table 1 enable us to make some interesting observations. We observe a considerable increase of the intensities obtained, by means of the FeK_α radiation, from heated specimens as compared with those obtained from natural specimens. The percentage increase of intensity is not constant and ranges from 20-30 % for the samples Or 2, Or 3 to $\sim$90 % for the sample A1.

This variation of intensity can not be related to the presence of unmixing in the natural alkali feldspars, because originally homogeneous alkali feldspars (Ab. A1, A2, A3, A4, A5, HS) also show a noticeable increase in the intensities after

the heat-treatment. A complete interpretation of this behaviour is very difficult but it may be reasonable to suppose that a fair recrystallization consequent to heat treatment can, at least in part, be responsible for that. On the basis of the foregoing discussion, it appears necessary to carry out a heat-treatment of the specimen, for a quantitative X-ray diffraction analysis of the alkali feldspars, also in the case of originally homogeneous alkali feldspars.

In figure 1 the intensity measurements obtained on heated specimens, by means of CuK$_\alpha$ radiation and corrected by the absorption factor are plotted against Or content of the alkali feldspar specimens. The set of intensity values is normalized to a maximum of 100 for the Ab specimen. In the case of the Na rich feldspars the relation is linear, within the limits of what we consider to be our experimental error. The intensities of the potash-feldspars, within the composition range Or$_{75}$-Or$_{90}$, on the contrary, are practically indipendent from the Or-content because the maximum percentage deviation between the intensities of the $\overline{2}01$ reflection is comparable with the standard deviation of the $\overline{2}01$ intensity for replicate slides. For the k-feldspars, the influence of the structural state on the $\overline{2}01$ intensity seems of negligible importance, while for the Na-feldspars this influence is not evaluated here due to the lack of a sufficient number of low structural state specimens. In figure 2, as for figure 1, the intensities are plotted against Or-content, but in this case the measurements are unnormalized and uncorrected by the absorption factor. For the Na-rich feldspars, the lines of best fit, as determined by the least-squares method, are drawn on the figure. This diagram is useful to evaluate the diffracted intensity by a pure K-Na feldspar of known Or-composition.

Quantitative X-ray diffraction analysis

In order to check the validity of the $\overline{2}01$ reflection in the quantitative analysis of alkali feldspars, we analyzed prepared ternary mixtures of alkali feldspars with quartz. The six sets of mixtures are presented in table 3 where in column two and three are indicated the three mineralogical components the mixture and their percentage weights (wt%) respectively. The mixtures were homogenized by mixing the components in alcohol with a ball mill for 40 minutes. The quantitative analysis of the Na-K feldspars was made by measuring the integrated intensities of the $\overline{2}01$ reflection, by using of the CuK$_\alpha$ radiation, in the instrumental conditions described above. These measurements are listed in table 3. The interference or overlap of the $\overline{2}01$ reflection of the k-rich feldspars, utilized in the mixtures (Or 1, MM and HS samples) with the 100 reflection of the quartz was corrected as previously described. The concentrations of the components of the mixture were computed by means of the relation:

$$X_i = I_i \mu K_i \qquad (1)$$

where μ is the total mass absorption coefficients of the sample at the diffracted wavelength, K_i is a constant which depends on the characteristics of the apparatus

TABLE 3

Values of the computed and theoretical concentrations, diffracted intensities, values of μ for $\lambda = 1.50$ Å, of the mixtures alkali-feldspar-quartz

SAMPLE		Wt%		$\mu \ (\lambda=1.50$Å$)$	$I_{\bar{2}01}$	$I_{102\text{quart}}$
	Or 1	19.26*	19.10▼		1718	
M1	Ab	38.58	41.70	33.76	4245	
	Quartz	42.15	40.60			3423
	Or 1	9.18	10.70		1005	
M2	Ab	53.37	56.80	32.31	6046	
	Quartz	37.44	35.90			3161
	MM	48.00	49.30		4217	
M3	Ab	24.73	26.00	36.83	2413	
	Quartz	27.22	27.30			2109
	HS	27.60	25.62		2205	
M4	Ab	40.11	39.20	34.08	3950	
	Quartz	32.29	33.00			2757
	A1	40.71	42.30		3463	
M5	HS	39.37	35.87	35.94	2928	
	Quartz	19.92	21.20			1683
	Or 1	30.07	35.80		3091	
M6	Ab	36.40	34.00	35.06	3328	
	Quartz	33.52	31.40			2545
(esd)•%	for k-feldspar 12.00					
	for Na-feldspar 6.50					

* Theoretical concentrations. ● Estimated standard deviation%. ▼ Concentrations computed from Eq. (I) using experimental mass absorption coefficients.

and on the structure of the component i, I_i is the diffracted intensity of a crystalline component (i) contained in the sample and X_i is its concentration (wt%).

The mass absorption coefficient μ of the sample mixtures was estimated following the procedure developed by BATTAGLIA et al. (1977). These coefficients are listed in table 3.

In table 3 the concentrations of the alkali feldspars and quartz calculated with the equation (1) (column 4) are summarized.

The values of the K_i constants in (1) were obtained through a simple linear regression program utilizing all the measurements performed on the mixtures. These computed values of the K_i constants were then used to calculate the concentrations of the alkali feldspars and quartz in the mixtures.

Procedure for quantitative analysis

The proposed method, for a quantitative analysis of alkali feldspars, may readily be applied in other laboratories.

A simple procedure for doing this is as follows:

1) the specimen must be heated at 1000° C for 4 hours;
2) the X-ray intensity of the $\overline{2}01$ reflection of the Na-k feldspar must be normalized to our intensity measurements. For this propose it is possible to utilize either the $\overline{2}01$ integrated intensity of the international standard Or 1 (see table 1) as the 100 integrated intensity of a pure sample of quartz, with a particle size of about 10 microns. This last intensity, for the CuK_x radiation and with the same instrumental condition above described, is been determined. It is resulted of 28544 counts, with a standard deviation for replicate slides of $\sim 1 \%$;
3) the quantity of alkali feldspar, in the sample, can be determined by the relation:

$$X_i = \frac{I_c}{I_s} \cdot \frac{\mu_c}{\mu_s}$$

where X_i is the concentration (wt%) of a alkali feldspar in the sample, I_c is the diffracted intensity of the alkali feldspar to be quantitatively estimed, I_s is the diffracted intensity of a pure feldspar with similar Or-composition to the feldspar being quantitatively estimed (this intensity can be evaluated, knowing the Or-content of the pure feldspar, by the diagram of figure 2); μ_c and μ_s are the total mass absorption coefficients of the sample and of the pure feldspar respectively, at the diffracted wavelenght;
4) the mass absorption coefficients, μ_c and μ_s can be estimated following the procedure developed by FRANZINI et al. (1975).

Conclusions

The results of our investigation demonstrate that the use of the $\overline{2}01$ reflection, for a quantitative X-ray powder diffraction analysis of the alkali feldspars is a reliable semiquantitative method. For the k-feldspar no relation was observed between the $\overline{2}01$ intensity and their Or-content, in the range of Or composition examined; a linear relation between the two variables, instead, was found for the Na-feldspar. The plot of figure 2 can be used to evaluate the intensity of a feldspar of known Or-content. In addition we recall that for the use of this method, the alkali feldspars could be heated at 1000° C for 4 hours in all cases (unmixed or homogeneous specimen). The estimated standard deviation, using this method for a quantitative analysis is about 12 % for the k-feldspar and about 7 % for the Na-feldspar.

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