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THE DETERMINATION OF FELDSPARS IN MUDROCKS USING AN X-RAY POWDER DIFFRACTION METHOD

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Abstract—Low albite and maximum microcline were the two feldspars identified in Coal Measures mudrocks. Standard feldspars were then used to spike a mudrock base to construct standard working curves based on X-ray powder diffraction peak areas. Boehmite was added as an internal standard and also to correct for orientation effects. The samples were ignited at 950°C before the addition of the internal standard. This is advantageous for several reasons, but a disadvantage is that albite was found to undergo partial conversion to K-feldspar. The conversion was not total and the original albite content could be determined. This method is an extension of an existing method for quartz and therefore feldspars and quartz can be determined simultaneously.

Key Words—Albite, Feldspar, Microcline, Mudrock, Orthoclase, Plagioclase.

INTRODUCTION

There is little geological information on feldspars in mudrocks. According to Blatt et al. (1972, p. 133) very little is known about the relative abundance of microcline, orthoclase and plagioclase in sandstones and nothing is known concerning these species in mudrocks. Apart from not having any information on what could be an important component in mudrocks the lack of quantitative information of feldspar content in mudrocks creates uncertainties in the interpretation of major element analyses, as in the calculation of normative clay minerals following the schemes such as those proposed by Imbrie and Poldervaart (1959) and Nicholls (1962).

Quartz is an important component in mudrocks and a number of methods are in use for its determination. One widely used method involves a potassium pyrosulphate fusion (Trostel and Wynne, 1940). Quartz is isolated by this method and is quantitatively retained for a gravimetric determination. Feldspars undergo partial solution and they too are retained with the quartz. Kiely and Jackson (1965) modified the method so that the attack on the feldspars was reduced in order that the feldspars could also be determined. Changes they suggested were a reduction in the concentration of some of the solutions and use of sodium pyrosulphate. They noted that in the potassium pyrosulphate fusion the plagioclase feldspars gained K. Although dissolution of the feldspars was reduced it was not entirely eliminated, and Kiely and Jackson (1965) gave correction factors, based on standard feldspars, which allow the extent of the dissolution to be calculated. This was found to vary both with the composition and grain size of the feldspars and thus in unknown mudrocks some difficulty could be encountered in applying an appropriate correction factor.

An X-ray powder diffraction method (Till and Spears, 1969) for quartz can also be used. This method is based on the use of an internal standard, boehmite (5 μm Cera hydrate*), which is added to the samples after they have been ignited at 950°C for 3 hr. Igniting the sample destroys the clay minerals and removes interfering peaks from the X-ray powder diffraction traces. The ignition also concentrates the quartz, thus increasing the sensitivity of the method. A standard working curve was produced using samples of known quartz content. Quartz was determined using the method of Trostel and Wynne (1940). In the present work it was hoped to extend the quartz X-ray powder diffraction method to include the feldspars.

FELDSPARS IDENTIFIED IN COAL MEASURES MUDROCKS

In unorientated powder mounts of mudrocks, feldspars can be identified by peaks occurring on the X-ray diffraction traces in the range 27–29°2θ (CuKα radiation). Although the feldspars are an extremely complicated group and many reflections are possible in the 27–29°2θ range, it was observed that in Coal Measures mudrocks the feldspar mineralogy was relatively simple. In the mudrocks examined only a low albite and a maximum microcline were recorded. This identification was made from the comprehensive X-ray powder diffraction powder patterns published by Borg and Smith (1968, 1969).

The feldspar assemblage recorded is simple, particularly when the possible feldspar complexity is considered. Clearly, if the assemblage had been complex then the problems of developing a method for feldspar determination would have appeared insurmountable. On the other hand, in these Coal Measures mudrocks a complex assemblage would not have been predicted. Feldspars crystallizing at high temperatures will be less resistant to alteration in the low-temperature weathering environment than those crystallizing at lower temperatures. Provenance also will play a part in the production of a simple assemblage. Thus the Coal Mea-

* Cera hydrate was obtained from the British Aluminium Co.

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sures rocks were derived from the Caledonian orogenic belt, where, in addition to recycling of sedimentary rocks, granite plutons and metamorphic rocks were exposed containing the feldspars now recorded from the Coal Measures rocks.

The identification of K-feldspar is based mainly on the position of the diffraction peak at about 27.50°2θ which is due in large part to the 002 reflection. The $\bar{2}01$ reflection at 21.08°2θ is also important for identification although the intensity is about half that of the former peak.

In the mudrocks examined it was found that, when microcline is a minor part of a complex mixture, there is a broad peak spanning the 2θ value, but averaging 27.52–27.67°2θ. Other K-feldspars have the main diffraction peak at values of 2θ lower than 27.50°2θ and the second most intense peak increases in intensity to about 60% of the main peak. Triclinic microcline is unequivocably differentiated from monoclinic K-feldspars by the presence of the 131–$1\bar{3}1$ doublet at 26.44 and 30.24°2θ. The separation of these peaks is used to calculate the degree of triclinicity after Goldsmith and Laves (1954).

Plagioclase feldspars give a main diffraction peak, which is also composite, at about 28°2θ. For low albite the main peak at 27.95–28.02°2θ is accompanied by a peak at 24.32°2θ which is only a third of the intensity of the former. Differentiation from K-feldspars is thus possible. As the calcium content increases so the main peak shifts to lower 2θ values. There is also a shift in the second peak to 23.52°2θ and a lowering of intensity. To identify a specific plagioclase, it is useful to scan the 2θ range from 20 to 28°2θ for this usually gives four or five recognizable peaks even when the plagioclase content is low.

The boehmite internal standard peaks occur at 14.51°2θ for the 020 reflection and 28.28°2θ for the 021 reflection. These peaks also provide a check on the X-ray intensity and the 2θ calibration.

PREPARATION OF STANDARD WORKING CURVES

Sample preparation and operating conditions

The advantages of igniting samples at 950°C were noted earlier in describing the X-ray determination of quartz. The same advantages of removing interfering clay peaks and enhancing the diffraction intensities should also apply to the feldspars provided that ignition either does not have an appreciable effect, or the effect is predictable. In the work of Kiely and Jackson (1965) reaction between the potassium pyrosulphate and plagioclase feldspars was noted. In the present work we observed that mudrocks in which only albite could be detected before ignition contained a significant amount of microcline after ignition. Plagioclase feldspar reacts with K released when the clay minerals are destroyed. The importance of this reaction and ways to circumvent it were considered.

Standard feldspars were chosen from reference minerals to correspond with the feldspars identified in the mudrocks. The behavior of the standards in a mudrock base following ignition was also checked. The mudrock base was chosen because feldspars were not detected although the mineralogy was otherwise typical, based on the major element composition. The matching of standards and unknowns is made a little easier by the fact that small variations in composition of the albite and up to 20% perthite in the microcline can be tolerated without affecting the peak intensity.

The choice of suitable standards must be based on the correct identification of the feldspars in the unknown mudrocks. This can usually be achieved from X-ray diffraction traces of unfired samples and using the tables of Borg and Smith (1968, 1969). In some cases it may be necessary to concentrate the unknown feldspars by ignition, but the possibility of reaction must be borne in mind. Once the unknown feldspars are identified suitable standards can be selected. We used pure massive minerals from our reference mineral collection. The purity of the standards was checked by X-ray diffraction on powder mounts run from 4 to 44°2θ. The heating properties of the pure feldspars were also checked. Plagioclase feldspars, for example, should not be antiperthitic and muscovite impurities should be avoided because of the release of K_2O at 950°C.

Differentiation of monoclinic orthoclase and triclinic microcline was achieved using the method of Goldsmith and Laves (1954). Monoclinic K-feldspar has a single 131 reflection and triclinic K-feldspar a 131 and $1\bar{3}1$ doublet. The separation of the doublet increases the more triclinic the feldspar and thus Goldsmith and Laves (1954) suggested the following formula: triclinicity $\Delta = 12.5\ (d131 - d1\bar{3}1)$, such that $\Delta = 1$ for the most triclinic, or maximum microcline and $\Delta = 0$ when the feldspar is monoclinic.

Small amounts of plagioclase within the K-feldspar can be tolerated; these feldspars are very commonly microperthitic. Luth and Querol-Sũné (1970) demonstrated that some 2% Na can be tolerated in the microcline structure without affecting ordering or spacing. At the grain size used in the method, any crytoperthite with either the standard or unknown K-feldspar would be homogenized at 950°C to give a single phase. It is important, however, to make sure that the perthite is only a minor phase in the standards in order to avoid exchange reactions with the standard K-feldspar or modification of the ordering (which is stable if the albite molecule is less than 2%). Estimation of the perthite content is done using Wright's (1968) equation from the unfired K-feldspar powder trace utilizing the position of the $2\bar{0}1$ peak. Wright's equation, maximum microcline/low albite series; microcline percentage in perthite = $2031.77 - 92.19 \times (2\theta_{\bar{2}01})$ peak.

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Standard feldspars were then added to a suitable mudrock base and the procedure followed as outlined. A sample of mudrock was dry-sieved to pass 200 mesh (75 μm). A 2-g sample was ignited in a shallow vitrosil dish at a temperature of 950°C for 3 hr. The ignition loss was recorded and the sample was hand-ground to a talc-like consistency in an agate mortar. The ignited sample was then mixed with boehmite (5 μm Cera hydrate) in the weight proportion 9 (sample) to 1 (boehmite). This sample was then mechanically homogenized. The same treatment was used for the mudrock base spiked with feldspar standards. The feldspar was ground to pass 200 mesh and added to the mudrock base before ignition. Standards were prepared in this manner covering the range 0.5–10.0% albite and 0.5–10.0% microcline.

The X-ray diffraction traces were obtained using back-filled A1 holders and a 2kW Philips diffractometer operating under the following conditions: CuKα–Ni filtered radiation; 1, 0.1, 1° slits; 36 kV, 26 mA; scan rate ½°2θ/min, chart speed 120 cm/hr. The samples were scanned from 13.0 to 15.5°2θ and from 25.5 to 29.5°2θ.

A constant base line was drawn on the diffractograms and the areas of the peaks measured. A polar planimeter was not used; instead it was found more accurate to weigh peaks prepared from an overlay of high quality drafting film.

Problems due to preferred orientation

The two main boehmite peaks are at 14.50 and 28.20°2θ. The former is more intense and on average, using the back-filled Al mounts, the ratio of the areas was found to be 0.50. The ratio does vary and it was noted that as it did so there was an antipathetic relationship between the microcline and albite peak areas. This was proved to be due to a variation in orientation by comparing back-filled mounts with sedimented mounts. The boehmite peak at 14.5°2θ is the 020 reflection and the peak at 28.2°2θ, is the 021 reflection. Boehmite has a {010} cleavage and therefore orientation should enhance the 020 reflection and reduce the 021 reflection. The ratio of the boehmite peak areas will therefore be reduced (peak area 28.2°2θ/14.5°2θ). The ratio for a sedimented mount was 0.29, whereas in the back-filled mounts the variation was from 0.47 to 0.53, which is relatively small (±6%). In the feldspars cleavage will also influence the peak areas. The main cleavages are {001} and {010}. The albite peak at 27.9°2θ is due to, in decreasing importance, the 002 (I = 100), 040 (I = 67) and 220 (I = 37) reflections. The microcline peak at 25.7°2θ is due to the 002 (I = 100), $\bar{2}$20 (I = 62) and 040 (I = 36) reflections. Preferential orientation should therefore favor albite more than microcline and this was observed in practice. Standard feldspars and unknowns behaved in an identical manner as the degree of preferred orientation was varied. Although care was taken in hand-grinding the samples and in packing the samples, it proved difficult to eliminate entirely a small variation in orientation. The peak areas were therefore standardized to a boehmite peak area 28.3°2θ/14.5°2θ of 0.5 using the calculation given below, which was established from the repeated diffraction traces. These are: for albite:

$$\frac{\text{Albite peak area} \times 0.5}{\text{Boehmite (28.2°2}\theta\text{ peak area)/(14.5°2}\theta\text{ peak area)}}$$

for microcline:

$$\frac{\text{Microcline peak area} \times 2.0}{\text{Boehmite (14.5°2}\theta\text{ peak area)/(28.2°2}\theta\text{ peak area)}}$$

The reaction between potassium and plagioclase at the ignition temperature

The advantages in igniting the sample, apart from the fact that this is done in the X-ray quartz method which we are attempting to extend to include the feldspars, are that interfering clay X-ray reflections are removed following a 3-hr ignition at 950°C and the concentrations of quartz and feldspars are increased. Another important advantage is that these minerals which have cooled slowly through the solidus as homogeneous feldspars can show unmixing effects as well as structural inversions such as the conversion of monoclinic to triclinic K-feldspar. In feldspars present in mudrocks these would be represented by only cryptoperthites (and the converse) at this order of grain size. While this exsolution component could be unimportant on a weight % basis, subsidiary diffraction peaks of differing feldspar species could appear for unfired samples. The advantage therefore of heating at 950°C is that homogenization occurs for these feldspars and the diffraction patterns are attributable to a single plagioclase or K-feldspar mineral depending which is dominant in the perthite-antiperthite.

A disadvantage of ignition is that the plagioclase feldspars undergo reaction to form K-feldspar. This reaction was investigated by Viswanathan (1971a, b). In low albite the structure is deformed around the Na atom, but as the temperature increases so the structure expands until K can be accommodated (Smith, 1974). The K-feldspar produced in our work had an identical diffraction pattern to the standard microcline. The possibility of suppressing the reaction by adding a sodium salt was investigated. NaCl was added and reaction between the K released from the clay minerals and the albite was prevented. However, we had also inadvertently produced a fusion mixture in which quartz, in particular, was soluble. Although in the Coal Measures samples investigated in this work the K_2O% (3.0–5.0%) was always in excess of that required to convert all the albite to microcline only partial conversion was observed.

Apart from the changes in the feldspar contents the

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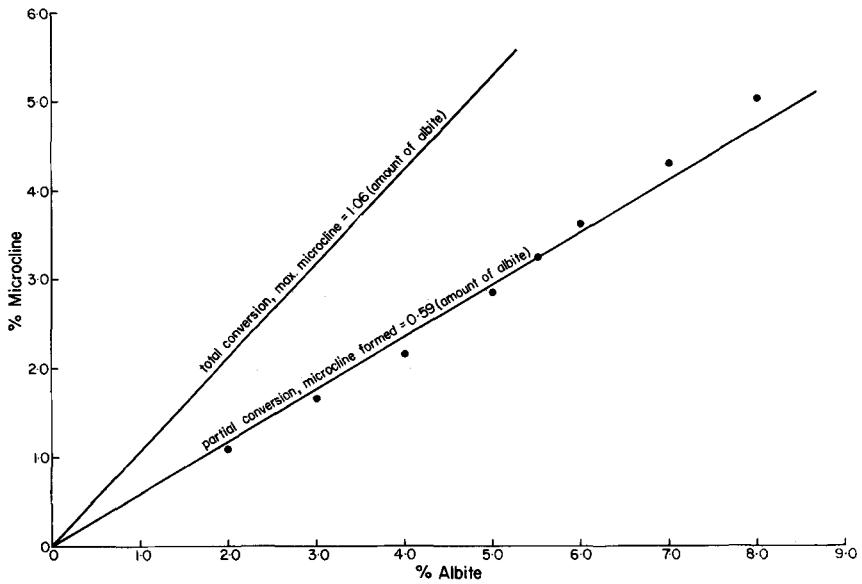


Fig. 1. The partial conversion of albite to microcline at the ignition temperature at 950°C microcline formed = 0.59 (amount of albite). Also shown is the line denoting total conversion maximum microcline = 1.06 (amount of albite).

experimental conditions remained constant including the ignition temperature, the duration of heating and the grain size of the samples. The results are shown in Figure 1, where it will be seen that for a given albite percentage the microcline produced during ignition is 56% of the theoretical maximum and furthermore that these proportions remain constant over the range of albite values studied. This means that for these Coal Measures samples the problems resulting from reaction during ignition can be overcome. Thus from the albite remaining after ignition the original albite content can be determined and the amount of microcline produced during reaction. This latter figure can then be deducted from the total amount of microcline.

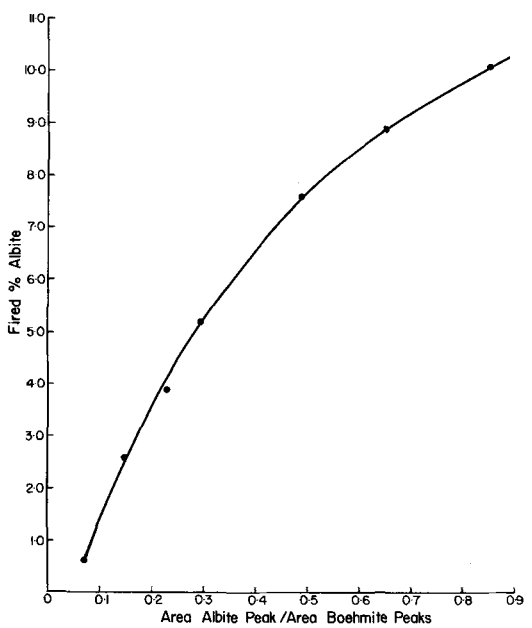


Fig. 2. The relationship between the percentage albite, in ignited samples, and the ratio of area albite diffraction peak to area combined boehmite diffraction peaks.

Standard working curves

The working curves for albite and microcline are given in Figures 2 and 3. The peak areas, measured by weighing, are expressed as a ratio of the boehmite area. Because of a variation in the relative intensities of the 28.2 and 14.5°2θ boehmite peaks, the total area of the two peaks was taken. This gave marginally more consistent results than using the area of the main boehmite peak alone. The albite peak area is measured, the effect of orientation allowed for using the ratio of the two boehmite peaks as described earlier, and this value expressed as a ratio of the boehmite peak area. The albite percentage is then determined from Figure 2, and the ignition loss taken into account. Figure 1 is then used to give the percentage microcline produced from the albite during the ignition and this figure is deducted from the total microcline percentage. The latter value is found from Figure 3, again expressing the microcline peak area as a ratio of the total boehmite area.

It will be noted on Figures 2 and 3 that the curves do not pass exactly through the origin. This stems from our measurement of small feldspar peak areas and the choice of a suitable and constant baseline.

Detection limits, precision and accuracy

The detection limits for the method were found to be 0.4% albite and 0.4% microcline. The feldspar contents

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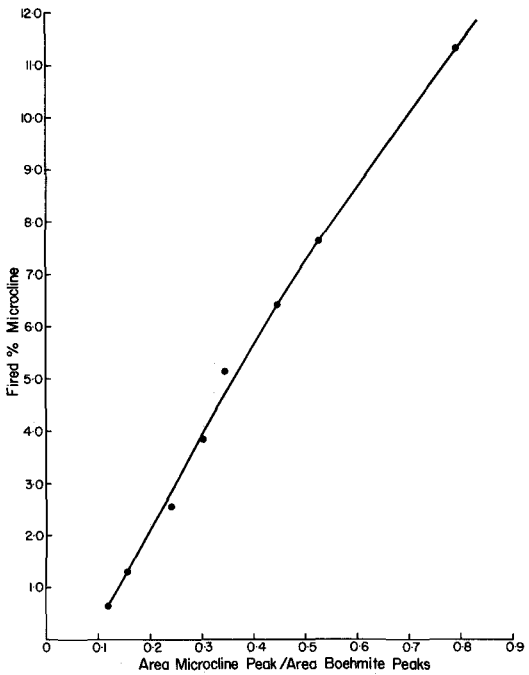


Fig. 3. The relationship between the percentage microcline, in ignited samples, and the ratio of the area microcline diffraction peak to area combined boehmite diffraction peaks.

in the mudrocks examined was typically in the range 1.0–3.5% and no sample exceeded the upper limit of the standards. Repeat determinations on standards containing 3.0–4.0% albite and microcline gave an average coefficient of variation of 5.4%. However, close to the detection limit the precision is understandably lower and the coefficient of variation was 17%.

The accuracy of the method is difficult to estimate because it is very much dependent on the choice of the correct feldspar standard. Unknown mudrocks containing feldspars were spiked with standard feldspars and the feldspar content determined before and after spiking. Sample R2G, which was thought to contain 3.80% microcline from the standard curve, when spiked with 2.45% microcline gave a total of 6.25% microcline and when spiked with 4.40% microcline gave a total of 8.20%. Likewise sample R2F, which was thought to contain 1.15% albite, when spiked with 1.99% albite gave a total of 3.15% and when spiked with 4.3% albite gave a total of 5.45%. Although these figures are very good, the standards with which the samples were spiked were the same as those on which the standard curves were based and therefore they demonstrate that the precision is good and possibly also is the accuracy.

CONCLUSIONS

A method for the determination of the feldspars present in Coal Measures rocks has been developed using standard feldspars. The feldspar assemblage in these mudrocks is relatively simple, consisting of low albite and maximum microcline. We would suggest that in other mudrocks the feldspar assemblage will not be complex, because it is only the low-temperature feldspars which will generally survive in the sedimentary cycle. Immature mudrocks in which this is not the case will undoubtedly occur, but these will be associated in the stratigraphic column with immature sandstones falling in the arkose category. The Coal Measures sandstones do not classify in this category. Thus we believe that the choice of suitable feldspar standards may not be as difficult as the vast number of feldspars present in igneous and metamorphic rocks suggests it might be.

The conditions adopted in this work are the same as those used in a quartz method using boehmite as an internal standard (Till and Spears, 1969) including the ignition of the samples at 950°C. Apart from the advantage of concentrating quartz and feldspars and reducing background on the X-ray diffraction scan, ignition also simplifies the feldspar reflections. A disadvantage of ignition, however, is the reaction of albite with K released from the clay matrix to give K-feldspar. Reaction is, however, incomplete under the conditions used and the amount of albite remaining after ignition can be used to give the original albite content. Likewise, the microcline produced can be deducted from the total microcline present to give the original microcline content. Some variation was encountered due to orientation. Using the boehmite peaks this difficulty can be circumvented and thus the internal standard serves more than one purpose.

We do not claim that the method described for the determination of feldspars in Coal Measures mudrocks can be used for all other mudrocks. In mudrocks of a comparable composition to those analyzed in this work little modification should be necessary, however, and the method should provide a viable alternative to the fusion method of Kiely and Jackson (1965).

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Резюме- Низкое содержание альбита и максимальное - микроклина было установлено в аргиллите "Коул Межез".Эталонные полевые шпаты были затем использованы,чтобы вызвать пик от аргиллитовой основы для построения эталонных рабочих кривых,базирующихся в зонах пиков порошковых дифракций рентгеновских лучей. Бемит был добавлен в качестве внутреннего эталона,а также для устранения искажений за счет эффектов ориентации.Образцы прокаливались при 950°С перед добавкой внутреннего эталона.Это дает преимущества по нескольким причинам,но отрицательной стороной является то,что альбит частично превращается в К-полевой шпат.Превращение не является полным и первоначальное содержание альбита может быть определено.Этот метод является развитием существующего метода определения кварца,и,таким образом,полевые шпаты и кварц могут определяться одновременно.

Kurzreferat- Tieftemperatur Albit und maximum Microclin waren die zwei Feld späte, die in 'Coal Measures' Schieferton identifiziert wurden. Dem Schieferton wurden Standart Feldspäte zugegeben, um Eichkurven herzustellen,die auf Flächeninhalten von Röntgenpulverdiagrammen beruhen. Als innerer Standart,und um Orientierungseffekte zu korrigieren, wurde Boehmit zugegeben. Die Proben wurden um 950°C angezündet-vor der Zugabe des Standarts. Das ist aus verschiedenen Gründen vorteilhaft, aber ein Nachteil ist, daß es sich herausgestellt hat, daß Albit eine teilweise Umwandlung in K-Feldspat untergeht. Die Umwandlung ist nicht vollständig und der Originalgehalt des Albiten konnte bestimmt werden. Diese Methode ist eine Erweiterung einer schon exsistierenden Methode für Quartz, und daher können Feldspäte und Quartz nebeneinander bestimmt werden.

Résumé-L'albite basse et la microcline maximale étaient les deux feldspaths identifiés dans les argilites"Coal Measures".Des feldspaths standards ont alors été utilisés pour étalonner une base argilite pour construire des courbes de travail standard basées sur des régions de pics de diffraction aux rayons-X.De la boehmite a été ajoutée comme étalon interne et aussi pour corriger les effets d'orientation.Les échantillons ont été oxidés à 950°C avant l'addition de l'étalon interne.Ceci est avantageux pour plusieurs raisons, mais un désavantage est que l'albite subit une conversion partielle en feldspath-K.La conversion n'est pas totale et le contenu d'albite à l'origine n'a pas pu être déterminé.Cette méthode est une extension d'une méthode existante pour le quartz,et c'est ainsi que les feldspaths et le quartz peuvent être déterminés simultanément.

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