^{29}Si AND ^{27}Al CPMAS NMR QUALITATIVE AND QUANTITATIVE ANALYSIS OF KAOLINITE AND DICKITE IN KOS ISLAND KAOLINS, GREECE

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Abstract

The application of ^{27}Al and ^{29}Si CPMAS NMR spectroscopy to the investigation of selected kaolinite and dickite bearing samples from hydrothermally altered rhyolites of Kos island is tested using also XRD and analytical SEM-EDS data. Kaolinite and dickite, can be detected by both their tetrahedral Si and octahedral Al CPMAS NMR spectra. It was found that the interference of the peaks become less significant and the shape of the peaks narrow when the pulse recycling delay is high (up to 10s). The octahedral Al / tetrahedral Si ratios of kaolinite group mineral forms from samples showing various degrees of alteration, calculated from the NMR spectra, were found to be very similar to these derived from the structural formulae of SEM-EDS microanalyses. In this work it is presented for the first time an approach to provide narrow CPMAS NMR peaks. The narrow shape of the peaks provides accurate measurements of the exact position of the peaks and the octahedral Al / tetrahedral Si ratios.

Key words: NMR, Kaolinite, Dickite.

Περίληψη

Η μέθοδος του Πυρηνικού Μαγνητικού Συντονισμού (NMR) και οι τεχνικές ^{27}Al και ^{29}Si CPMAS NMR εφαρμόστηκαν στην έρευνα επιλεγμένων δειγμάτων υδροθερμικά εξαλλοιωμένων ρυολίθων της νήσου Κω. Επιλέχθηκαν δείγματα πλούσια σε καολινίτη και δικίτη που είχαν ήδη αναλυθεί και με τη χρήση της Περιθλασιμετρίας Ακτίνων Χ και σημειακών χημικών αναλύσεων (που ελήφθησαν από το Ηλεκτρονικό Μικροσκόπιο). Ο καολινίτης και ο δικίτης μπορούν να ανιχνευτούν βάση των φασμάτων του τετραεδρικού Πυριτίου και του οκταεδρικού Αργιλίου (με τις τεχνικές ^{27}Al και ^{29}Si CPMAS NMR). Βρέθηκε ότι η αλληλεπίδραση των ανακλάσεων υποβαθμίζεται και το σχήμα των ανακλάσεων γίνεται οξύληκτο όταν ο χρόνος αποφόρτισης (pulse recycling delay) είναι υψηλός (10 δευτερόλεπτα). Ο λόγος οκταεδρικό Αργίλιο / τετραεδρικό Πυρίτιο των ορυκτών της ομάδας του καολινίτη όπως μετρήθηκε από τις τεχνικές του Πυρηνικού Μαγνητικού Συντονισμού βρέθηκε παρόμοιος με αυτόν που προέκυψε από τις σημειακές χημικές αναλύσεις. Σε αυτήν την εργασία παρουσιάζεται για πρώτη φορά μια προσέγγιση που κάνει εφικτή τη λήψη οξύληκτων ανακλάσεων Πυρηνικού Μαγνητικού Συντονισμού σε στερεά δείγματα (^{27}Al and ^{29}Si CPMAS NMR). Το οξύληκτο σχήμα των ανακλάσεων μεγιστοποιεί την ακρίβεια των μετρήσεων της θέσεων των ανακλάσεων και του λόγου οκταεδρικό Αργίλιο / τετραεδρικό Πυρίτιο.

Λέξεις κλειδιά: Πυρηνικός Μαγνητικός Συντινισμός, Καολινίτης, Δικίτης.

1. Introduction

The application of NMR spectroscopic methods to solids is fast becoming an important tool in mineralogy. ^{29}Si and ^{27}Al have been the most important nuclides for MAS NMR studies of clay minerals and over the last two decades, a large data base for the MAS NMR behaviour of these minerals have been accumulated. It is well known that Si linked via oxygens to three other Si atoms with no nearest Al neighbors has a chemical shift of -92 to -98 ppm in the ^{29}Si MAS NMR spectrum, whereas Si with one nearest Al neighbor has a shift -85 to -90 ppm. ^{27}Al MAS NMR can readily distinguish 4, 5 and 6-coordinated Al, providing thus significant information about site occupancies. Calculations, based on NMR studies can provide direct quantitative values for the fractions of Si-sites with different numbers of Al next-nearest beigbour and can also be used to determine tetrahedral / octahedral Al ratios (Lipmaa *et al.* 1980, Kirkpatrick 1988).

In this study ^{29}Si and ^{27}Al CPMAS NMR spectroscopy has been used to examine representative kaolin samples containing kaolinite and dickite reflecting various degrees of kaolinization, with the aim to: a) discriminate among the minerals kaolinite and dickite and to determine of the exact position of their resonance, b) to provide quantitative values for octahedral Al and tetrahedral Si in these clay minerals present and c) to investigate the impact some details of the analytical technique to the octahedral-Al / tetrahedral Si ratios of kaolinite and dickite.

2. Geological Settings

Kos Island lies at the southeastern part of the Aegean Sea, and it is a part of the South Aegean Active Volcanic Arc (Fig. 1). The lowermost unit comprises a metamorphic series of Permocarboniferous marls, impure limestones and sandstones, phyllites and rare mafic intercalations (Altherr *et al.* 1976). At 12 Ma, this series was partly contact metamorphosed by the intrusion of a large quartz monzonite (Fig. 1; Altherr *et al.* 1982, Henjes-Kunst *et al.* 1988, Kalt *et al.* 1998). Jurassic to Eocene limestones and dolomitic limestones tectonically overlie the above metamorphic basement. A successive series of volcanic rocks, mainly of rhyolitic-dacitic composition and pyroclastic formations covered the island of Kos (Fig. 1), while Pliocene and Pleistocene sediments occur mainly at the peripheral parts of the island (Keller 1969, Dürr and Jacobshagen 1986, Allen *et al.* 1999, Allen 2001). The volcanic products of Kos derive from two periods of intense volcanic activity. The first began 10.4 Ma ago and continued until about 7.3 Ma ago, with effusions of magma belonging to the K–alkaline series and characterised by ignimbrite deposits. The second period began 3.4 Ma ago, with effusions of magma belonging to the Ca–alkaline series and continued up to the most recent volcanic activity on the island, some 140 ka ago (Boven *et al.* 1987, Dalabakis 1987, Keller *et al.* 1990, Dalabakis and Vougioukalakis 1993, Allen *et al.* 1999).

Rhyolite occurrences of Pliocene age (Boven *et al.* 1987) at Kefalos display variable degrees of kaolinization. The kaolinized rocks are generally white in colour, however they are frequently stained reddish by iron oxides; they extend over an area of about 0.5 km^2. Rhyolitic dykes at Asfendiou penetrate the metamorphic basement. The studied rocks were sampled from a completely kaolinized rhyolitic dyke (Papoulis 2003).

3. Materials and Methods

Representative kaolinite rich and dickite rich samples from Kos island were analysed using ^{27}Al and ^{29}Si CPMAS NMR. The application of ^{27}Al and ^{29}Si CPMAS NMR spectroscopy to the investigation of the selected kaolinite and dickite rich samples from hydrothermally altered rhyolites of Kos island were tested using also XRD and analytical SEM-EDS data.

A Bruker DPX400MHz spectrometer operating at 79.50 MHz on the ^{29}Si and 104.26 MHz on the ^{27}Al was used for CPMAS NMR experiments. Cross-polarisation with magic angle spinning (CPMAS) was applied at 5-10 kHz. A contact time of 1-6 ms was used, while a pulse delay of 1-10sec was chosen. Spectra were obtained using a tuned probe equipped with a SB-MAS probe - 4mm rotor- double bearing CPMAS assembly. The rotor filled with sample was allowed to spin before each experiment in order to stabilize sample packing and improve field homogenization. The spinning speed was detected optically by a glass fibre. Short, powerful radio-frequency pulses (0.6 μs equivalent to 10 pulse angle), with high-power B1 field amplitude ~70 kHz ^{1}H decoupling was used. Chemical shifts-given in parts per million (ppm) were referred to the resonance signal of tetramethylsilane (TMS) for the ^{29}Si and Al(H2O)$^{+3}_6$ for the ^{27}Al (external standards). More than 7500 scans were needed to obtain acceptable S/N (signal/noise) ratio for both nuclides for these samples. For optimum performance the spectrometer was calibrated before and during the NMR spectra acquisition as suggested by Bruker.
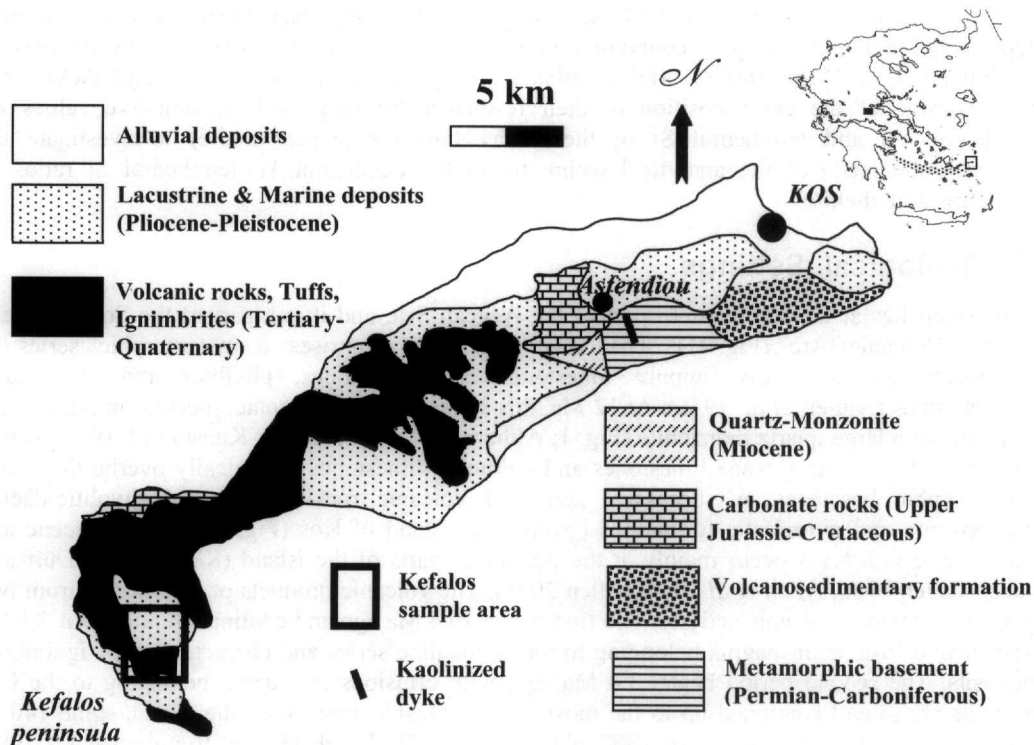

Figure 1 - Geological sketch map of Kos Island (after Triantaphyllis 1994, 1998); inset shows the position of Kos Island and the relative position of the South Aegean Active Volcanic Arc (SAAVA; dotted area)

XRD patterns of the samples were acquired on powdered samples using a Philips PW1050/25 diffractometer with Ni-filtered CuKα radiation. Oriented clay powders were prepared by the dropper method and were scanned at 1°2θ/min from 3 to 60°2θ. Random powder mounts for selected samples were prepared by gently pressing the powder into the cavity holder. For each <2 μm specimen, clay minerals were identified from three XRD patterns (air-dried at 25 °C, ethylene-glycol solvated, and heated at 490 °C for 2h).

4. Results and Discussion

4.1. ^{27}Al and ^{29}Si MAS NMR spectra of representative kaolin samples containing book-type kaolinite and dickite

^{27}Al and ^{29}Si CPMAS NMR spectra of representative kaolin samples containing book-type kaolinite and dickite are presented in Fig 2. Figs 2a, b shows CPMAS NMR spectra of ^{27}Al and ^{29}Si for the highly kaolinized sample K48. The ^{27}Al spectrum (Fig. 2a) contains a single peak at -2.93 ppm which is assigned to six-coordinated Al atoms in phyllosilicates (Rocha and Klinowski 1990, Rocha and Pedrosa de Jesus, 1994, Miyawaki et al. 1992). The ^{29}Si MAS NMR spectrum (Fig. 2b) consist also of a single resonance at -91.93 ppm, characteristic of layer silicates assigned to Si linked via oxygens to three other Si atoms (Rocha and Klinowski 1990, Guo et al. 1997). X-Ray powder diffraction study of this sample (Fig. 3a) revealed the presence of kaolinite (Papoulis et al. 2005). Based on fully consistent XRD and SEM observations (Papoulis et al. 2004), the ^{29}Si and ^{27}Al CPMAS NMR spectra of the sample K48 are therefore assigned to kaolinite.

The XRD pattern derived from random powder mounts of clay fractions (<2 μm) of the highly altered sample K35 (Fig. 3b) revealed the presence of the clay mineral dickite (Papoulis et al. 2005). The ^{29}Si and ^{27}Al MAS NMR spectra of sample K35 are characterized by the presence of one peak which must is attributed to the six-coordinated Al (Al VI) and tetrahedral Si (Si IV) of dickite, the phase which was found according to XRD and SEM-EDS data.

The ^{27}Al NMR peak of the dickite (Fig. 2c) appears at -0.13 ppm, 2.80 ppm relative to that of kaolinite and the ^{29}Si spectra of kaolinite appears at -93.01 ppm, -1.08 ppm relative to that of dickite (Fig. 2d).

It is known that phases bearing paramagnetic components or impurities, gives very broad NMR peaks (Oldfield et al. 1983, Grimmer et al. 1983, Sheriff and Harman 1985) and according to Altaner et al. (1988) the presence of 1-2 oxide wt % Fe at least for ^{29}Si, broadens the peaks sufficiently to cause poor resolution. However because Fe^{2+} has more unpaired d-electrons than Fe^{3+} in principle, should have a larger peak broadening effect than Fe^{3+} (Kirkpatrick 1988). The CPMAS NMR in the spectra of the sample K35 provides relatively less sharp peaks especially for ^{29}Si and relatively high noise level suggest that the iron in the phases present is in its Fe^{2+} rather than Fe^{3+} state. Data from chemical analyses shows that the iron oxide content of sample K35 is higher than 2 % (3.19 %) and the iron content of sample K48 is lower than 2 % (Papoulis 2003). It should be noted that in order to obtain a satisfactory resolution and to avoid interference of the peaks in the ^{29}Si and ^{27}Al NMR spectra of the two kaolinite group mineral forms bearing samples, we performed multiple spinning speeds experiments at various pulse recycling delays. The observation show that the pulse recycling delay is a magnitude significant parameter in achieving accurate measurements. It was found that the interference of the peaks become less significant when the measuring time of the samples which and eventually we extended the pulse recycling delay up to 10 seconds.

The comparative study of the CPMAS NMR spectra of the samples K35 and K48 reveals that : The line shapes of the octahedral Al and tetrahedral Si signals of the kaolinite group mineral present (kaolinite) in sample K48 exhibit lower noise level and better formed, narrow peaks this is probably due to the relatively low amount of iron in the sample. The line shapes of the octahedral Al and tetrahedral Si signals of the kaolinite group mineral present (dickite) in sample K35 is characterized by high noise level attributed probably to the presence of relatively high amount of iron. The high amount of iron of the sample K35 (Papoulis 2003), broadens the peaks sufficiently to cause relatively poor resolution and not well formed peaks.
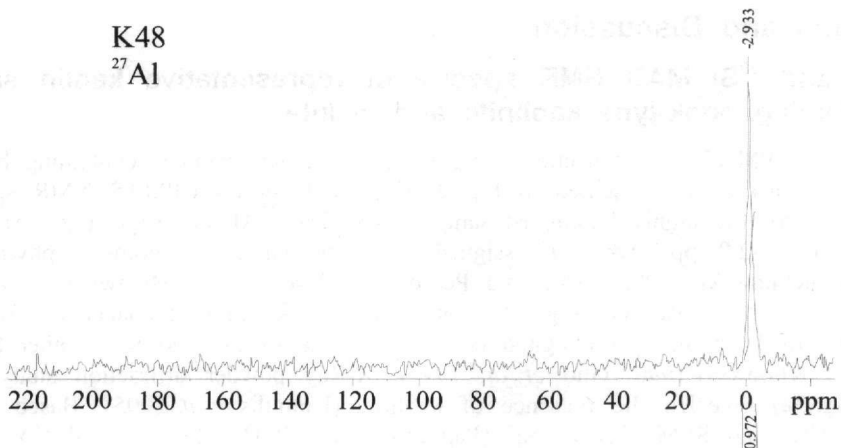
K48

^{27}Al

220 200 180 160 140 120 100 80 60 40 20 0 ppm

Figure 2a - ^{27}Al CPMAS NMR spectra of sample K48 (kaolinite rich sample)

K48

^{29}Si

120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 ppm

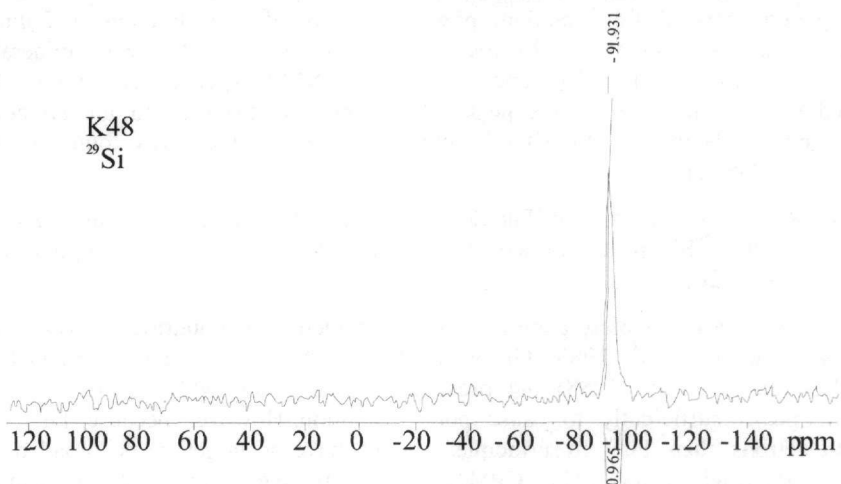**Figure 2b - ^{29}Si CPMAS NMR spectra of sample L48 (kaolinite rich sample)**

4.2. Octahedral-Al / tetrahedral Si ratios of kaolinite and dickite

By using curve fitting procedures the areas of the kaolinite and dickite ^{29}Si and ^{27}Al CPMAS NMR peaks from the spectra of the samples K48 and K35 were calculated. The octahedral Al / tetrahedral Si ratio of the kaolinite in sample K48 (Figs 1a, b) was found to be 1.01, a value which is similar to the theoretically expected and only slightly higher than the value (1.00) derived from the structural formulae of SEM EDS microanalyses on aggregates of kaolinite.

The calculated octahedral Al / tetrahedral Si ratio of dickite in the most altered sample K35 (Figs 1c, d) were found to be 1.00. Previously published and unpublished work by Papoulis *et al.* (2001) and Papoulis (2003) has provided useful information about the chemical composition of kaolinite and dickite of both areas of Kos island. The octahedral Al and tetrahedral Si CPMAS NMR peaks of the dickite of sample K35 are probably broadened and not well formed as the result of the relatively high iron amount of the sample and this may account for the small difference between the octahedral-Al / tetrahedral-Si ratios obtained by NMR and analytical SEM methods (1.00 and 1.04 respectively). The relatively high amount of iron seems to be the critical factor that causes the small error of the
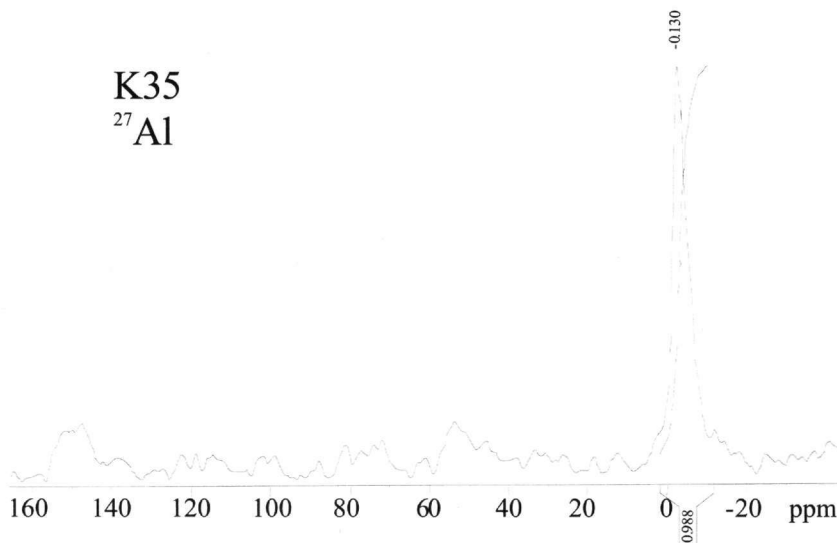
K35
^{27}Al

-0.130

160 140 120 100 80 60 40 20 0 -20 ppm

0.988

Figure 2c - ^{27}Al CPMAS NMR spectra of sample K35 (dickite rich sample)

-93.013

K35
^{29}Si

40 20 0 -20 -40 -50 -80 -100 -120 -140 -160 -180 -200 -220 ppm
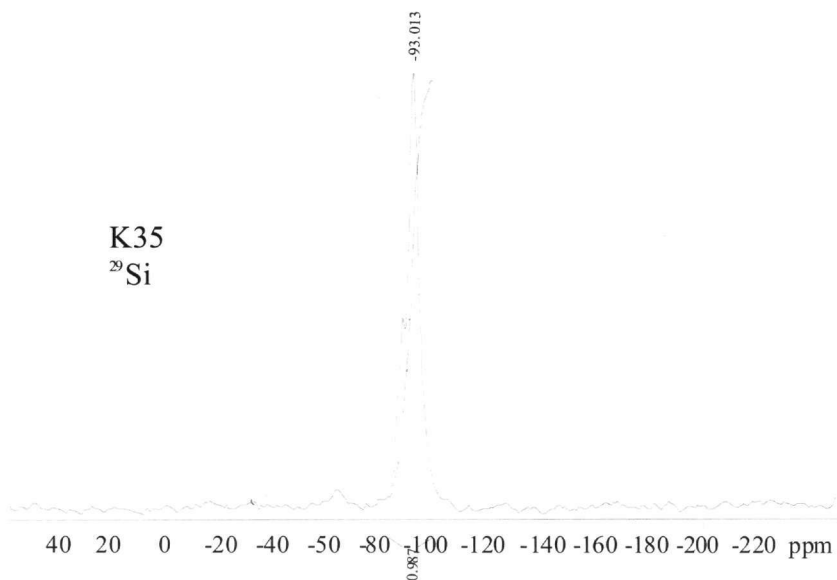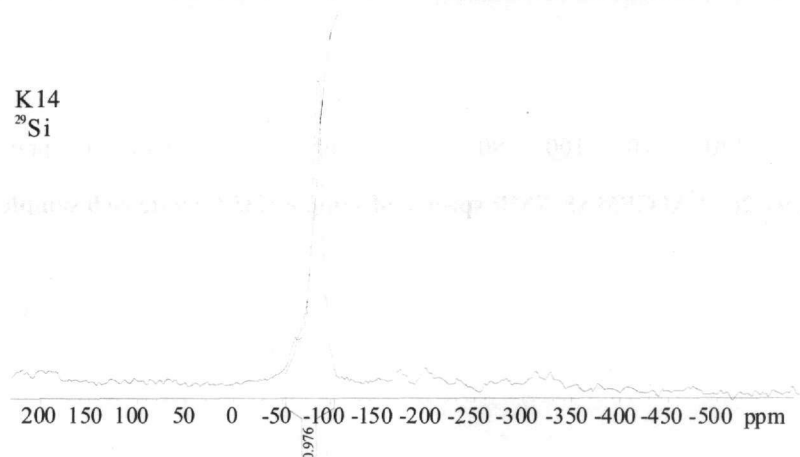
0.987

Figure 2d - ^{29}Si CPMAS NMR spectra of sample K35 (dickite rich sample)

octahedral-Al / tetrahedral-Si ratio measurement of dickite obtained by NMR of the sample K35. The relatively low iron amount of sample K48 is not causing problems to the octahedral-Al / tetrahedral-Si ratio of kaolinite obtained by NMR and as a result this measurement is accurate and significantly more accurate than those of dickite of the sample K35. It should be noted that the difference of the measurements is not significant and could be explained. The microanalyses measures a "spot" on the contrary NMR measures the whole sample and therefore is the average value of the mineral in the sample.

K14
^{27}Al

180 160 140 120 100 80 60 40 20 0 -20 ppm
0.985
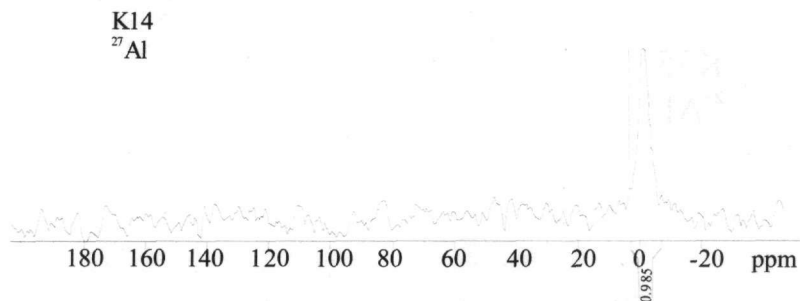
Figure 2e - ^{27}Al CPMAS NMR spectra of sample K14a (kaolinite rich sample)

K14
^{29}Si

200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 -400 -450 -500 ppm
0.976

Figure 2f - ^{29}Si CPMAS NMR spectra of sample K14a (kaolinite rich sample)

4.3. The impact some "details" of the analytical technique to the octahedral-Al / tetrahedral Si ratios of kaolinite and dickite

In order to get rid of the baseline noise the spectra was processed using absolute value spectra. This technique however, most of the times sweeps off the small nearby peaks. The kaolinite peaks observed in the spectra of sample K14a (Figs 2e, f), a kaolinite rich sample (Fig. 3c), are much weaker than the signals assigned to Al VI and Si IV in dickite and kaolinite bearing samples (Figs 2a, b, c, d), but relatively sharpen than dickite peaks of sample K35 and kaolinite peaks of other samples provided under the same technique. The kaolinite peaks of the sample K14a are relatively very broad. The broadening of the peaks has relatively low but not insignificant affect on the octahedral Al / tetrahedral Si ratios. It should be noted that all previously published NMR spectra of kaolinite group minerals (e.g. Bobos *et al.* 2001) are relatively very broad peaks and as it is shown in this work a small but significant error on the octahedral Al / tetrahedral Si ratios observed in these cases. This is due to the impact of some "details" of the analytical technique that was referred in the methodology and especially to the high pulse recycling delays, the improved field homogenization, the proper tuned of both channels and the calibration of the spectrometer. In this work it is presented for the first time an approach to provide narrow MAS NMR or CPMAS NMR peaks. The narrow shape of the provided peaks is accommodating by accurate measurements of the exact position of the peaks and the octahedral Al / tetrahedral Si ratios. These is critical in order to identify the mineral and to measure its octahedral Al / tetrahedral Si ratio especially in cases that two or more polymorphs coexists.
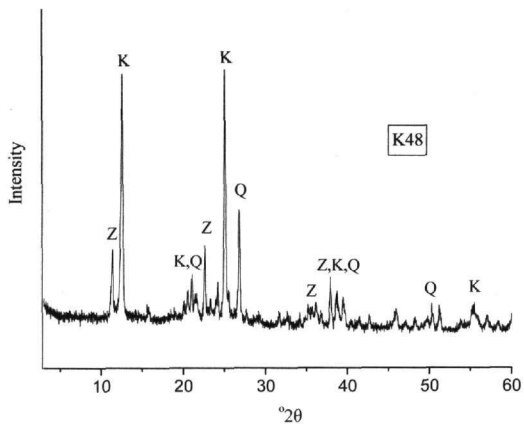
Figure 3a - XRD pattern of the bulk sample K48 (K: kaolinite, Z: Zunyite, Q: quartz)
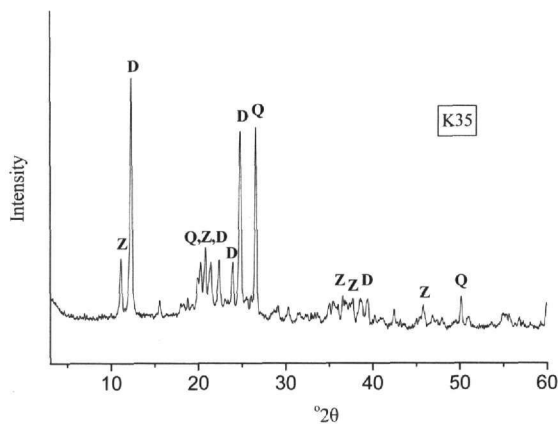

Figure 3b - XRD pattern of the bulk sample K35 (D: dickite, Z: Zunyite, Q: quartz)
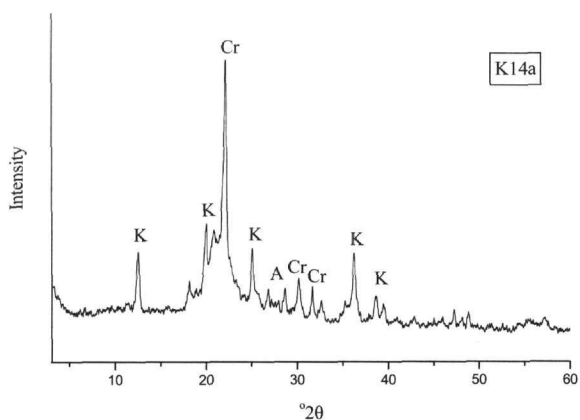

Figure 3c - XRD pattern of the bulk sample K14a (K: kaolinite, Cr: cristoballite, A: Feldspars)

5. Conclusions

The applications of ^{29}Si and ^{27}Al CPMAS NMR spectroscopy to the study kaolinite and dickite showed that kaolinite group of minerals could be easily detected by NMR techniques. However, it was found that in order to obtain a satisfactory resolution in the NMR spectra it was necessary to perform multiple spinning speed experiments at various pulse recycling delays; by increasing the pulse recycling delays, the interference of their peaks become less significant. The impact of some "details" of the analytical technique and especially the high pulse recycling delays, the improved field homogenization, the proper tuned of both channels and the calibration of the spectrometer is significant in order to obtain satisfactory resolution.

The octahedral-Al / tetrahedral-Si ratios of the kaolinite group of minerals estimated from ^{29}Si and ^{27}Al CPMAS NMR spectroscopy are in general agreement with the values calculated from (previously published) SEM-EDS microanalyses.

In this work it is presented for the first time an approach to provide narrow CPMAS NMR peaks. The narrow shape of the peaks provides accurate measurements of the exact position of the peaks and the octahedral Al / tetrahedral Si ratios.

The ^{27}Al NMR peak of the dickite appears at -0.13 ppm, 2.80 ppm relative to that of kaolinite. The ^{29}Si spectra of kaolinite appear at -93.01 ppm, -1.08 ppm relative to that of dickite.

6. Acknowledgments

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