

MINERAL QUANTIFICATION IN SEPIOLITE-PALYGORSKITE DEPOSITS USING X-RAY DIFFRACTION AND CHEMICAL DATA

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ABSTRACT: A quantification technique useful in analysis of clay-rich deposits containing sepiolite and/or palygorskite has been developed by combining diffractometric and chemical data and represents a considerable improvement on classic quantification based on X-ray diffraction. The required data are: intensity ratios between certain diffraction peaks of calcite-dolomite and sepiolite-palygorskite-smectites, and also the CaO, MgO, K₂O, Al₂O₃ and SiO₂ contents. The validity of this method was tested by analysis of artificial mixtures of pure phases of the minerals found in such deposits.

The quantitative analysis of mineral phases in clay-rich samples has always been subject to discussion. The classic techniques based on X-ray diffraction (XRD) have proved useful as a semi-quantitative method (Schultz, 1964; Biscaye, 1965; Barahona, 1974), although the degree of precision varies considerably, depending on errors inherent to the process and errors caused by the relative complexity of the mineral assemblage (cf. Mellinger, 1979; Moore & Reynolds, 1989; Pevear & Mumpston, 1989). The degree of accuracy in mineral quantification of clay-rich samples improves considerably if chemical data are used together with the parameters obtained by XRD (Pearson, 1978; Hodgson & Dudeney, 1984; Johnson *et al.*, 1985; Leoni *et al.*, 1988; Calvert *et al.*, 1989, and references therein). However, the increase in accuracy usually involves tedious additional techniques that make this quantification process slow and expensive and, therefore, of little use as a routine procedure.

Pearson (1978) proposed a method for mudstones in which the clay minerals belong to the chlorite, mica and kaolinite groups, although he pointed out that errors are significant when the mineral composition includes >35% chlorite and the smectite content is >10%. Apart from XRD, this method requires determination of SiO₂, Al₂O₃,

K₂O, Fe₂O₃, MgO and CO₂. Quartz is determined by XRD and carbonates by the CO₂ content. Literature data on average chemical compositions of mudstones and phyllosilicates were used in Pearson's calculations.

Hodgson & Dudeney (1984) proposed a method for estimating phyllosilicates in mixtures of chlorite, vermiculite, smectite, kaolinite and serpentine based on a combination of XRD and chemical analyses of Si, Al, Fe and Mg. They applied the method to hydrothermally altered kimberlites, obtaining an overall error for a particular phase proportion in the range 7–25%, the error decreasing with an increasing estimate of mineral proportion.

The method of Johnson *et al.* (1985) is useful for samples of soils or sediments containing kaolinite, illite, smectite, vermiculite, chlorite, interstratified vermiculite-chlorite, quartz and non-crystalline phases. Apart from XRD, this method requires determination of several analytical variables, such as cation exchange capacity (Ca/Mg, K/NH₄), contents of K₂O, SiO₂, MgO and weight loss at different temperature ranges (100–300°C and 300–950°C).

Another method for quantification of pelitic rocks and sediments with quartz, calcite, feldspars, kaolinite, illite, chlorite and smectite is that by

Leoni *et al.* (1988). This includes: (1) identification and approximate quantitative estimation of the mineral phases in the whole sample and in the <4 μm fraction by powder XRD; (2) chemical analysis by fluorescence of the major components in the whole sample saturated with NH_4 ; (3) determination of CO_2 and H_2O as loss by calcination.

Calvert *et al.* (1989) proposed another computerized method useful for mineral quantification of geological samples based on the following requirements: identification and semi-quantitative estimation by XRD in the whole sample and the <2 μm fraction, analysis of major elements in the whole sample saturated with NH_4 , and specific surface analysis.

In recent years, Merodio *et al.* (1992) and De Caritat *et al.* (1994) developed computer programs for the calculation of the normative composition of pelitic rocks based on XRD data and chemical analysis of the bulk sample and individual phases. These programs are applicable to samples containing illite, chlorite, smectite and kaolinite.

None of these methods includes fibrous clay minerals (sepiolite and palygorskite) in the determined phases. In this study we propose a method based on XRD and chemical data that is appropriate for samples from sepiolite and/or palygorskite deposits. Apart from these two phases, the most common minerals in these types of deposits are: calcite, dolomite, quartz, amorphous silica, feldspars, illite, interstratified illite-smectite (I-S), Al-smectite and Mg-smectite. Very small quantities of clinoptilolite-heulandite, gypsum, halite, kaolinite and apatite occur in some samples (cf. Jones & Galán, 1988).

Previous studies on these types of deposits (Torres-Ruiz *et al.*, 1994) revealed the difficulty of quantifying certain mineral phases by XRD. The most significant errors affected: (1) determination of the percentage of illite, I-S and palygorskite (due to overlapping of their principal reflections); (2) differentiation of Mg-smectite from other types of smectite; and (3) quantification of amorphous silica. In the first two cases errors can be extremely high, as these phases are major components in many samples.

METHODOLOGY

Ten artificial mixtures were prepared using pure phases of the major minerals typically present in this type of deposit: quartz, calcite, dolomite, illite, sepiolite, palygorskite, Al-smectite and Mg-smec-

tite. Practically pure illite was obtained in a sample from Vicálvaro (Madrid, Spain) consisting of illite, quartz and feldspars, by treating with heavy liquids and centrifugal separation. The pure palygorskite was obtained in a sample from Pareja (Guadalajara, Spain) made up of palygorskite, calcite and illite, by dissolving calcite with 1 N acetic acid, followed by heavy liquid separation and centrifuge treatment. The other minerals were obtained from monomineralic samples. Table 1 shows the origin and chemical analysis of the pure minerals and Table 2 shows the different mineral mixtures and their chemical analyses.

Chemical analyses were carried out by X-ray fluorescence by X-RAL Laboratories (Ontario, Canada). The lower reporting limit is 0.01% for all elements.

The accuracy of the method is intimately connected to the knowledge of the chemical composition of those mineral phases that may have broad compositional variation (basically, palygorskite, illite and smectites in these deposits). The composition of these phases must be previously determined from monomineralic samples or by mean of EDX analysis. In particular knowledge of the CaO content in the phyllosilicates may be important for a correct quantification of carbonates. In any case, if these data are not available, the use of the average compositions of these minerals based on published data (Table 3) can substantially improve the initial XRD quantification.

Development of the suggested method involved the stages described below.

X-ray diffraction

X-ray diffraction was carried out on the whole sample, previously milled to 50 μm , and on oriented aggregates treated with ethylene glycol. On the diffractograms we determined: (1) proportions of the phyllosilicates and other minerals present using the classic method based on areas of certain peaks and reflective power (the peaks and reflective powers used for sepiolite and palygorskite are those indicated by Huertas (1969) and the others by Schultz (1964) and Barahona (1974)); (2) determination of the intensity ratio between the calcite and dolomite peaks (3.03 Å and 2.88 Å in the whole sample); (3) determination of the intensity ratios between the sepiolite and smectite peaks (12.1 Å and 17 Å) and palygorskite and smectite peaks (10.6 Å and 17 Å) in the oriented aggregates solvated with ethylene glycol.

TABLE 1. Chemical composition and origin of the pure phases used.

	Calcite (1)	Dolomite (2)	Sepiolite (3)	Palygorskite (4)	Illite (5)	Al-smectite (6)	Mg-smectite (7)
SiO ₂	0.10	0.25	55.21	56.50	50.20	59.07	58.74
Al ₂ O ₃	0.05	0.07	0.43	7.87	26.88	19.83	1.37
Fe ₂ O ₃	0.05	0.03	0.15	3.63	3.55	3.82	0.78
MgO	0.23	21.75	24.26	10.81	2.92	5.26	26.11
CaO	55.45	30.29	0.20	0.20	0.41	1.42	1.00
Na ₂ O	0.05	0.03	0.10	0.07	0.15	1.40	0.10
K ₂ O	0.02	0.03	0.15	0.28	7.24	1.20	0.24
TiO ₂	0.00	0.02	0.05	0.05	0.35	0.50	0.10
MnO	0.01	0.01	0.02	0.04	0.04	0.05	0.01
LOI	43.85	47.25	19.21	19.84	8.42	8.00	11.56
Total	99.81	99.73	99.78	99.29	100.16	100.55	100.01

(1) Calcite from Almazán (Duero Basin)

(2) Dolomite from Almazán (Duero Basin)

(3) Sepiolite from Vicálvaro (Madrid)

(4) Palygorskite from Pareja (Tajo Basin)

(5) Illite from Vicálvaro (Madrid)

(6) Al-Smectite from Cabo de Gata (Almería)

(7) Mg-Smectite from Vicálvaro (Madrid)

Chemical analysis

The chemical composition of any sample is related to its mineralogy by equations of the type: $a_iX + b_iY + c_iZ = 100K_i$, where a_i , b_i and c_i are the

percentages of an element or oxide in the minerals x , y and z ; K_i is the percentage of this element or oxide in sample K ; X , Y and Z are the percentages of the minerals x , y and z .

TABLE 2. Mineralogical and chemical composition of the different artificial mixtures.

	Mixt. 1	Mixt. 2	Mixt. 3	Mixt. 4	Mixt. 5	Mixt. 6	Mixt. 7	Mixt. 8	Mixt. 9	Mixt. 10
Mineralogy										
Quartz	0	0	4	1	12	7	0	10	5	3
Calcite	0	15	21	6	0	0	3	0	3	48
Dolomite	20	0	10	5	0	25	0	3	43	0
Sepiolite	50	30	20	0	65	0	17	6	0	18
Palygorskite	0	10	25	42	0	43	0	5	9	5
Illite	20	5	6	8	3	20	5	60	35	11
Al-smectite	10	20	10	30	0	5	0	10	5	10
Mg-smectite	0	20	4	8	20	0	75	6	0	5
Chemical analyses										
SiO ₂	43.20	47.00	40.10	48.40	61.10	44.30	55.93	55.38	30.46	30.15
Al ₂ O ₃	7.99	5.65	5.47	10.50	1.40	9.64	2.42	18.35	10.92	5.42
Fe ₂ O ₃	1.04	1.76	2.14	3.56	0.46	2.61	0.88	3.21	2.02	1.13
MgO	17.20	14.80	11.30	9.11	20.80	10.93	23.75	6.45	11.55	7.04
CaO	6.80	8.93	15.40	6.04	0.55	7.82	2.48	1.28	14.94	27.15
Na ₂ O	0.26	0.25	0.15	0.32	0.15	0.16	0.10	0.30	0.19	0.19
K ₂ O	1.90	0.66	0.64	0.99	0.42	1.70	0.57	4.35	2.63	0.96
TiO ₂	0.15	0.19	0.27	0.39	0.11	0.14	0.10	0.31	0.19	0.11
MnO	0.05	0.05	0.05	0.05	0.05	0.04	0.01	0.04	0.04	0.03
LOI	20.80	20.60	24.00	19.70	14.50	22.53	13.69	10.22	25.94	27.89
Total	99.39	99.89	99.52	99.06	99.54	99.86	99.93	99.90	99.88	100.08

TABLE 3. Average compositional data obtained from the literature on phyllosilicates usually appearing in these deposits.

	Sepiolite (1)	Palygorskite (1)	Illite (2)	Al-smectite (3)	Mg-smectite (4)	Mixed-layer I-S (4)
SiO ₂	52.5–56.1	52–58	49.8	59.5	53–57	49–54
Al ₂ O ₃	0.25–0.6	8–12	26.4	21.9	0–1.1	22–28
MgO	21.3–25.3	9–13	2.8	3.6	24.5–27.5	2–3
CaO	0.3–0.5	0.5–2	0.3	1.2	0.5–1	0–0.6
K ₂ O	0–0.6	0.1–0.5	7.0	0.3	0–0.4	5–9

(1) Mean compositional range. Data taken from Weaver & Pollard (1973) and Jones & Galán (1988)

(2) Mean composition of 24 illites (Weaver & Pollard, 1973)

(3) Mean composition of 101 montmorillonites-beidellites (Weaver & Pollard, 1973)

(4) Mean oompositional range. Data taken from Weaver & Pollard (1973)

For most samples it will only be necessary to determine SiO₂, CaO, MgO, K₂O and Al₂O₃. In some deposits with significant proportions of gypsum and/or halite it will also be necessary to determine the content of sulphate and chloride.

Determination of typical accessory phases. If feldspars, gypsum and/or halite are found by XRD, their proportions are calculated on the diffractogram using the classic technique of reflective powers. More precisely, on the basis of the data on sulphates and chlorides in the chemical analysis we obtain: % gypsum = $100 \times (\%)SO_4^{2-}/55.81$ and % halite = $100 \times (\%)Cl^-/60.68$.

Determination of carbonates. Given that Ca is found almost exclusively in carbonates, its distribution between calcite and dolomite is as follows:

$$CaO_{\text{carbonates}} = CaO_{\text{total}} - CaO_{\text{gypsum}} - CaO_{\text{phyllosilicates}}$$

$$CaO_{\text{gypsum}} = \% \text{ gypsum} \times 23.256/100,$$

$$CaO_{\text{phyllosilicates}} = \% \text{ phyllosilicates} \times a/100$$

($a = \% \text{ CaO in phyllosilicates}$),

$$CaO_{\text{calcite}} = 1.843 \times \text{ratio (XR)}_{\text{cal/dol}} \times$$

$$CaO_{\text{carbonates}}/[1 + (1.843 \times \text{ratio (XR)}_{\text{cal/dol}})],$$

$$CaO_{\text{dolomite}} = CaO_{\text{carbonates}} - CaO_{\text{calcite}}.$$

With these values we therefore obtain:

$$\% \text{ calcite} = CaO_{\text{calcite}} \times 100/56 \text{ and}$$

$$\% \text{ dolomite} = CaO_{\text{dolomite}} \times 184.3/56.$$

Determination of illite and interstratified illite-smectite. Considering that the only phases containing significant quantities of K in their structure are illite, interstratified illite-smectite and potassium feldspar, and that a small proportion of K can be found in neoformed clays, we suggest the following:

$$K_2O_{\text{illite + illite-smectite}} = K_2O_{\text{total}} - K_2O_{\text{FdK}} - K_2O_{\text{fibrous clays}}$$

$$K_2O_{\text{FdK}} = \% \text{ FdK} \times 17/100,$$

$$K_2O_{\text{fibrous clays}} = \% \text{ phyllosilicates} \times b/100$$

($b = \% \text{ K}_2\text{O in the fibrous clays}$),

$$\% \text{ illite + illite-smectite} = K_2O_{\text{illite + illite-smectite}} \times 100/c$$

($c = \% \text{ K}_2\text{O in illite and illite-smectite}$).

Determination of palygorskite and Al-smectite.

The Al datum is most useful in calculating the proportions of palygorskite and Al-smectite. Since we already know the (illite + illite-smectite) and feldspar values, we find that:

$$Al_2O_3_{\text{palygorskite + Al-smectite}} = Al_2O_3_{\text{total}} - Al_2O_3_{\text{I + I-S}} - Al_2O_3_{\text{feldspars}}$$

$$Al_2O_3_{\text{illite + illite-smectite}} = \% \text{ I + I-S} \times d/100$$

($d = \% \text{ Al}_2\text{O}_3 \text{ in I + I-S}$)

$$Al_2O_3_{\text{feldspars}} = \% \text{ feldspar}_i \times e_i/100$$

($e_i = \% \text{ Al}_2\text{O}_3 \text{ in each feldspar}$)

To distribute the Al between palygorskite and Al-smectite, we use the ratio between both minerals as calculated on the diffractogram. The calculations are as follows:

$$F1 = 100/1 + \text{ratio (XR)}_{\text{palygorskite-smectite}}$$

$$R1_{\text{palygorskite}} = F1 \times \text{ratio (XR)}_{\text{palygorskite-smectite}} \times f/100$$

($f = \% \text{ Al}_2\text{O}_3 \text{ in palygorskite}$),

$$R2_{\text{Al-smectite}} = F1 \times g/100$$

($g = \% \text{ Al}_2\text{O}_3 \text{ in Al-smectite}$),

$$S1 = R1 + R2.$$

$$\% \text{ palygorskite} = (R1/S1) \times Al_2O_3_{\text{palygorskite + Al-smectite}} \times 100/f,$$

and

$$\% \text{ Al-smectite} = (R2/S1) \times Al_2O_3_{\text{palygorskite + Al-smectite}} \times 100/g.$$

Determination of sepiolite and Mg-smectite.

$$\text{MgO}_{\text{sepiolite}} + \text{Mg-smectite} = \text{MgO}_{\text{total}} - \text{MgO}_{\text{dolomite}} - \text{MgO}_{\text{I} + \text{I-S} + \text{palygorskite}}$$

$$\text{MgO}_{\text{dolomite}} = \% \text{ dolomite} \times 40.3/184.3$$

$$\text{MgO}_{\text{illite}} + \text{illite-smectite} + \text{palygorskite} = [\% (\text{I} + \text{I-S}) \times h/100] + [\% \text{ palygorskite} \times i/100]$$

(h = % MgO in illite and illite-smectite and i = % MgO in palygorskite)

The Mg is then distributed between sepiolite and Mg-smectite:

$$F2 = 100/1 + \text{ratio} (\text{XR})_{\text{sepiolite-smectite}}$$

$$R3_{\text{sepiolite}} = F2 \times \text{ratio} (\text{XR})_{\text{sepiolite-smectite}} \times j/100$$

(j = % MgO in sepiolite),

$$R4_{\text{Mg-smectite}} = F2 \times k/100$$

(k = % MgO in Mg-smectite),

$$S2 = R3 + R4.$$

$$\% \text{ sepiolite} = (R3/S2) \times \text{MgO}_{\text{sepiolite}} + \text{Mg-smectite} \times 100/j,$$

and

$$\% \text{ Mg-smectite} = (R4/S2) \times \text{MgO}_{\text{sepiolite}} + \text{Mg-smectite} \times 100/k.$$

Determination of quartz and amorphous silica.

Once we have established the phases containing silica (feldspars and phyllosilicates), we can determine the quantity of quartz and/or amorphous silica, the latter being a phase that is frequently not detected by XRD:

$$\text{SiO}_2_{\text{phyllosilicates}} = \% \text{ phyllosilicate}_i \times I_i/100$$

(I_i = % SiO₂ in each phyllosilicate)

$$\text{SiO}_2_{\text{feldspars}} = \% \text{ FdK} \times 64.7/100$$

$$\begin{aligned} &+ \% \text{ plagioclases} \times 68.2/100 \\ \% \text{ quartz and amorphous silica} &= \text{SiO}_2_{\text{total}} \\ &- \text{SiO}_2_{\text{phyllosilicates}} - \text{SiO}_2_{\text{feldspars}} \end{aligned}$$

All the calculations described above and the necessary repetitions are tedious, unless we use a computer program. We have developed such a program using Excel for Windows 5.0 (Microsoft) and a disk copy is available to anyone requesting it.

DISCUSSION AND CONCLUSIONS

The aim of the method proposed is to improve the quantification obtained by the classic XRD method and is particularly suitable for samples with a high fibrous clay mineral content. In these types of deposits the rest of the major phases are quartz, carbonates, smectites, illite and interstratified illite-smectite. Other phases (feldspars, zeolites, kaolinite, apatite, chlorite, Fe-oxides, gypsum and halite) usually appear in small quantities or are absent, so that the errors occurring during quantification by XRD are not especially significant.

The following observations can be made from comparison of the XRD method and the method proposed (Table 4):

(1) The values obtained by the proposed method are very similar to those of the prepared artificial

TABLE 4. Quantification percentages of the artificial mixtures obtained by XRD and the proposed method.

	Mixt. 1	Mixt. 2	Mixt. 3	Mixt. 4	Mixt. 5	Mixt. 6	Mixt. 7	Mixt. 8	Mixt. 9	Mixt. 10
Data obtained by X-ray diffraction										
Quartz	0	0	5	3	10	10	0	18	9	2
Calcite	0	12	22	7	0	0	2	0	1	52
Dolomite	20	0	9	5	0	20	0	3	52	0
Sepiolite	59	56	32	0	72	0	23	6	0	22
Palygorskite	0	8	22	59	0	57	0	7	18	9
Illite	12	3	3	5	5	10	4	58	15	7
Smectites	9	21	7	21	13	3	71	8	5	8
Data obtained by the proposed method										
Quartz	0	0	3	0	12	6	1	10	4	3
Calcite	0	15	21	7	0	0	4	0	3	48
Dolomite	21	0	10	4	0	25	0	3	43	0
Sepiolite	49	32	20	0	66	0	15	6	0	17
Palygorskite	0	9	25	42	0	42	0	5	9	5
Illite	19	4	6	7	3	21	5	60	36	11
Al-smectite	11	19	10	30	0	5	0	10	4	10
Mg-smectite	0	21	5	10	19	1	75	6	1	6

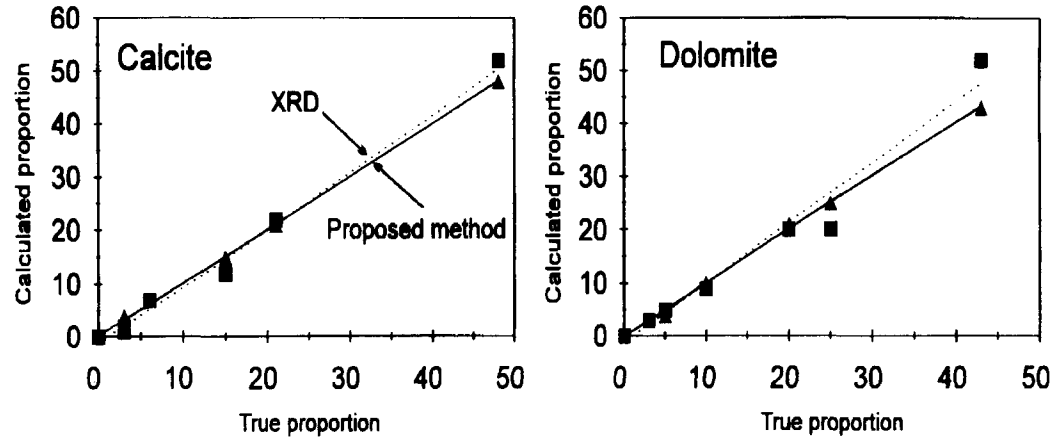


FIG. 1. Comparison of the true proportion of calcite and dolomite present in the mixtures and the experimental data obtained by XRD and the method proposed. Regression lines are shown. Squares and dotted line = XRD data; triangles and continuous line = data obtained by the proposed method.

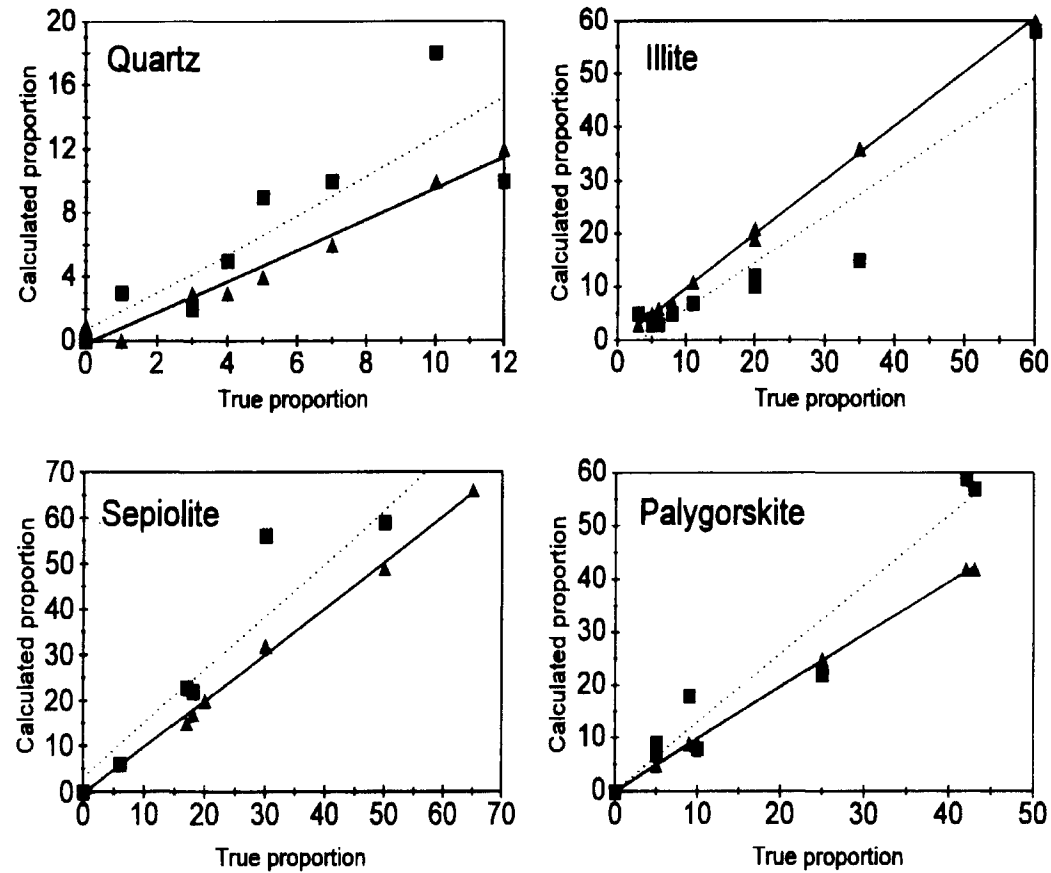


FIG. 2. Comparison of the true proportion of quartz, illite, sepiolite and palygorskite present in the mixtures and the experimental data obtained by XRD and the method proposed. Symbols as for Fig. 1.

mixtures, and present a high degree of linear correlation. However, the data obtained by XRD show higher dispersion of values, that vary from one phase to another (Figs. 1 to 3).

(2) The carbonate (calcite and/or dolomite) percentages obtained by the two methods are not

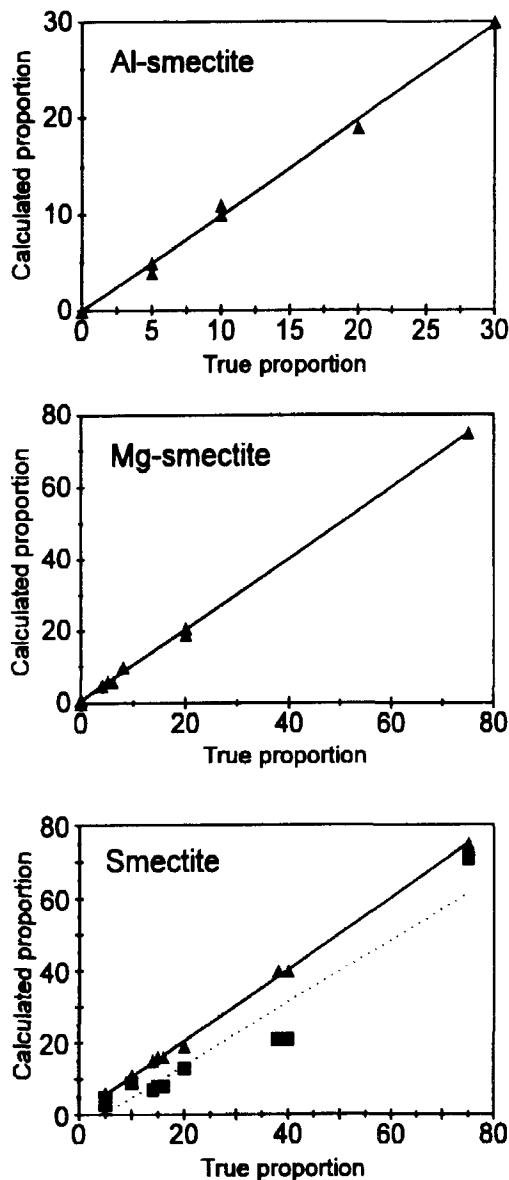


FIG. 3. Comparison of the true proportion of smectite present in the mixtures and the experimental data obtained by XRD and the method proposed. Symbols as for Fig. 1.

substantially different (Fig. 1). However, errors become significant at carbonate percentages >20–25%.

(3) The differences between the two methods are significant for quartz, fibrous minerals, illite and smectite. The XRD quantification of illite and smectite gives values lower than both the true ones and those obtained by the method proposed here. The contrary is true for the other minerals mentioned.

(4) The XRD quantification of illite has serious disadvantages when the samples are rich in palygorskite, as the 10.6 Å peak of the latter can completely mask the 10 Å peak of illite. This is illustrated in Fig. 4, corresponding to artificial mixture 6, which contained 20% illite and 43% palygorskite.

(5) Determination of the percentages of the different types of smectite is the most difficult case to solve, although the spacing of the 060 reflection on powder samples gives some idea of whether the smectites are dioctahedral or trioctahedral. In addition, a comprehensive study of Spanish deposits of sepiolite/palygorskite by Torres-Ruiz *et al.* (1994) showed that Mg-smectite is normally either the only neoformed phyllosilicate or it is associated with sepiolite. No sample was found presenting Mg-smectite together with palygorskite, at least in significant amounts, which simplifies the problem in most cases. However, where the two types of smectite coexist, the only approximation to quantification can be made by progressive adjustments of the sepiolite/Mg-smectite and palygorskite/Al-smectite ratios in order to obtain a perfect fit between the chemistry deduced from the mineralogical composition and the chemical components analysed. Despite these disadvantages, very good results were obtained

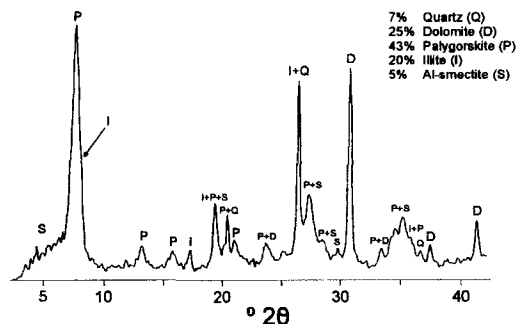


FIG. 4. X-ray diffraction diagram of artificial mixture no. 6. Note that the main diffraction peaks of illite are overlapped by the palygorskite and quartz peaks.

by this method for quantification of artificially prepared mixtures (Fig. 3).

(6) The method proposed also allows estimation of amorphous silica, a phase frequently found in these deposits that cannot be quantified by XRD. This estimate is carried out by calculation of the quartz content by XRD and fit between the chemical composition deduced from the mineralogical characteristics and the total SiO₂ content of the sample. The presence of amorphous silica in considerable quantities in samples from the sepiolite deposits in the Madrid Basin was confirmed by scanning electron microscopy, which detected it in the form of opal lepispheres covered by sepiolite fibres (Medina *et al.*, 1993).

As already stated, use of this quantification method for these types of samples represents a significant improvement over XRD. However, the degree of accuracy achieved depends on adequate prior information on the chemical composition of the different mineral phases present, particularly the different phyllosilicates, which can have a broad range of compositional variety.

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