

ОСАДОЧНАЯ ГЕОЛОГИЯ И НЕФТЕГАЗОНОСНОСТЬ

КОЛИЧЕСТВЕННОЕ ИЗУЧЕНИЕ ГЛИНИСТЫХ МИНЕРАЛОВ В ПОРОДАХ-КОЛЛЕКТОРАХ ГАЗОНОСНОГО ГОРИЗОНТА ШУРИДЖЕ (*Северо-Восточный Иран*)
КОМПЛЕКСОМ МЕТОДОВ РЕНТГЕНОВСКОГО АНАЛИЗА

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Породы-коллекторы горизонта Шуридже (неоком) на газовом месторождении Гонбадди в Копетдагском бассейне Северо-Восточного Ирана представлены песчаниками, местами — с прослоями сланцев. Глинистые минералы горизонта Шуридже были изучены методами рентгенодифракционного и рентгенофлуоресцентного анализа в 76 ядрах, отобранных из двух глубоких скважин Гонбадди. При рентгенофлуоресцентном анализе были выявлены высокое процентное содержание Si и варьирующие от умеренных до низких содержания Al, S, Ca, K, Na, Mg и Fe в обеих скважинах. Согласно результатам рентгенодифракционного анализа, вышеназванные элементы сконцентрированы в форме кварца, ангидрита, доломита, кальцита, плагиоклаза, калиевого полевого шпата, гематита и глинистых минералов. Дальнейшее изучение глинистой фракции с помощью данного метода показало, что основными типами глинистых минералов являются иллит, хлорит и каолинит. С другой стороны, глауконит, смектит и смешанослойные глинистые минералы (иллит-смектитовые и хлорит-смектитовые глины) были обнаружены лишь в немногих образцах. Определения процентных содержаний отдельных глинистых минералов были выполнены методом внешнего стандарта с использованием калибровочных кривых и успешно подтверждены системой линейных уравнений, полученных на основе детальных данных изучения элементов рентгенофлуоресцентным методом. Погрешность определения составила $\pm 5\%$ для главных минеральных компонентов и $\pm 15\%$ для второстепенных минералов. Кроме того, на основе данных рентгенофлуоресцентного изучения элементов было получено локальное регрессионное соотношение, позволяющее оценить содержание глинистой фракции в других пробуренных скважинах на Шуридже с применением данных импульсной нейтронной спектроскопии. При использовании предложенного количественного подхода наблюдались значительные вариации содержания иллита, которое достигало 18.3%. Напротив, содержания каолинита и хлорита, как правило, были низкими (менее 8.4%). Суммарное содержание глинистых минералов резко изменялось от минимального, составлявшего 5%, до максимального, равного 32.5%. Рост содержания иллита по мере увеличения глубины погружения и температуры явно свидетельствует о глубинном диагенезе в данном горизонте.

Минералогия глин, рентгенодифракционный метод, рентгенофлуоресцентный метод, количественный минералогический анализ, горизонт Шуридже.

QUANTITATIVE ANALYSIS OF THE CLAY MINERALS IN THE SHURIJEH RESERVOIR FORMATION USING COMBINED X-RAY ANALYTICAL TECHNIQUES

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The Shurijeh reservoir Formation of Neocomian age is represented by a sandstone sequence, occasionally interbedded with shale, in the Gonbadli gas field, Kopet-Dagh Basin, North-eastern Iran. In this study X-ray diffraction (XRD) and X-ray fluorescence (XRF) techniques were used to characterize the Shurijeh clay minerals in 76 core samples, collected from two deep Gonbadli wells. The results of XRF analysis showed high percentages of silicon and moderate to low percentages of aluminum, sulfur, calcium, potassium, sodium, magnesium, and iron in both wells. The XRD analysis indicated that the above elements were concentrated in the form of quartz, anhydrite, dolomite, calcite, plagioclase, K-feldspar, hematite and clay minerals. Further XRD exami-

nation of the clay fraction, revealed that illite, chlorite, and kaolinite were the major types of clay minerals. Unlike, glauconite, smectite and a mixed layer clays of both the illite-smectite and chlorite-smectite types were observed only in very few samples. The percentages of individual clay minerals were determined using external standard calibration curves, and successfully validated by a system of simultaneous linear equations acquired from detailed elemental information based on the XRF analysis. The amount of error reached $\pm 5\%$ for the main mineral constituent and $\pm 15\%$ for minor minerals. A local regression relationship was also derived, based on the XRF elemental information, which can be used to estimate the clay contents of other Shurijeh drilled wells with data of pulsed-neutron spectroscopy tools. According to the proposed quantitative approach, the amount of illite varied considerably reaching up to 18.3%. In contrast, the amount of kaolinite and chlorite were generally small, i.e. less than 8.4%. The amount of total clay minerals changed greatly from a minimum of 5% to a maximum of 32.5%. An increase in illite with increasing burial depth and temperature was an obvious indication of deep burial diagenesis in this Formation.

Keywords: clay mineralogy, Shurijeh reservoir Formation, X-ray diffraction, X-Ray fluorescence, Quantitative mineralogical analysis

1. INTRODUCTION

Clay minerals are of prime importance in the hydrocarbon reservoirs, due to their direct contribution to the production strategy. The most abundant clay minerals in the sandstone reservoirs are kaolinite, illite, chlorite, smectite and a mixed layer of illite-smectite. Since they can greatly affect the chemical and physical properties of the reservoirs (Worden and Morad, 2003), a good knowledge of types as well as the absolute amounts of clay minerals is necessary for the characterization studies of clastic reservoir. The important role of quantitative clay mineralogy in the provision of a successful and reliable reservoir description has been intensely studied (Sarkisyan, 1972; Wilson and Pittman, 1977; Hurst and Archer, 1986; Hurst, 1987; Bandaru, 2010; Soto Becerra et al., 2010). In most studies, X-ray diffraction (XRD) method has shown the remarkable ability to calibrate the well logs in terms of mineralogy; especially for the fine grained clay minerals (Pierce and Siegel, 1969; Causey, 1991; Crain, 2000; Bouchet et al., 2000; Krinari et al., 2014). It is known that under ideal conditions, the peak intensities of an XRD diffractogram are proportional to the concentrations of individual minerals present in the sample. Hence, the qualitative mineralogical data obtained from X-ray diffraction method can be quantified, using either the internal or external standard methods (Chung, 1974a, 1974b), or the whole pattern methods (Smith et al., 1987) such as the Rietveld algorithm (Rietveld, 1967, 1969), Arquant model (Blanc et al., 2007), and the so-called Le-Bail and Pawley method. Explanation of some other methods using absorption intensity factors or just intensity factors can be also found in Kahle et al. (2002). The conventional XRD standardization is mainly based on conducting a regression analysis against datasets obtained from the standard patterns. The external standard quantification method is based on using standard samples with identical diffraction characteristics to the same minerals in the original samples.

Johns et al. (1954), Sudo et al. (1961) (see also Aoki et al., 1974), Biscaye (1965), and Siegel et al. (1981), have studied clay minerals semi-quantitatively, assuming 100% of the < 2 mm fraction represented by the sum of the weighted peak areas of the clay minerals. A review of quantitative analysis of clay minerals is given by Ronald (1967), Alexiades and Jackson (1966); Pierce and Siegel (1969), Cody and Thompson (1974), Heath and Piasias (1979), Brindley (1980), Smith et al. (1987), Snyder and Bish (1989), Thornley and Primmer (1995), Moore and Reynolds (1997), Hillier (2000), Ottner et al. (2000), Ruan and Ward (2002), Kahle et al. (2002), Ouhadi and Yong (2003), Chittoori and Puppala (2011), and Wang et al. (2011). However, if very accurate quantitative mineralogical data are required, then the X-ray method alone is unable to obtain it, due to many factors such as the peak interferences (Moor and Reynolds, 1989), varying microstructures and different mass absorption coefficients in minerals (Ouhadi and Yong, 2003), various defects in crystals (Środoń et al., 2001), the suitability level of standard sample (Mitchell and Soga, 2005), amorphous existence (Jackson and Barak, 2005), disaggregation state (McManus, 1991), various possible alterations from initial chemical pretreatments (Moor and Reynolds, 1989), separation of particle sizes (Brindley, 1945), some variation in the packing of samples (Jackson and Barak, 2005), preferred crystallites orientation in the prepared slides (Dollase, 1986), and, finally, method of assessing proportions from the diffraction pattern (McManus, 1991). Klute (1986) has reviewed the detailed influence of the mentioned factors on the diffraction maxima. The clay contents of sandstones represent only a very small fraction of the whole sample and since the other phases, notably quartz, dominates in them, quantification becomes more difficult. As a result, if a more precise quantification is needed, it should be achieved by the help of elemental composition information obtained from the X-ray fluorescence or any other instrumental techniques of the elemental analysis (Calvert et al., 1989; Thornley and Primmer,

1995). In this combined method, the percentages of each mineral identified by the XRD are obtained by solving a number of simultaneous equations. The results of many studies (McNeal and Sansoterra, 1964; Hussey, 1972; Pearson, 1978; Hodgson and Dudney, 1984; Johnson et al., 1985; Braun, 1986; Engler and Iyengar, 1987; Kolka et al., 1994; Laird and Dowdy, 1994; Paktunc, 2001; Rosen et al., 2004; Prandel et al., 2014) imply that employing both methods can provide efficient quantitative mineralogical data with sufficient accuracy, which is applicable to the technical needs.

Although many previous studies of the quantitative clay mineralogy in the sandstone reservoirs have been carried out, comparatively little attention has been given to the study of clay minerals in the clastic reservoirs with complex lithology. The heterogeneous sandstone Shurijeh Formation is one of the most important as well as the most challenging gas reservoirs, which properly characterize the eastern Kopet-Dagh sedimentary Basin, Northeastern Iran. In this study, having known the types of clay minerals in the Shurijeh Formation, relevant percentages present in 76 core samples from two deep drilled wells in the Gonbadli gas field were calculated by the external standard method and validated by the detailed elemental information obtained from the XRF analysis.

2. GEOLOGICAL SETTING

The core data for this study were collected from a gas producing and other non-producing deep vertical wells drilled in the Gonbadli gas field of Eastern Kopet-Dagh sedimentary Basin, NE Iran. The Kopet-Dagh, an Iranian tectono-sedimentary unit, extends from east of the Caspian Sea to Northeast Iran (Fig. 1). It formed in an extensional regime after the closure of Palaeo-Tethys in the Middle Triassic (Alavi et al., 1997) and the opening of Neo-Tethys during the Lower to Mid Jurassic (Buryakovskiy et al., 2001). The sedimentation in the eastern Kopet-Dagh went on rather continuously and over 8000 m sediments were deposited from Jurassic through Miocene (Afsharharb, 1979). The Jurassic–Cenozoic sedimentary sequences unconformably overlie the Palaeozoic basement and Triassic rocks (Ulmishek, 2004). This region hosts both the Khangiran and Gonbadli gas fields.

The Gonbadli gas field was drilled in 1969 on the Gonbadli structure, an elongated and symmetrical anticline, located in the eastern part of the Kopet-Dagh sedimentary Basin, some 25 km southwest of Sarakhs town, between two productive structures of Dowlat-Abad in the east and Khangiran in the west (NIOC, 1986). The reservoir rock in the Gonbadli field consists of the Lower Cretaceous, Shurijeh sandstones, deposited under arid and warm conditions, in a variety of continental, coastal, and marine environments (Moussavi-Harami and Brenner, 1993). The Shurijeh Formation includes mixed red bed siliciclastic sediments, mostly fine to medium

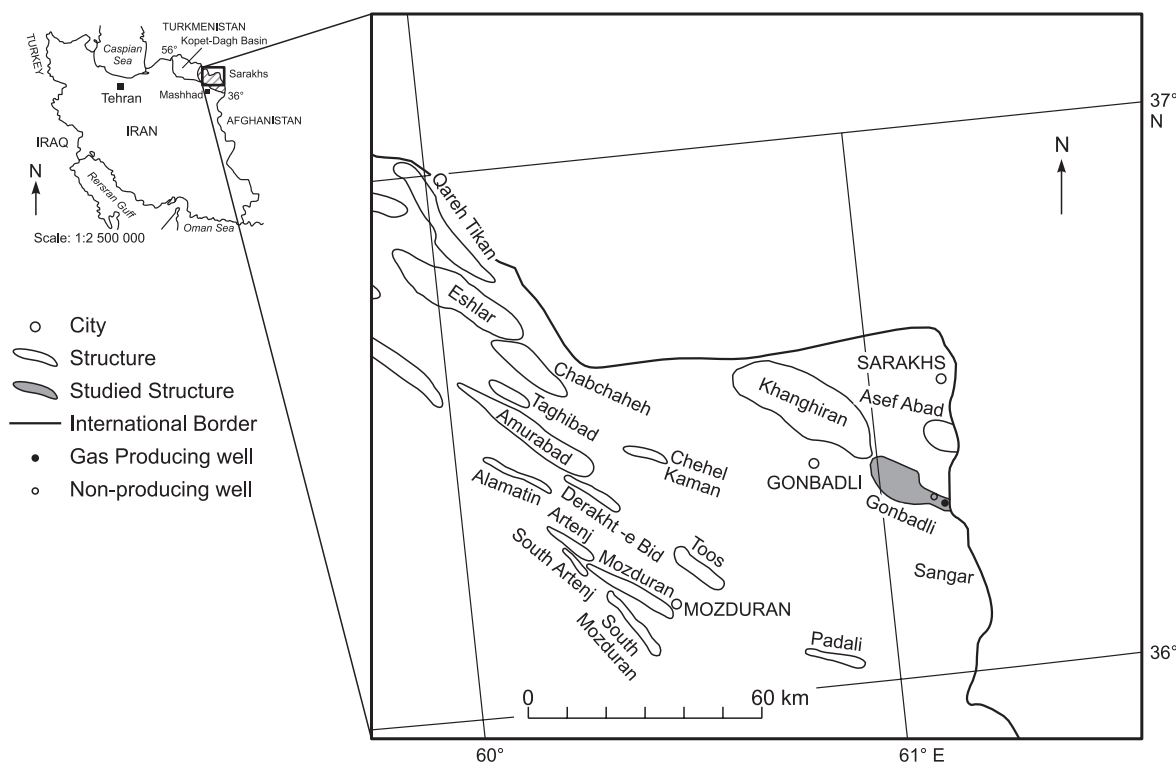


Fig. 1. Geographic location map of the studied area (modified from Jozanikohan et al., 2015).

Table 1.

The Shurijeh Formation classification (NIOC, 1986)

Division		Composition	Thickness (m)	
			Gas producing well	Non-producing well
Upper Part	E	Terrigenous evaporate minerals mixed with the sandstone, claystone	12.97	17.00
	D	Brownish gray whitish gray to bluish gray, medium coarse-grained, calcareous, partly friable and glauconitic sandstone with intercalation of reddish brown, anhydritic, silty claystone and greenish gray, calcareous siltstone	44.87	36.00
			D ₁	24.73
Middle Part	C	Reddish brown, calcareous siltstone, buff gray and brown, partly anhydritic claystone, alternating with thin-beds of buff gray fine-grained quartzitic, slightly glauconitic sandstone	46.35	21.23
			C ₁	34.05
Lower Part	B	Reddish brown, whitish gray, medium to coarse-grained, partly conglomeratic, quartzitic sandstone, interbedded with thin layers of reddish brown, anhydritic claystone and chocolate brown, calcareous siltstone	33.11	41.00
	A	Reddish brown, calcareous, anhydritic claystone and chocolate brown, calcareous siltstone	25.92	38.5

grained rocks (shales, siltstone and sandstones) with occasional intercalations of evaporates and carbonates lithofacies, overlying the limestone of Mozduran Formation (Upper Jurassic) and capped by the Tirgan Formation (NIOC, 1986). The Shurijeh Formation approximately starts some 3 km below the rotary tables with a varying thickness from 174.5 m to 259.1 m in the Gonbadli drilled wells (NIOC, 1986). Based on extremely variable lithology, Shurijeh was divided onto upper, middle and lower parts with five lithological units as lithofacies A, B, C (subdivided into C₁ and C₂ units), D (subdivided into D₁ and D₂ units) and E (Table 1) within which, the sand rich unit of D₁ is characterized as the main sweet gas bearing zone in the area under study, with production capacity of 1.1 Mcm/d (NIOC, 1986). Four of the main points of difference between D₁ and D₂ and C₁ and C₂ units, are summarized in the degree of cementation, formation fluid type, the amount of porosity and matrix (NIOC, 1986). The thickness of reservoir unit, D₁, varies between 24.5 m and 40.66 m in the Gonbadli field (NIOC, 1986). Two Gonbadli wells, one gas producing and the other non-producing, approximately located in the 8.5 km distance from each other in the eastern end of structure (Fig. 1), were chosen for this study. The Shurijeh Formation is situated between depths of 3125 m and 3347 m in the gas producing well and depths of 3121 m to 3377.5 m in the non-producing well.

3. MATERIALS AND METHODS

3.1. Core samples

A total of 76 core samples were taken almost every half a meter from D₁ and C₂ units of the Shurijeh Formation in the two Gonbadli wells. The relevant units and location of 20 samples of the producing well and 56 samples of non-producing well are shown in Fig. 2. The outer parts of each core sample were removed to prevent the possible contamination or oxidation effects. Then, 100 g of each sample was crushed to a preliminary coarse size (<mm) in a heavy mortar and grounded as a paste with propanol to avoid the possible phase changes in minerals. To obtain a homogeneous and evenly distributed grain size mixture, each sample was well mixed and ground with a constant grinding time. A special attempt was made in sample grinding in order to avoid adding the non-clay minerals into fine grained powders (<2 μm fraction). The ground samples were then properly disaggregated by the blender and ultrasonic methods for XRD analysis of clay minerals.

3.2. X-ray diffraction (XRD) analysis

The mineral identification/quantification of the Shurijeh Formation reservoir was accomplished using a computer controlled Bruker AXS, D8 Advance powder X-ray diffractometer with a two-theta/theta goniometer geometry. All core samples were scanned in the angular range from 4 to 70 and 4 to 40 two-theta degrees for the bulk and clay mineralogy purposes, respectively. The measurements were performed with the 0.02° two-theta degrees scan step sizes in a speed of 1.2 two-theta degrees per minute, using copper Ka radiation with a nickel filter at 40 kV voltage and 30 mA current of the generator. A dynamic scintillation detector with low background, and large dynamic range was used for the collection of X-ray diffraction data from samples. The total bulk and clay mineralogy scan times for each sample with the mentioned set up were 55 and 31 minutes, respectively.

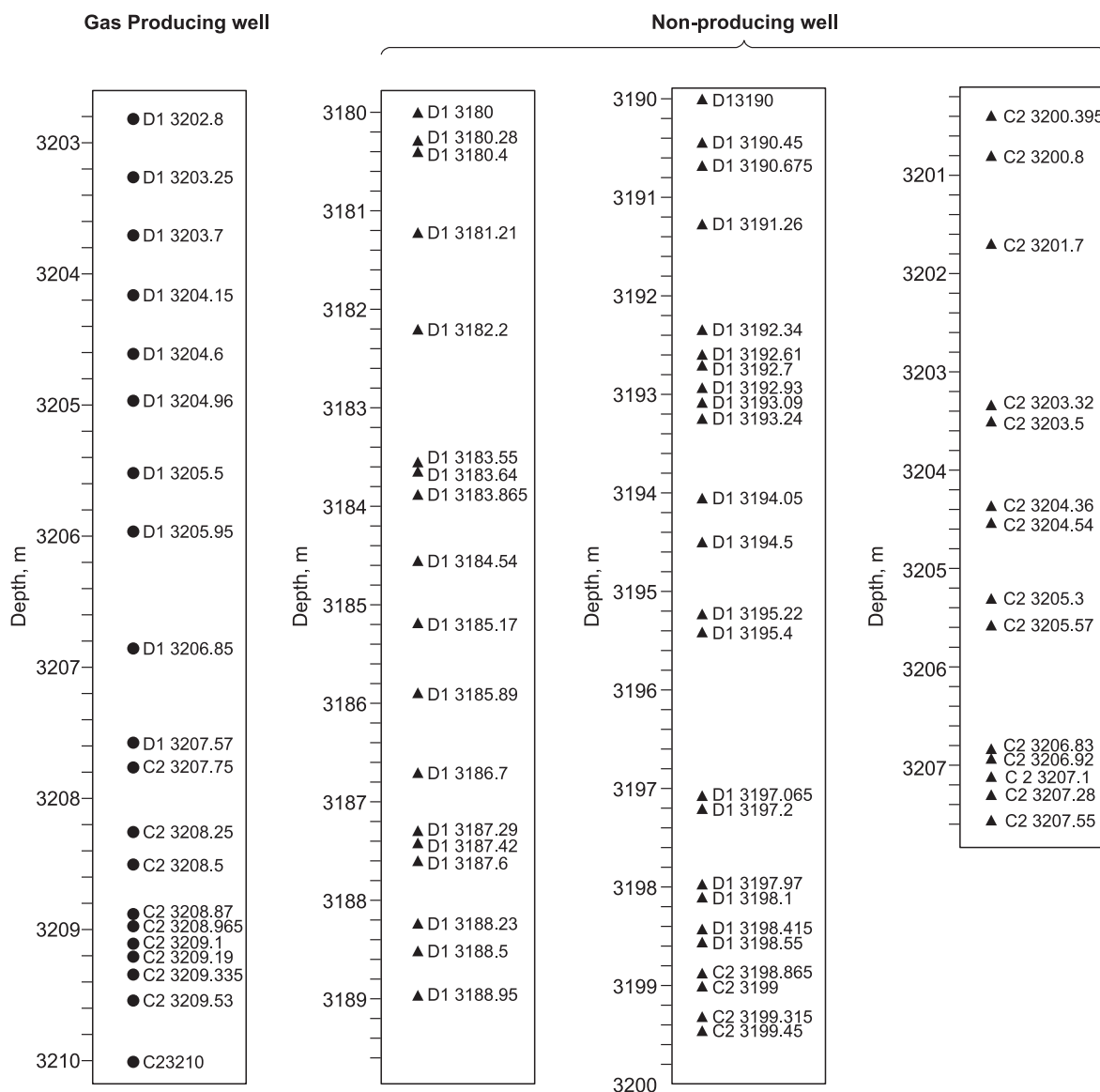


Fig. 2. The schematic locations of core samples in both wells. The relevant Shurijeh units and depth of each core samples are mentioned on the Figure. ● = gas producing well core samples and ▲ = non-producing well core samples.

3.2.1. Preparation

The most important first step in quantitative XRD analysis is to prepare the samples with respect to all possible sources of error. Non-clay minerals can mask some basic reflections of the clay minerals, especially when clay minerals are minor, the most common case in the hydrocarbon reservoirs, therefore the non-clay separation is necessary (Moore and Reynolds, 1997). Figure 3 shows the importance of removing the non-clays in enhancing of weak peaks of clay minerals in the Shurijeh Formation. Figure 3 shows that although the removal of non-clay minerals was not completely achieved (look to the 3.34 Å peak in both diffractograms), proper performing of the treatments resulted in significant decrease in the intensity of non-clay mineral peaks.

To gain a preliminary knowledge of the existing minerals, the randomly oriented powder samples were first exposed to the X-ray and analyzed. Fine whole-rock powder was packed into a circular shaped plastic cavity sample holder with an area of 4.91 cm² and a depth of 1 mm. A flat glass was used to press the surface of the packed powder and make it compact with the correct height and smooth surface. According to the whole-rock powder diffractometry, the main constituent of the samples from both wells was quartz with secondary minerals such as clays, anhydrite, carbonates (dolomite and calcite), plagioclase, K-feldspar, and in some sam-

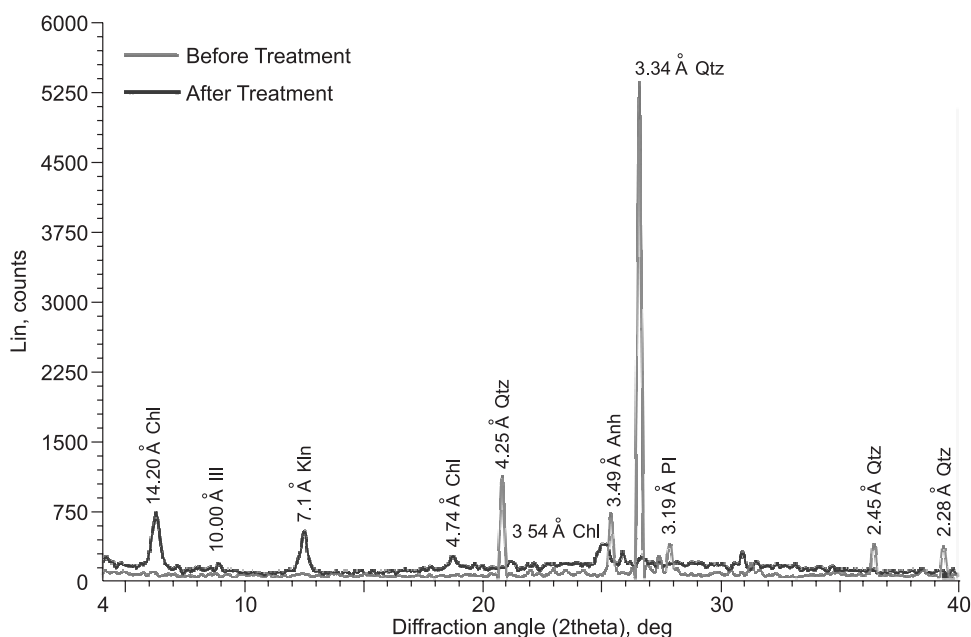


Fig. 3. Comparison of the XRD patterns before and after non-clay mineral removals. Although the removal of non-clay minerals was not achieved to a complete level (look to the 3.34 Å peak in both diffractograms), but the treatments resulted in significant decrease in intensity of non-clay minerals peaks.

Chl=Chlorite; Ill= Illite; Kln=Kaolinite; Qtz=Quartz; Anh=Anhydrite; Pl=Plagioclase.

ples hematite (Fig. 4). These results were found extremely useful in design of the subsequent non-clay mineral removal steps.

For each core sample, the carbonate and sulfate removals were accomplished by mild heating of crushed samples in a sodium acetate-acetic acid buffer at pH=5, according to Jackson and Barak (2005) procedure and by the sodium salt of ethylenediaminetetraacetic acid (EDTA) with the procedure described by Bodine and Fernald (1973), respectively. Since the removal of iron oxides and organic matter may alter the X-Ray diffraction response of mixed layer clay minerals or cause a partial dissolution in the high-Fe chlorite, the small amount of iron oxides or organic matter, which exist in some samples, were not removed. Unlike quartz, alkali feldspars and plagioclase were separated from clay minerals in a settling tube, based on the Stokes' law, leaving non-clay minerals in the coarser residue. An adequate amount of fine enough particle size fraction (<2 μm) was extracted after nearly 4 hours at 20 °C with at least three times of decantation. In each stage the clay minerals were dispersed into individual colloidal particles in the suspension, using a 0.1% solution of sodium metaphosphate to avoid the aggregation of submicroscopic polymineralic flocculates. A paste of <2 μm fraction was finally smeared onto three glass slides with a homogeneous size distribution and similar thickness of 1 mg/cm², leaving at room temperature to be dried. The glass substrate was weighted before and after each application of the clay minerals to calculate the sample density and make sure that all of the preparations were reached to the favourable density of 1 mg/cm². The X-ray diffraction analyses were conducted on oriented clay glass slides under three separated states of air-dried, saturated with the vapor of ethylene glycol for at least 24 h at 60 °C, and heated at 550 °C for 1 hour (Fig. 5). An additional treatment was chemically performed by boiling the suspected samples for 2 hours in 1 N HCl to distinguish the chlorite from kaolinite.

3.2.2. Qualitative Analysis

Having analyzed the oriented clay aggregates prepared from the less than two micron size fraction (Fig. 5), the obtained patterns were compared with the standard X-ray powder diffraction patterns of reference clay minerals (International Centre for Diffraction Data (ICDD), Mineral Powder Diffraction File Search Manual, 1988) to precisely identify the constituent minerals. Although the search/match computer program, applied to identify the phases, suggests the possible presence of non-clay minerals in trace amounts in the clay fraction, the removal procedure was considered to be successful in enhancing the weak peaks of clay minerals.

Illite was characterized by intense 10 Å, 5.0 Å, and 3.3 Å peaks of air-dried pattern, which remained unaffected by the ethylene glycol solvation, and heating to 550 °C. Glauconite was differentiated from illite by

a higher ratio of 001/003 peaks, 1.5 to 1.52 Å 060 peak, and, finally, by the presence of weak or nonexistent 5 Å peak. Chlorite was identified by its unaltered 14 Å, 7.1 Å, 4.74 Å, and 3.54 Å peaks in the three patterns of air-dried, solvated with ethylene glycol, and heated. Kaolinite was identified using the characteristic peaks at 7.1 Å, 3.58 Å and 2.3 Å in the air-dried pattern. Kaolinite was clearly distinguished from chlorite by comparisons of 3.58 Å kaolinite peak and 3.54 Å chlorite peak and also by performing a subsequent treatment with hydrochloric acid and thin section analysis. The small amounts of smectite in two samples were detected by swelling the 14 Å peak to 17 Å in the saturated pattern with ethylene glycol, and its collapse to about 10 Å in the heated pattern. Mixed layer clays of both illite-smectite and chlorite-smectite types were identified in a few samples by the basal diffraction peaks between 14 and 10 Å and 17 to 14 Å in the glycolated pattern.

Illite, chlorite and kaolinite were observed in all of the 76 core samples, while the glauconite was between the depths of 3202.80 m and 3206.85 m; 3208.97 m and 3209.19 m of the producing well, and it was only observed in 3 samples of the non-producing well, located between the depths of 3180 m and 3180.28 m. Smectite was present only in two samples of producing well, in depths of 3208.25 meters and 3208.87 meters. Mixed layer clay minerals were present just in the nonproducing well from the depth of 3192.61 to the end of the cored interval.

3.2.3. Quantification using calibration curves obtained from the standard samples

Pure identified minerals obtained from the same reservoir are preferred for calibration in the quantitative XRD analysis. In order to ensure homogeneity, including similar crystal growth habits and orientation between standards and samples under investigation as well as acquiring the more reliable calibration relationships be-

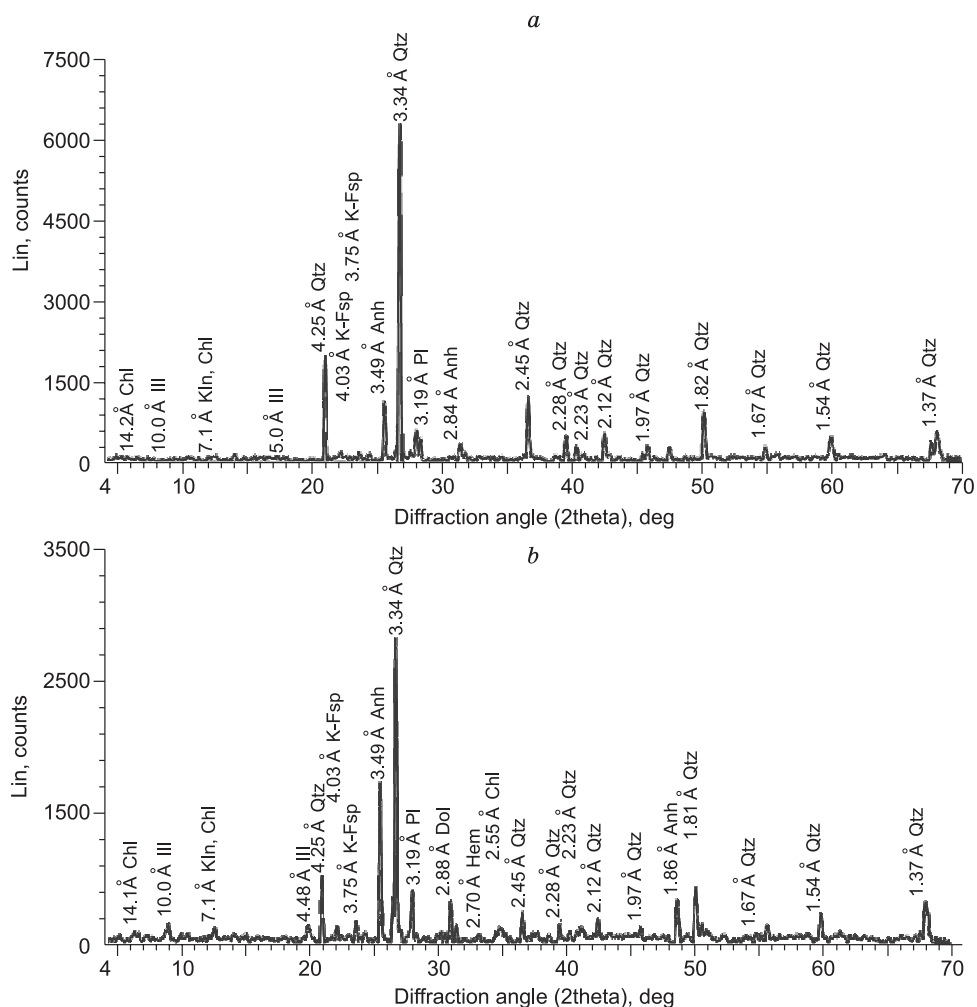


Fig. 4. The typical bulk powder XRD diffraction pattern of the samples in the gas producing well (a) and nonproducing well (b).

Chl=Chlorite; Ill= Illite; Kln=Kaolinite; Qtz=Quartz; K-Fsp=K-feldspar; Anh=Anhydrite; Pl=Plagioclase; Dol=Dolomite; Hem=Hematite.

Table 2. The best reflection with no interference in the Shurijeh core samples, used for quantification purpose

Mineral	Peak (Å)	Mineral	Peak (Å)
Quartz	4.25	Anhydrite	3.49
Plagioclase	3.29	Hematite	2.70
K-Feldspar	3.24	Kaolinite	2.34
Calcite	2.50	Chlorite	4.74
Dolomite	2.19	Illite	5.03

tween the major peak intensity and the weight percent of mineral contents, pure standard samples from the same reservoir were used. It is worthy to mention that the standard samples were extracted from the Shurijeh Formation by the technical sponsor of this study (National Iranian Oil Company, know as NIOC). The clay standards were weighted, and pre-treated according to the same procedures as the original samples. The standards were then mixed over the sufficient and different portions of known percentages which were varying from 10% to 100%. Figure 6 shows the XRD patterns of some selected mixtures. At least 4 runs were performed on each standard sample with the random orientation to obtain an accurate average. The best reflections of each mineral with the maximum intensity, no interference, and as close together as possible were selected from the range of intermediate diffraction angles to avoid many problems encountered in the low angle region (Table 2).

The intensity of peaks in high angles can be affected by the thin sample preparations (Moore and Reynolds, 1997). Two approaches were used to deal with the problem of thin preparations. First, the XRF data were used as the basis for intensity corrections to the values that the peaks would actually have, if the sample was infinitely thick. Second, only analytical near-neighbour peaks were used for the purpose of quantitative measurements. The diffraction traces were then modelled with respect to the Lorentz-polarization factor, the interference function, and the scattering amplitude of the unit cell according to what was described by Moore and Reynolds (1997). The atomic scattering factor was calculated by dividing the amplitude of a wave scattered by the atom by the amplitude of a wave scattered by an electron.

A series of calibration curves plotting the peak intensity of different minerals in the prepared standards (x -intercept) versus mineral weigh percentage fractions (y -intercept) was generated to calculate the percentages of each mineral in the samples, using the slope of a best fit line (Fig. 7). The linear calibration graphs revealed

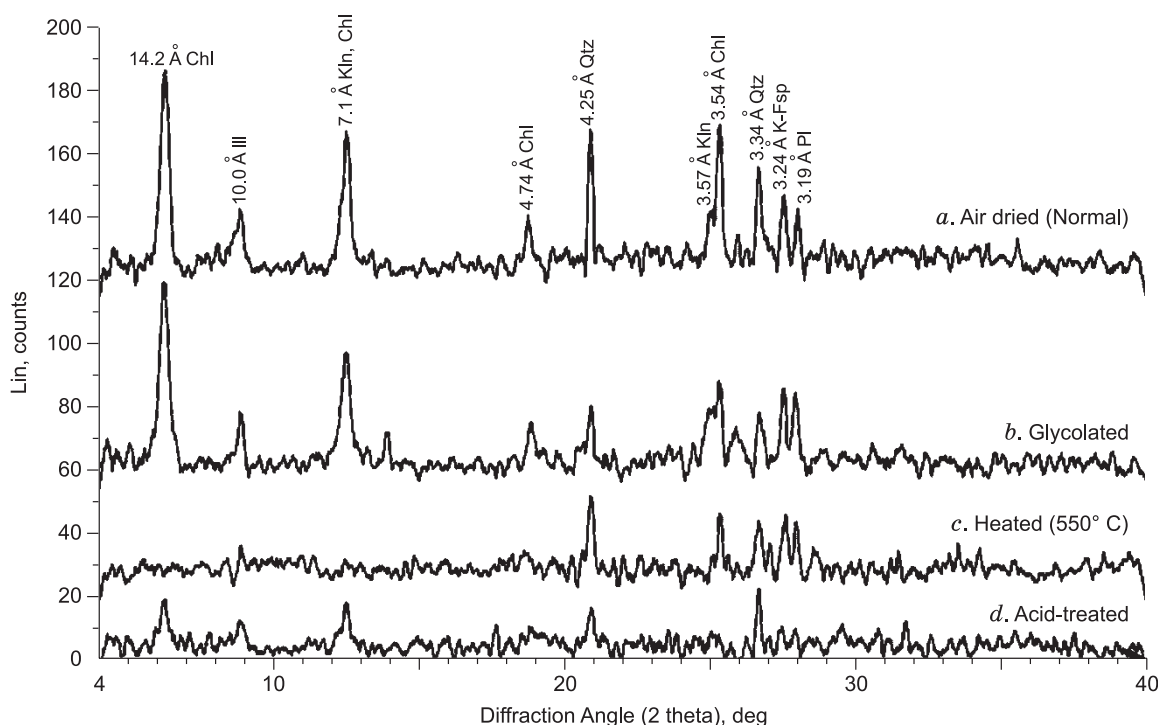


Fig. 5. The sharp, strong peaks of clay minerals in an oriented XRD diffraction pattern from a Shurijeh core sample.

Chl=Chlorite; Ill= Illite; Kln=Kaolinite; Qtz=Quartz; K-Fsp=K-feldspar; Pl=Plagioclase.

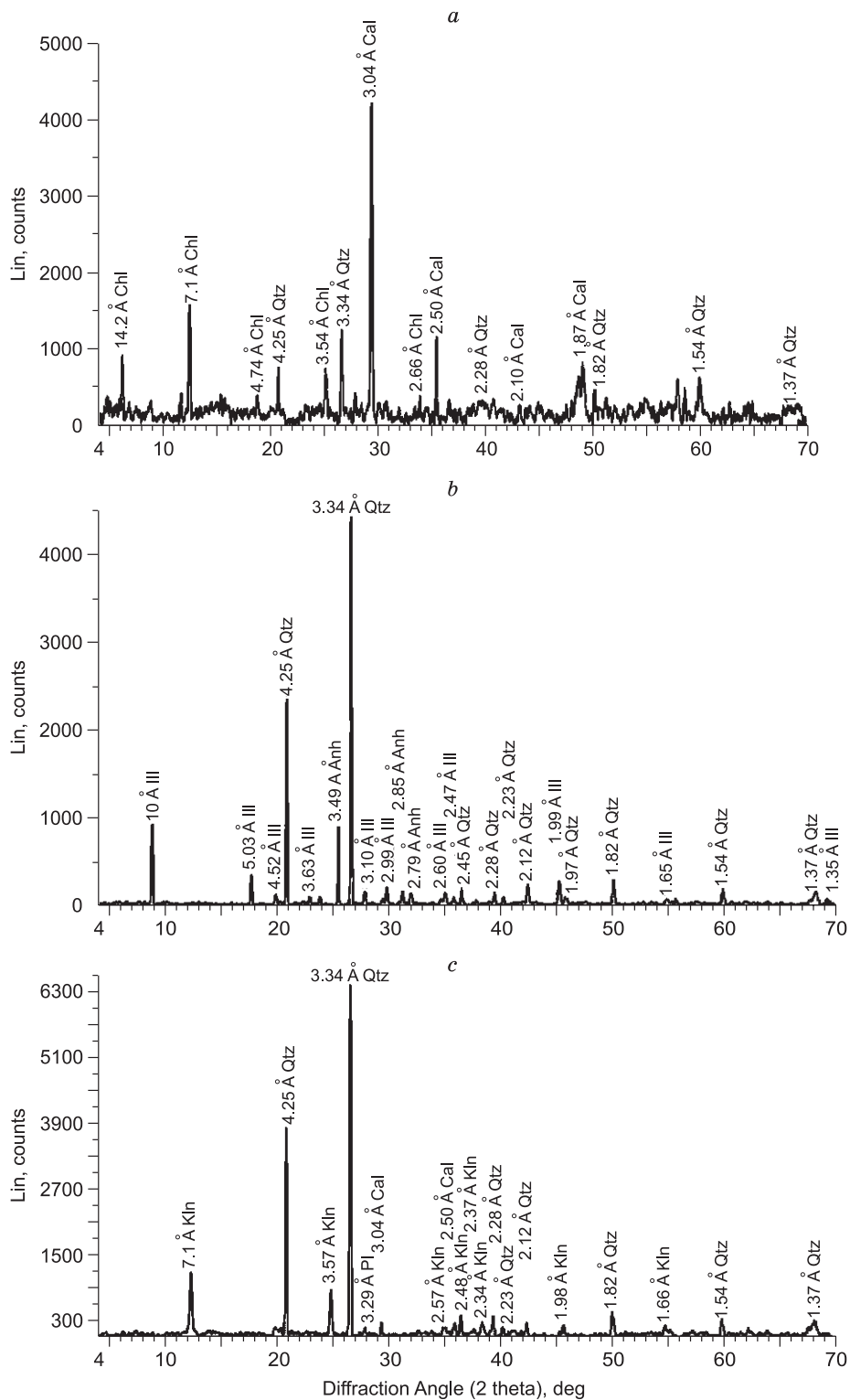
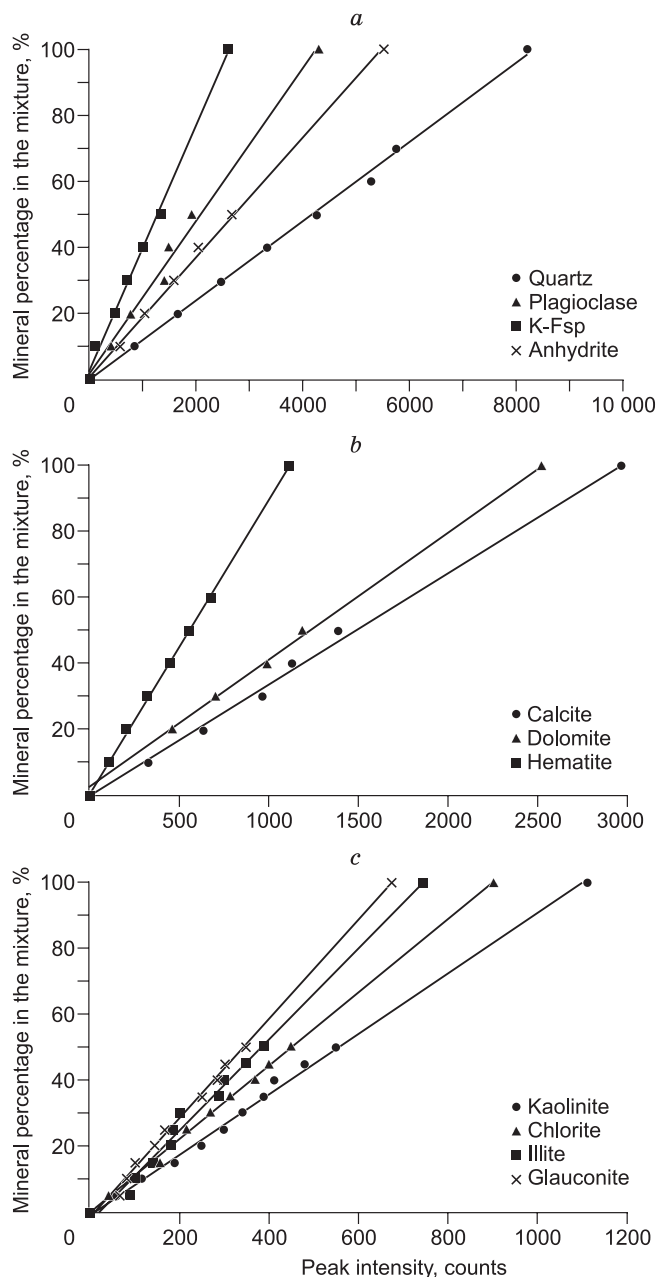


Fig. 6. The XRD patterns of some mixtures of standard samples: a, Calcite 50 wt%, Chlorite 40 wt%, Quartz 10 wt%; b, Illite 50 wt%, Quartz 30 wt%, Anhydrite 20 wt%; c, Quartz 50 wt%, Kaolinite 30 wt%, Calcite 10 wt%, Plagioclase 10 wt%.

Chl=Chlorite; Ill= Illite; Kln=Kaolinite; Qtz=Quartz; Anh=Anhydrite; Pl=Plagioclase; Cal=Calcite.

Fig. 7. Relationships of different mineral percentage in the mixture versus diffraction peak intensity: a, quartz, plagioclase, K-Feldspar, and anhydrite; b, calcite, dolomite, and hematite; c, kaolinite, chlorite, illite, and glauconite.



the correlation coefficients varying from 0.9912 to 0.9996. The accuracy of calibration curves was checked by perfect correlation between the actual known composition of standards and predicted ones obtained from the XRD calibration curves with an error of nearly $\pm 1\%$ for the main mineral constituent and $\pm 5\%$ or less for minor minerals.

The resulting standard calibration curves, based on the bulk XRD powder analysis, were then used to estimate the percentages of all mineral phases in 76 core samples as well as clay minerals within the less than two micron size fraction. A set of replicate analysis, provided a standard deviation of $\pm 5\%$ for the main mineral constituent and $\pm 15\%$ or less for minor minerals, showed that the proposed approach can produce highly precise analysis in the Shurijeh reservoir Formation.

3.3. X-ray fluorescence (XRF) analysis

The elemental analysis of the Shurijeh samples was performed on an automated Philips MagiX PRO wavelength-dispersive sequential X-ray fluorescence (WDXRF) spectrometer facility which was equipped with Rhodium (Rh) target end window tube. The maximum strength for signals was attained by using the close-coupled optics. The samples were analyzed for the elements in the range from oxygen to uranium, using a full set of analyzer crystals. A 4kW/ 125mA solid state X-ray generator with three detectors including a flow, a sealed proportional one in tandem, as well as a scintillation detector parallel with a range of beam filters and collimators were used. The system was utilized by the Philips SuperQ Data Collection and Evaluation Software, v3.0 and the data were evaluated by the Omega Data system's uniQuant 4.0 XRF data analysis software.

3.3.1. Preparation and data acquisition

In the present study, 0.4000 g of each dried ground sample were mixed with 4.0000 g ICPH Fluore-X 65 flux to prepare the fused beads of 32 mm in diameter. The mentioned flux was a mix of lithium tetraborate 66% and lithium metaborate 34%. Three drops of a lithium iodide solution (250 g/L) were added to act as the non-wetting agent in the melting process as well. The fusion was then conducted at 1150°C for 20 minutes. Air bubbles were removed by swirling the mixture every 10 minutes. After 15 minutes a platinum casting tray was placed in the furnace to bring it up to the casting temperature. The melt was then poured into the tray in the furnace and placed on a tripod to cool down and was finally removed after 5 minutes (Giles et al., 1995).

It is known that the intensities of the characteristic XRF peaks are directly related to the concentrations of present elements in the sample through some complicated relationships (Beckhoff et al., 2007). The recorded intensity of a single emission line is a function of several factors such as the X-ray source, the detector (and the window) sensitivity, the sample geometry, the detector efficiency, the energy spectrum, the matrix effects, and

the intensity of exciting X-rays (Beckhoff et al., 2007). All of these complexities can be dealt with in the quantitative XRF analysis software, such as the Omega Data system's uniQuant 4.0.

Having separated the peaks from the background, the intensity of each peak was determined. The separation of overlapping peaks was carried out as well as doing all of the required corrections for the escape peaks and other loss processes. A set of 49 certified reference materials (CRM), covering a wide elemental range, was then used for calibration purposes. The calibration was corrected for inter-element effects, using the Traill-La-chance model supplied with the software. The obtained empirical relationships between net intensity of peaks and concentrations were then used to determine the concentration of elements in the samples studied. A certified standard was also analyzed with the samples to check the accuracy of the results. The obtained data fell within the set limits of less than 5% relative standard deviation.

The measurements of loss on ignition were carried out on the 1-2 g dried ground sample. The samples were precisely weighted and placed into porcelain crucibles with known weights in a furnace at 1025 °C for 1 hour. The residual sample were then placed in desiccator and reweighed to calculate the LOI from Eq. (1).

$$LOI = \frac{(Weight\ of\ sample - Residue\ weight)}{(Weight\ of\ sample)} \times 100$$

3.3.2. Quantification using elemental information from the XRF analysis

The data in Fig. 8 describe average chemical composition of core samples in both wells of Gonbadli field. The linear correlation between the clay percentage from the XRD analysis and the elemental concentrations from the XRF analysis was checked. Fig. 9 shows plots of clay mineral percentages versus some selected elements. As it can be seen in Fig. 9, the clay mineral content correlates well with measured iron, aluminum, potassium, and magnesium concentrations. Based on the anti-correlation with the silicon, the plot of clay mineral percentage versus $100 - SiO_2$ was developed (Fig. 10). The anti-correlation is obviously disturbed by the presence of sulphate mineral (anhydrite), carbonate minerals (calcite and dolomite), and the Na-bearing minerals. These minerals are accounted for by measuring the calcium, sulfur, magnesium, and sodium. Therefore, having combined five elements (Si, Ca, S, Mg and Na) in terms of their oxides, a strong correlation with the total clay content was discovered in this research for the first time (Eq. (2)):

$$Clay\ Minerals\ Percentage = 0.481 [100 - SiO_2 - CaSO_4 - Ca,Mg(CO_3)_2 - CaCO_3 - 5Na] + 5.475$$

The Shurijeh clay contents from ten other core samples, which were not used to develop the regression relationship, verified both very low and the medium range clay mineral contents, estimated from the Eq. (2) with the minimum error.

Highly variable chemical and physical properties of clay minerals, with the exception of kaolinite, inherit some limitations in the reliability of external standards in the XRD analyses. Series of simultaneous equations (Eq. 3 to i) were formulated, using the whole-rock major elemental analyses (Si, Al, Mg, Fe, Ca, Na, K,

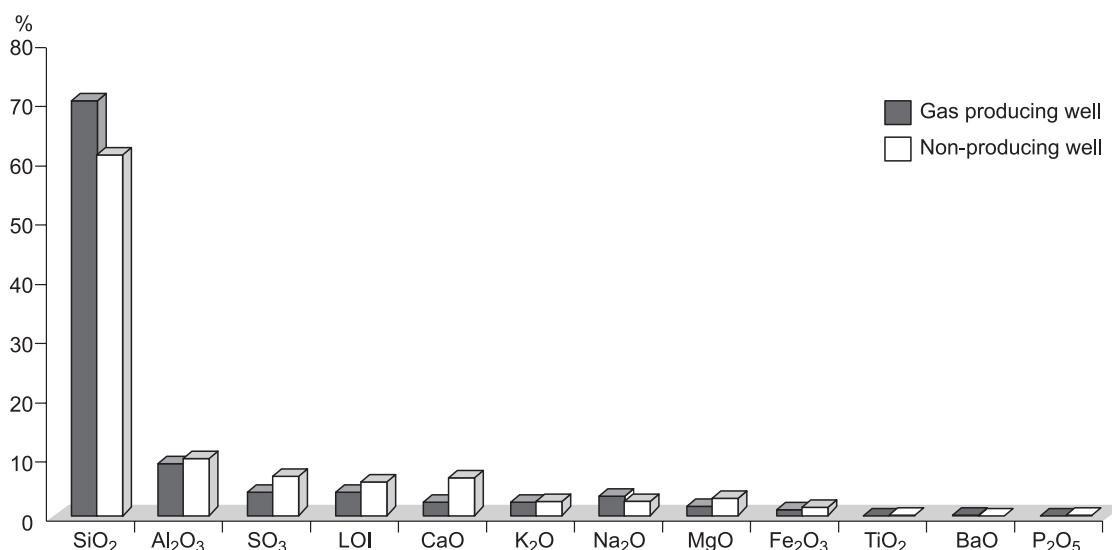


Fig. 8. The average chemical composition of the Shurijeh Formation from XRF analysis.

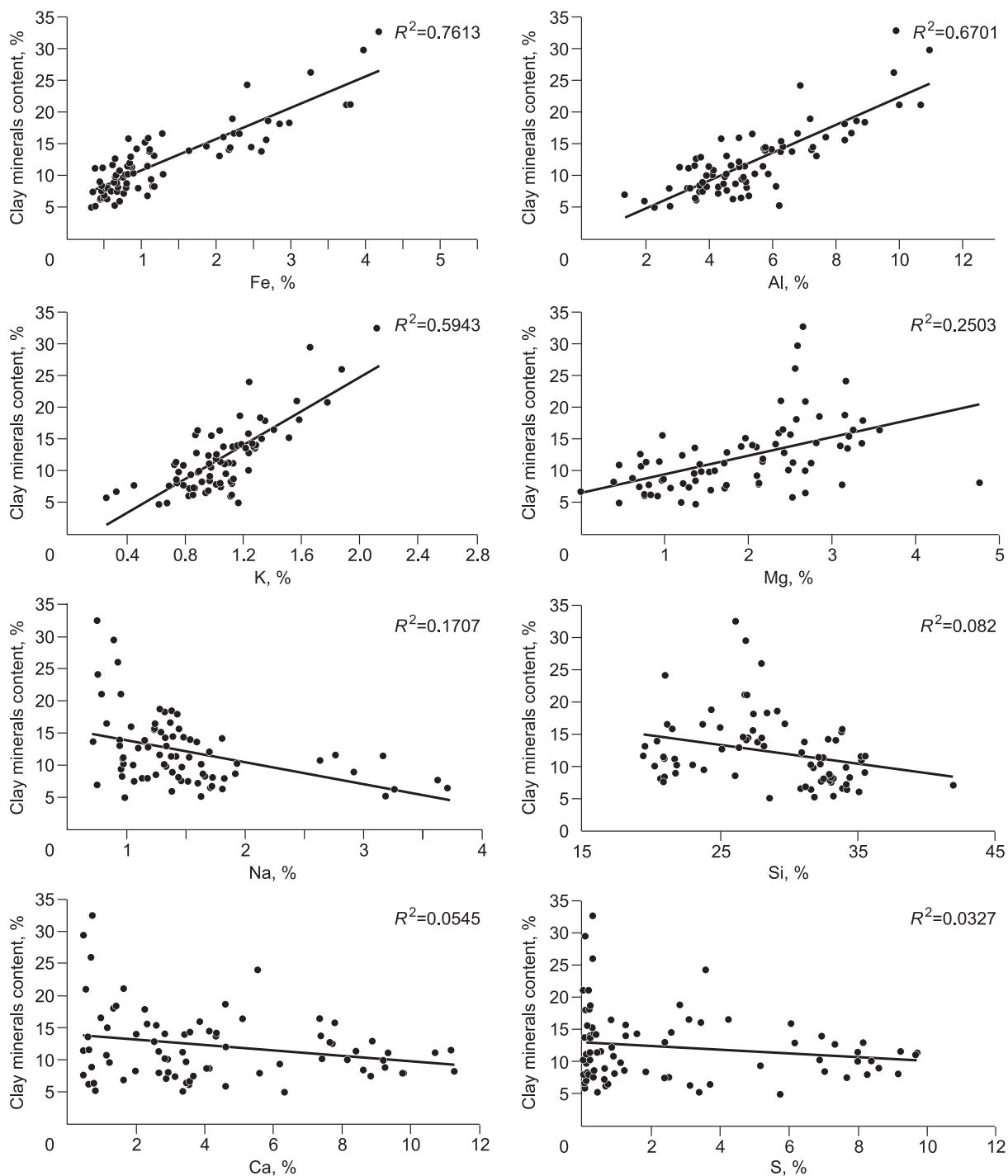


Fig. 9. The comparison of the concentrations of various elements measured by the XRF analysis with the Shurijeh XRD-measured clay contents from the best to poor correlations.

and S) and loss on ignition (LOI) data. The equations were then used to estimate the clay mineral abundances. The most important advantage of this method is to allow for the quantitative calculations without any standards.

$$a_1A + b_1B + \dots + z_1Z - 100g_1 \quad (3)$$

$$a_2A + b_2B + \dots + z_2Z - 100g_2 \quad (4)$$

$$a_3A + b_3B + \dots + z_3Z - 100g_3 \quad (5)$$

.....

$$a_iA + b_iB + \dots + z_iZ - 100g_i \quad (i)$$

where a_i, b_i, \dots, z_i and g_i are the i th element percentages in the mineral phases and the bulk rock, respectively. A, B, ..., and Z are the percentages of present phases in the sample.

The measured elemental ratios were calibrated to mineralogy, using 76 samples, based on the X-ray diffraction and X-ray fluorescence methods' data. The resulting estimates obtained from the chemical mass balance, compare favourably with those obtained by the XRD external standard method and in some cases improved them.

The minimum, maximum, and average percentages of individual clay minerals and total clay minerals, the sum of all different types of clay minerals respective mean concentrations, are given in Tables 3 and 4. From the mentioned Tables, it is clear that the most developed clay mineral in each well is illite and the other types of clay minerals are minor. The trend of different clay minerals over depth is shown in Figure 11. Higher levels of each clay mineral are only found in the non-producing well. In great depth in both wells, strong diagenesis with predominant illite and very small amounts of chlorite and kaolinite were observed. As seen in the Figure 11, the clay mineral types are rather constant and vertical variations in the amount of illite are remarkable.

4. RESULTS AND DISCUSSION

The bulk powder X-ray diffractometry of 76 core samples showed that the main constituent of the Shurijeh Formation was quartz with moderate to small amounts of some other minerals such as, the clay minerals, anhydrite, carbonates (dolomite and calcite), plagioclase, K-feldspar, and hematite. The reduction of associated non-clay minerals also proved that the weak peaks of clay minerals can be greatly enhanced upon the proper removal procedures to be performed (Fig. 3). Based on typical X-ray diffraction patterns, prepared from the treated oriented clay glass slides, the clay fractions of both wells were dominated by illite, chlorite and kaolinite. In very few samples, the mentioned clay types were accompanied by the subsidiary glauconite, smectite and mixed layer clay minerals such as illite-smectite and chlorite-smectite. Glauconite is a rarely occurred clay mineral, mainly found in the producing well. While smectite was only found in the gas producing well, and the mixed layer clays were only found in the non-producing well.

The XRD standards obtained from the reservoir under study produced reliable calibration curves and were considered to be more preferred for the quantitative XRD analysis. Both methods provided good results with absolute errors typically less than $\pm 5\%$ for the main mineral constituent and $\pm 15\%$ for minor minerals, which were better than this in the most cases. The error amount showed that the method is capable of providing accurate quantitative analysis.

It can be clearly seen in Fig. 8, that the silicon oxide was present in major quantities in both wells, while aluminum, sulfur, calcium, potassium, sodium, magnesium, and iron were present in moderate to minor amounts and other elements were present in trace amounts. There was a strong linear correlation between the clay percentage and the concentrations of iron, aluminum, potassium and magnesium (Fig. 9), which was not surprising due to the fact that the mentioned elements are the main chemical constituents in the dominant clay minerals of the Shurijeh Formation. A clear trend existed between the measured clay percentage and the $100\text{-SiO}_2\text{-CaSO}_4$, which improved even further once the carbonates (calcite and dolomite) had been subtracted. The correlation maximum improvement was achieved, when the sodium was subtracted. The Eq. (2) is generally applicable to

Table 3. The amount of each clay mineral in the D1 subunits of the Shurijeh Formation

Mineral	Gas producing well (D1)			Non-producing well (D1)		
	Min	Max	Average	Min	Max	Average
Illite	1.0	5.5	2.6	0.5	17.6	5.0
Chlorite	0.9	4.4	1.7	1.0	8.4	2.8
Kaolinite	0.8	3.1	1.8	0.6	6.5	2.5
Smectite		ND			ND	
Glauconite	0.0	4.2	2.3	0.0	6.2	0.4
Mixed layer clay minerals		ND		0.0	4.1	1.1
Total clay minerals	5.0	13.0	8.4	6.8	32.5	11.9

Table 4. The amount of each clay mineral in the C2 subunits of the Shurijeh Formation

Mineral	Gas producing well (C2)			Non-producing well (C2)		
	Min	Max	Average	Min	Max	Average
Illite	1.0	13.5	4.6	4.5	18.3	8.8
Chlorite	1.0	5.7	2.5	1.4	7.4	3.2
Kaolinite	1.0	4.7	1.8	1.2	6.4	2.9
Smectite	0.0	1.0	0.2		ND	
Glauconite	0.0	2.7	1.0		ND	
Mixed layer clay minerals		ND		0.6	2.4	1.3
Total clay minerals	5.2	21.0	10.1	8.0	29.5	16.2

estimate the clay contents of the Shurijeh Formation in all drilled wells in the Gonbadli field, with data of pulsed-neutron spectroscopy tools, a mineralogical special log which is able to measure the concentrations of some selected elements. The resulting clay contents estimates obtained from the chemical mass balance compared favourably with those obtained by the XRD external standard method and improved it in some cases.

Although, the results showed similar types of clay minerals in both wells, but very great differences also existed in the amounts of each clay mineral between the D₁ and C₂ units in two wells (Tables 3 and 4). Generally, the average amount of each clay mineral in C₂ unit was higher than D₁ unit and non-producing well was more shaly with a clay quantity of one and a half order of magnitude larger than that in the gas producing well. The amount of illite, the dominant clay mineral in both wells, vertically varied considerably, ranging up to 18.3%. In contrast, the amount of kaolinite and chlorite was generally small and less than 8.4%. Glauconite was seldom found in both wells with amounts of less than 4.2%. Smectite was only found in the C₂ unit of gas producing well in a very small amount. The amounts of both types of mixed layer clays were quite low. The amount of total clay minerals changed greatly from a minimum of 5% to a maximum of 32.5%. Detailed quantitative analysis based on the X-ray analytical techniques yielded an average clay mineral contents in the D₁ and C₂ units of Shurijeh Formation, varying from 8.4% to 11.9% and 10.1% to 16.2%, respectively.

The differences in clay minerals' characteristics in the Shurijeh Formation can be related to the different depths of core samples. It is clearly known that the diagenetic changes in K-feldspar and plagioclase occurred with an increase in temperature and burial depth, and as a result clay minerals like kaolinite, and illite got

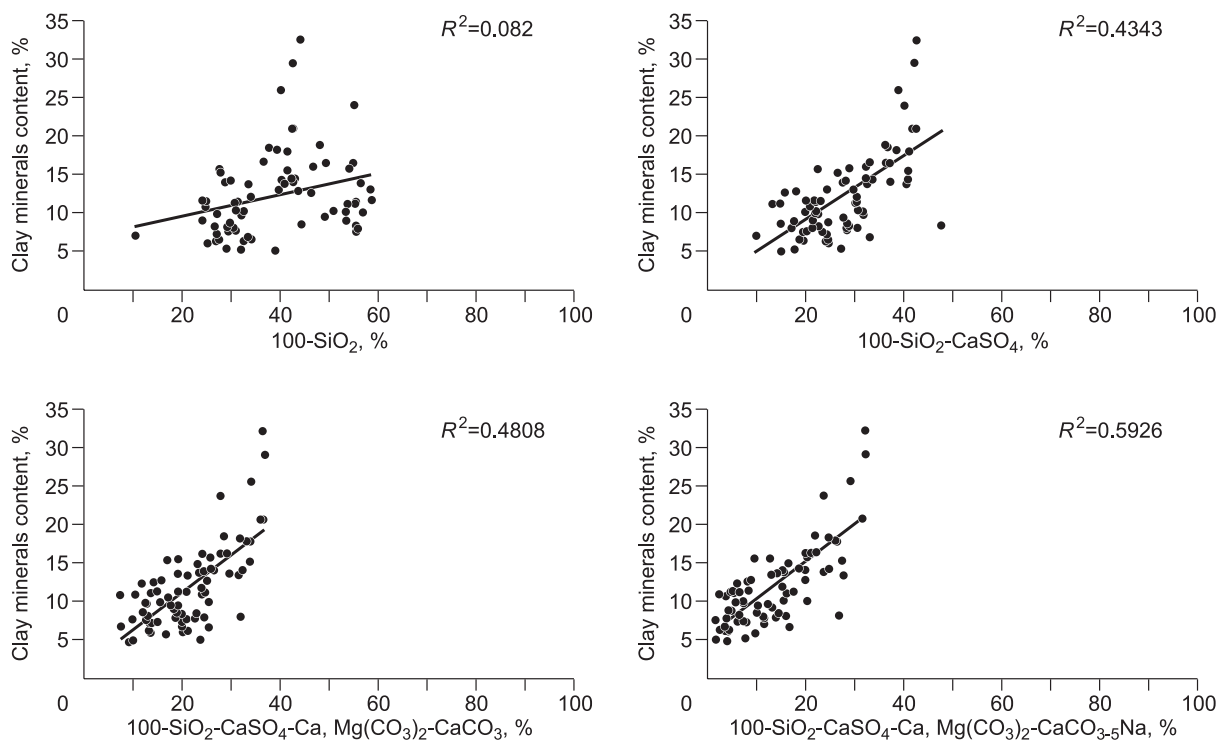


Fig. 10. The gradual correlation improvements derive a local clay content predictor relationship, based on the elemental information.

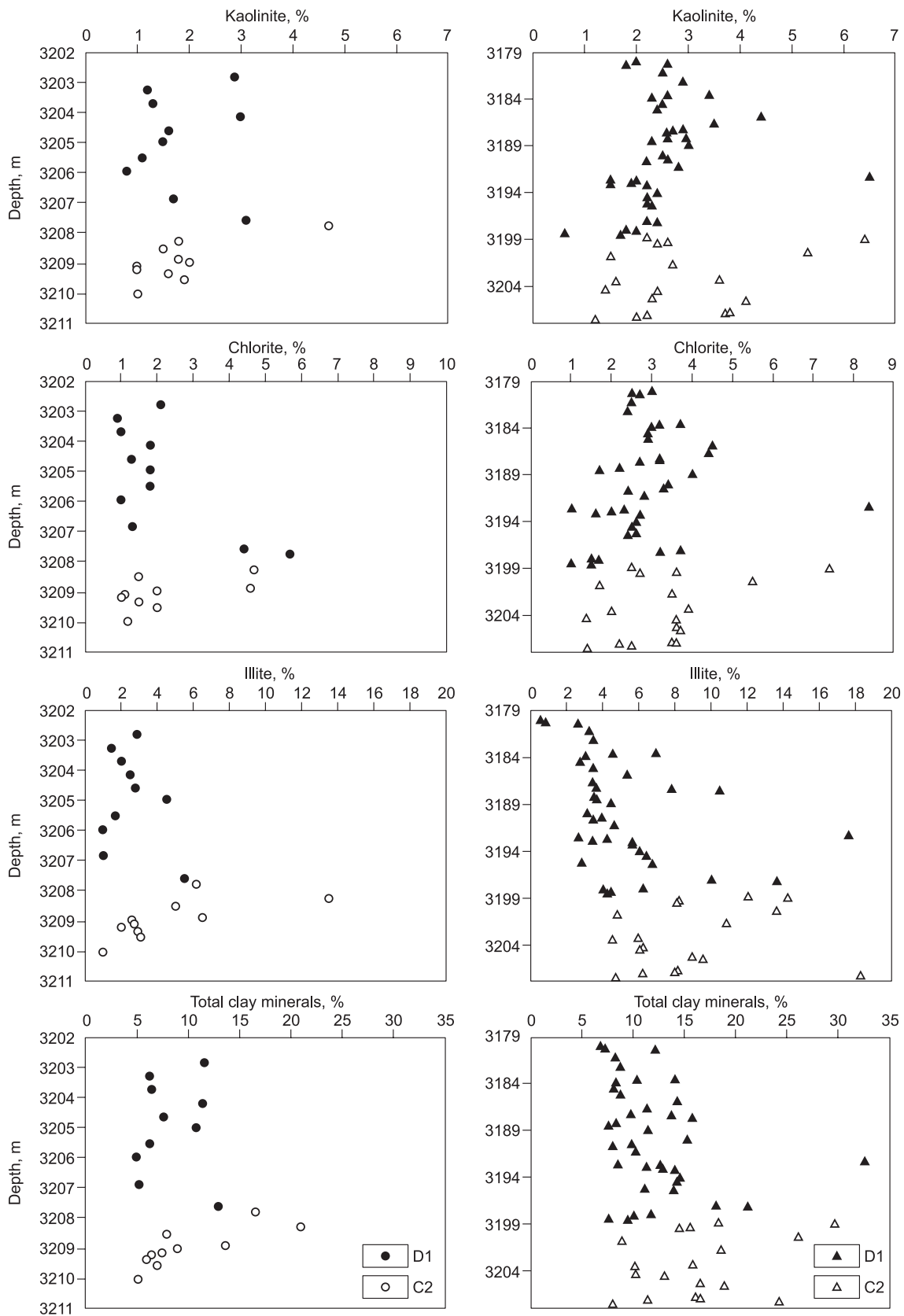


Fig. 11. Eight plots showing typical variation in the amount of kaolinite, chlorite, illite, and the total clay content of Shurijeh Formation over depth. Smectite, glauconite and mixed layer clay minerals were only seen in very few samples.

Circles = gas producing well data and triangles= non-producing well data.

formed. Apparently, K-feldspar and plagioclase alteration in the Shurijeh resulted in generally small amounts of kaolinite and chlorite and relatively high amounts of illite. It seems that transformation of smectite into illite and gradual dehydration process occurred in the Shurijeh Formation with increasing depth, during burial diagenesis. The presence of mixed layer chlorite-smectite and illite-smectite proved that smectite almost entirely changed into illite and chlorite. The smectite to illite conversion releases Mg^{2+} , Fe^{2+} and Fe^{3+} , which promotes the transformation from kaolinite to chlorite as well. With increasing depth, the amount of kaolinite in the Shurijeh declined, while the amounts of illite gradually increased (Fig. 11).

The overall results prove that the X-ray diffraction method supplemented by any elemental analysis, such as X-ray fluorescence, is highly applicable in the quantitative clay mineralogy investigations in the formations with complex lithology.

5. CONCLUSIONS

In this research, the X-ray analytical techniques such as XRD and XRF were employed to determine the quantitative clay mineralogy of Shurijeh Formation, based on a total of 76 core samples in two wells as deep as 3000 m, located in the Gonbaldi gas field, north-eastern Iranian part of Kopet-Dagh sedimentary Basin. According to the qualitative studies, the Shurijeh Formation was mainly composed of quartz along with smaller quantities of clay minerals, anhydrite, carbonates (dolomite and calcite), plagioclase, K-feldspar and in few samples hematite. Developed clay minerals in the Shurijeh Formation were illite, chlorite, and kaolinite. In very few samples smectite, glauconite and mixed layer clay minerals such as illite-smectite and chlorite-smectite were observed. By adopting standard quantitative XRD procedures, using measurement of peak intensities in the pure mineral samples obtained from the same reservoir as the external standards, the clay mineral percentages were precisely determined. A set of simultaneous equations formulated, using the whole-rock XRF analysis was used as well to validate the XRD quantifications and recalculate the clay mineral abundances, as a method free from many of the XRD pitfalls. Both quantification methods could successfully validate and improve each other. The success of the combined proposed method is believed to be independent from the standard samples. This clarified that the X-ray analytical techniques are quite reliable upon quantitative assessments in the field of clay mineralogy investigations in samples with complex lithology.

Based on the quantitative results, obtained from the X-ray analytical techniques, i.e., X-ray diffraction (XRD) and X-ray fluorescence (XRF), each Shurijeh well exhibits the high amount of illite, typically up to 18.3% and low contents of other clay minerals with increasing depth, an obvious sign of deep burial diagenesis. The outcomes of this research will affect the reservoir protection process and efficient gas recovery in the Gonbaldi field.

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