Quantitative XRD bulk and clay mineralogical determination of paleosol sections of Unayzah and Basal Khuff clastics in Saudi Arabia

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(Received 24 January 2012; accepted 16 February 2012)

Quantitative X-ray diffraction (XRD) analysis is performed on 172 samples mainly containing paleosol sections of Unayzah and Basal Khuff clastics taken from the core of one well drilled by Saudi Aramco. Quantitative XRD bulk mineralogical determination is achieved using the Rietveld refinement method whereas quantitative XRD clay mineralogical determination of clay-size fraction is obtained using the reference intensity ratio method. The XRD results indicate that the samples from paleosol sections consist mainly of quartz and feldspar (microcline and albite) as framework constituents. Cement minerals include dolomite, hematite, anhydrite, siderite, gypsum, calcite, and pyrite. Clay minerals are important constituents in paleosols. The XRD results show that clay minerals in the samples are illite, mixed-layer illite/smectite, kaolinite, and chlorite. No discrete smectite is present in the samples. The clay mineral associations in these samples of paleosol sections can be classified into three types: Type I predominantly consists of illite and a mixed layer of illite/smectite; Type II of kaolinite; and Type III of illite and a mixed layer of illite/smectite, but also significant amounts of kaolinite. The change of clay mineral association type with sample depth can indicate the change of paleoclimate and paleoenvironment. For example, kaolinite usually forms under strongly leaching conditions such as abundant rainfall, good drainage, and acid waters. Therefore, XRD mineralogical data of paleosol sections are important for petroleum geologists to study paleoclimate and paleoenvironment and to predict the reservoir quality of the associated rock formations. © *International Centre for Diffraction Data* [doi:10.1017/S088571561200022X]

Key words: quantitative XRD analysis, paleosol, clay-size fraction, Rietveld refinement, reference intensity ratio

I. INTRODUCTION

Paleosol is a soil formed in the geological past. Like modern soils, it was formed during times of relatively slow or no accumulation of sediment. During these times, the land surface and near-subsurface were exposed to chemical and physical weathering processes. Features within paleosols can give important clues about the climate and other environmental conditions during their formation (Mack and James, 1994). Quantitative X-ray diffraction (XRD) analysis is performed on 172 samples containing paleosol sections of Unayzah and Basal Khuff clastics taken from the core of one well drilled by Saudi Aramco. The objective is to characterize the mineral compositions, including clay mineral type and abundance, in the paleosols to help geologists interpret the paleoclimate and paleoenvironment and understand the relation of paleosols to the underlying reservoirs.

II. ANALYTICAL METHOD AND PROCEDURE

XRD is the best available technique for the identification and quantification of minerals in paleosols. The application of the Rietveld refinement method in XRD quantitative phase analysis shows great advantages over conventional methods such as the reference intensity ratio (RIR) method for accuracy and convenience (Bish and Howard, 1988; O'Connor and Raven, 1988; Bish and Post, 1993; McCusker *et al.*, 1999; Gualtieri, 2000; Hillier, 2000). The advantages are: (1) using the full XRD profile rather than single-peak integrated intensity reduces the possible effect of mineral-preferred orientation; and (2) no standard or reference material is needed. However, a limitation of the Rietveld refinement method is that it restricts quantitative analysis of clay minerals such as montmorillonite and mixed-layer clays in the samples. A combination of the Rietveld refinement method and the RIR method was used to solve this problem in the XRD analysis of paleosols (see the procedure in Figure 1). For this study, a PANalytical XPERT PRO X-ray diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å) was used. A monochromator and a proportional detector were used in conjunction with a fixed 1° divergent slit, a 0.3-mm receiving slit, and a fixed 2° anti-scattering slit at instrument settings of 45 kV and 40 mA. All bulk samples were briefly disaggregated and lightly crushed in a mortar and pestle, and, then, ~3 g of sample were ground for 5 min in a McCrone micronizing mill (Figure 2) to get 10–20 μm of fine powder that can reduce the preferred orientation of particles (Figure 3) and does not affect the structure of clay in

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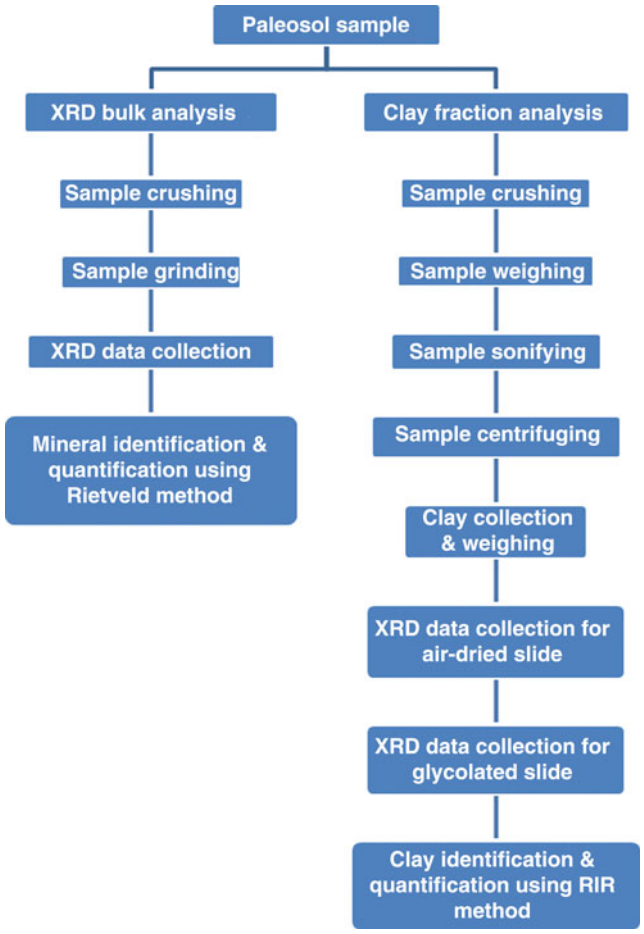

Figure 1. (Color online) Procedure of XRD bulk and clay fraction analysis.

Figure 2. (Color online) McCrone micronizing mill and its accessories.

the sample as the sample can be kept at the room temperature while grinding by using isopropanol as a grinding agent, unlike a ball mill that increases temperature dramatically. The dried powdered samples were back-loaded by hand into sample holders and run in the XRD instrument from 4° to 70° 2θ, using a step size of 0.02° and a count time of 1 s per step.

The Rietveld refinement method used the PANalytical HighScore Plus software for quantitative analysis of the mineral compositions of bulk samples. The semi-auto mode and background available were used during refinement. The parameters refined were zero shift, scale factor, unit-cell parameters, and profile function. The accuracy of the results was reasonable according to accuracy checking and quality control by the test of artificial mixture samples of standards (Tables I and II). For clay fraction analysis, the centrifuge

Table I. Quantitative results of artificial mixture samples by the Rietveld refinement method.

Mixture samples	Illite (wt%)	Quartz (wt%)
Actual	10	90
Calculated	9	91
Actual	1	99
Calculated	2	98
Actual	5	95
Calculated	5	95
Actual	22	78
Calculated	23	77
Actual	43	57
Calculated	43	57
Actual	64	36
Calculated	63	37

Table II. Reproductivity of the results from the Rietveld refinement method.

Artificial mixture sample	Illite	Kaolinite	Quartz
Actual wt%	24	38	38
1st Run and calculated	22	37	41
2nd Run and calculated	25	35	40
3rd Run and calculated	23	36	41

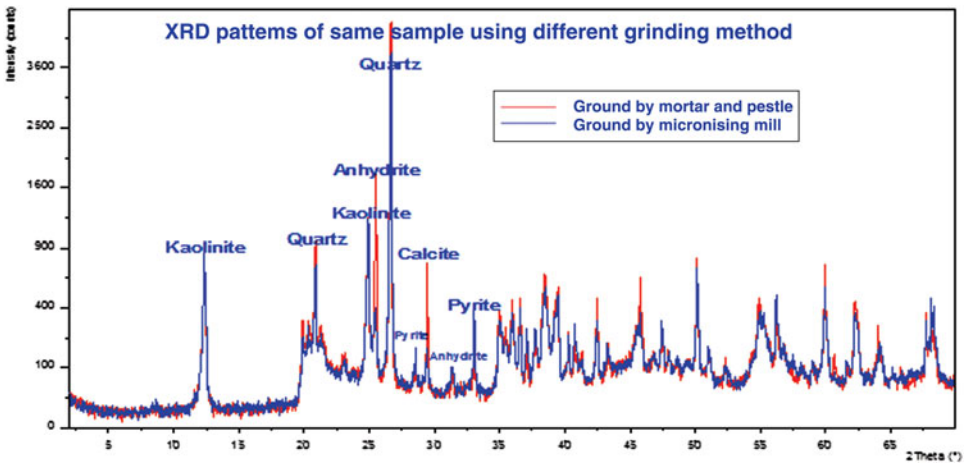

Figure 3. (Color online) Micronizing mill grinding reduces particle-preferred orientation.

https://doi.org/10.1017/S088571561200022X Published online by Cambridge University Press

Table III. Reference intensity ratio (RIR) factors of clay minerals.

Mineral	d (Å)	RIR (mineral/kaolinite)[a]
Kaolinite	7.15	1.00
Chlorite	7.12	1.00
Illite	10.0	0.40
Ordered illite/smectite	10.5–13.5	0.40
Random illite/smectite	15–17	1.50
Smectite	17	1.50
Quartz	4.26	0.42

[a]RIR factors for clay minerals in glycolated slide sample.

technique was used to separate clays (<2 μm) from paleosols and prepare clay slurry with preferred orientations. Clay slurry was laid on a glass slide and exposed to ethylene glycol vapor for a minimum of 24 h to aid in detection and characterization of expandable clays. The total clay (<2 μm) was calculated from the separating weight percentage. The relative percentages of individual clay minerals were quantified using RIR factors (Chung, 1974a, b). To obtain the RIR factor of each clay mineral, artificial mixture samples of clay mineral standards were made and compared with the intensities of each clay mineral (Table III).

III. ANALYTICAL RESULTS AND INTERPRETATION

Quantitative XRD results indicate that the samples from paleosol sections consist mainly of quartz and feldspar (microcline and albite) as framework constituents. In addition to silica cement, which can be identified only by petrographic analysis, the cement minerals detected are dolomite, hematite,

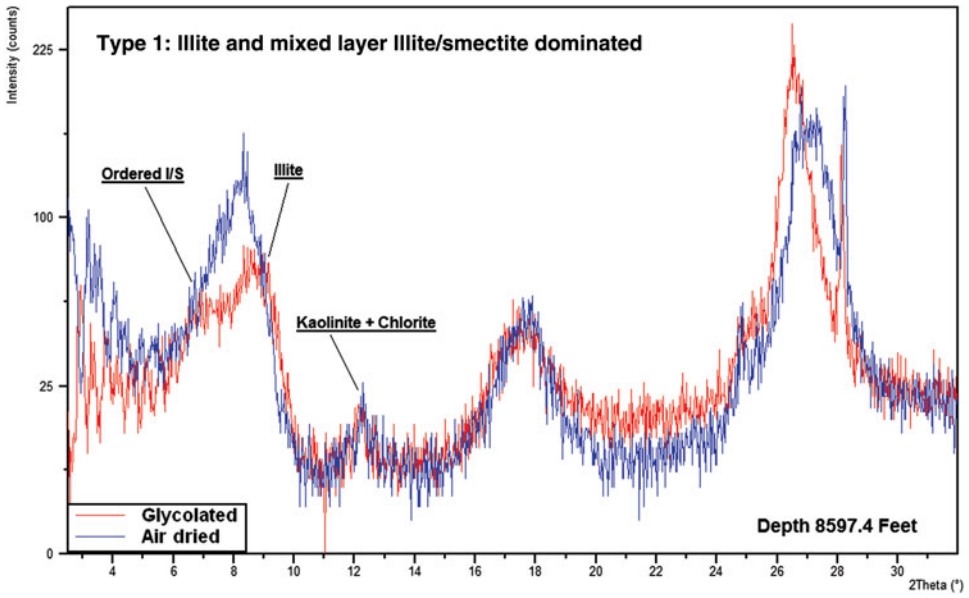

Figure 4. (Color online) XRD patterns of clay mineral association: Type I.

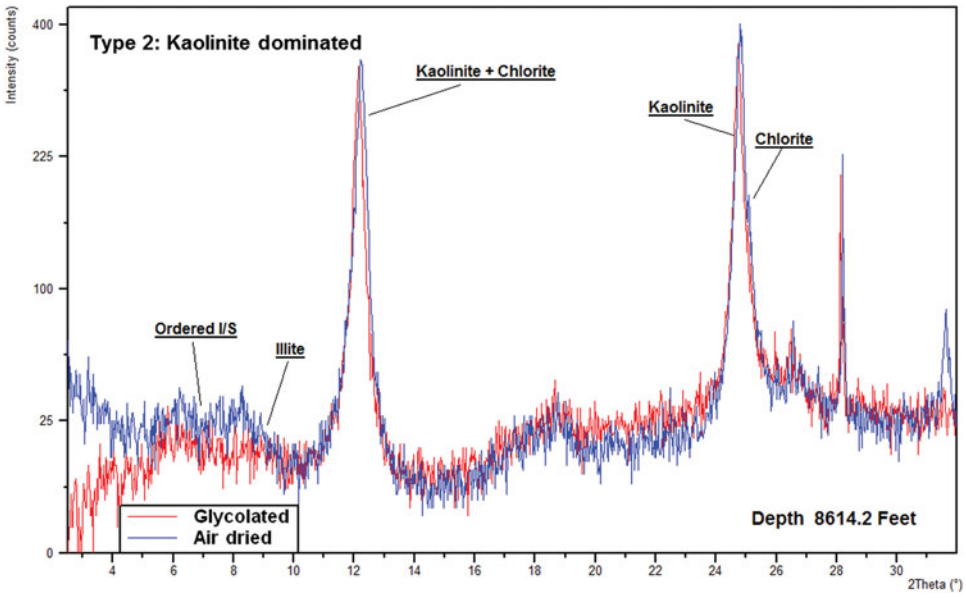

Figure 5. (Color online) XRD patterns of clay mineral association: Type II.

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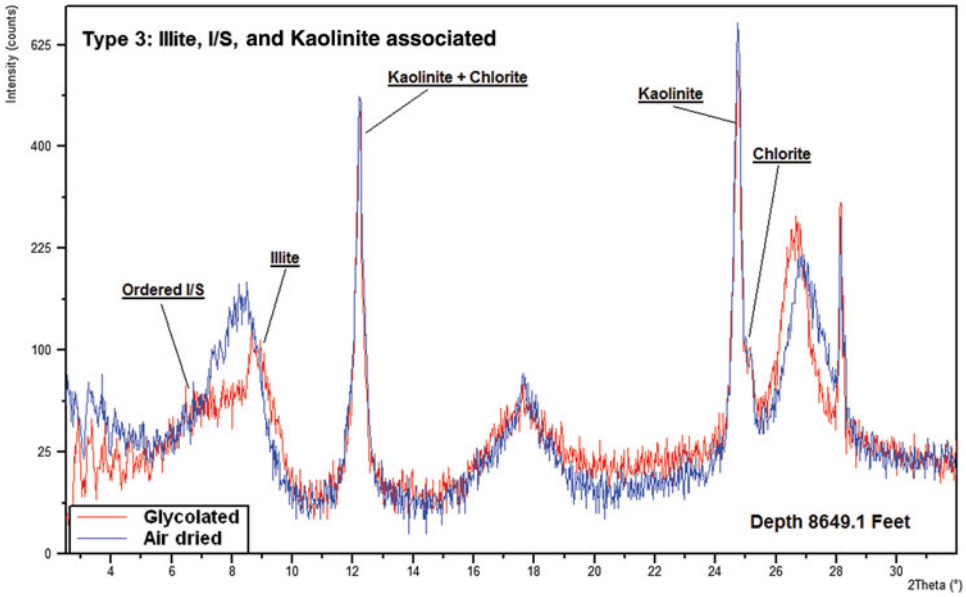

Figure 6. (Color online) XRD patterns of clay mineral association: Type III.

Table IV. Clay mineral association type change with sample depth.

X-ray diffraction No.	Depth (ft)	Illite (%)	Illite/smectite (%)	Kaolinite (%)	Chlorite (%)	Clay mineral association type	Paleoclimatic condition
00229	8596.9	52	46	1	1	I	Relatively cool and dry
00230	8597.4	57	40	2	1	I	
00231	8599.1	44	41	10	5	I	
00232	8599.6	47	49	2	2	I	
00233	8600.1	52	44	2	2	I	
00234	8600.4	55	37	6	2	I	
00235	8607.7	50	36	9	5	I	
00236	8608.1	39	28	17	16	I	
00237	8608.5	48	41	8	3	I	
00238	8609.2	19	22	40	19	III	Transitional
00239	8609.5	17	19	38	26	III	
00240	8610.2	19	20	40	21	III	
00241	8610.9	13	20	43	24	III	
00242	8611.1	10	8	68	14	II	Relatively warm and humid
00243	8611.8	22	15	23	40	I	
00244	8612.3	8	9	59	24	II	
00245	8612.6	4	3	61	32	II	
00246	8613.2	17	13	57	13	II	
00247	8613.5	7	15	64	14	II	
00248	8614.2	5	3	75	17	II	
00249	8614.5	9	4	75	12	II	
00250	8615.5	5	4	77	14	II	
00251	8615.8	3	2	74	21	II	
00252	8616.2	8	6	70	16	II	
00253	8616.6	4	8	77	11	II	
00254	8617.2	7	5	76	12	II	
00255	8617.6	6	4	71	19	II	
00256	8618.5	8	6	76	10	II	
00257	8620.0	43	38	14	5	I	
00258	8621.5	13	13	59	15	II	
00259	8623.0	9	33	51	7	II	
00260	8624.5	44	39	11	6	I	Relatively cool and dry
00261	8626.0	38	48	11	3	I	
00262	8627.5	44	48	7	1	I	
00263	8629.0	34	29	31	6	III	
00264	8630.5	40	43	13	4	I	
00265	8632.0	37	35	20	8	I	
00266	8633.5	34	38	22	6	I	
00267	8641.0	46	32	19	3	I	
00268	8642.5	42	29	22	7	I	
00269	8645.0	38	31	26	5	I	
00270	8647.1	64	31	3	2	I	

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anhydrite, siderite, gypsum, calcite, and pyrite. Hematite mainly occurs in the section with a depth of 8617.2–8649.1 ft, where the rocks are red and usually contain relatively high amounts of clays. Hematite is a common mineral in paleosols. It is generally formed in warm and humid climates, which facilitates chemical weathering (Blatt *et al.*, 1980). Clay minerals are important constituents in paleosols. The XRD results show that clay minerals in the samples are illite, a mixed layer of illite/smectite, kaolinite, and chlorite. No discrete smectite is present in the samples. On the basis of comparison of the data from XRD bulk mineralogy and XRD clay fraction analysis, the total percentages of clay minerals (illite, a mixed layer of illite/smectite, kaolinite, and chlorite) determined from XRD bulk analysis are usually found to be bigger than clay-size fractions determined using separation techniques. This is because some clay minerals (especially kaolinite) may be larger than clay size (<2 μm). The total clay data from XRD bulk analysis indicate that clay contents are variable by an average of 11.4% (0–43.5%), of which 5.0% is kaolinte (0–28.9%), 4.9% is illite and a mix of illite/smectite (0–28.1%), and 1.5% is chlorite. Many clayey paleosols were reported to be predominantly composed of illite, and in many soils illite or a mixed layer of illite/smectite is the main clay mineral, especially in young soils of desert regions with strong wet–dry seasons (Robinson and Wright, 1987). The predominantly illitic composition of many paleosols is also because of the alteration of smectite to illite during burial, a process now widely documented from studies of boreholes. The samples of paleosol sections in this study were collected from a depth of 8596.9–8988.7 ft, where temperatures are favorable to the transition of smectite to illite through a mixed layer of illite/smectite. The percentages of the smectite layer were 10–30% in these mixed-layer samples, which indicates the type is ordered illite/smectite. The clay mineral associations in these samples of paleosol sections can be classified into three types: Type I: illite and mixed layer of illite/smectite dominated (Figure 4); Type II: Kaolinite dominated (Figure 5); and Type III: illite, mixed layer of illite/smectite, and kaolinite associated (Figure 6). Most samples are of Type I, in which illite and a mixed layer of illite/smectite are predominant, whereas kaolonite is <30%. Type II mainly occurs at depths of 8612.3–8618.5 ft, in which the relative percentage of kaolinte is >50%. Type III mainly occurs at depths of 8609.2–8610.9 ft and 8915.8–8988.7 ft, in which illite and a mixed layer of illite/smectite are still major constituents, but kaolinite is >30%. The change of clay mineral association type with depth (Table IV) may indicate the change of paleoclimate and paleoenvironment. For example, kaolinite usually forms under strongly leaching conditions such as abundant rainfall, good drainage, and acid waters. Therefore, XRD mineralogical data of paleosol sections are important for petroleum geologists to study paleoclimate and paleoenvironment and predict the reservoir quality of the associated rock formations. However, the interpretation of clay mineral association should consider all factors including provenance and diagenesis.

IV. CONCLUSION

On the basis of the quantitative XRD analysis of 172 samples from paleosol sections, (1) the McCrone micronizing mill is highly recommended for grinding a bulk sample to reduce the particle-preferred orientation; and (2) the combined method of Rietveld refinement and RIR is a good solution for quantitative XRD analysis of geological samples containing clay minerals. The change of clay mineral association type with sample depth in paleosol sections may indicate the change of paleoclimate and paleoenvironment, and help petroleum geologists predict the reservoir quality of the associated rock formations.

ACKNOWLEDGMENTS

The authors would like to acknowledge Abdulelah A. Al-Naser, Yazeed A. Al-Dukhayyil, Awad M. Al-Mofleh, and Abbas S. Al-Ghamdi of Saudi Aramco for their help and support. Thanks are also given to Saudi Aramco for the permission to publish this paper.

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