Appendix 4
Minerals characterisation for sorption experiments

Contents

A4.1 Introduction

The characterisation of the minerals selected to study the sorption of U(IV) is essential to verify their purity. All minerals were characterised by x-ray diffraction (XRD) and x-rays fluorescence (XRF). These analyses were performed at the Cellule Interdépartementale d'Analyse, Faculty of Sciences, University of Louvain-la-Neuve (Belgium). In this annex, the XRD patterns and the chemical compositions are given and discussed.

A4.2 Characterisation techniques

A4.2.1 X-ray diffraction

X-ray diffraction (XRD) analyses allow to qualitatively identify the mineralogical phases present in the sample. They were performed on bulk sample of all selected minerals and on the clayey fraction of the clay minerals. A Siemens D500 diffractometer working with the mean Cu Kα line (λ=1.5418 Å) was used for standard powder diffraction. The scan speed was 0.5°2θ per 60 seconds. Scans of the various diffraction peaks were recorded in the 4°-90°2θ range, except for the clayey fraction for which the range was 2°-30°2θ. The results were interpreted with SOCABIM DiffracPlus version 5.1 software.

The clayey fraction was analysed on oriented mounts. The preparation procedure involves suspending the clay sample in distilled water, disaggregating it using ultrasound (Soniprep 150 MSE), and settling gravitationally to extract the less than 2 μm size-fraction. This suspension is pipetted onto a glass plate and allowed to dry under room temperature. Three oriented plates were analysed: under ambient room conditions (N), after heating at 500°C (F) and after exposure overnight to an ethylene glycol atmosphere (EG).

A4.2.2 X-ray fluorescence

The major (>1%) and minor elements (0.1-1%) were analyzed by x-ray fluorescence (XRF) with a Siemens-Bruker SRS 3000 spectrometer. The data acquisition and treatment were achieved by the SOCABIM SpectraPlus version 1.4 software.

The sample was prepared by mixing 8 g of the powdered mineral with 0.8 g of a synthetic resin (elvacite) in an agate mortar. This mixture was then pressed at 40 tons to obtain a pastille. The loss of ignition (L.O.I.) is determined by heating the sample for 24 hours at 900°C. The total iron content is expressed as Fe_2O_3.

A4.3 Results

A4.3.1 Clay minerals

XRD analyses on the bulk sample are performed to identify the minerals other than clay minerals present in the sample (data not shown). XRD analyses of the clayey fraction on oriented mounts are conducted to identify the mineralogical composition of the clay minerals. The chemical composition of the bulk clay minerals samples is compared with the data given on the website of the Source Clay Minerals Repository (http://cms.lanl.gov/chem.htm), at least when they are available.

A4.3.1.1 Kaolinite (Ka-1)

The only detected mineral phase by XRD on the bulk sample is kaolinite. The sharp peaks indicate a good crystallization. The diffraction spectra of the clayey fraction are given in Figure A4.1. The N and EG spectra show the characteristic 7.1 Å (00l) and (002)-reflections occurring at 12.4 and 24.9°2θ, respectively. The (00l) and (002) peaks do not change on ethylene glycol saturation (EG) meaning that no swelling occurs. After heating at 500°C (F), the peaks disappear pointing out the kaolinite transformation into metakaolinite (dehydroxylation) and the absence of well-crystallized chlorite.

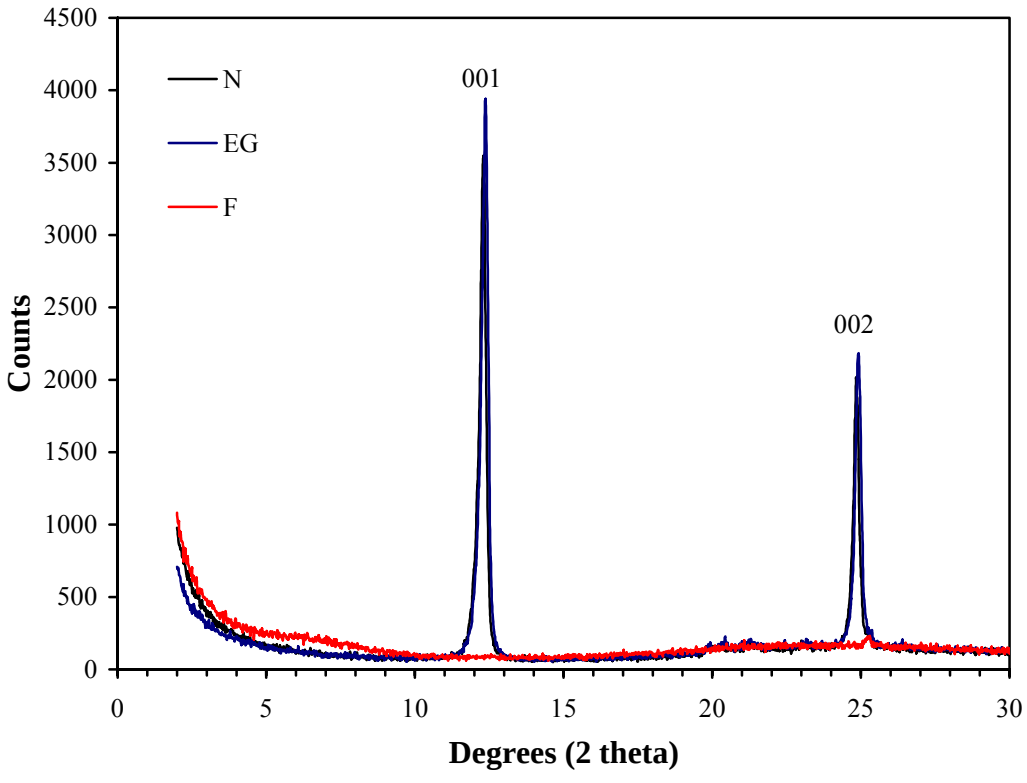

Figure A4.1. XRD patterns of the clayey fraction of the kaolinite sample. N, F and EG are described in the text.

The chemical composition of the kaolinite bulk sample is reported in Table A4.1. The composition determined by XRF and that provided by the Source Clay Minerals Repository are very similar. The kaolinite sample contains about 1 wt.% of titanium oxide. The presence of anatase and rutile in KGa kaolinite from the Source Clay Minerals Repository has been reported (*e.g.* Payne *et al.*, 1998; Chipera and Bish, 2001). Anatase is the more abundant TiO_2 polymorph, and occurs in grains generally less than 0.2 to 0.3 μm in size, and also as single crystals up to 0.5 μm. Rutile is less common, but several single crystals up to approximately 1 μm in length were observed by Payne *et al.* (1998).

Table A4.1. Chemical composition in weight percentage of the kaolinite sample determined by XRF and as given on the website of the Source Clay Minerals Repository (SCMR).

Compounds	**XRF wt.%**	**SCMR wt.%**
L.O.I.	14.1	13.8[#]
SiO_2	43.3	44.2
Al_2O_3	41	39.7
TiO_2	1.3	1.4
Fe_2O_3	0.3	0.2[§]
P_2O_5	< 0.1	< 0.1
Total	100.1	99.4

#: L.O.I. determined at 1000°C

§: Fe_2O_3 + FeO

A4.3.1.2 Illite (Il-1)

The detected minerals on the bulk sample besides clay minerals are quartz and microcline (feldspar). The XRD spectra of the clayey fraction are shown in Figure A4.2. All diffractograms are very similar. The 10 Å (001) and (003)-reflections are the most intense and occur at 8.8 and 26.8°2θ, respectively. The peaks remain unaffected by the ethylene glycol treatment and the heating at 500°C. The intensity ratio of the peaks (001) and (002) can be used to distinguish illite and muscovite. This ratio is between 0.7 and 1 for the muscovite. The calculated ratio for our sample is about 4 indicating that it consists of illite. A ratio higher than 3 is in agreement with the reported values for Fe-rich illites (Thorez, 1976). XRF analysis indicates a Fe_2O_3 content of 5.8 wt.% while the Fe content reported by the Source Clay Minerals Repository is 7.9 wt.% (Table A4.2).

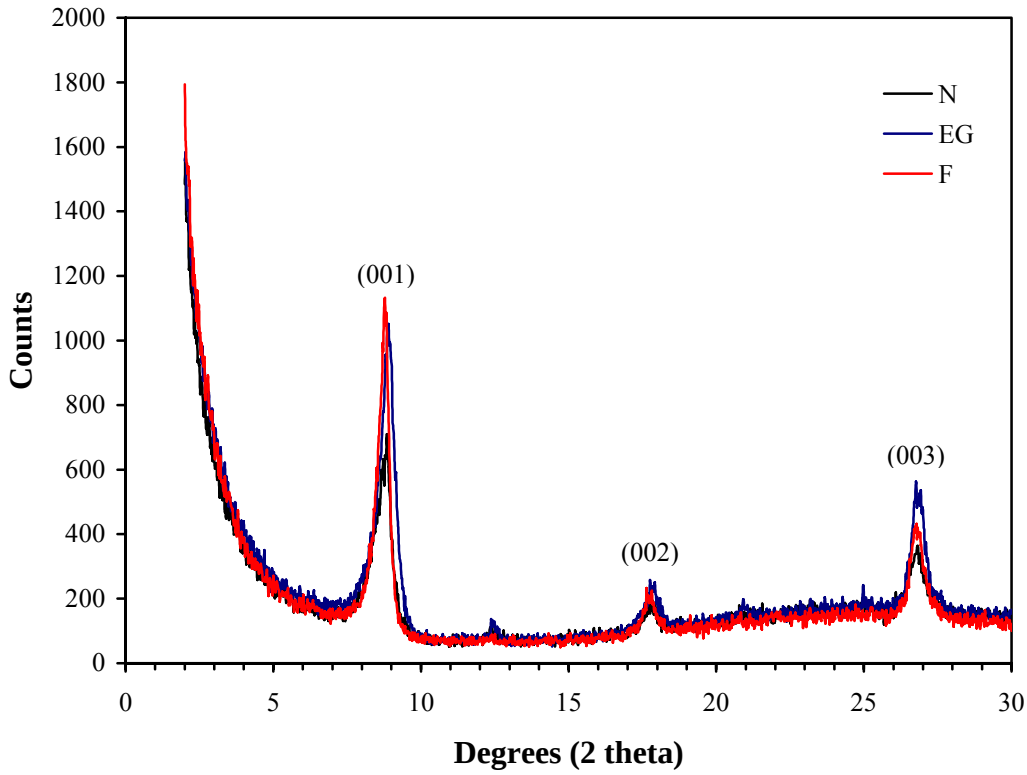

Figure A4.2. XRD patterns of the clayey fraction of the illite sample. N, F and EG are described in the text.

Table A4.2. Chemical composition in weight percentage of the illite sample determined by XRD and as given on the website of the Source Clay Minerals Repository (SCMR).

Compounds	**XRF wt.%**	**SCMR wt.%**
L.O.I.	6.49	—
SiO_2	54.3	49.3
Al_2O_3	22.8	24.3
K_2O	7.2	7.8
Fe_2O_3[#]	5.8	7.9
MgO	2.1	2.6
TiO_2	0.6	0.6
CaO	0.2	0.4
P_2O_5	0.1	0.1
SO_3	0.1	—
Na_2O	< 0.1	0
Total	99.8	93

#: Fe_2O_3 + FeO

A4.3.1.3 Na-montmorillonite (Mt-1)

Montmorillonite is a dioctahedral species of the expanding clay minerals group of smectite. Again, the only impurity detected by XRD on the bulk sample is quartz. The spectra of the clayey fraction are given in Figure A4.3. On the N pattern, the most intense peak, corresponding to the basal one, occurs at a *d*-spacing of 12.8 Å (6.9°2θ). The *d*(001)-spacing expands to 17.3 Å (5.1°2θ) on ethylene glycol treatment and collapses to 9.8 Å (9°2θ) after the heating at 500°C. This behaviour is characteristic of the smectite group (Thorez, 1976). Nevertheless, the appearance of a 8.6 Å peak at 10.3 2θ on the EG pattern reveals that the clay is composed of smectite-illite mixed layer with an illite content of about 10 % (Reynolds, 1980).

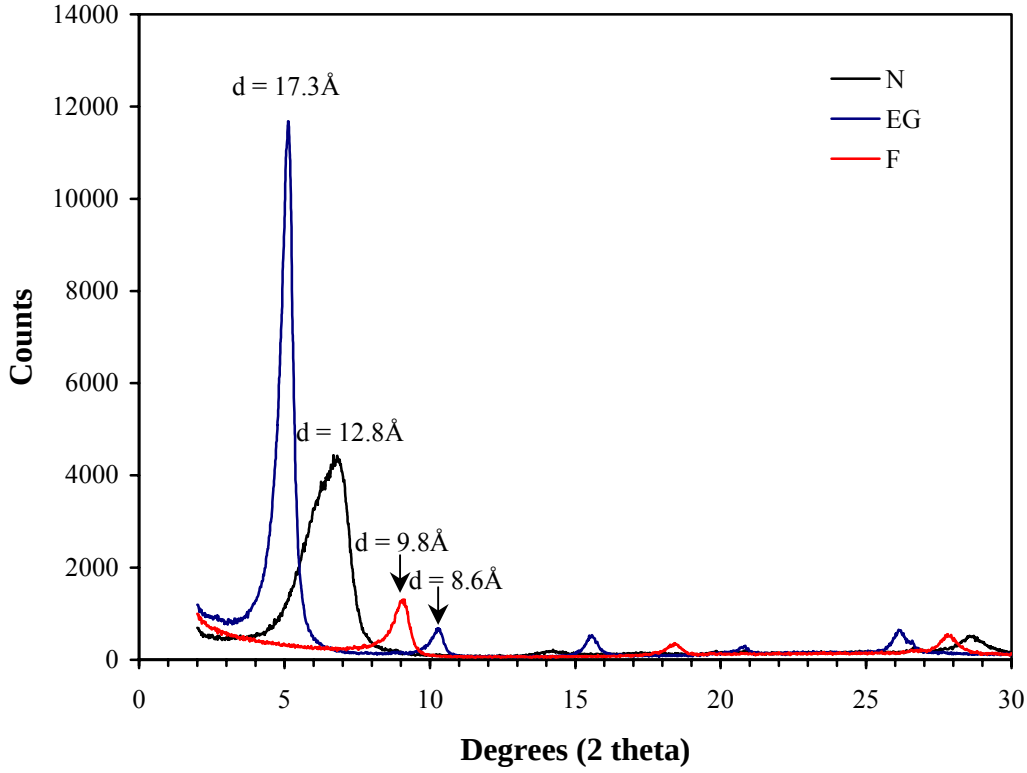

Figure A4.3. XRD patterns of the clayey fraction of the Na-montmorillonite sample. N, F and EG are described in the text.

The chemical composition is reported in Table A4.3. The relatively high content in Fe_2O_3 (3.7 wt.%) is usual for the smectite from Wyoming (Grim and Kulbicki, 1961; Van Olphen and Fripiat, 1979). This is explained by the fact that 5 to more than 15% of the octahedral positions are populated by iron (Grim and Kulbicki, 1961). As the sample contains about 0.3 wt.% of SO_3, it is possible that sulphide minerals are present but in minor amount since they are not detected by XRD.

Table A4.3. Chemical composition in weight percentage of the Na-montmorillonite sample determined by XRD and as given on the website of the Source Clay Minerals Repository (SCMR).

Compounds	**XRF wt.%**	**SCMR wt.%**
L.O.I.	9.3	6.06[#]
SiO_2	60.6	62.9
Al_2O_3	20.0	19.6
Fe_2O_3	3.7	3.7[§]
MgO	2.6	3.1
Na_2O	1.4	1.5
CaO	1.4	1.7
K_2O	0.5	0.5
SO_3	0.3	0.12*
TiO_2	0.1	0.1
P_2O_5	< 0.1	< 0.1
Total	100	99.4

#: L.O.I. determined at 1000°C

§: Fe_2O_3 + FeO

*: recalculated from 0.05 % elemental sulphur.

A4.3.1.4 Illite-smectite mixed layer (Il/sm-1)

The only non-clay mineral detected in the bulk sample is quartz. The (001)-reflection, the most intense, occurs at a *d*-spacing of 11 Å (8°2θ) on the N pattern (Figure A4.4). The *d*-spacing increases to 13 Å (6.8°2θ) on the glycolated sample and collapses to 10 Å (8.8°2θ) after the heating at 500°C (Figure A4.4). The limited swelling and collapsing suggest that the clay contains more illite than smectite. This assumption is confirmed by the appearance of the 9.4 Å reflection (9.4°2θ) on the EG pattern that indicates that the sample contains about 65% of illite (Reynolds, 1980). This value is in agreement with the composition given by The Source Clays Minerals Repository that defines the clay as a 70/30 ordered illite-smectite mixed layer.

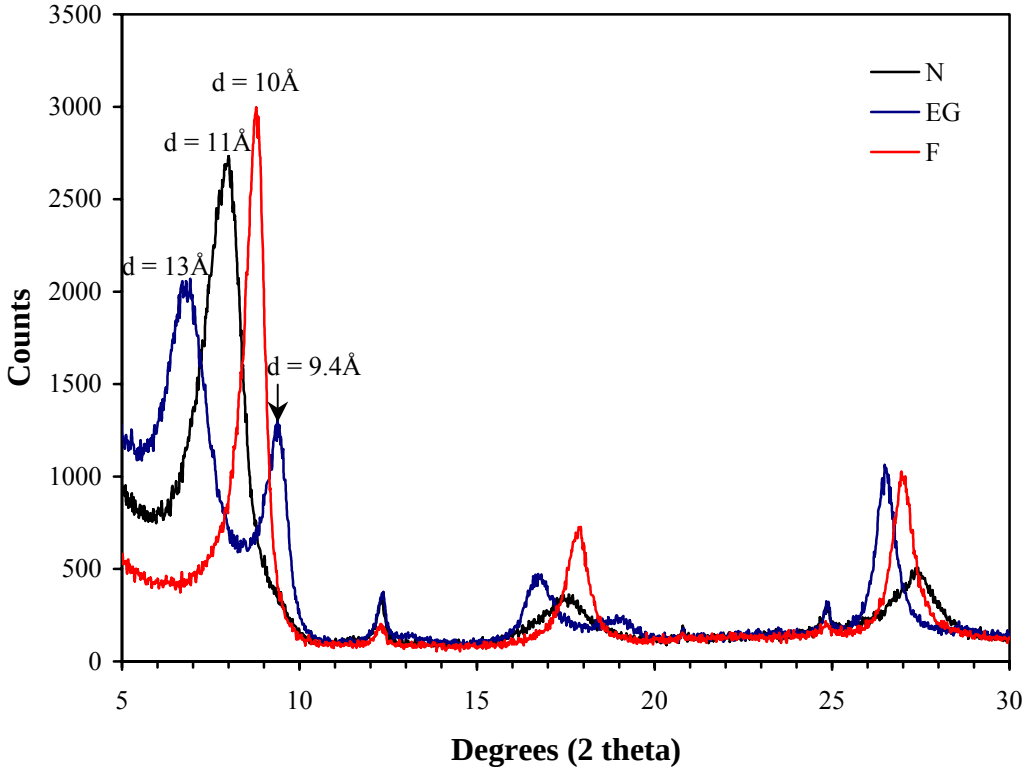

Figure A4.4. XRD patterns of the clayey fraction of the illite-smectite mixed layer sample. N, F and EG are described in the text.

The chemical composition obtained by XRF and from the Source Clay Minerals Repository are compared in Table A4.4. Both analyses mainly differ by their SiO_2 content.

Table A4.4. Chemical composition in weight percentage of the illite-smectite mixed-layer sample determined by XRD and as given on the website of the Source Clay Minerals Repository (SCMR).

Compounds	**XRF wt.%**	**SCMR wt.%**
L.O.I.	8.9	—
SiO_2	62.5	51.6
Al_2O_3	21.7	25.6
K_2O	4.0	5.4
MgO	1.9	2.5
Fe_2O_3	1.0	1.1
CaO	—	0.7
TiO_2	< 0.1	< 0.1
Total	100.1	87

A4.3.1.5 Ripidolite (Ri-1)

Ripidolite is defined as a ferroan clinochlore, clinochlore being a tri-octahedral Mg-rich chlorite: $(Mg_{10}Al_2)(Si_6Al_2)O_{20}(OH)_{16}$. Besides ferroan clinochlore, quartz is the only impurity in the bulk sample. Chlorite is recognised by its strong 14 Å second and fourth order basal reflections at 12.5 and 25.2°2θ, respectively (Figure A4.5). As generally in iron-rich varieties of chlorite, the (001) and (003) reflections are weak. The ethylene glycol (EG) and heating treatments (F) do not affect the *d*-spacing (Figure A4.5). However, the peak intensity changes: it increases on the EG pattern and decreases on the F pattern, except for the (001) peak which slightly increases. The sensitive lowering of the peaks intensity after heating at 500°C is a characteristic of some chlorites and in particular the iron-rich varieties (Thorez, 1976).

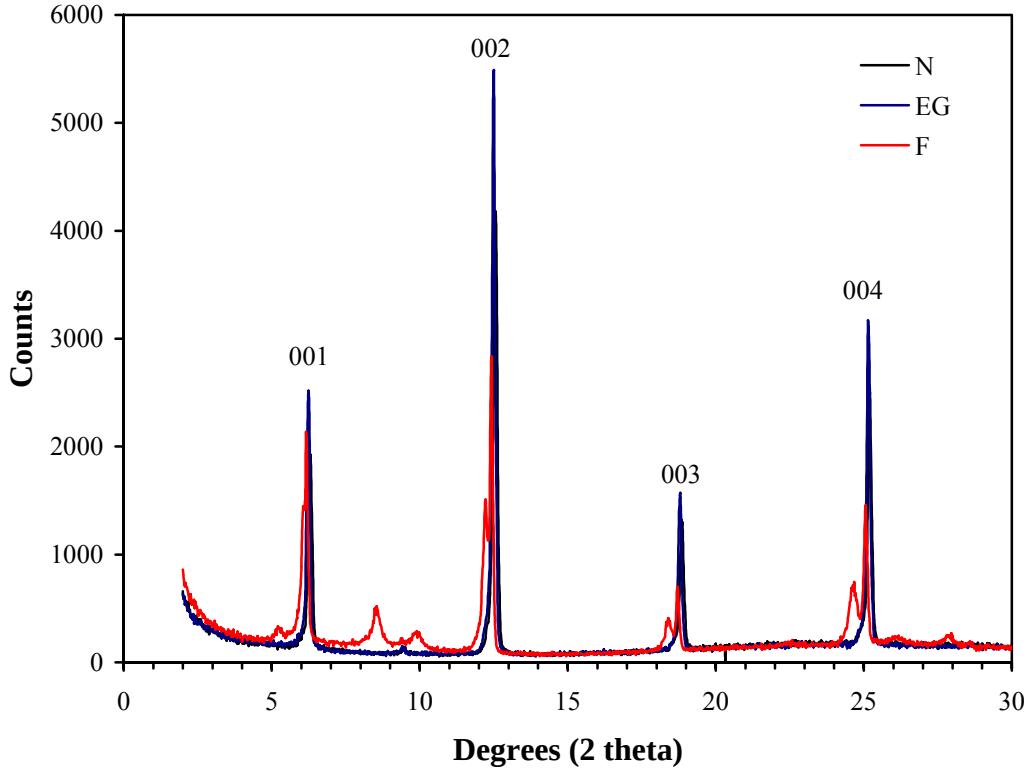

Figure A4.5. XRD patterns of the clayey fraction of the ripidolite sample. N, F and EG are described in the text.

The chemical composition of the ripidolite bulk sample is given in Table A4.5. The compositions obtained from XRF and the Source Clay Minerals Repository are comparable, except the iron content. The iron content reported by Source Clay Minerals Repository is extremely high and we assume that it results from an error.

Table A4.5. Chemical composition in weight percentage of the ripidolite sample determined by XRD and as given on the website of the Source Clay Minerals Repository (SCMR).

Compounds	**XRF wt.%**	**SCMR wt.%**
L.O.I.	9.3	—
SiO_2	26.5	26.0
Al_2O_3	22.8	20.0
Fe_2O_3	22.4	47.4§ ?
MgO	18.2	17.2
Ti_2O	0.6	0.5
CaO	—	0.3
MnO	< 0.1	0.1
Total	99.9	111.5

§: Fe_2O_3 + FeO

A4.3.2 Non clay minerals

A4.3.2.1 Rutile (Ru-1)

The XRD pattern shows that rutile is the predominant mineral in the sample (Figure A4.6). The small peak at 25.3°2θ is due to anatase which occur in small amount. Anatase is a polymorph of rutile. The sharp peaks indicate well-crystallized mineral.

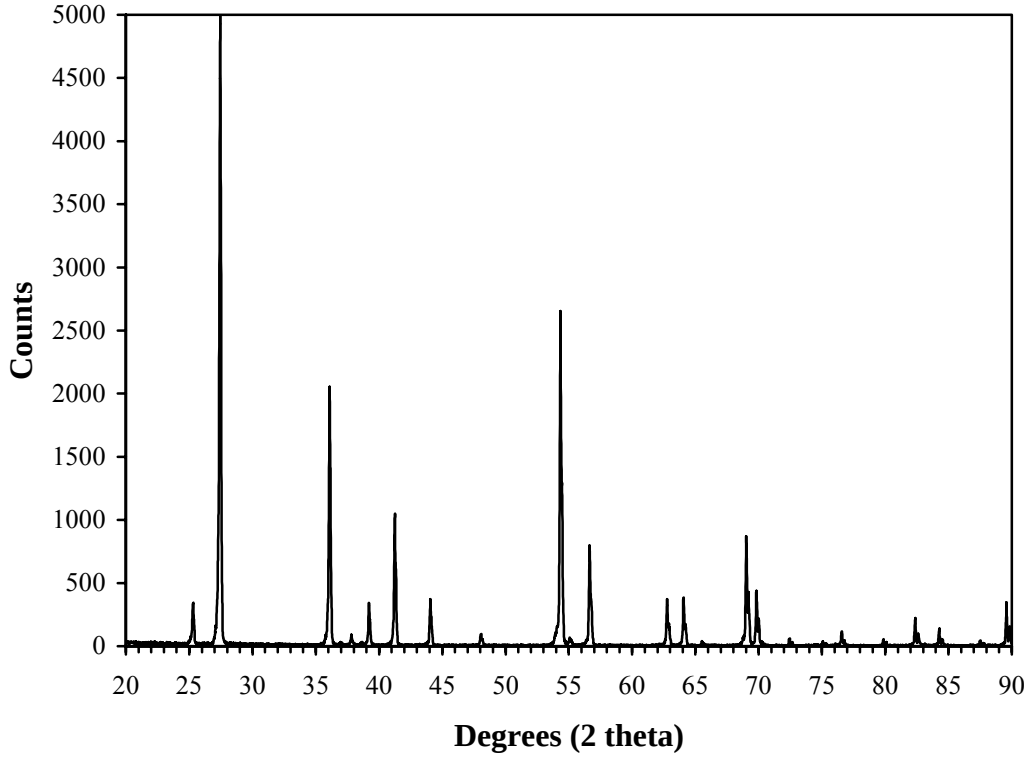

Figure A4.6. XRD pattern of rutile.

The product is very pure since TiO_2 represents 99.7 wt. %. The chemical composition is summarized in Table A4.6.

Table A4.6. Chemical composition in weight percentage of rutile determined by XRF.

Compounds	wt.%
L.O.I.	0.1
TiO_2	99.7
SiO_2	0.1
Al_2O_3	< 0.1
Total	100

A4.3.2.2 Ca-carbonate (Bel-1)

The mineralogical purity of the calcium carbonate is attested by the XRD analysis. Only one mineral constitutes the sample and it is pure calcite (Figure A4.7).

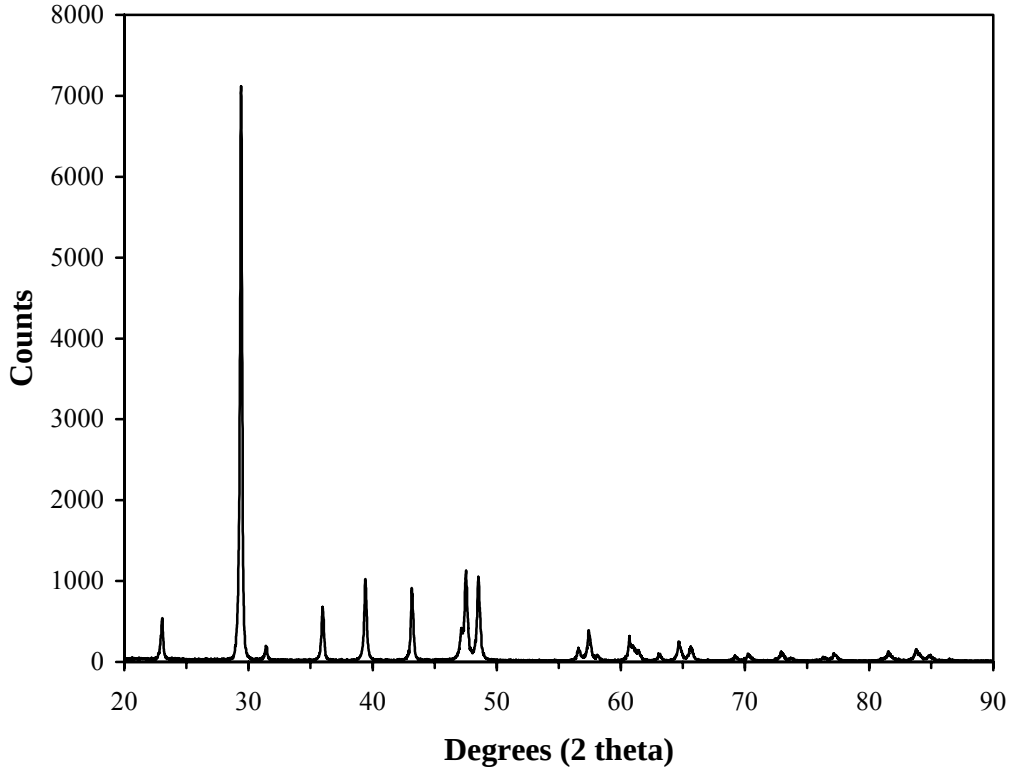

Figure A4.7. XRD pattern of calcium carbonate

The chemical composition confirms that the calcium carbonate consists in a pure calcite. Both the CaO and CO_2 (L.O.I.) content represents more than 99 wt. % of the sample (Table A4.7).

Table A4.7. Chemical composition in weight percentage of calcium carbonate determined by XRF.

Compounds	wt.%
CO_2	43.6
CaO	55.9
MgO	0.2
SiO_2	0.1
Fe_2O_3	< 0.1
Total	99.9

A4.3.2.3 Apatite (Kola-1)

According to the information received from the sample provider (Prayon, Liège, Belgium), Kola-1 is initially composed of hydroxyl-fluoro-apatite ($Ca_5(PO_4)_3(OH,F)$), ilmenite ($FeTiO_3$), sphene ($CaTiO(SiO_4)$) and nepheline ($NaAlSiO_4$). A process of flotation allows to remove nepheline, sphene and ilmenite. Indeed, the XRD analysis only detects fluoro-apatite in the Kola-sample (Figure A4.8).

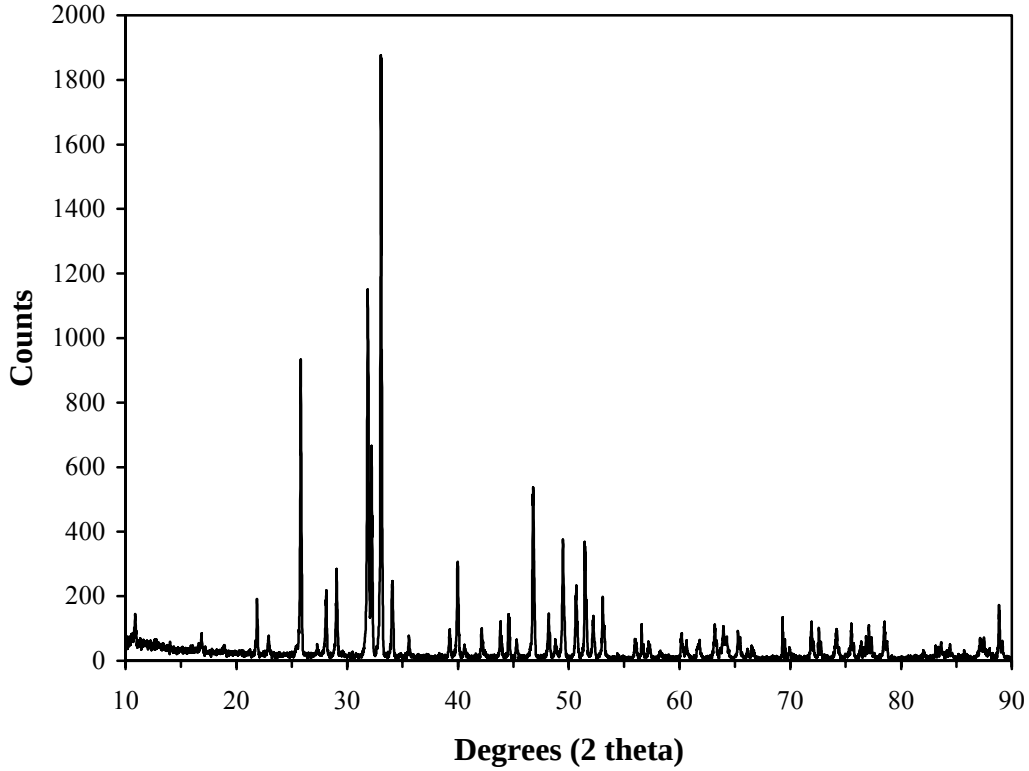

Figure A4.8. XRD pattern of apatite.

The compound $Ca_5(PO_4)_3(F)$ represents more than 90 wt.% of the sample (Table A4.8). SrO and SiO_2 are the other major elements.

Table A4. 8. Chemical composition in weight percentage of apatite determined by XRF.

Compounds	wt.%
L.O.I.	0.5
$Ca_5(PO_4)_3F$	92.3
SrO	2.7
SiO_2	1.4
Al_2O_3	0.6
Na_2O	0.6
Fe_2O_3	0.4
TiO_2	0.3
SO_3	0.2
MgO	0.2
K_2O	0.2
Total	99.4

A4.3.2.4 Pyrite (BC py-1)

The Boom Clay pyrite sample is mainly composed of pyrite. The XRD pattern shows that the only mineral present besides pyrite is quartz (Figure A4.9). The presence of quartz is identified by the occurrence of a small peak at 26.64°2θ.

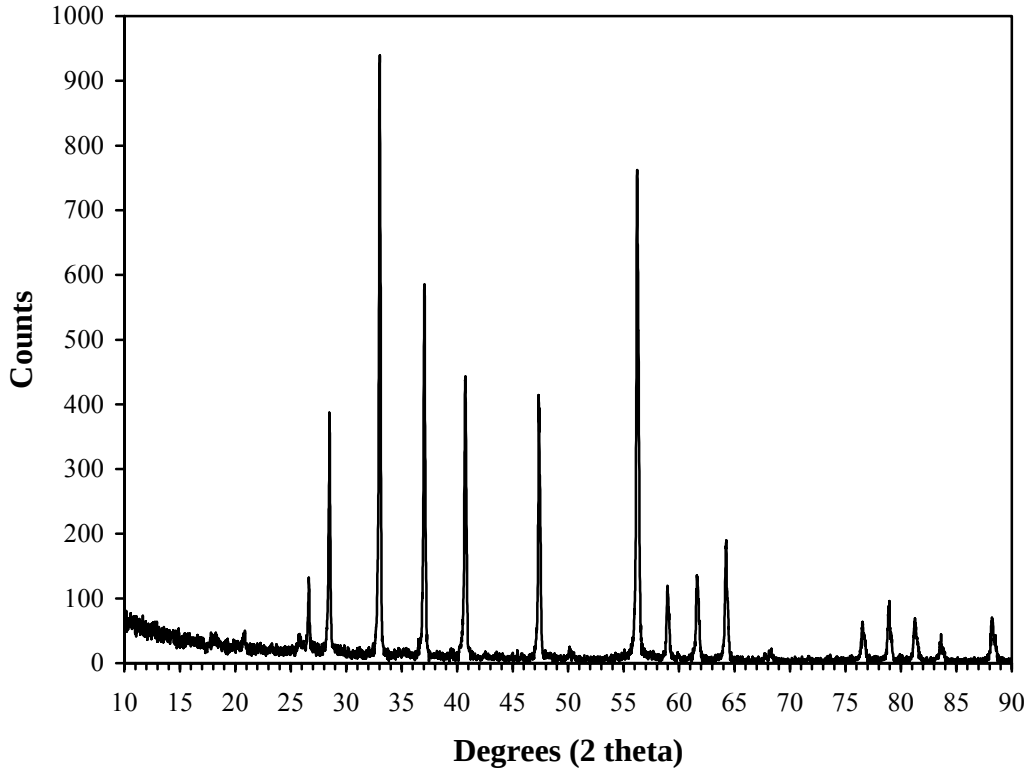

Figure A4.9. XRD pattern of Boom Clay pyrite.

The XRF analysis reveals that pyrite represents more than 90 wt. % of the sample and quartz about 6 wt. % (Table A4.9).

Table A4.9. Chemical composition in weight percentage of Boom Clay pyrite determined by XRF.

Compounds	**wt.%**
FeS_2	90.7
SiO_2	6.1
Al_2O_3	1.6
CaO	0.9
K_2O	0.3
MgO	0.2
TiO_2	< 0.1
Ni	< 0.1
Total	100

A4.4 Conclusion

On the basis of the Boom Clay mineralogical composition, nine minerals have been selected to perform the sorption study of U(IV). The XRD and XRF characterisations indicate that the selected minerals are sufficiently pure to be used as representative components of the Boom Clay mineral assemblage.

The bulk sample of kaolinite contains about 1 wt. % of TiO_2, mainly anatase. Quartz is the only mineral present besides the clay minerals in the bulk samples of illite-smectite mixed-layer, Na-montomorillonite and ripidolite. The bulk sample of illite also contains minor amounts of quartz but also feldspar. The presence of quartz and feldspar is not considered as a problem since they are common minerals in the Boom Clay. The XRD patterns of the clayey fraction of the clay minerals from the Source Clay Minerals Repository confirm the purity of kaolinite, illite, ripidolite and illite-smectite mixed layer of which the ratio illite to smectite is 70/30. About 10 % of illite could be present in the clayey fraction of Na-montmorillonite.

The purity of the non-clay minerals is also verified. The rutile sample is composed for more than 99 wt. % of TiO_2. Rutile is the predominant TiO_2 polymorph but anatase is detected by XRD in minor amounts. The calcium carbonate consists for more than 99 wt. % of a pure calcite. The apatite sample is identified by XRD as a fluoro-apatite which constitutes more than 92 wt. % of the sample. Finally, the Boom Clay pyrite sample mainly contains pyrite, about 91 wt. %. The main impurity is quartz which represents 6 wt. %.

A4.5 References

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