

# Mineralogical Report on Sample TN211041: Gypsiferous Claystone

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A drill core sample of friable, grey-brown coloured claystone from a Cenozoic Basin overlying the Ngalia Basin (NT) was examined under the binocular microscope and the scanning electron microscope. The core material is radioactive and portable XRF readings indicate that several hundred ppm of uranium is present. Under the binocular microscope abundant fine flakes of detrital muscovite together with less common mm-sized clasts of angular to sub-angular clear quartz and rare tourmaline can be identified. These clasts are all set within a soft, clay-dominant matrix although less common mm-sized patches of light-coloured coarser grained material are also present. Black-coloured material, which appears to be largely carbonaceous matter and/or sulphide form wispy zones, patches, spots and clusters of rod-like forms scattered throughout the specimen. Efflorescent crusts of a pale yellow material coat the external core surface and are also present in voids within the interior of the core sample but are not present within the matrix. The crusts commonly contain tiny specks or dustings of an orange-coloured mineral.

The rock is too soft to allow preparation of conventional polished sections. Particles of interest were therefore selected from the core external surface or from the broken pieces of the core interior and mounted on SEM stubs. This material was then carbon-coated and examined under the SEM with excellent results. A series of illustrative backscattered electron images are provided below.

The matrix was found to consist of very fine (<10 micron size) particles of clay and quartz in which are set fine (10 to 20 micron sized) clasts of detrital muscovite, K-feldspar and occasional flakes of Fe-rich chlorite (Figs 1-3). The matrix also contains scattered gypsum crystals up to about 20 microns in size but some parts of the matrix were found to be gypsum-rich and dominated by bladed gypsum crystals of 20-100 microns size (Fig. 4). The clay mineral(s) could not be identified with certainty; analyses show variable K<sub>2</sub>O contents (1 to 4% K<sub>2</sub>O) suggesting the clay is a mixture of illite and kaolinite; XRD analysis would be required for definitive identification.

An investigation of the black material that occurs as clusters and spots, shows that it is composed of aggregates of fine pyrite particles (Fig.5). The pyrite has variable nickel and cobalt contents ranging from trace levels up to 22% Co and 12% Ni. The Co, Ni-rich pyrite (bravoite) is relatively common in the specimen. Black material that occurs in larger, more diffuse patches is organic matter that in particular occupies grain boundaries and coats detrital grains. Organic matter appears black under backscattered imagery and can be difficult to identify under the SEM, so organics are likely to be more widespread in the specimen than suggested by this description.

Under backscattered electron imaging, numerous tiny particles (mostly 2 to 5 microns size) of uranium-bearing minerals were found scattered throughout the clay matrix; concentrations are highest in the vicinity of pyrite clusters. The uranium minerals fall into five different types all with distinct and reproducible compositions. The most abundant species encountered was an yttrium-uranium-Al-silicate-phosphate with ~50% UO<sub>2</sub>, but it does not appear to correspond to any known mineral. The other uranium-bearing minerals encountered include: altered uraninite, an APS (aluminium-phosphate-sulphate) mineral of the Crandallite-series, altered uraniferous zircon and an

unidentified Ca-Ti-U-Al -silicate. A list is provided below and representative analyses are provided in Table 1.

- Altered uraninite or “gummite” ( ~76% UO<sub>2</sub>)
- Unknown: (Ca,Fe)-Ti-U-Al-Silicate, (~58% UO<sub>2</sub>)
- Unknown: (Y,Nd,Sm,Dy)-U-Al-Silicate-Phosphate (~50% UO<sub>2</sub>),
- Uraniferous APS mineral: (Ca,Ce)-Al-Phosphate-Sulphate-Hydrate (~5% UO<sub>2</sub>)
- Altered Uraniferous Zircon (~18% UO<sub>2</sub>)

Other accessory minerals occurring as small particles in the matrix include anatase, barite and florencite-(Ce).

The yellow efflorescent material common as crusts on the exterior surface of the core was found not to be a uranium mineral, but instead a mixture of gypsum and the secondary hydrous sulphate copiapite: Fe<sub>5</sub>(SO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>•xH<sub>2</sub>O. The orange dustings are iron oxide; a hydrous zinc sulphate-chloride mineral was also identified in the efflorescent crust. The crusts presumably crystallized from acidic waters containing dissolved Fe and sulphate once the core samples dried-out post-recovery.

Table 1. Analyses of Uranium Minerals

	Altered Uraninite "Gummite"	Ca-U-REE-Al Silicate-Phosphate	Ca-U-Ti-Al Silicate	Uraniferous APS mineral	Altered Uraniferous Zircon
SiO <sub>2</sub>	6.9	19.8	18.5	bdl	23.7
TiO <sub>2</sub>	bdl	bdl	2.7	bdl	0.7
Al <sub>2</sub> O <sub>3</sub>	5.1	10.3	10.4	36.8	3.2
FeO	0.6	0.6	0.9	2.1	0.8
MgO	0.4	0.4	bdl	bdl	bdl
CaO	1.4	1.0	1.3	7.4	1.1
Na <sub>2</sub> O	0.7	bdl	bdl	bdl	bdl
P <sub>2</sub> O <sub>5</sub>	0.4	3.8	bdl	13.2	1.5
SO <sub>3</sub>	bdl	1.2	1.1	17.5	bdl
Y <sub>2</sub> O <sub>3</sub>	0.6	4.8	bdl	bdl	bdl
Ce <sub>2</sub> O <sub>3</sub>	bdl	bdl	bdl	7.8	bdl
Nd <sub>2</sub> O <sub>3</sub>	1.4	1.6	1.2	bdl	bdl
Sm <sub>2</sub> O <sub>3</sub>	bdl	1.1	bdl	bdl	bdl
Dy <sub>2</sub> O <sub>3</sub>	bdl	1.7	bdl	bdl	bdl
UO <sub>2</sub>	75.6	49.6	58.2	4.9	18.5
ZrO <sub>2</sub>	bdl	bdl	bdl	bdl	47.4
Total	93.1	95.9	94.3	89.7	96.9

Area scans of the SEM stub material (Table 2) gives a guide to the bulk composition of the rock. Scans #1 and #2 of the normal clay-rich areas give a composition of approx. 72% clay minerals, 10% quartz, 10% detrital muscovite plus K-feldspar, 5% gypsum and 3% pyrite. In a dark area rich in organic matter, less quartz is present and there is more gypsum, pyrite and possibly some halite (as indicated by higher Na and measurable Cl) together with >1% UO<sub>2</sub>. An association between pyrite, organic matter and uranium minerals in the black-coloured patches is indicated.

Table 2. Area Scans

	Area Scan #1	Area Scan #2	Area Scan #3 Black patch rich in organic matter/pyrite
SiO <sub>2</sub>	54.96	55.12	38.05
TiO <sub>2</sub>	0.97	1.02	0.68
Al <sub>2</sub> O <sub>3</sub>	30.45	33.89	31.61
FeO	2.04	1.38	3.31
MgO	0.50	0.71	1.44
CaO	3.26	2.22	4.22
Na <sub>2</sub> O	0.36	0.36	1.46
K <sub>2</sub> O	1.56	1.45	1.96
SO <sub>3</sub>	5.25	3.73	8.65
Cl	bdl	bdl	0.14
UO <sub>2</sub>	bdl	bdl	1.54
Total	99.35	99.88	93.06

### Backscattered Electron Imagery

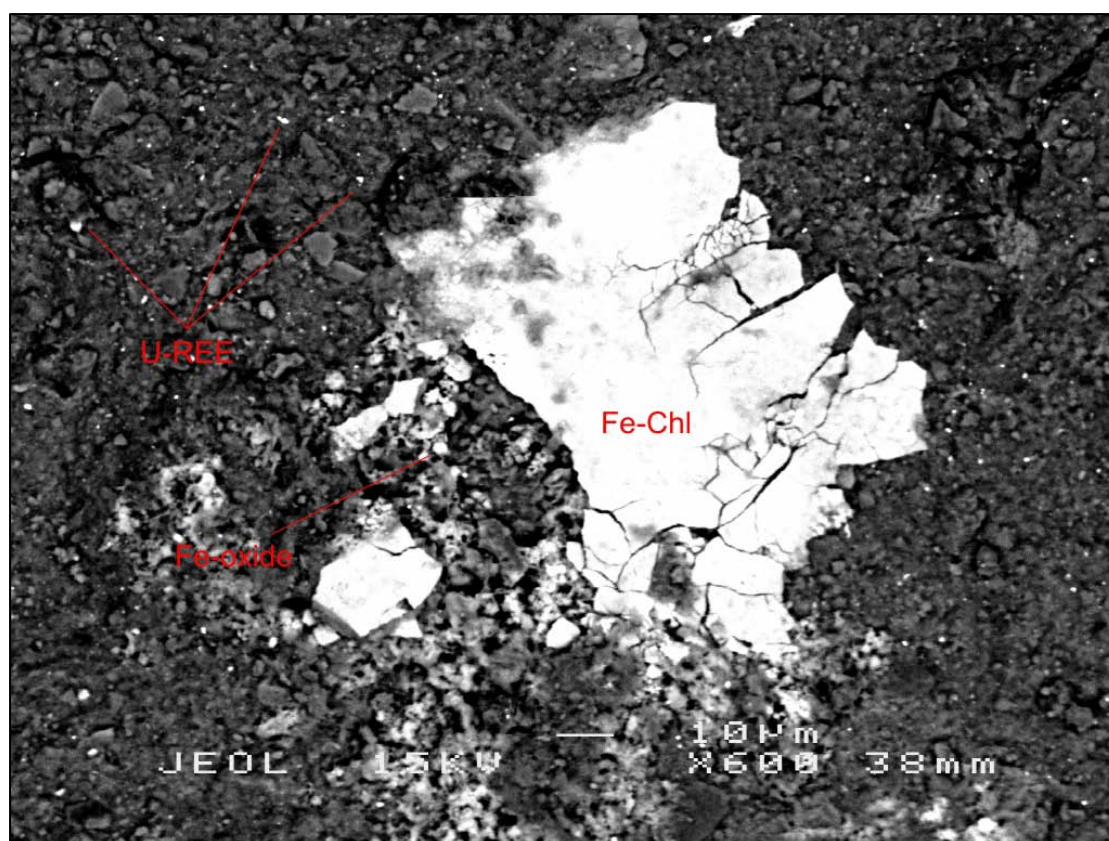


Fig.1. Plate of Fe-rich chlorite (Fe-Chl) on the clay-rich matrix. Tiny bright particles include Fe-oxide and an unidentified Ca-U-REE-Al-Silicate-Phosphate mineral (U-REE).

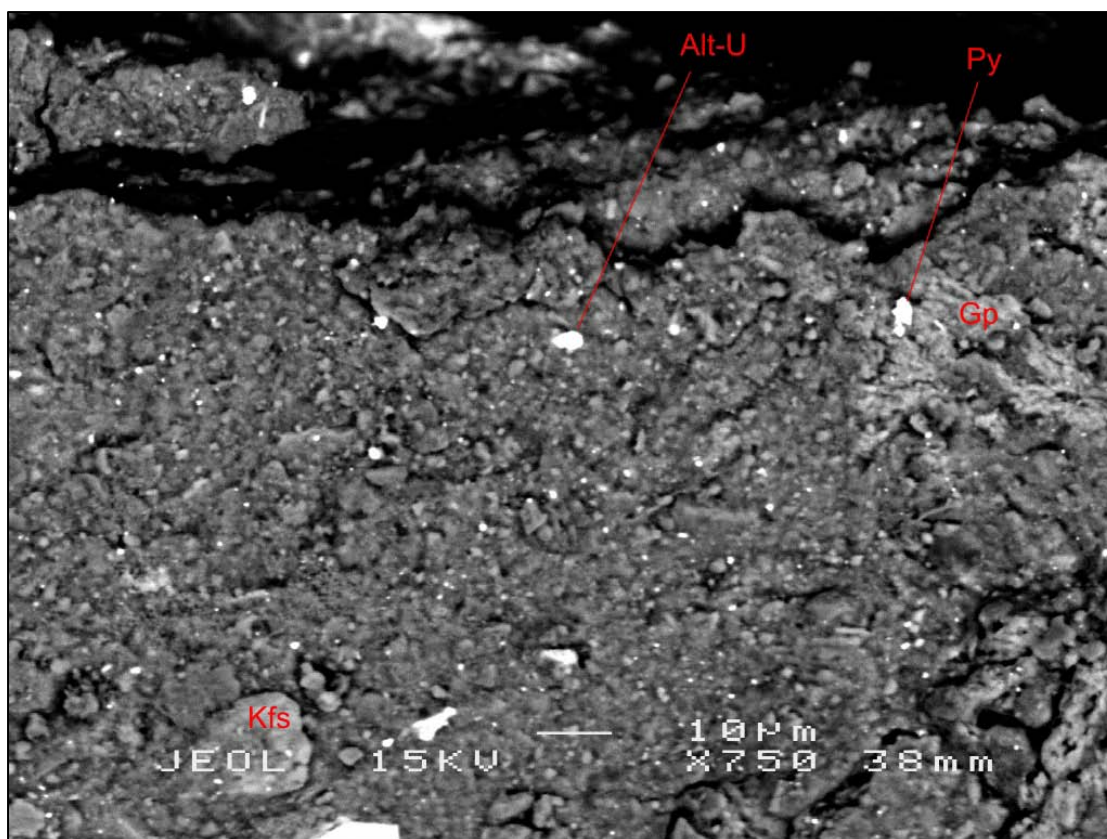


Fig.2. Clay matrix showing detrital K-feldspar (Kfs), matrix gypsum (Gp) and ~5 micron sized particles of altered uraninite (Alt-U; "gummite") and pyrite (Py).

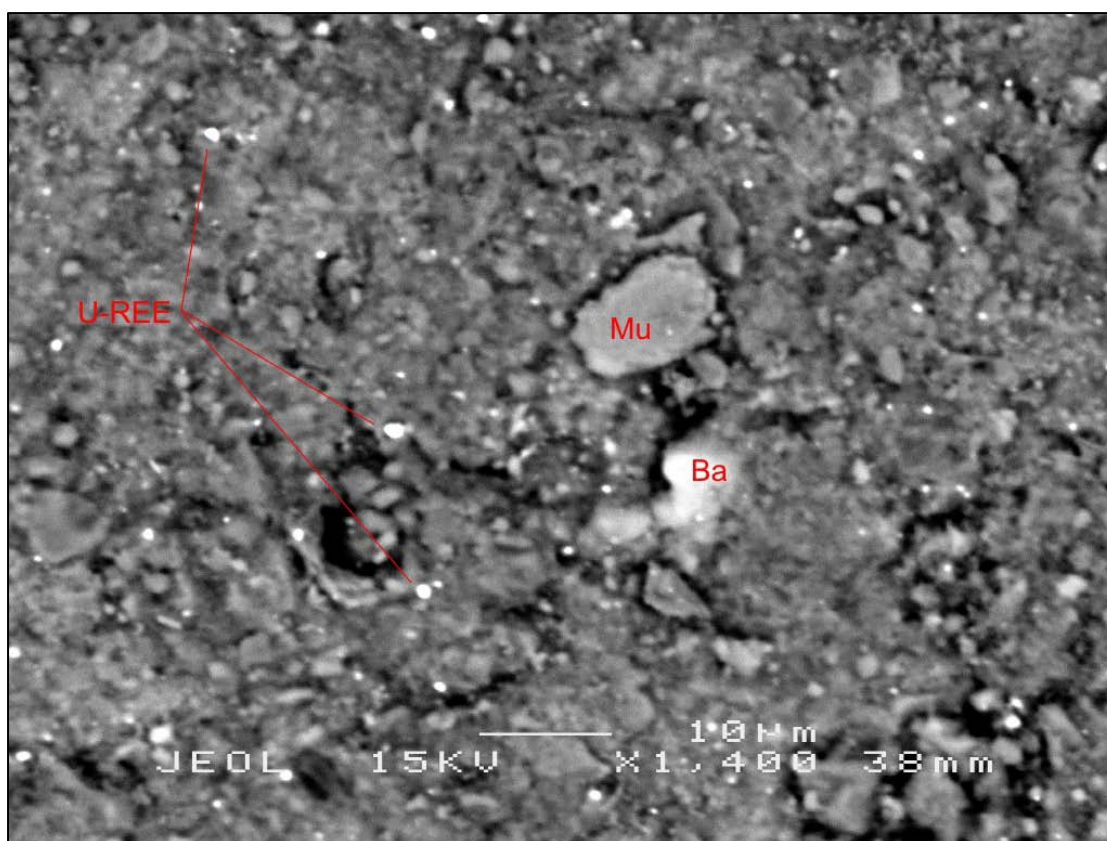


Fig.3. Clay matrix showing detrital muscovite (Mu), barite (Ba) and <5 micron sized particles of a Ca-U-REE-Al-Silicate-Phosphate mineral (U-REE).



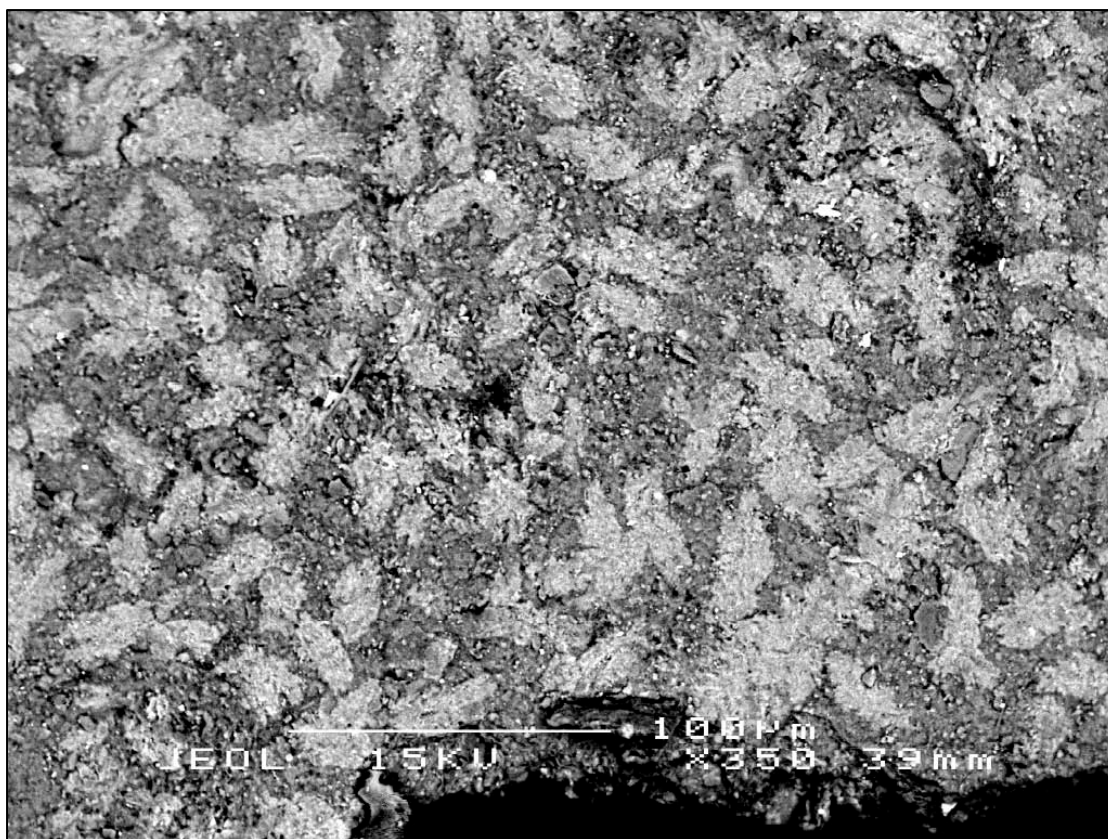


Fig.4. Gypsum-rich area showing 20-100 micron sized gypsum crystals in the clay matrix.

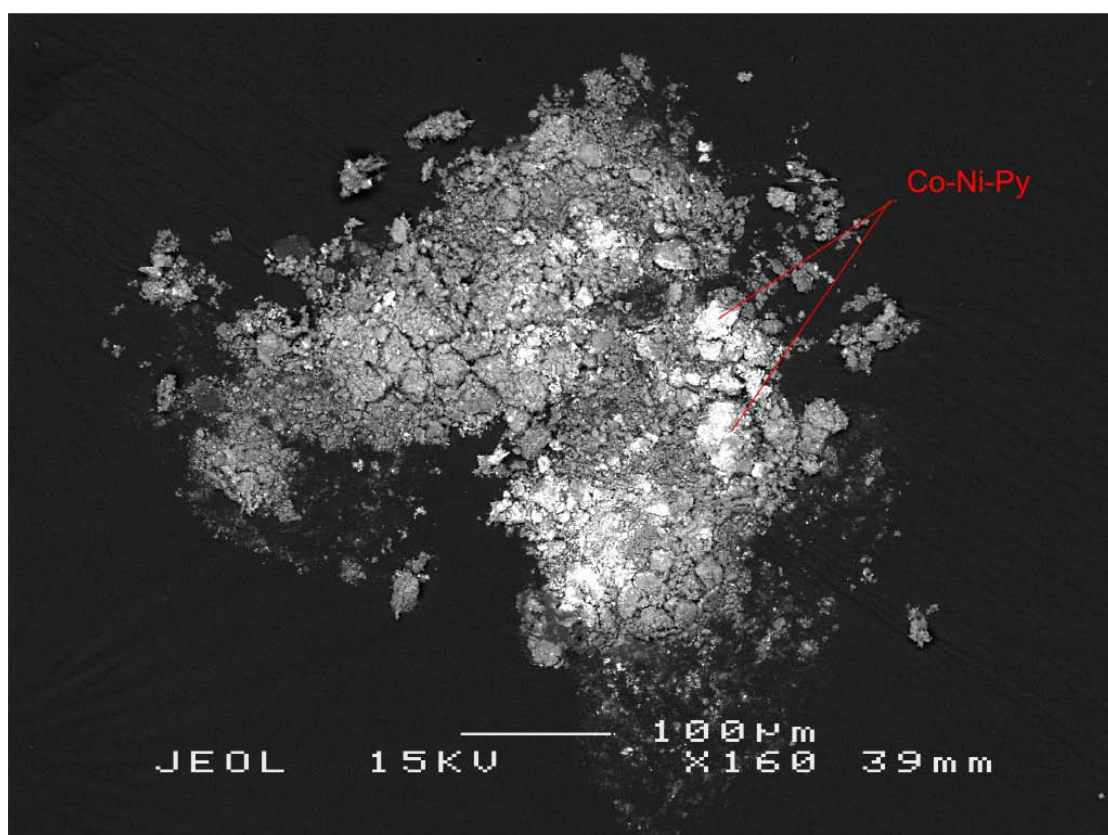


Fig.5. Black spot in hand specimen identified as an aggregate of cobaltiferous pyrite (22% Co, 14% Fe, 11% Ni), which appears bright under backscattered imagery.

## Discussion:

The Cenozoic gypsiferous claystone described here is very similar to equivalent rocks from Cenozoic basins across central and southern Australia which are generally comprised of interbedded micaceous/pyritic/carbonaceous clays, sands and silts. For example, the Eocene formations of the Otway Basin in Victoria and South Australia comprise micaceous silt and fine sand passing up into interbedded dark grey clay and mudstone. The clays carry copiapite, gypsum, pyrite and are fossiliferous. The copiapite is derived from oxidation of pyrite and implies acidic conditions (pH ~1-2), however, the oxidation in the present case seems confined to the external core surface, and may therefore have occurred on exposure of the claystone to the atmosphere post-core recovery (Fig.6). The original claystone environment must have been quite reducing in order to immobilise uranium in the various mineral species described above.

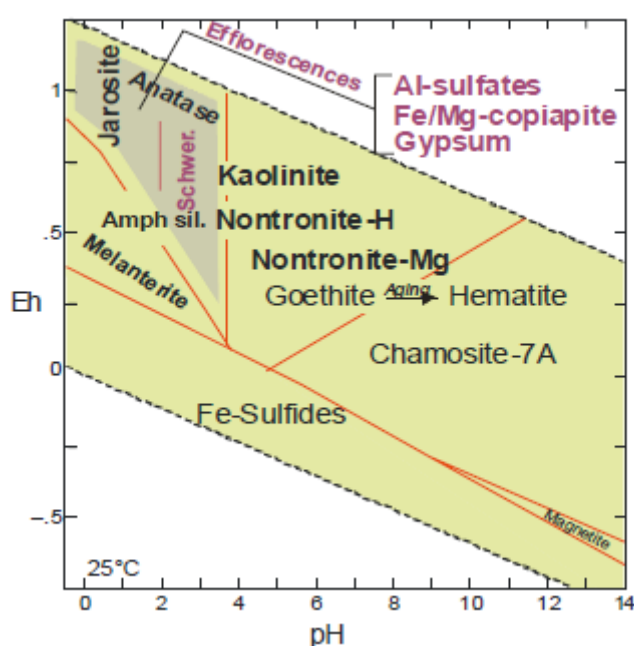


Fig. 6. pH-Eh mineral stability diagram of the Fe-S-Si system showing stability of Fe sulphate minerals and pyrite.

A variety of uranium-bearing minerals are present in the claystone including altered uraninite, altered urano-zircon, an aluminium phosphate-sulphate mineral (APS) similar to woodhouseite:  $(\text{Ca,Ce})\text{Al}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$ , and unidentified aluminosilicate minerals which contain U and REEs (yttrium, neodymium and dysprosium in particular); the REEs are probably breakdown products of original monazite and xenotime. These minerals occur in association with organic matter and pyrite; much of the pyrite is cobaltiferous and nickeliferous (bravoite); the Co and Ni perhaps being originally scavenged by bacterial activity. No vanadium minerals were encountered. The extent to which U was introduced into the rock versus that which was intrinsic to the claystone is difficult to judge. However it should be noted that the claystone is unlikely to be very permeable to fluids.

Recommended elements for geochemical assay are: Fe, K, P, S, U, Co, Ni, Y, La, Ce, Nd, Dy, Zr, Th, V