Two-fluids (oxic and reduced) model for the formation of uraninite in early proterozoic quartz-pebble conglomerates of the Elliot Lake District, Ontario, Canada

S. Ono
R. Mock
H. Ohmoto

Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, USA

Two contrasting models for the origin of uraninite

Uraninite in quartz-pebble conglomerate beds of ~2.8 to ~ 2.2 Ga has been considered to be detrital in origin by many previous researchers because of the presence of rounded grains of uraninite and pyrite. The survival of these minerals during fluvial transport and deposition has been used as an important line of evidence for an anoxic atmosphere prior to 2.2 Ga, because both minerals are unstable under an oxygen-rich environment. An alternative model, diagenetic/hydrothermal model, has been suggested for uraninite and pyrite in the quarts-pebble conglomerate beds in the Witwatersrand district, South Africa (e.g. Barnicoat et al., 1997).

If uraninite and pyrite are not of detrital in origin, the occurrence of this type of deposits may not be used as evidence for an anoxic atmosphere. On the other hand, if these minerals were formed by diagenetic or hydrothermal processes, a series of redox reactions must have occurred to form uranium-bearing minerals, such as the reactions between U^{6+}-bearing, oxic groundwater and reductants (e.g. organics and sulphides) to precipitate UO_2 (uraninite). Such formational processes would have been favoured under an oxic atmosphere. The objective of this research is, therefore, to better understand the origin(s) of uraninite in quartz conglomerate beds of >2.2 Ga, and to constraint the atmospheric pO_2 level. This objective has been pursued mostly from a detailed study, using ore microscopy and electron microprobe analyser, of the textures and paragenesis of U-Th-bearing minerals in ores from the Stanleigh mine, Elliot Lake district, Ontario, Canada. The ores are hosted in quartz-pebble conglomerate beds of the Matinenda Formation which is ~2.4 Ga in age.

Paragenesis and textures of U-Th-bearing minerals

Based on the observation of small-scale textures in a variety of minerals occurring in about 10 doubly-polished thin sections of ore-bearing quartz conglomerates from the Stanleigh mine, Mock and Ohmoto (1997) suggested that most of the U and Th in the deposits were introduced in the quartz-pebble beds as detrital grains of uranothorite (($U,Th)SiO_4$), rather than as uraninite, and that diagenetic alteration of uranothorite and ilmenite resulted in the formation of uraninite (UO_2) and brannerite (UTi_2O_6). These suggestions are substantiated by a further study on more than 1000 grains of U-Th-bearing minerals in about 60 polished thin sections.

Uranothorite grains occur as ~50 to ~100 μm, subhedral to rounded grains. The occurrence of rounded grains suggests some of the uranothorite grains were detrital in origin. Most uranothorite grains suffered replacement by uraninite from the rims. The intensity of replacement varies greatly. Most of uraninite grains contain small amounts of remnants of uranothorite in their interior. These uraninite/ uranothorite grains show mymekitic texture, one of the typical texture for replacement products. A whole spectrum of intensity of replacement, from unaltered uranothorite to almost pure uraninite with small amounts of uranothorite, was observed. Uraninite predominant grains are abundant. These mineralogical features suggest that most of the uraninite grains are replacement products of uranothorite.

In one of the 60 thin sections, some uraninite grains (~50 to ~100 μm) contain blebs (inclusions) of uranothorite; there is no replacement texture between the uranothorite and the uraninite. Similar inclusions of uranothorite occur in some detrital grains of monazite (($Ce, La)PO_4$; ~50 to ~200 μm). The uraninite and monazite grains that contain

uranothorite blebs are typically 'muffin' shaped. These features suggest that these uraninite and monazite grains are probably detrital in origin, retaining some of the mineral textures in the parental rocks, probably U-Th-*REE* rich pegmatites.

Uraninite/uranothorite grains are often associated with brannerite. Brannerite occurs as needle-like crystals (~10–50 μm) or aggregates of fine subhedral crystals. Brannerite is often associated with rutile and forming pseudomorphs of detrital crystals, probably ilmenite. Brannerite and rutile often make microscale (~mm to cm) veinlets in clay minerals or cutting quartz and pyrites. These features suggest that most (if not all) brannerite and rutile are diagenetic (or hydrothermal) origin. Brannerite are as abundant as uraninite as a whole, suggesting that a significant amount of uranium was remobilized after deposition of uranothorite.

In some thin sections, uraninite/uranothorite grains are surrounded and/or veined by hydrocarbon. The veins of hydrocarbon cut uraninite and uranothorite grain indicates that these hydrocarbon was once in a liquid form as it invaded pre-existing fractures, and injection of hydrocarbon was later than the replacement of uranothorite by uraninite. This supports the pyrobitumen origin for hydrocarbon closely associated with uraninite (Barnicoat *et al.,* 1997), and also suggests that the replacement of uranothorite by uraninite occurred mostly during the early diagenesis of the host rocks. Selective dissolution of Th from uranothorite is observed along hydrocarbon veins in some uranothorite grains.

Two-fluids mixing model for the formation of uraninite and brannerite

The paragenetic and textural features of the U-Th-bearing minerals in the Stanleigh mine suggest a model of mixing of two fluids to form most uraninite and brannerite in this deposit: one fluid was oxic, shallow groundwater that traveled downward through the conglomerate bed, and the other was reduced and petroleum- and H_2S-bearing fluid that was generated in a deep sedimentary basin (probably >100 km away) and migrated upward through the conglomerate bed. The Matinenda Formation, which hosts the uranium ores, is fluvial deposits, but it was probably graded into a marine facies ~100 km downstream. The source rocks for the petroleum-bearing fluid could have been this marine facies, or one of the argillite-bearing formations overlying the Matinenda Formation.
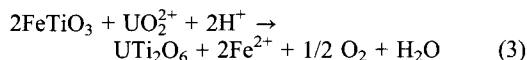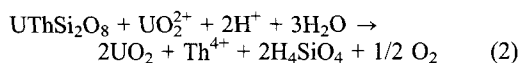
The ore deposit site was probably the site where the influence of the above two fluids was most intense, but fluctuated with time. When the ore deposit site was invaded by the petroleum-bearing fluid, Th and Si could have been preferentially leached from uranothorite, forming porous uraninite-rich rims through reactions such as:

$$UThSi_2O_8 + 4H^+ + 2H_2O \rightarrow \\ Th^{4+} + 2H_4SiO_4 + UO_2 \quad (1)$$
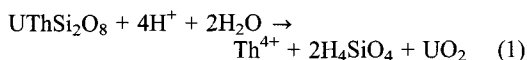
The solubilities of Th-bearing minerals (e.g. thorianite and thorite) are extremely low in organic-free, low temperature fluids, but significantly increase in the presence of abundant organic ligands (Langmuir, 1997). The solubility of silica may also be increased in petroleum-bearing fluids.

The oxic, shallow ground water were probably enriched in U^{6+} because of preferential dissolution of U^{4+} from the detrital grains of uraninite and uranothorite. Therefore, when the oxic fluid invaded the ore deposit site and reacted with reductants (e.g. the remnants of petroleum and H_2S; detrital pyrite), the U^{6+} in the fluid would have precipitated uraninite and/or brannerite through reactions such as:

$$UThSi_2O_8 + UO_2^{2+} + 2H^+ + 3H_2O \rightarrow \\ 2UO_2 + Th^{4+} + 2H_4SiO_4 + 1/2\,O_2 \quad (2)$$

$$2FeTiO_3 + UO_2^{2+} + 2H^+ \rightarrow \\ UTi_2O_6 + 2Fe^{2+} + 1/2\,O_2 + H_2O \quad (3)$$

Precipitation of uraninite may have occurred in the porous, uraninite-rich rims of uranothorite to convert them to solid uraninite, or near pyrite grains and petroleum blebs.

The influence of oxic groundwater in the ore deposit site appear to have ceased before the compaction of the host sediments, but the influence of reduced fluids appear to have continued long after the compaction. This is suggested by: the occurrences of veinlets of organic carbon through fractured grains of uraninite; the occurrence of inclusions of galena in most of uranothorite and uraninite grains, indicating sulphidization continued after some Pb was generated by the radioactive decay of U and Th, i.e. at least a few hundred million years after the deposition of the detrital minerals.

The above model for the formation of uraninite is essentially identical to that proposed by Gauthier-Lafaye (1989) for uranium deposits at Oklo, Gabon, which has been considered by many (e.g. Holland, 1994) as the oldest (2.0 Ga) uraninite deposits formed by oxic ground water. Our genetic model for the pre-2.2 Ga uraninite deposits is compatible with the atmospheric evolution model of Dimroth and Ohmoto (Ohmoto, 1997) which postulates an oxic atmosphere since ~4.0 Ga.