Surface weathering conditions of minerals of natural fission reactors

L. Pourcelot
F. Gauthier-Lafaye

Centre de Géochimie de la Surface, Unité Mixte de Recherche n°
7517 CNRS and Université L. Pasteur 1, rue Blessig F67084
Strasbourg Cedex, France

The sixteen natural reactors of Gabon, in the U deposits of Oklo-Okelobondo and Bangombé can be considered as 2 Ga natural waste repositories of fission products and actinides. Indeed uraninites of the reactors (UO_{2+x}) act as good traps for actinides and fissiogenic *REE*. However, because of high solubilities of uraninites in oxidizing fluids, these minerals are geochemically unstable in most surficial environments and are particularly susceptible to weathering by meteoric fluids. This explains why in the shallow Bangombé reactor, located 10 m below the surface, loss of U and fissiogenic *REE* has been observed. On the other hand those elements tend to remain in uraninite and surrounding clays of the deeper reactor 10 (400 m depth). Thus these natural reactors provide a good opportunity to study surface weathering conditions of uraninites, since they are located at different depths between 10 and 550 m (Fig. 1). The aim of the present study is to trace surface weathering of the uraninites by two means (1) structural and chemical characterization of the rocks (X-ray diffraction and electron microprobe analyses of uraninites) and (2) Oxygen isotopic tracing of subsequent interactions of uraninites with surface fluids (Pourcelot and Gauthier-Lafaye, 1998a). The same methods were also applied to trace the weathering of the clay matrix surrounding the reactors (Pourcelot and Gauthier-Lafaye, 1998b). Indeed, clays may act as a barrier preventing large *REE* scavenging during weathering of the reactors.

Results and discussion

X-ray patterns of the uraninites show that the uraninites from surface (10 m deep) and subsurface reactors (100–150 m deep) are poorly crystallized compared to deeper samples (250–550 m deep). Furthermore, calculated cell parameters of the uraninites of surface and subsurface reactors are smaller (5.43 to 5.44 Å) than the uraninites of the deeper reactors (cell parameters are close to 5.45 Å). We assume that such a decrease is due to oxidation of U since U^{6+} radius (0.086 nm) is smaller than U^{4+} (0.10 nm). Also chemical compositions of uraninites reveal contrasts between surface and underground uraninites. Uraninites from surface and subsurface reactors contain more impurities (Fe and Si) than samples from the deep mine. Such elements are known to be easily mobilized during chemical surface weathering processes under a wet equatorial climate and they must have been incorporated into the uraninite lattice.

Unlike the mineralogical data, the strong ^{18}O depletion of the uraninites ($\delta^{18}O$ range between −15.0 and −22.0‰ SMOW) is not correlated with depth. Furthermore uraninites are not in isotopic equilibrium with present day surface fluid ($\delta^{18}O$ range between −2 and −5‰ SMOW), but with strongly ^{18}O depleted fluid ($\delta^{18}O$ range between −3 and −13‰ SMOW). Thus although structural and chemical impacts of surface weathering fluids flows on uraninites can be recognized, no isotopic exchange between surface fluids and uraninites has been observed. We assumed that ^{18}O depleted fluids

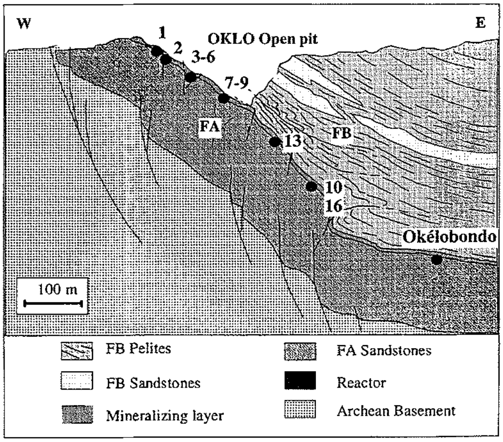

FIG. 1. Location of the reactors.

in equilibrium with the uraninites originate from isotopic fractionation effects of water radiolysis. Reactors can be considered as a nearly closed system, in which trapped water has been submitted to α radiations due to U decay for 2 Ga. Such oxidizing fluids produced by water radiolysis may be responsible for UO_2 corrosion and subsequent isotopic exchange.

Clays of deep reactor 10 (450 m deep) consist only of high temperature chlorite species (Mg chlorites and sudoites). Oxygen isotopic compositions of Mg chlorites and sudoites show that those species still record the high temperature of criticality (about 380°C) and the following cooling stage of the reactor. In addition to illite and some kaolinite, subsurface reactor 9 (150 m deep) contains also weathered vermiculitized chlorites. These types of chlorites are ^{18}O enriched ($\delta^{18}O = +18‰$ SMOW). These minerals have undergone oxygen isotopic exchange with present day ^{18}O depleted surface fluids ($\delta^{18}O$ range between -2 and $-5‰$ SMOW) during the weathering of the chlorites. ^{18}O enrichment of the clay fractions is also accompanied by contamination of fissiogenic *REE* (traced with anomalous $^{149}Sm/^{147}Sm$) that can reach 3 meters. Around the reactor, correlation of surface fluid flow (tracing with ^{18}O enrichment of the clays) with migration of fissiogenic Sm, illustrates the effect of acidic and oxydative surface fluids percolating through the reactors. Clays of the surface reactor of Bangombé (10 m depth) are mainly composed of illite as well as newly formed weathered kaolinite and metahalloysite. Thus mineralogical and isotopic data from the clays are also consistent with progressive surface weathering of the reactors as they rose to the oxidizing surface conditions.

Conclusion

Uraninite may be affected by weathering without exchanging its oxygen with meteoric water. This implies that no break of U-O bond nor any recrystallisation of uraninite has taken place. However, extensive dissolution of uraninite (without precipitation of newly crystallised uranium minerals) occurred in the most altered reactors, when oxidation conditions were strongly aggressive to uranium dioxide minerals. Such dissolution leads to significant removal of U from the core of the surface and near-surface reactors and to the transport of fission products in the reactors vicinity. Clay also underwent surface weathering. However, it was recognized that clays retained fissiogenic *REE*.

References

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