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# Zircon: an immobile index in soils?

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## 1. Introduction

Interpretation of any element's mobility in soils needs rigorous means of calculating losses or gains in relation to parent rock. The first mass-balance calculations were based on iso-element changes (major elements) during conversion of fresh rocks to weathered materials (Harrisson, 1933; Leneuf, 1959). Isovolumetric mass-balance calculations were applied for the first time in 1955 to determine mass transfers in saprolite (Millot and Bonifas, 1955). Since that time, numerous works have been carried out on mass-balance calculations in determining transfers during weathering (Brimhall and Dietrich, 1986).

Recently, equations used to calculate volumetric changes and net mass gain or loss of mobile elements have been based on zirconium, mostly from the mineral zircon. The aim of the paper is to question the axiomatic immobility of zircon in soils, and then to assess the limit of mass-balance calculations in surficial weathering systems.

## 2. Geography and geology of the Dondo Mobi soil system

We chose to conduct our study on a well-characterized soil system at Dondo Mobi, Gabon, which has developed under undisturbed equatorial rainforest conditions from homogeneous Archean Gneiss. These mature soils are the result of the long-term physical and chemical evolution of the upper part of the stable Congolese cratonic lithosphere. The studied soil system is located downslope of the Dondo Mobi Hill (Fig. 1) and consists from the fresh rock to the surface of a deep kaolinitic saprolite, a gibbsitic saprolite, a transitional nodular-saprolite layer, a nodular layer and a surficial sandy–clayey layer. A thin organic layer overlies the whole system. The active root zone extends to the nodular layer. Weathering profiles developed upslope from gold-rich rocks, and from detrital Proterozoic rocks very rich in zirconium (200–600 ppm).

## 3. Results

### 3.1. *The physical mobility of zircons*

Total zirconium concentrations for fresh Archean Gneiss and weathered layers range from 100 to 500 ppm. Zr mapping performed on polished thin sections by routine microprobe analyses as well as punctual microprobe analyses of each primary and secondary phases (with a 50 ppm detection level) demonstrate that Zr is linked to zircon in the whole weathering system (Fig. 2).

Digitalized microscope, image processing and SEM have been carried out on zircons extracted from each layers, by heavy-mineral separations, in order to study statistically their distribution, size and morphology. Two mor-

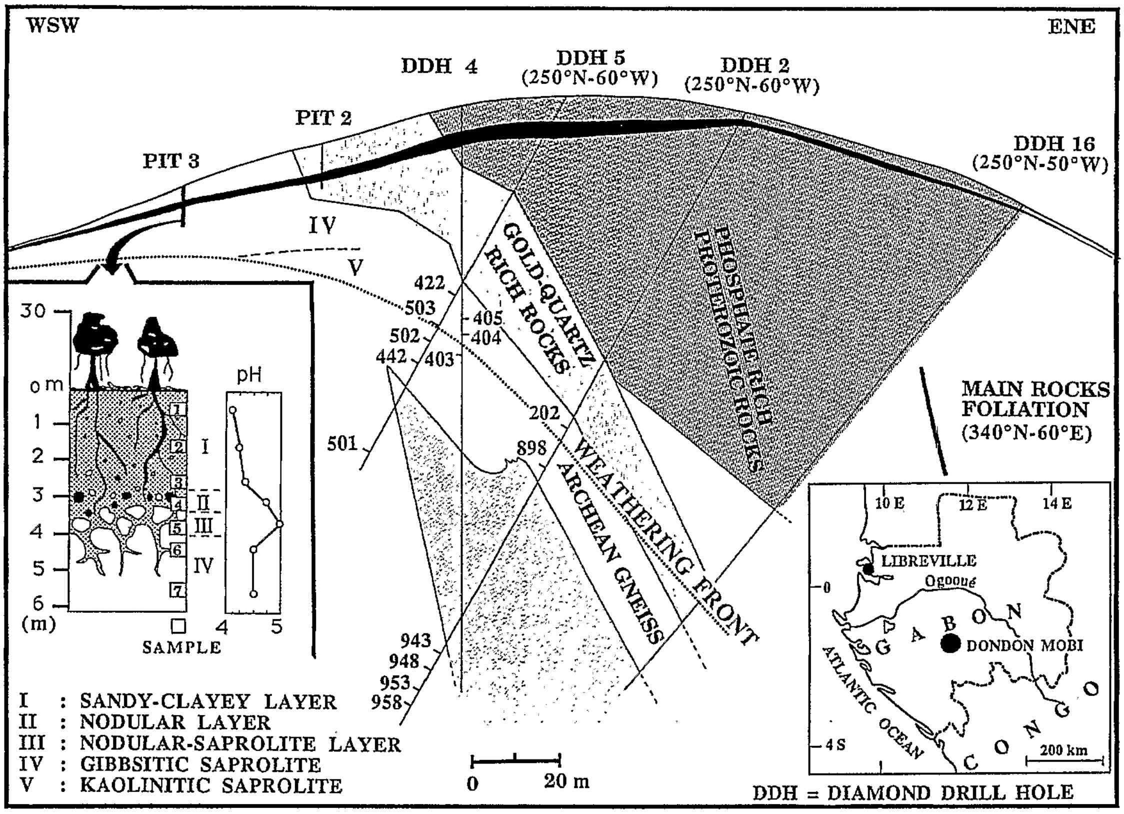


Fig. 1. Dondo Mobi weathering profile: sandy–clayey layer (samples 1–3), nodular layer (sample 4), nodular-saprolite layer (sample 5), gibbsitic saprolite (samples 6 and 7), and kaolinitic saprolite (samples 422, 503, 405, 404 and 202).

photypes of zircons have been identified (Fig. 3): euhedral cloudy zircons, and subrounded cloudy grains. The euhedral zircons are ubiquitous from the unweathered Archean Gneiss upward to the sandy–clayey layers, while the rounded ones are found only in the upper part of the profile, increasing progressively in weight % from the nodular-saprolite layer to the surface (Fig. 4). These rounded zircons are responsible for the corresponding increase in the total zirconium contents.

Petrological and chemical data of the gneiss-derived weathering system demonstrate that the whole profile has been formed in situ. For example, very close to the surface, gibbsitic pseudomorphs after feldspar can be recognized within the microaggregate kaolinitic-rich matrix. In the whole Dondo Mobi Hill, feldspar is present only in fresh Archean Gneiss and in its derived kaolinitic saprolite. Euhedral zircons are interpreted as residual from in situ weathering of the Archean formations.

The fact that the two populations of zircons coexist in the upper part of the weathering profile, reinforced by the absence of significant trace of dissolution at the surface of the euhedral zircons (Fig. 3), points out that the rounded zircons are not derived from in situ weathering of the euhedral ones.

As shown in Fig. 4, the upward progressive increasing amount of rounded zircons indicates that the sources of such zircons are external to the gneiss-derived profile.

Looking for the different possibilities of external sources, rounded zircons found in the upslope formations have been studied. Shape, size and morphology of these zircons were totally similar to those found in the upper part of the gneiss soil system. Thus we conclude that rounded zircons have been mechanically im-

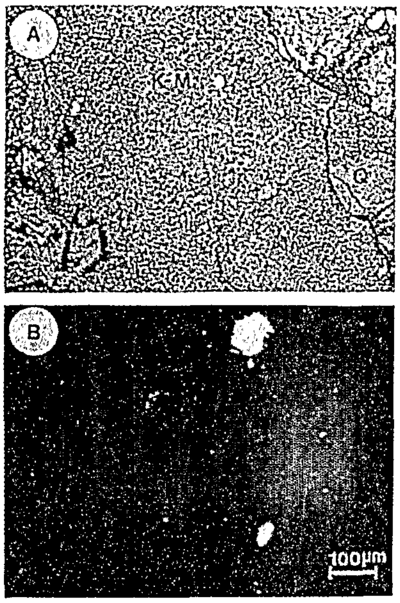


Fig. 2. 8-hr Zr mapping performed on sandy–clayey layer polished thin section: Zr is related to zircons ($Q$=quartz; $KM$=kaolinitic matrix).

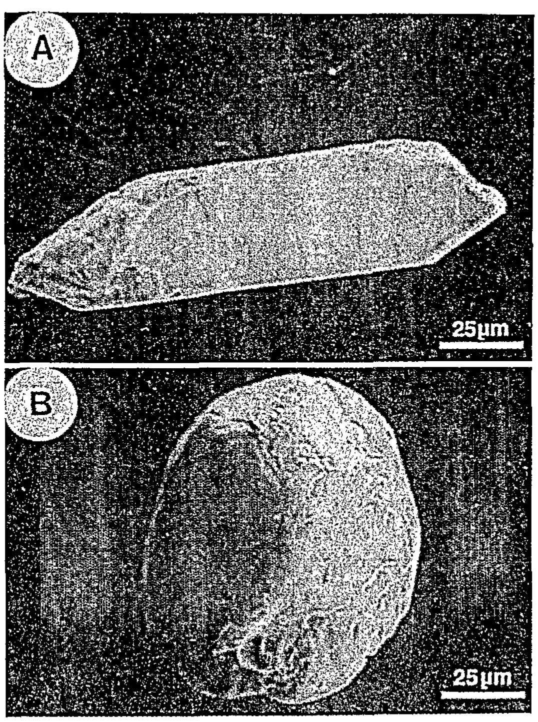


Fig. 3. Euhedral (A) and rounded zircon (B) under SEM.

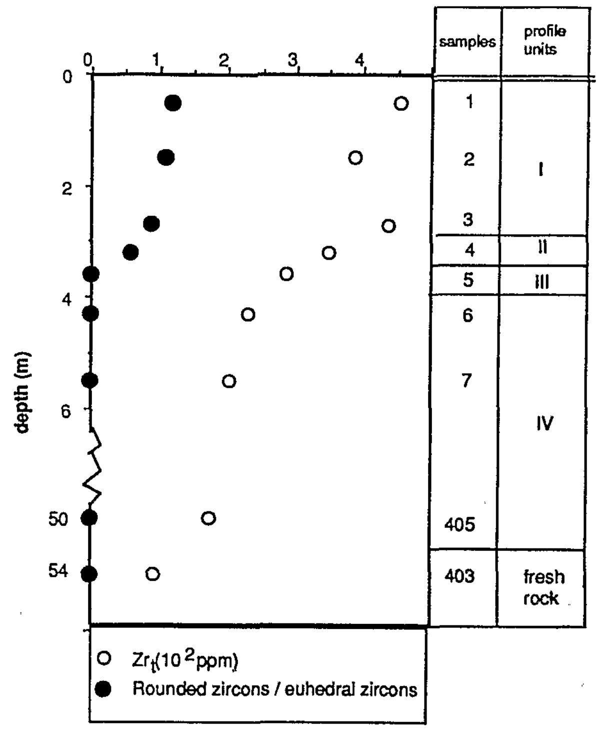


Fig. 4. Variation in total Zr contents and in rounded zircon/euhedral zircon ratio (*r.z./e.z.*) with depth (sample numbers are related to Fig. 1).

ported downslope and then translocated downward into the root zone.

### *3.2. The chemical mobility of zircons at Dondo Mobi*

The euhedral zircon surfaces do not exhibit significant dissolution features under SEM. Nevertheless, the solubility of zircon has been thermodynamically calculated in the natural conditions of Dondo Mobi (Fig. 5). We used here, as potential ligand, chloride of marine origin, measured in source water around the hill and ranging from $10^{-5}$ to $10^{-3.8}$ mol l$^{-1}$. The total concentration of Zr in the solution is extrapolated from seawater content. In the Dondo Mobi soil system, zircon should not dissolve. However, an increase in the chloride concentration of 1 order of magnitude will induce the dissolution of zircons near the ob-

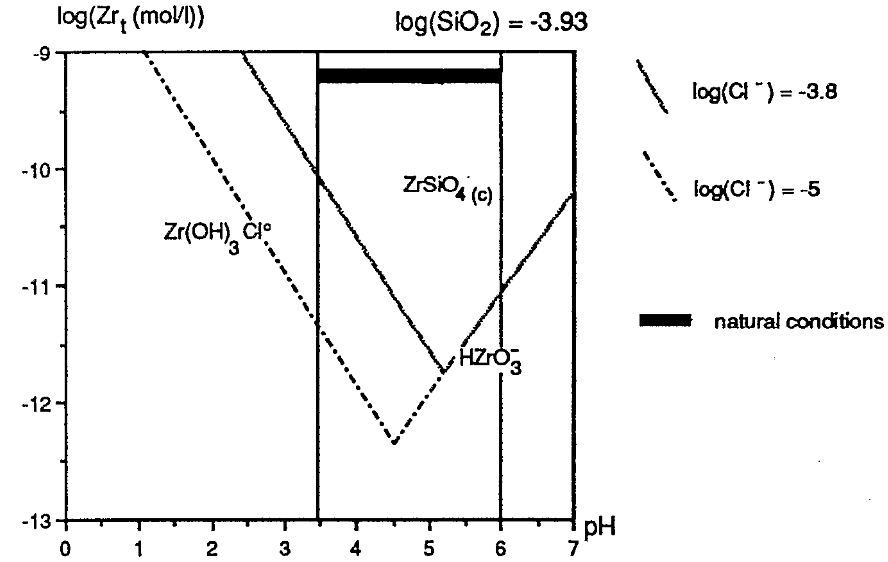


Fig. 5. Solubility of zircon vs. pH at Dondo Mobi.

served pH, or pH below 3 may induce a zircon dissolution in the range of natural chloride concentrations.

Organic matter may also play a role in the potential dissolution of zircon as reported by Berrow et al. (1978) and Tejan Kella (1991), but no dissociation constant is reported in the literature for zirconium with organic acid.

## 4. Conclusions

Zircons are physically mobile in the root zone at Dondo Mobi. We may expect such mobility in most surficial soils of the world.

Zircon dissolves under acid pH with significant chloride concentrations, conditions we may expect for example in most of the surficial lateritic soils developed along the sea coast. Zircon may also be unstable in very acid media such as podzols.

In addition, metamict zircons with hydrous species and disordered crystalline structure with isolated silica tetrahedra (Woodhead et al., 1991) may be sensitive to weathering.

We conclude that, to be able to use zirconium from zircon as an immobile index in soil systems, and especially in the surficial root zone, it is necessary to investigate such axiomatic immobility and potentially to take into account the mobility of zirconium in correcting mass-balance calculations.

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