INTRODUCTION

Hematite, goethite and gibbsite are with kaolinite the main mineral components of laterite. A better understanding of lateritisation processes implies a reconstitution of secondary mineral nucleation and growth conditions and the determination of their stability fields.

Various morphologies, texture and spatial arrangements of hematitic, goethitic and gibbistic materials have been described in numerous fields and petrographic studies of metric weathering profiles. Thermodynamic and kinetic modelling, together with laboratory experiments, have attempted to afford global valuable interpretations of the facts. However, at the same time, independent mineralogical data obtained by different physical methods emphasized the variability of the structural and crystal-chemical characters of hematite, goethite and, to a lesser extent, gibbsite. These characters reflect the initial weathering conditions, but depend also on the subsequent and continuing processes of dissolution and crystallization which have affected the materials.

Deciphering the part of each phenomenon implies combined studies at different scales. Particularly, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (CTEM and HRTEM) and selected area diffraction, coupled with in-situ chemical analysis (EDS), allows morphological and crystal chemical characterizations of particles and aggregates at the micrometer scale. The objective of this present study is to report results on investigations carried out at this scale on a petrographically well defined laterite from Cameroon, in order to get more informations about goethite, hematite and gibbsite geneses and the interrelationships between these oxy-hydroxides and kaolinite.

MATERIALS

The studied samples come from vertical lateritic profiles which present an ordered development of three main zones from the bottom to the top: (1) a lower weathering zone or yellow and loose saprolite, (2) an intermediate nodular zone in which ferruginous and indurated nodules are embedded in soft and mainly red clayey materials, and (3) an upper loose topsoil zone, composed of soft clayey and mainly yellow materials. This type of weathering profile is representative of most tropical countries under forest cover and permanently humid and percolating environment.

GOETHITE AND HEMATITE

Goethite presents a global variability according to the sampling place in lateritic profiles and local evolution in a very place, in terms of morphology, particle size, crystal association and mineral interrelationships. However, these characters lead to the distinction of three main types of goethitic materials corresponding to the three zones which characterize the weathering profiles: (1) in the yellow saprolite, goethite forms multidomainic almond or netting-needle like crystals frequently associated with complex tridimensional star-shaped aggregates; (2) in the red nodular zone, goethite forms large multidomains platelets together with anhedral dumpy crystals often associated with hematite and laths or acicular crystals filling voids and cracks; (3) in the yellow topsoil zone, goethite appears as rodshaped...
particles or minute rounded crystallites. No distinctive signs of destabilization of these various types of goethite crystals have been evidenced.

This diversity of goethite morphologies according to sampling place reveals unambiguously differences in the environmental growth conditions. The observed morphologies and the existence of intermediate forms suggest goethite development proceeds with a dissolution and reprecipitation growth mechanism or "reconstructive transformation". Goethite epitaxial growth upon kaolinite, evidenced within the nodular zone, represent another mode of development, with "heterogeneous nucleation".

Whatever the sampling place, hematitic materials do not display such major or significant differences: hematite crystals always present a typical hexagonal outline. In contrast to kaolinite which remains preserved in the same zones, hematite crystals undergo a later weathering and constitute a secondary source of iron. Moreover, and in contrast to goethite, hematite crystals do not exhibit direct interrelationships with kaolinite.

Morphological characters of hematite crystals support the assumption of formation of hematite after nucleation from amorphous Fe(III) hydroxides in a aqueous system. Moreover, these morphological characters being observed whatever the size of the particle and the location of the sample, this formation process can be considered as unique.

Close associations of hematite and goethite, either in a same and one particle (intermediate phase) or as intergrowths, have been found. In these cases, goethite, which is associated with hematite or hematite-like particles presenting dissolution marks, seems often to postdate hematite and tends to develop in more open microsites: hematite particles are precursors for goethite growth, in a hematite-goethite transformation involving a dissolution-crystallization mechanism.

GIBBSITE
Gibbsite appears mainly in the soft red clayey materials of the nodular zone. It is particularly concentrated in the porous core of gibbsitic micronodules rimmed by an hematitic and dense cortex.

Two types of nucleation of gibbsite crystals are distinguished: (i) a heterogeneous nucleation, characterized by a topotaxial relationship between gibbsite crystals and kaolinite, and (ii) a homogeneous nucleation within the microvoids.

An orderly modification of the crystal habit of gibbsite from the core to the cortex of gibbsitic micronodules is related to variations of crystal growth conditions at a microscale:

(i) in the core, the gibbsite crystals are of relatively equal grain size, and have a massive and prismatic habit with smooth crystal faces. Some of the crystals present overgrowths centered on basal faces. These features correspond to steady state conditions of growth at low supersaturation, in a quiet medium and relatively pure solutions.

(ii) near the cortex, gibbsite crystals have a variable grain size. Overgrowths are frequently observed as macrosteps at the edges of the basal faces and hollow prismatic crystals with closed or open surrounding surface. Moreover, some crystals present granular inclusions containing Fe and Si. These features are interpreted as the result of a rapid rate of crystallization, at high supersaturation or under transient conditions, of fluctuations in the transport conditions with a directional flow of the solutions, and of impurity effects in crystal growth. The different habits observed correspond to equilibrium forms or are characteristic of growing crystals.

PETROLOGICAL IMPLICATIONS

At the scale of the weathering profiles, the above data would imply:

(i) The existence of three successive generations of iron oxy-hydroxides: (i) a first generation of goethitic material, resulting from in-situ direct weathering of iron-bearing rock-forming minerals, present in each of the three zones; (ii) iron transfers via solutions inducing in the intermediate nodular zone nucleation and growth, as achieved experimentally, of hematite, hematite-goethite and goethite particles; and (iii) again within the intermediate nodular zone, next generations of goethite, resulting from dissolution-crystallization processes affecting hematite and intermediate particles.

(ii) An in-situ differentiation of gibbsitic micronodules within the soft red and clayey materials of the intermediate nodular zone: Gibbsite crystallization is due to incongruent dissolution of kaolinite and is related to local centrifugal transfers of iron and silicon and aluminum transfers take place only at micro-size scales. Moreover, the observed crystal habits attest that gibbsite is a stable mineral. It can be then inferred that kaolinite from the topsoil zone cannot result, even partially, from a "silicification" or "kaolinization" of the gibbsite from the intermediate nodular zone.