

PARAMAGNETIC CENTERS IN KAOLINITE AND THE HISTORY OF WEATHERING CRUSTS

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One of the most crucial problems raised by the weathering crusts concerns the relationships between weathering materials and their genetical significance. On account of the monotonous mineralogy developed in most laterites, it is necessary to use the structural and physico-chemical properties which may characterize the major components in order to decipher the various stages of formation of these crusts. It is of special importance to correlate these observations with the geochemical environment, which would allow a better understanding of the weathering crusts differentiation. Paramagnetic centers in kaolinite, a widespread soil component, may be used as geochemical tracers. We present the results obtained in kaolinite sampled in orderly arranged vertical sequences of a laterite from Cameroon.

Seven common types of lateritic vertical sequences from Cameroon (1) have been investigated (about 150 samples). They consist of a succession of three main layers with contrasted facies (2) : (i) a lower saprolite, which preserves the preexisting gneiss texture and structure; (ii) an intermediate nodular zone composed of two types of indurated ferruginous nodules, large irregular nodules with gneiss-inherited texture and small subrounded nodules with soil texture, which are embedded in soft clay-ferruginous materials; (iii) an upper topsoil zone mainly composed of soft clayey materials. Kaolinite and iron oxihydroxides are the main weathering phases all along these weathering sequences (3). The major changes for kaolinite occur at the transitions between materials with gneiss inherited texture (saprolite and large nodules) and those with soil fabric (small nodules and soft clayey

materials). From (i) to (iii), these transitions correspond to changes in kaolinite crystal packing (oriented to randomly arranged), a decreasing crystal size (from large booklets to very fine platelets), and a decreasing structural order (4). Various paramagnetic centers have been systematically looked for with Electron Paramagnetic Resonance (EPR), including substitutional trivalent iron, divalent manganese and hole-trapping defects (5), with a special attention devoted to their spatial distribution and concentration inside one profile. Two frequencies have been used to separate the various centers, X and Q band.

Substitutional trivalent iron gives rise to a complex EPR signal at low field values (5, and references therein). It consists of an isotropic line I and a triplet II, attributed to Fe^{3+} ions in rhombically distorted and more symmetric sites, respectively. The relative concentration of I and II centers, S(I) and S(II) respectively, show some regularities as a function of depth : (i) S(I) values keep a constant value in materials with gneiss-inherited texture but increase from these materials to the materials with soil texture and from the bottom to the top of the sequence (excepted the organic accumulation zone); (ii) on the contrary, S(II) values for materials with gneiss-inherited texture decrease significantly from the basis of the sequence to the nodular zone and then remain quite unchanged up to the top of the sequence; (iii) S(I) and S(II) are both the lowest for large nodules with gneiss-inherited texture. These general trends are confirmed in each of the seven sequences examined in detail. Thus, kaolinite from the different materials can be clearly distinguished both by the content and the distribution of

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substitutional-Fe³⁺.

Divalent manganese gives rise to a characteristic EPR signal with a hyperfine sextet Q-band spectra indicate the presence of two EPR-distinguishable Mn(II) species whose superimposed signals are characterized by different hyperfine splitting constant (A), line-width of the first and the sixth hyperfine splitting components (ΔH_1 and ΔH_6) and variation in the component linewidth, $\Delta = \Delta H_1 - \Delta H_6$, related to site distortion. Species one (A=90+1G; $\Delta H_1 = 40G$; $\Delta H_6 = 55G$) is clearly identified as Mn(II) ions substituted in distorted site in the octahedral sheet of residual muscovite. Species two is associated with weathering minerals. It remains after kaolinite extraction including several washings and different treatments (heating, oxidation, Na⁺-saturation) of this kaolinite. Moreover, it is stable up to 400°C. The corresponding A value (95G) is those of a hydrated Mn(II) in the form $[Mn(H_2O)_6]^{2+}$. The Δ values ($\Delta H_1 = \Delta H_6 = 30$; $\Delta = 0$), correspond to a site with a nearly cubic symmetry. The requirement concerning the site symmetry is not fulfilled by normal substitutional sites within kaolinite lattice. However, hydrated Mn(II) is by some means or other trapped and then protected from the environmental changes, for two main reasons: (i) hydrated Mn(II) ions exchanged in inter-layers sites or on crystal faces demonstrate solution-like mobility at relative humidities between 75 and 100% and (ii) these ions would be in a distorted axial electric field in dried samples. As the measured spectral parameters for species two are the same than those measured for Mn(II) in water-filled sodalite cage of zeolites, stable up to 400°C, it is inferred that these traps are closed folders between adjacent layers which have been visualized earlier by lattice imaging in electron microscopy and whose diameter (8 to 9 Å) are in the same range than sodalite cage.

The variation of Mn(II) concentration as a function of both depth and nature of materials has been appreciated by measuring the fifth line intensity: Mn(II) is to a great extent concentrated in ferruginous nodules and to some one in their surrounding soft-clayey materials and in saprolite. Besides, 2M1-muscovite progressively disappears from the bottom to the top of the weathering sequences and is almost absent in the ferruginous nodules (1). Comparison between relative content of kaolinite and muscovite and relative EPR contribution of the two Mn(II) species show that species one is responsible for Mn(II) signature of

saprolitic samples, where residual muscovite is abundant, while species two is dominant in ferruginous nodules, whatever their textural characteristics. Then, trapped hydrated Mn(II) species attest that particular geochemical conditions have prevailed during the formation of kaolinite from the ferruginous nodules: it is suggested that these conditions, probably controlled by past water-table fluctuations, were less oxidizing than the present-day ones.

At least three distinct hole-trapping defects give rise to a complex EPR spectra centered near $g=2$. Only one (A-center) (6) is stable up to 400°C and is observed in all natural kaolinites. Its stability may extend over geological periods near ambient temperature. It is a positive hole associated to Si. A-centers concentration [hereafter referred as S(A), (6)] has been evaluated in all deferrated samples. Two sets of materials appear clearly separated according to S(A) when plotting S(A) values obtained for the different materials as a function of depth: (i) the soft materials (saprolite, soft clayey materials) which exhibit both low iron content and low values of S(A), and (ii) the indurated ferruginous nodules characterized by high iron content and high S(A). Besides, while the variations of the concentration of A-centers in the kaolinite more or less follow those of iron and U-Th content of the raw sample, these variations appear unrelated to textural differences (6).

These results can be also discussed as a function of the geochemical conditions prevailing during kaolinite formation. As a matter of fact, A-centers arise from an external irradiation of kaolinite (7). In the weathering sequence studied, a possible radiation source has to be sought in radioactive elements disseminated through the weathered materials and mainly accumulated in ferruginous materials. However, the present day U-Th content is too low to explain the measured S(A) values. By taking into account the efficient chemisorption of radioactive elements on poorly crystallized iron oxides, A-defects are attributed to an irradiation of the kaolinites during the first stages of rock weathering and their subsequent crystallization. The subsequent evolution of iron oxides towards a more crystalline structure leads to a release of the radioactive elements, and the A-centers are thus the memory of their past transit.

Paramagnetic centers are then efficient fingerprints of the successive generations of kaolinites during weathering and they give some indications on the

conditions prevailing during the formation of kaolinite crystals. The data obtained give new constraints in discussing laterite history : the present occurrence of various generations of kaolinites all along the studied lateritic sequences might reflect changing conditions of weathering which are "memorized" by kaolinite crystallites under the stable paramagnetic centers kept in the kaolinite lattice.

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