

ROLE OF FERRIC IRON IN THE OXIDATION OF HYDROCORTISONE BY SEPIOLITE AND PALYGORSKITE

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Abstract—The role of adsorbed and structural Fe³⁺ in palygorskite and sepiolite with respect to the oxidation of hydrocortisone in aqueous suspension has been evaluated using electron spin resonance and UV-visible spectroscopy. Natural surface-adsorbed Fe³⁺ showed an important activity in the oxidation process, although smaller than octahedral Fe³⁺. The kinetics of oxidative degradation of hydrocortisone by palygorskite appear to be composed of two apparent first order reactions which may be associated with two kinds of sites for Fe in palygorskite. The lower oxidizing power of sepiolite for hydrocortisone degradation is due to its very low Fe³⁺ content.

Key Words—Catalysis, Electron spin resonance, Hydrocortisone, Iron, Oxidation, Palygorskite, Sepiolite.

INTRODUCTION

The ability of clay minerals to catalyze certain reactions of organic molecules is well known; however, the mechanisms of the catalytic processes have been the subject of considerable speculation. The color reaction of benzidine with some silicate minerals is perhaps the most widely used example of this kind of reaction (Theng, 1974). The presence of structural Fe³⁺ in clays is considered at least partly responsible for the oxidation reactions, but Al³⁺ at edge sites (Solomon *et al.*, 1968), as well as surface-adsorbed hydrated metal ions, such as Fe³⁺ and Cu²⁺, have been suggested as active sites in the oxidation of organics on clays containing little or no structural iron (McBride, 1979). Examination of these surface reactions by electron spin resonance (ESR) and UV-visible (UV-VIS) spectroscopic techniques can provide a better understanding of the mechanisms of clay-organic interactions (McBride, 1979). The role of certain impurities in clays in these processes can also be elucidated by using Mössbauer and ESR spectroscopy (Goodman, 1978).

The fibrous clay minerals, sepiolite and palygorskite (attapulgitite), have numerous industrial and pharmaceutical applications, due mainly to their high surface area and intracrystalline channels. It has been shown that Fe³⁺ is the principal source of oxidizing action of the surface of palygorskite (Miller *et al.*, 1964). This fact has been checked in a study of the oxidation of hydrocortisone in the presence of that clay (Cornejo *et al.*, 1980). As sepiolite generally contains less iron than palygorskite, its effect on the oxidative degradation of hydrocortisone is much smaller than that of palygor-

skite (Hermosin *et al.*, 1981). The present investigation examines the role of Fe³⁺ in the catalytic oxidation of hydrocortisone by palygorskite and sepiolite.

MATERIALS AND METHODS

Natural sepiolite from Vallecas, Spain, and palygorskite (Pharmasorb, a commercial variety of attapulgitite) were used in all experiments. Free iron oxides were removed from a portion of the palygorskite by a citrate-bicarbonate-dithionite (CBD) extraction procedure (Jackson, 1956) in order to evaluate the influence of non-structural Fe impurities on the ability of the clay to oxidize hydrocortisone. ESR spectra of the palygorskite (before and after CBD treatment) and the untreated sepiolite were obtained on a Varian Model No. E109 (X-band) spectrometer using oriented clay films aligned perpendicular (⊥) or parallel (∥) to the magnetic field of the spectrometer. The UV-VIS spectra of the same films were recorded on a Cary 17-D NIR-UV-VIS spectrophotometer.

The hydrocortisone-clay interactions were carried out in an aqueous medium as described earlier (Cornejo *et al.*, 1980; Hermosin *et al.*, 1981). The quantity of hydrocortisone adsorbed by the clays was measured by the decrease in the intensity of the UV absorbance of the supernatant liquid at 254 nm after centrifuging to separate the clay. High-pressure liquid chromatography (HPLC) was also used to measure the amount of hydrocortisone degraded by the clays (Cornejo *et al.*, 1980; Hermosin *et al.*, 1981).

RESULTS AND DISCUSSION

Forms of Fe³⁺ in palygorskite and sepiolite

Palygorskite has been shown to cause oxidation of hydrocortisone, and structural Fe³⁺ and surface-ad-

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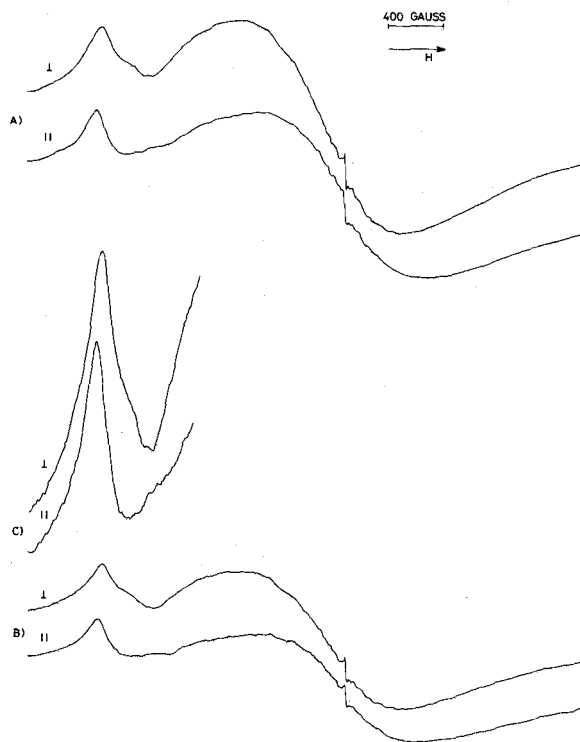


Figure 1. The ESR spectra of air-dried palygorskite films: A = untreated clay; B = CBD-treated clay. The films were oriented \perp and \parallel to the magnetic field. The region of $g = 4.2$ is shown at higher gain in spectrum C.

sorbed free iron oxides have been suggested as possible sources of its reactivity (Cornejo *et al.*, 1980). The ESR spectra in Figure 1 show that both of these components are present in palygorskite. The ESR signal at $g = 4.2$ is indicative of octahedral Fe^{3+} in the clay, whereas the very broad signal close to $g = 2$ can probably be attributed to ferromagnetic, surface-adsorbed iron oxides or hydroxides (Angel and Vincent, 1978; McBride, 1979) because it is reduced by a single citrate-dithionite treatment (Figure 1b). The ESR signal at $g = 4.2$ has been assigned to structural Fe^{3+} in the octahedral layer; this signal appears to be composed of two resonances: a low-field, strong resonance which could be attributed to Fe^{3+} - Al^{3+} pairs with orthorhombic symmetry (Angel and Hall, 1972) and a weaker signal which most likely arises from Fe^{3+} - Mg^{2+} pairs (McBride *et al.*, 1975).

The anisotropy of the $g = 4.2$ signal of palygorskite is clearly shown in Figure 1c. This orientation-dependence of the Fe^{3+} signal is opposite that observed in Upton, Wyoming, montmorillonite (Berkheiser and Mortland, 1975), but similar to that shown by hectorite (McBride, 1979). The higher field should appear for the \perp rather than the \parallel orientation of the palygorskite film relative to the magnetic field. No apparent correlation exists between dioctahedral (montmorillonite and palygorskite) or trioctahedral (hectorite) character of min-

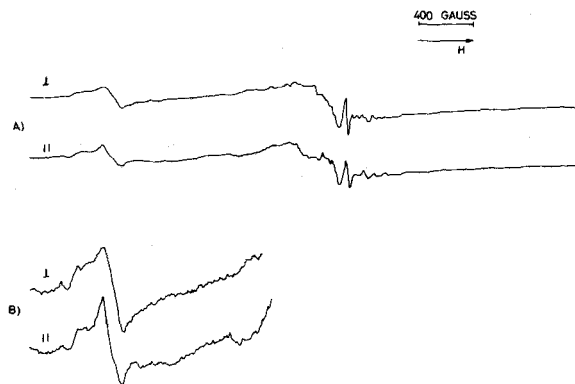


Figure 2. The ESR spectra of air-dried sepiolite films: A = untreated clay; B = same sample as in A, but with the $g = 4.2$ signal recorded at higher gain.

erals and orientation-dependence of the Fe^{3+} signal in the $g = 4.2$ region, as suggested by McBride (1979). The very broad signal attributable to surface-adsorbed iron oxides also shows anisotropy (shifting upfield) when the clay platelets are aligned parallel to the magnetic field (Figure 1a). The narrow feature with $g = 2$ probably arises from an unpaired electron at a surface or bulk-defect site.

The lesser oxidizing power of sepiolite than that of palygorskite in the presence of an aqueous solution of hydrocortisone has been attributed to the very low iron content of sepiolite (Hermosin *et al.*, 1981). The ESR spectra of sepiolite (Figure 2) also show the same two features observed for palygorskite: a structural Fe^{3+} signal at $g = 4.2$ and a surface-adsorbed iron oxide or hydroxide at $g = 2$. Both signals are weaker in sepiolite than in palygorskite and depend on the amount of total iron in the clays. These values for sepiolite and palygorskite are 3.2 mg/g and 26.6 mg/g, respectively (Cornejo *et al.*, 1980; Hermosin *et al.*, 1981). The low iron content of sepiolite minimizes the possibility of electron-electron interactions arising from neighboring paramagnetic ions in the structure.

The ESR signal at $g = 4.2$ is essentially anisotropic (Figure 2b) and very similar to the orientation-dependent Fe^{3+} signal in palygorskite (Figure 1c), but in the opposite sense. The $g = 2$ feature is essentially isotropic, and the weak, narrow feature with $g = 2$ probably arises, as in the palygorskite sample, from an unpaired electron at a surface or bulk-defect site.

The UV-VIS spectra of palygorskite and sepiolite clays (Figure 3) also indicate the presence of Fe^{3+} in both minerals. The palygorskite spectrum (Figure 3a) shows a strong absorbance at 250 nm (comparable to some montmorillonites) that can be assigned to charge transfer (oxo to Fe^{3+} octahedral), which is indicative of an octahedral Fe^{3+} content of about 2–3% range (Karrickhoff and Bailey, 1973). No appreciable difference was observed in the UV-VIS spectra of palygorskite

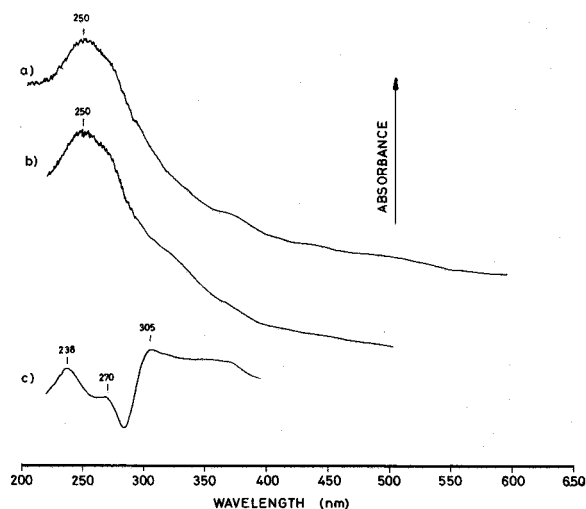


Figure 3. UV-visible spectra of palygorskite and sepiolite films: A = untreated palygorskite; B = CBD-treated palygorskite; C = untreated sepiolite.

before and after CBD treatment (Figure 3b). The sepiolite spectrum (Figure 3c) shows a weak band at 238 nm that can be assigned to charge transfer (oxo to Fe^{3+} octahedral). The assignment of the weak 270-nm shoulder is difficult, however, it has been attributed in some clays to Fe^{2+} - Al^{3+} metal-metal charge transfer from octahedral Fe^{2+} (Karickhoff and Bailey, 1973).

Mechanism of hydrocortisone reaction on the clay

Hydrocortisone exhibits very slow degradation in aqueous solution at pH 8.4 (Takubo *et al.*, 1962; Pitman *et al.*, 1972; Cornejo *et al.*, 1980). However, degradation occurs more rapidly in contact with sepiolite (Hermosin *et al.*, 1981) and even more rapidly in contact with palygorskite (Cornejo *et al.*, 1980) and seems to consist of two, apparent first-order reactions rather than the simple apparent first-order reaction observed for hydrocortisone solutions. Treatment of palygorskite by the CBD-extraction procedure reduced the catalytic effect of palygorskite and produced a degradation profile similar to that observed in the presence of sepiolite. The effect of the CBD-extraction procedure on palygorskite suggests that surface-adsorbed iron oxides are active in the oxidation of hydrocortisone. Freshly precipitated ferric hydroxide produced no catalytic effect; thus an intimate association of the iron with the clay surface appears to be necessary for the oxidation of hydrocortisone.

The reduced degradation rate of hydrocortisone in the presence of CBD-treated palygorskite may be attributed to the Fe^{3+} present in palygorskite as surface-adsorbed oxides or hydroxides as shown by ESR spectra in Figures 1a and 1b (broad signal close to $g = 2$). However, the two-phase degradation reaction of hydrocortisone observed in the presence of palygorskite

before and after CBD-treatment may be an indication that two additional kinds of sites for iron exist in palygorskite. As the oxidizing potential of the more accessible sites are exhausted, the rate of degradation decreases. These two kinds of sites for iron in palygorskite may be associated with the ESR $g = 4.2$ signal, which is composed of a low-field strong resonance, attributed to Fe^{3+} - Al^{3+} pairs with orthorhombic symmetry, and a weaker signal arising from the Fe^{3+} - Mg^{2+} pairs (Figure 1c).

The observation that the oxidizing power of sepiolite is less than that of palygorskite in hydrocortisone degradation can be explained on the basis of the very low Fe^{3+} content of sepiolite. Although ESR spectra of sepiolite (Figure 2) show two kinds of sites for Fe^{3+} which are similar to those in palygorskite, the amounts present are so small that the hydrocortisone degradation rate is very slow.

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Резюме—Оценивалась роль адсорбированного и структурного Fe^{3+} в палыгорските и сепиолите по отношению к окислению гидрокортизона в водных растворах путем электронного спинового резонанса и Уф-видимой спектроскопии. Естественные Fe^{3+} , адсорбированные на поверхности, показали значительную, хотя меньшую, чем октаэдрические Fe^{3+} , активность в процессе окисления. Кинетика окислительной деградации гидрокортизона палыгорскитом, по-видимому, состоит из двух кажущихся первого порядка реакций, которые могут быть связаны с двумя типами мест для Fe в палыгорските. Низшая окислительная сила сепиолита для деградации гидрокортизона обусловлена его низким содержанием Fe^{3+} . [E.C.]

Resümee—Der Einfluß von Fe^{3+} , das an Palygorskit und Sepiolith adsorbiert ist oder sich in deren Struktur befindet, wurde im Hinblick auf die Oxidation von Hydrocortison in wässriger Subspension mittels Elektronenspinresonanz und UV-VIS-Spektroskopie untersucht. Natürliches, an der Oberfläche adsorbiertes Fe^{3+} zeigt einen erheblichen Einfluß auf den Oxidationsprozeß, der jedoch kleiner ist als der von oktaedrischem Fe^{3+} . Die Kinetik der oxidativen Degradation von Hydrocortison durch Palygorskit scheint aus zwei Reaktionen erster Ordnung zu bestehen, die anscheinend mit zwei Arten von Fe-Plätzen im Palygorskit zusammenhängen. Das geringe Oxidationsvermögen von Sepiolith bei der Hydrocortison-Degradation hängt mit dessen sehr geringem Fe^{3+} -Gehalt zusammen. [U.W.]

Résumé—Le rôle de Fe^{3+} adsorbé et structural dans la palygorskite et la sépiolite vis à vis de l'oxidation de l'hydrocortisone en suspension aqueuse a été évalué en utilisant la résonance à spin d'électrons et la spectroscopie UV-visible. Le Fe^{3+} naturel adsorbé à la surface a montré une activité importante dans le procédé d'oxidation, quoique plus petite que Fe^{3+} octaédral. La cinétique de dégradation oxidative de l'hydrocortisone par la palygorskite semble être composée de deux réactions de premier ordre qui pourraient être associées à deux sources de sites pour Fe dans la palygorskite. La capacité d'oxidation moindre de la sépiolite pour la dégradation de l'hydrocortisone est due à son très bas contenu en Fe^{3+} . [D.J.]