

Applications of electron spin echo modulation to transition metal ions in smectite clays

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Abstract- The location and solvation environment of cupric ions and silver atoms in nonpillared montmorillonite, beidellite and hectorite clays has been determined by electron spin echo modulation spectroscopy.

INTRODUCTION

Electron spin echo modulation (ESEM) is becoming increasingly useful for probing the surroundings of paramagnetic transition metal ions on a variety of oxide surfaces of catalytic and potential catalytic importance. Since commercial instrumentation for electron spin echo spectroscopy is now available this type of pulsed spin resonance spectroscopy should find increasing application in this area. It is of particular importance to trace changes in the location of a catalytically active metal ion with respect to the oxide surface as a function of thermal pretreatment, molecular absorption and other cocations present. With respect to catalysis by transition metal ion species on oxide surfaces, it is of particular importance to determine the coordination geometry of an adsorbate in terms of the number, distance and orientation of the absorbed molecules and also whether such coordination distances correspond to direct bonding distances or to longer indirect interaction distances. With a paramagnetic valence state of a transition metal ion, one can use electron magnetic resonance techniques to probe the surroundings of that catalytically active ion in a rather detailed fashion. Analysis of electron spin echo modulation patterns can often answer such questions by resolving very weak electron nuclear dipolar interactions in disordered systems such as powders which are generally not resolved by ordinary electron spin resonance (ESR).

Previous work has shown the efficacy of ESEM to studies of transition metal ions in zeolite molecular sieves (ref. 1). Current work also involves aluminophosphate-based molecular sieves (ref. 2) which constitute a new class of microporous materials for which the catalytic applicability is largely undeveloped. The background of ESEM has been well described (ref. 3) together with the simulation of modulation patterns to determine magnetic parameters such as the distance and number of interacting nuclei as well as some of the limitations involved in such analyses.

In this brief review we detail studies of transition metal ions in layered oxide materials as represented by the smectite clays. Smectite clays generally have some cation exchange capacity and also have the advantage of potentially larger molecular spaces than are realized in zeolite and aluminophosphate molecular sieve materials.

SMECTITE CLAY STRUCTURE

Smectite clays are swelling clays that contain an interlayer space which can expand by the absorption of a suitable solvent. Figure 1 shows a typical structure of smectite clays where only the oxide lattice is explicitly shown. Each clay layer is made up of three sheets consisting of two tetrahedral sheets sandwiching an octahedral sheet. In the center of each tetrahedron or octahedron are cations such as aluminum, silicon, magnesium, etc. The thickness of this

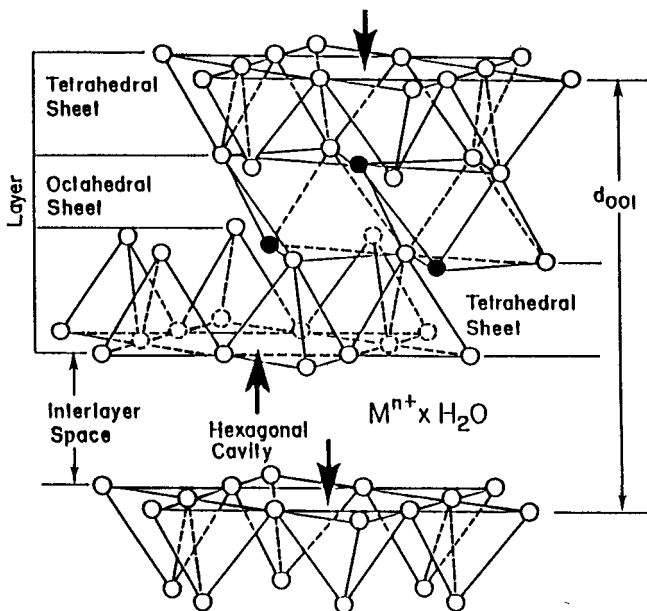
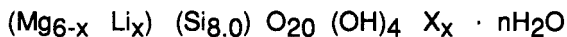
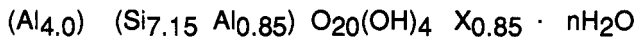
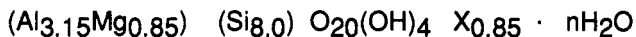


Fig. 1.
Smectite clay structure

clay layer is 0.096 nm and the interlayer space can range from nil to complete separation or delamination of the layers. For a well ordered system that has not delaminated, x-ray diffraction peaks are observed corresponding to the distance (d_{001}) between the basal oxygen surfaces of two successive layers as shown in Figure 1. Also shown in Figure 1 is the interlayer space. A hexagonal cavity is indicated by the arrow which corresponds to a cation location when it interacts strongly with a basal oxygen surface of the interlayer space such as when most solvent molecules have been removed.

Three common clay structures will be discussed: montmorillonite, beidellite and hectorite (ref. 4). The ideal unit formulas are shown below in order, where the first parenthesis represents the cation composition of the octahedral sheet and the second parenthesis represents the cation composition of the two tetrahedral sheets in each layer.



X represents a monovalent exchangeable cation in the interlayer space. Note that both montmorillonite and beidellite have only four ions in the octahedral sheet. This means that some of the octahedra are vacant since there are six octahedral vacancies per unit formula. Thus montmorillonite and beidellite are called dioctahedral clays. Hectorite is a trioctahedral clay which contains six cations in its octahedral sheet and has all of the octahedra occupied by a cation. Laponite is a trade name of a commercially available synthetic hectorite. All three clays are found in nature. In addition hectorite and beidellite have been synthesized in the laboratory.

CUPRIC IONS

Cupric ion was exchanged into natural montmorillonite to the extent of about 5 % of the exchange sites and was studied as a function of dehydration (ref. 5). Both ESR and ESEM experiments were carried out. It should be noted that it is not always possible to observe electron spin echoes in solid materials. This seems to be a sensitive function of the amount of aggregation of the paramagnetic species. In general in oxide materials it is found that the electron spin echo signal becomes weaker as the material is dehydrated. The ESR parameters, g_{\parallel} and A_{\parallel} , are characteristic of the environmental symmetry of the

TABLE 1. ESR parameters of Cu-montmorillonite and Cu-Al₁₃ Laponite.Cu-montmorillonite and Cu-Al₁₃ montmorillonite^a

	← Reversible →		
	Cu ^{II} (H ₂ O) ₆	→ Cu ^{II} (H ₂ O) ₄	→ Cu ^{II} (H ₂ O)
d(001)	2.0 ^b nm	1.5 ^b nm	1.0 ^b nm
g	2.39	2.35	2.42
A	145	175	117 x 10 ⁻⁴ cm ⁻¹

^aOne or more waters may be part of the pillar. ^b1.8 nm in Al₁₃ pillared material.

Cu-Al₁₃ Laponite (delaminated)

g	2.36
	→ Cu ^{II} (H ₂ O) ₂ (O _p) ₂ (H ₂ O) ₂
A	145 x 10 ⁻⁴ cm ⁻¹

Cu-Zr₄ montmorillonite

	← Not Reversible →		
	Cu ^{II} (H ₂ O) ₆	→ Cu ^{II} (H ₂ O) ₄	→ Cu ^{II} (H ₂ O) ₄
d(001)	1.93 nm	1.8 nm	1.64 nm
g	2.39	2.34	2.31
A	140	177	177 x 10 ⁻⁴ cm ⁻¹

cupric ion. Table 1 summarizes these results. It can be seen that three sets of values are observed during dehydration. For fully hydrated copper montmorillonite the ESEM results show that six waters are directly coordinated to copper and the ESR parameters are consistent with octahedral symmetry. An isotropic line is observed at room temperature indicating that this hexahydrated cupric ion is rapidly tumbling. If the temperature is lowered to 77 K the ESR spectrum shows an anisotropic spectrum whose parameters are given in Table 1. As dehydration occurs by evacuation at room temperature and then at higher temperatures it is found that square planar and tetrahedral species are relatively cleanly produced. They are distinguished by a different set of ESR parameters and a smaller number of coordinated waters. No electron spin echo is observed for the completely dehydrated cupric ion although an ESR spectrum is still observed.

It is particularly interesting that no ²⁷Al modulation is seen in this system even though aluminum is in the octahedral sheet of the montmorillonite. As the dehydration proceeds it is thought that the cupric ion moves toward the hexagonal cavity in the basal surface of the interlayer space. In this location it should be within about 0.4 nm from an aluminum in the octahedral sheet at least part of the time. This should give detectable modulation but none is seen so perhaps the cupric ion does not approach the hexagonal opening that closely.

It is noted under fully hydrated conditions that cupric ion is coordinated to the same number of water molecules as it is in bulk solution. However when cupric ion is solvated with ethanol and methanol (ref. 6) the analysis of the ESEM pattern shows that cupric ion is coordinated by only four methanols and four ethanols whereas in bulk solution the coordination number is six in both cases. The methanol-solvated cupric ion shows an isotropic ESR spectrum at room temperature characteristic of rapid tumbling within the interlayer space, however the ethanol-solvated cupric ion shows an anisotropic ESR spectrum even at room temperature. This presumably reflects the larger size of the ethanol-solvated cupric ion relative to the methanol-solvated cupric ion.

Pillared smectite clays have also been studied. Pillared clays are of interest because the incorporation of large robust inorganic cations into the interlayer space can serve as pillars which prevent the collapse of the interlayer space on dehydration and form a more thermally stable material. The most common type of pillar that has been used is an Al_{13} polyhydroxy species and this $\text{Al}_{13}\text{mont}$ system has been studied with cupric ion exchange (ref. 7). It has a d_{001} value of 1.8 nm which is retained on dehydration up to 350 °C. However, after pillaring and calcining at the high temperature no electron spin echo is observed. Even upon rehydration no spin echo is observed. Perhaps the calcination part of the pillaring process causes the impurity iron in the natural montmorillonite to redistribute such that it shortens the phase memory time to make the echo nonobservable. Although no electron spin echo is observed, the ESR spectrum is observed. Since we have calibrated the ESR parameters with respect to the number of waters directly coordinated to the cupric ion in the unpillared montmorillonite, one finds that the same three hydrated species are observed in the pillared montmorillonite. Also the dehydration process in $\text{Cu-Al}_{13}\text{mont}$ is reversible as it is in Cu-mont . The main difference in the pillared system is that little isotropic ESR at room temperature is seen. At low pillar density a small amount of isotropic spectrum is seen but as the pillar density is increased, little of the isotropic ESR spectrum is seen at room temperature. This means that the hexacoordinated cupric ion either does not have enough space to freely tumble in the pillared material or that it is coordinated at one or more sites on a pillar. The pillar has waters and hydroxyls on its external surface and to the extent that these are partially removed by calcination an oxygen remains which is a good coordination site for the cupric ion. Because of the lack of an isotropic ESR spectrum at room temperature we conclude that the cupric ion in the hydrated state and partially dehydrated state is indeed coordinated to an oxygen of the pillar. The cupric ion should be able to freely tumble if the d_{001} distance is greater than 1.5 nm which it is in the pillared montmorillonite.

Some support for the possibility that the intrinsic Fe^{3+} in natural montmorillonite affects the observation of an electron spin echo after pillaring comes from experiments on Al_{13} -pillared Laponite which is a synthetic hectorite and contains little or no iron as an impurity. Also recall that the hectorite has no aluminum in its octahedral or tetrahedral sheets and therefore the only aluminum present in Al_{13} -pillared Laponite is in the pillars. The Al_{13} -pillared Laponite is delaminated as indicated by the lack of any distinct reflections by x-ray diffraction. However, an electron spin echo signal is observed (ref. 8) and it shows aluminum modulation indicating clearly that the hydrated cupric ion is coordinated to a pillar. The ESR parameters indicate approximate octahedral symmetry but the ESEM pattern analysis of the cupric ion hydrated with D_2O shows that it is coordinated to two waters at 0.28 nm and two additional waters at 0.35 nm. Since the ESR parameters indicate approximate octahedral symmetry, it is concluded that the cupric ion is coordinated to two oxygens of the pillar also and that these oxygens plus two of the waters form equatorial ligands and the two other more distant waters are axial ligands. It is also interesting that no isotropic ESR is observed at room temperature at any pillaring density which also supports direct coordination to the pillar.

A different pillar that can be utilized is a Zr_4 polyhydroxy cation and cupric ion has been studied in Zr_4 montmorillonite (ref. 9). Here the results are significantly different from cupric ion in Al_{13} -montmorillonite. The same octahedral cupric species in the fully hydrated state is seen and also an isotropic spectrum is seen at room temperature indicating rapid tumbling. On dehydration the ESR parameters change to those characteristic of square planar symmetry but on further dehydration when most of the water is lost in Al_{13} montmorillonite the ESR parameters remain characteristic of the square planar symmetry suggesting that the cupric ion do not lose further water in Zr_4 montmorillonite. Also, this dehydration process is not reversible in Zr_4 -montmorillonite. Both of these facts argue that copper coordinates very strongly to the Zr_4 -pillar. If one examines the structure of the pillar it is seen that cupric ion can locate inside the pillar

and coordinate to four oxygens or hydroxyls which would be a very stable situation. This is consistent with the fact that on full hydration the cupric ion does not move into a hexagonal cavity near the basal surface of the interlayer space.

In addition to studying exchanged cupric in smectite clays it is also of interest to see if copper can be incorporated into the lattice. This has been recently achieved by synthesizing fluorohectorite with cupric ion in the synthesis mixture (ref. 10). Support of lattice substitution is shown by the fact that ethylenediaminetetraacetic acid (EDTA), which is a good complexing agent for cupric ion, only removes less than 20 % of the cupric ion in the synthesized CuFhct material. Also x-ray diffraction shows single phase fluorohectorite formed. In contrast, if fluorohectorite is synthesized without cupric ion in the synthesis mixture and subsequently cupric ion is exchanged into the fluorohectorite, then EDTA removes more than 90 % of the cupric ion.

Table 2 shows the cupric ion species observed in CuFhct. Three species are observed and it is possible to observe electron spin echo signals so coordination to adsorbates can also be studied. Two cupric ion species predominate and are termed A and B as shown in Table 2. They are distinguished by the fact that Cu(A) shows no lithium modulation whereas Cu(B) does show lithium modulation which can be analyzed in terms of one lithium nucleus about 0.3 nm distant. This is consistent with the distance expected if cupric ion were in the octahedral sheet of the fluorohectorite layer and adjacent to a lithium in an adjacent octahedron. When there is no lithium in the adjacent octahedron, then you have the Cu(A) species. It is also found by electron spin echo studies that these cupric ion species do not show direct coordination to water or other adsorbates. This is consistent with these cupric ion species being in the octahedral sheet.

TABLE 2. ESR parameters of Cu(II)-substituted fluorohectorite.

	Cu ^{II} (A)	Cu ^{II} (B)	Cu ^{II} (C)
g	2.40	2.26	not resolved
A	118 x 10 ⁻⁴ cm ⁻¹	50 x 10 ⁻⁴ cm ⁻¹	not resolved
	No Li-mod	Li-mod	Directly
		N = 1	Coordinates
		R = 0.30 nm	Ammonia (3)
	No direct coordination to adsorbates		Pyridine(2-3)

A third species Cu(C) is also observed in lesser abundance. The parallel ESR parameters are not resolved but it is possible to show that this third species directly coordinates to ammonia and pyridine adsorbates by resolved nitrogen hyperfine structure that is observed. The Cu(C) species directly coordinates with three ammonia molecules and two or three pyridine molecules. It is suggested that this species is at a edge lattice site in the octahedral sheet such that it has uncompleted coordination which allows coordination to adsorbates with lone pair electrons. There seems to be considerable future potential for exploring transition metal ion substitution into synthesized smectite clays.

SILVER ATOMS

Monovalent silver atoms can also be ion exchanged into smectite clays. They are not paramagnetic but they can be easily reduced by gamma radiation to produce silver atoms which are an excellent probe of the local environment because the silver atom has a very large isotropic hyperfine interaction. Thus silver atoms have been studied for this purpose in montmorillonite and Al₁₃-pillared montmorillonite (ref. 11). In hydrated Ag-montmorillonite the ¹⁰⁹Ag isotropic hyperfine constant is 2001 MHz. This is even larger than the value of 1978 MHz found in the gas phase and is characteristic from previous studies in frozen aqueous solutions of a frozen aqueous glass. This indicates that the environment of the water in the interlayer space of the montmorillonite is highly disordered as in an aqueous glass. For contrast in polycrystalline aqueous frozen solutions the analogous silver isotropic hyperfine coupling is only 1550 MHz.

TABLE 3. Number (N) and distance (R) of deuteriums from D₂O interacting with Ag(0) in smectite clays as a function of dehydration based on ESEM analysis.

	Hydration	d(001)	water layers	N	R
<u>Montmorillonite</u>	wet	> 2.0 nm	> 4	8	0.33 nm
	100 % RH	1.54	2	4	0.31
	48 % RH	1.22	1	2	0.31
	0 % RH	0.97	0	No echo	
<u>Al₁₃-Pillared Montmorillonite</u>	wet	1.82 nm	3	6	0.32
<u>Fluorohectorite</u>	wet	> 2.0 nm	> 4	4	0.31
				4	0.38
	100 % RH	1.91	~ 4	4	0.31
				4	0.36
	48 % RH	1.26	1	2	0.28
	0 % RH	0.98	0	0	
<u>Beidellite</u>	wet	> 2.2 nm	> 5	4	0.28
				4	0.35
	100 % RH	2.22	~5	4	0.30
				4	0.40
	48 % RH	1.58	2	4	0.24
	0 % RH	0.98	0		

Electron spin echo studies were carried out and showed that the silver is fully solvated in the montmorillonite with four waters directly coordinated to the silver atom. This is the same as is found in bulk solution. However for methanol and ethanol the coordination numbers in the montmorillonite are less than they are in frozen bulk solutions. For methanol the coordination number is two in montmorillonite versus four in bulk solution. For ethanol the coordination number is only one in montmorillonite versus four in bulk solution.

Dehydration was also studied. As with cupric ion, the electron spin echo signal becomes weaker upon dehydration. It is shown that the silver atom loses its waters and distinct species with two coordinated waters and one coordinated water can be observed. These results are summarized in Table 3. It can also be noted from Table 3 that the number of coordinated waters at various relative humidities deduced by the electron spin echo modulation analysis correlates very well with the number of water layers suggested from the basal plane spacing determined by x-ray diffraction. This lends support to the analysis of the electron spin echo modulation data.

As with cupric ion no aluminum modulation is seen for silver atoms in hydrated or dehydrated montmorillonite. However when the montmorillonite is pillared with the Al₁₃ polyhydroxy cation, aluminum modulation is seen and is in fact seen at all relative humidities. This indicates pillar coordination of the silver atom in the Al₁₃-pillared montmorillonite. In addition, as shown in Table 3, the ESEM results show that the silver atom in the pillared montmorillonite is coordinated to only three water molecules instead of four. This suggests that it coordinates to one oxygen of a pillar which is consistent with the observation of ²⁷Al modulation.

Recall that in the Al₁₃-pillared montmorillonite exchange of cupric ion did not show any electron spin echo signal, however when silver ion is exchanged into the Al₁₃-pillared montmorillonite and then partially converted to silver atoms electron spin echo modulation can be seen. The reason for this is not clear although it probably has to do with the location of the cupric ion and silver atom with respect to the basal oxygen surface.

One other fact that is particularly interesting in the silver atoms in montmorillonite is that in neither montmorillonite nor in pillared montmorillonite are silver clusters seen during dehydration. This contrasts with zeolite materials where silver cluster formation is very common and has been studied in detail (ref. 12).

Silver atoms have also been studied in synthetic fluorohectorite and synthetic beidellite and the results are shown in Table 3. The hydration geometry determined from ESEM analysis is shown as a function of relative humidity. One interesting result is that in the fully hydrated state four water molecules are still seen to be interacting with silver atoms in both fluorohectorite and beidellite but they are not equivalent. Two water molecules are directly coordinated and two are at a greater distance. This contrasts with montmorillonite. Also the echo is significantly stronger in the synthetic clays than in the natural montmorillonite and an electron spin echo can be observed at 0 % relative humidity. In the fluorohectorite at 0 % relative humidity fluorine modulation can be seen which implies that the silver atom is not too far from fluorines which are located between the tetrahedral and octahedral sheets. This suggests that with increasing dehydration the silver moves closer to the basal oxygen surface although probably not as close as the cupric ion is considered to do.

Beidellite is a particularly interesting smectite clay in that it has aluminum substitution in the tetrahedral sheets as well as in the octahedral sheets. Thus its center of negative charge in the layer is closer to the interlayer space than occurs in either hectorite or montmorillonite in which the layer charge is in the octahedral sheet. In beidellite, aluminum modulation is seen at all relative humidities and it has about the same modulation depth. This suggests that the silver atom location does not change with respect to the basal oxygen surface of the interlayer space during dehydration as controlled by the relative humidity.

This suggests a model where the silver ion or atom is directly coordinated to a tetrahedron containing aluminum of the tetrahedral sheet bordering the interlayer space. In this case the four direct coordination sites silver requires can be provided by two oxygens from the tetrahedron and two waters. In addition there are two further indirectly coordinated waters as indicated by the ESEM results under full hydration. This model for the location of silver atoms, and by implication silver ions before their conversion to silver atoms, is consistent with no change in the silver location during dehydration since it is already bonded directly to the basal surface of the interlayer space.

It is also found that in the fully hydrated or wet beidellite a second ESR spectrum of a silver atom is observed which has an isotropic silver hyperfine coupling of only 1565 MHz which is similar to that found in polycrystalline ice. The simulation of the echo modulation for this species gives eight deuteriums at 0.35 nm which is consistent with four equivalent waters at a direct coordination distance as expected for a silver species in bulk polycrystalline water. Thus in beidellite the arrangement of the water in the interlayer space seems to be glassy near the basal oxygen surface and polycrystalline further away from this surface. Whether this is a reflection of the charge in the tetrahedral sheet is not yet known. However it is clear that the location of the layer charge does have an effect on the hydration of transition metal ions in the interlayer space and on their location with respect to the basal oxygen surface. In montmorillonite where the charge is in the octahedral sheet the silver atom is fully coordinated by four equivalent waters and then as the dehydration proceeds it coordinates to some oxygens of the hexagonal cavity and moves to the basal oxygen surface.

In fluorohectorite which also has the charge in the octahedral sheet the silver atom solvation involves two waters and two oxygens of the basal oxygen surface with two further waters and as dehydration proceeds the silver appears to move more toward the hexagonal cavity based on the observation of ^{19}F modulation. However the picture here is not too well defined at present. In beidellite where the charge is in the tetrahedral sheet the picture is more clear. There the silver is directly coordinated to two waters and two oxygens of the basal oxygen surface and its location does not change as dehydration proceeds. It stays coordinated to two oxygens of the basal oxygen surface.

It is interesting to note that the order of dehydration efficiency varies with the particular smectite clay. Table 4 shows that the dehydration is most efficient in

TABLE 4. Data showing the differential ease of dehydration in smectite clays

Hydration	Ag-mont		Ag-Fhct		Ag-beid	
	d(001)	H ₂ O layers	d(001)	H ₂ O layers	d(001)	H ₂ O layers
100 % RH	1.54 nm	2	1.91 nm	~ 4	2.22 nm	~ 5
48 % RH	1.22	1	1.26	1	1.58	2
0 % RH	0.97	0	0.98	0	0.98	0

TABLE 5. Contrast of Cu(II) and Ag(0) Solvation in Montmorillonite

Solvent	Ag(0)		Cu(II)	
	Mont	Bulk	Mont	Bulk
D ₂ O	4	4	6	6
MeOH	2	4	4	6
EtOH	1	4	4	6

montmorillonite and least efficient in beidellite. It is also interesting to contrast the amount of solvation of cupric ion and silver atom in montmorillonite for different solvents. This is done in Table 5 and it can be seen that cupric ion seems to be more completely solvated than the silver atom in the interlayer space of smectite clays. Whether this is a charge effect or not has not yet been resolved.

CONCLUSIONS

It has been shown that electron spin echo modulation spectroscopy can be very useful for delineating the location and the solvation environment of paramagnetic transition metal species in smectite clays. Most of the work has been done with ions exchanged into the interlayer space where they can be moved around by changing the degree of hydration. It is particularly exciting that direct interaction or coordination with pillars can be observed. Much less work has been done on the substitution of transitional metal ions into the clay lattice itself. This is also synthetically possible in many cases and ESEM spectroscopy can monitor the environment of lattice-substituted transition metal ions.

One factor that is not fully understood is why an echo cannot be observed in certain systems, particularly those natural clays containing significant amounts of iron. Also the echo generally gets weaker as dehydration or desolvation occurs although in the synthetic fluorohectorite and beidellite systems an echo is still observable after complete dehydration. It appears that with synthetic materials electron spin echo spectroscopy can be fairly generally applied to incisive studies of transition metal ion location, solvation and movement in the clay interlayer space and location in direct substitutional sites in the clay lattice.

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