

Mecanismos de retenção do COS: superfícies minerais do solo

Prof. Yuri Lopes Zinn

Superfícies minerais no solo

- Os solos são compostos em média por 95% partículas minerais, e 5% MOS;
- Embora constante pelo mundo, essa proporção sugere um grande efeito da fase sólida mineral sobre a orgânica;
- Não obstante, a MOS, seus componentes e dinâmica são muitas vezes entendidos ou modelados como se fossem independentes da matriz mineral em que ocorrem.

Superfícies minerais no solo: área

- Textura: distribuição de tamanho das partículas primárias do solo: areia (2-0.02 mm), silte (20-2 μm) e argila (<2 μm);
- Areia e silte, por seu tamanho e forma granulares, são caracterizadas por baixa área superficial específica – ASE (até 6 $\text{m}^2 \text{g}^{-1}$);
- As argilas, em geral laminares, possuem maior ASE variando com expansividade e tamanho: <40 $\text{m}^2 \text{g}^{-1}$ para a caulinita a 800 $\text{m}^2 \text{g}^{-1}$) para esmectitas (montmorillonita);

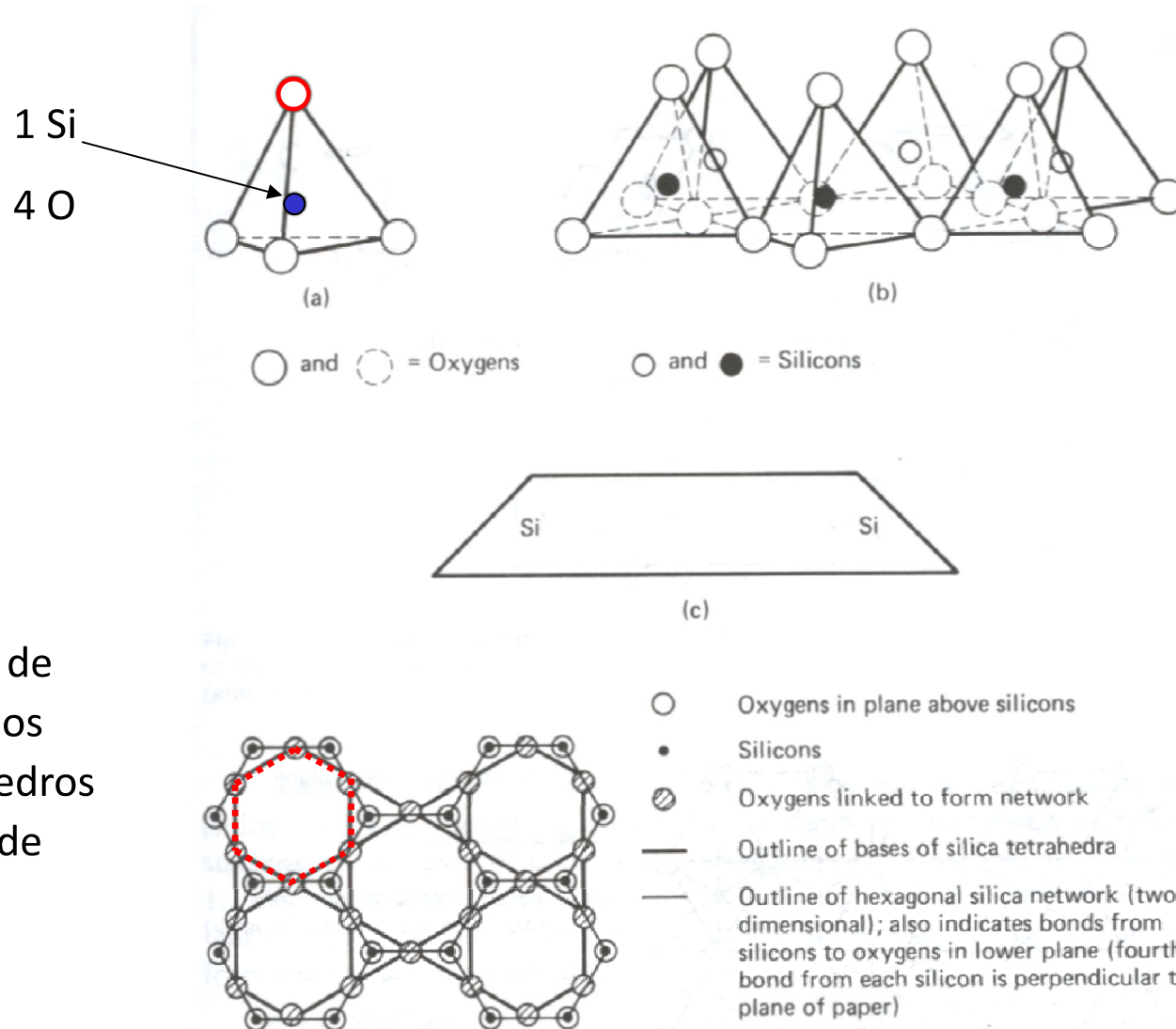
Superfícies minerais: cargas

- Cada componente da fase mineral do solo possui uma típica carga elétrica superficial (permanente e/ou variável),
- As cargas de cada mineral, multiplicadas por sua ASE, resultam numa capacidade de atração e (ad)sorção de íons e/ou outras partículas
- A compreensão da estrutura e natureza dos minerais mais comuns no solo é necessária para interpretar a retenção da MOS.

Geoquímica da crosta terrestre

Elemento	% g e vol.	Coordenação (carga/raio)
O	47 e 93	n.a. (-2/0.136 pm)
Si	28 e 0.2	Tetraedral (4/0.026 pm)
Al	8.1 e 0.2	Octaedral (3/0.039 pm)
Fe	5 e 0.5	Octaedral (3/0.078 pm)
Ca	3.6 e 1.1	Cúbica (3/0.1 pm)

O Tetraedro de Sílica e os filossilicatos



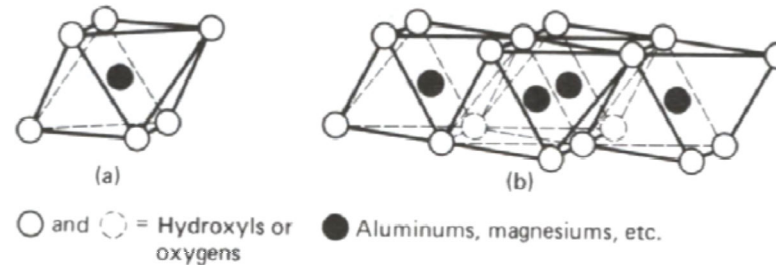
Em filossilicatos, os tetraedros são dispostos como hexágonos que se ligam pelo ápice formando lâminas.

A superfície basal é chamada siloxane e está em contato com o meio. A apical se liga à lâmina octaedral

Camada de hexágonos de tetraedros e cavidade central

O octaedro de Al, Mg, Fe etc. e sua camada

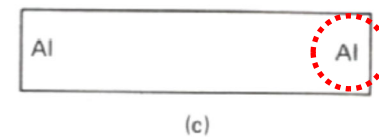
- 1 Cátion
- 6 O or OH



Há 2 tipos de minerais principais:

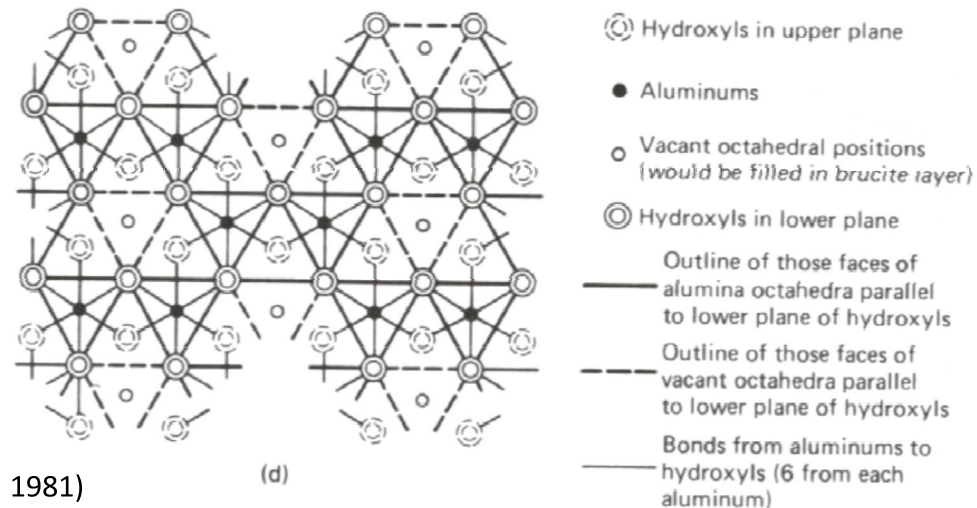
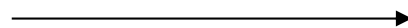
Gibbsita (com Al^{3+}): $\text{Al}_2(\text{OH})_6$, com 2/3 dos espaços catiônicos preenchidos. 1 OH é ligado a 2 Al:

Dioctaedral



Representação: retângulo

Brucita (com Mg^{2+}): $\text{Mg}_3(\text{OH})_6$, todos os espaços catiônicos preenchidos. 1 OH é ligada a 3 Mg: **Trioctaedral**



(Holtz e Kovacs, 1981)

Lâminas octaedrais

- Em 3 modelos, segundo Schulze (2002)
- Soil mineralogy with environmental applications. SSSA, Madison, 2002

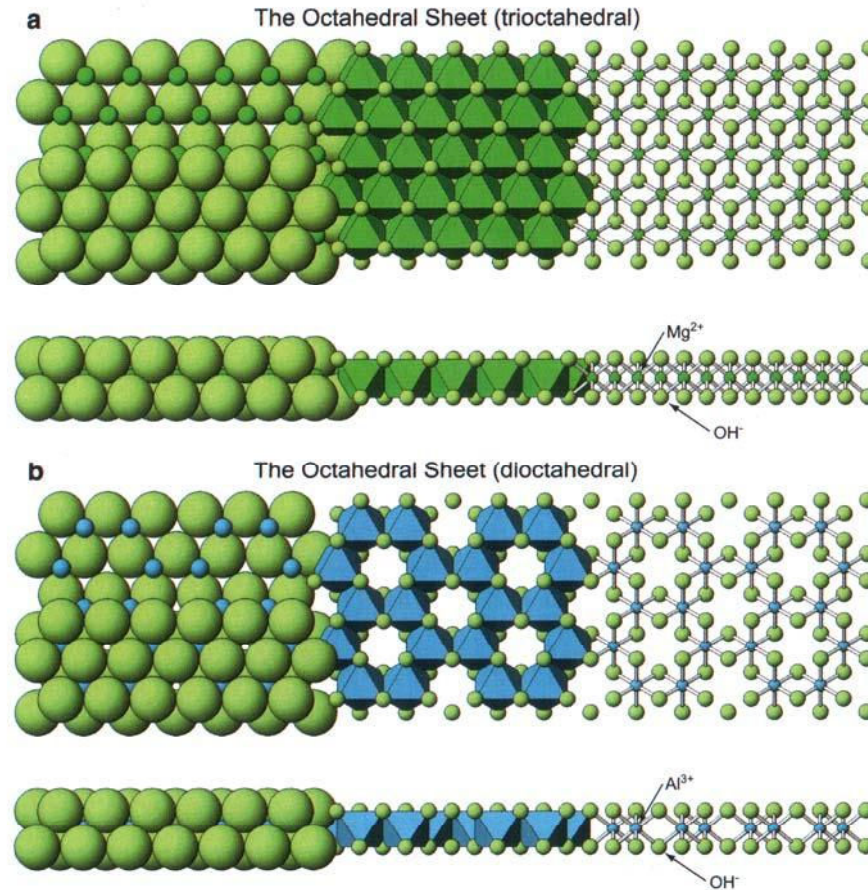


Plate 1-4. The octahedral sheet. (a) A trioctahedral sheet. (b) A dioctahedral sheet.

Cargas elétricas permanentes

- ◆ Em filossilicatos, são geradas por substituição isomórfica (SI) de um Si^{4+} por Al^{3+} na lâmina tetraedral, ou **especialmente** de Al^{3+} por Mg^{2+} ou Fe^{2+} na lâmina octaedral;
- ◆ Assim sendo, as cargas permanentes são sempre negativas, devido à SI por cátion de carga menor;
- ◆ Em sílica e óxidos de Fe/Al há pouca SI e portanto carga permanente desprezível

Cargas elétricas variáveis

- Em minerais, estão sempre associadas aos limites físicos dos cristais: em minerais laminares, às arestas quebradas
- Dois tipos: potencialmente neutras (O^- ligado a Si), e nunca neutras (O^- ligado à octaedros de Al, Fe, Mg)
- São sempre maiores em sólidos pouco cristalinos, que tem maior ASE
- A MOS só possui cargas variáveis, nunca as permanentes

Tipos de superfícies minerais ativas

- Siloxane neutra: ex. plano basal da caulinita.
Afinidade por substâncias apolares
- Siloxane de carga permanente: ex. planos basais de esmectitas, vermiculita, devida à SI.
- Silanol – aresta quebrada do plano basal da lâmina de tetraedros de sílica: varia entre -1,0, +1
- Hidroxil neutra – ex. segundo plano basal da caulinita, planos basais da gibbsita, goethita – permite pontes de H, afinidade por polares
- Hidroxil carregada – aresta quebrada de lâminas octaedrais: varia entre -1/2, +1/2, e até +3/2

Cargas e neutralidade em ácido húmico

- Possíveis sítios de interação mineral:
- Áreas claras: neutra, hidrofóbica
- Azul: carga –
- Vermelho: carga +
- Johnston & Tombacz, 2002

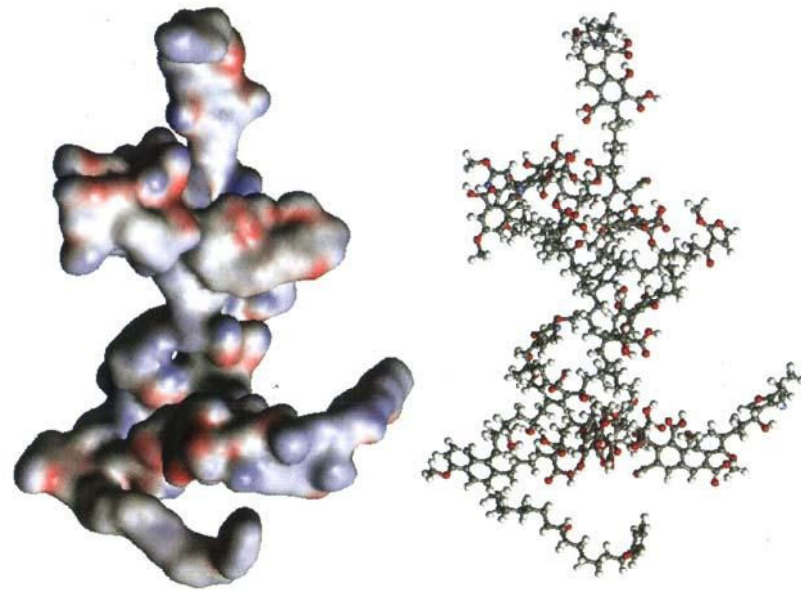


Plate 2-8. Three-dimensional structure of humic acid shown using a ball and stick representation on the left side and as the electrostatic potential surface on the right side. The gray regions of this surface correspond to neutral portions of humic acid, blue regions represent negatively charged areas and red regions to portions of the humic acid surface with a slight positive charge. Using the Molecular Simulations Cerius2 and Weblab ViewerPro programs, structures were plotted based on the two-dimensional structure of Schulten and Schnitzer (1995).

Minerais: Quartzo e sílica

- Extremamente comum em solos (resistente ao intemperismo), carga permanente e SI desprezíveis
- ASE baixa devido à forma granular e tamanho >silte
- Carga variável nas arestas quebradas (O^- sub-coordenado), como -1 , 0 e $+1$: $Si-O^-$, $Si-OH$, $SiOH_2^+$

- ASE e CTC na fração argila:

$2 \text{ m}^2 \text{ g}^{-1}$, 5 cmol kg^{-1} .

- Porém, o Qtz é instável neste tamanho ($pK_s = 3.1$)

- Segundo Monger & Kelly, 2002

SILICA MINERALS

615

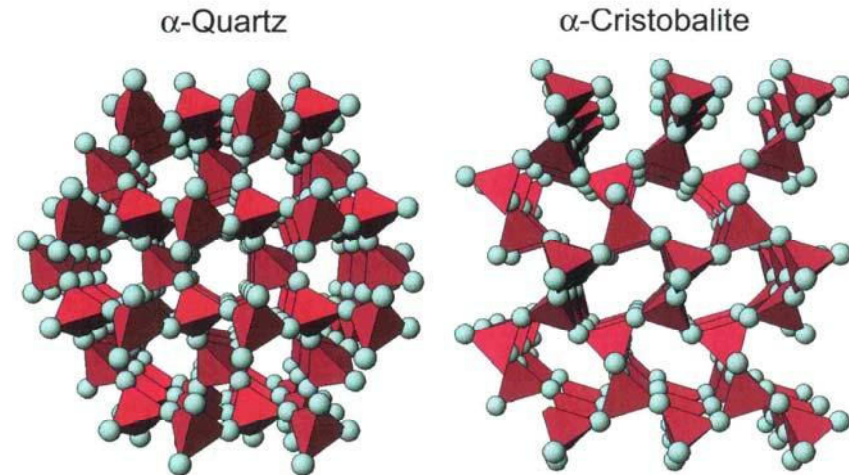
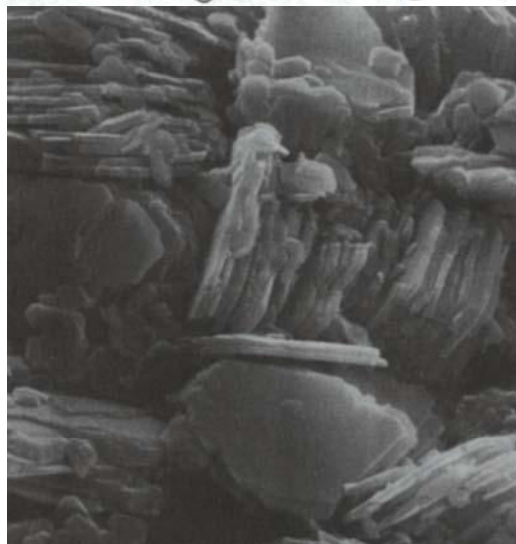
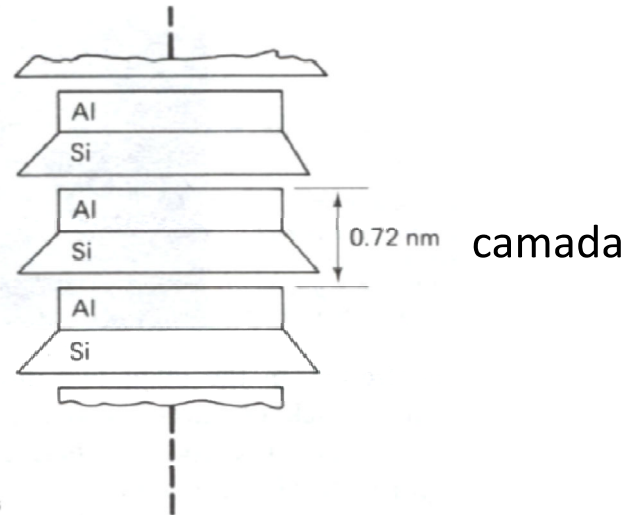
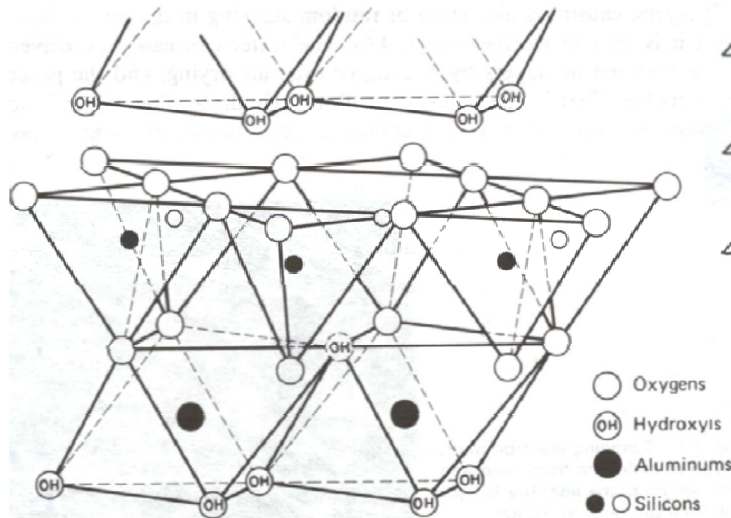


Plate 20-1. The crystal structures of α -quartz and α -cristobalite consist of SiO_4 tetrahedra linked in two different ways. Each structure is viewed down a structural axis that shows the maximum spacing between adjacent tetrahedra. Note the much more compact arrangement of tetrahedra in α -quartz. The more open packing of tetrahedra in α -cristobalite is why it has lower density and why it is more likely to contain more impurities than α -quartz.

Minerais 1:1 - caulinita (*kaolinite*)



17 μm

Trovey, 1971 (from Mitchell, 1993)

- Espaçamento Basal : 7.2 Å. Ligação entre camadas: van der Waals e pontes de hidrogênio: **não-expansiva**. $\text{Si}_4\text{Al}_4\text{O}_{10}(\text{OH})_8$.
- O mineral de argila **mais frequente** no mundo e **predominante** no Brasil, estável.
- ASE < 40 $\text{m}^2 \text{g}^{-1}$, baixa SI e portanto, **baixa CTC permanente** – CTC total 1 a 5 cmol kg^{-1}
- Carga variável na superfície silanol (aresta quebrada) com (-1,0,+1) e na alumina ($\pm 1/2$). PZC=5.25

Neutralidade e cargas na caulinita

- Área em verde:
superfície
neutra,
hidrofóbica

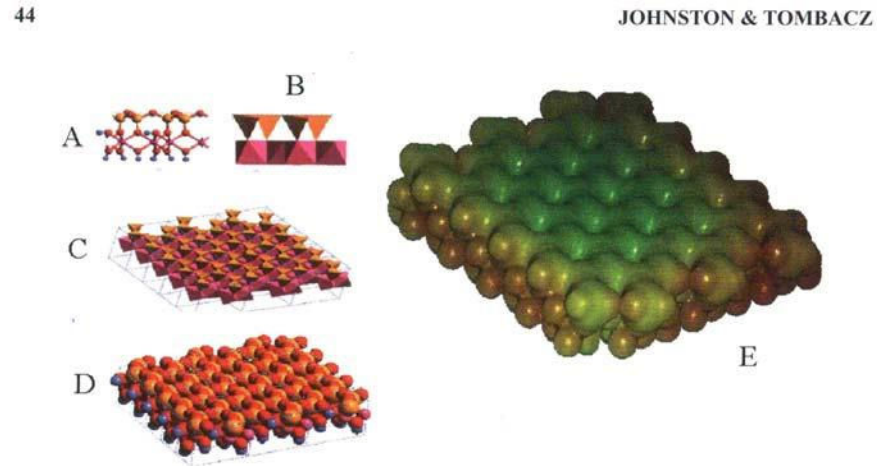


Plate 2-3. Representation of the kaolinite surface shown in (A) ball-and-stick and (B) polyhedral, (C) a 5 by 5 by 0.7 nm section of the kaolinite surface in polyhedral, and (D) ball-and-stick and space-filled models. (E) is an electrostatic surface potential map of the kaolinite surface (courtesy of Randy Cygan at Sandia National Laboratory).

- Cargas pH-
dependentes
(White &
Dixon, 2002)

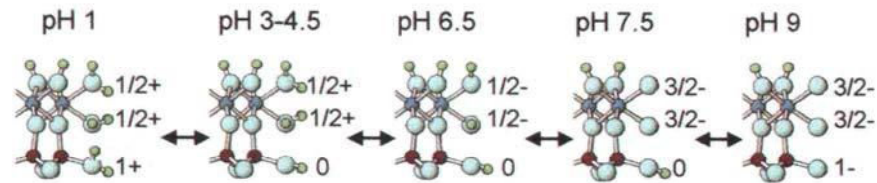
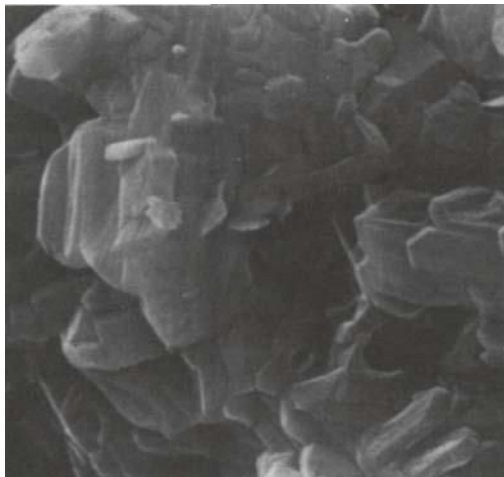
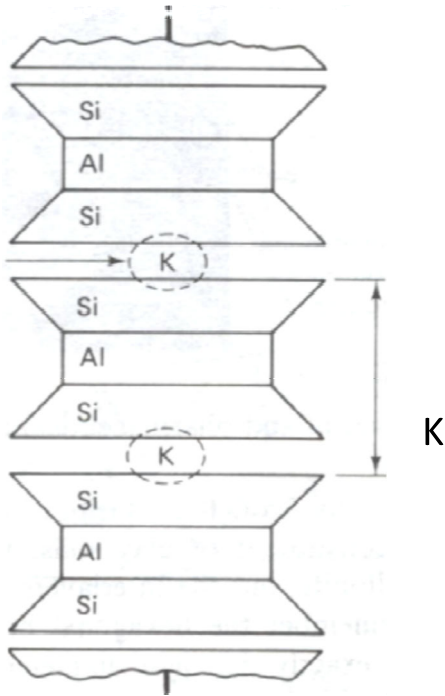


Plate 12-2. Effects of pH on the charge of the kaolinite edge that is affected by pH (modified from White and Zelazny, 1988). Color code for model is same as for Plates 12-1 and 12-3.

Minerais 2:1 – Micas (Illita)

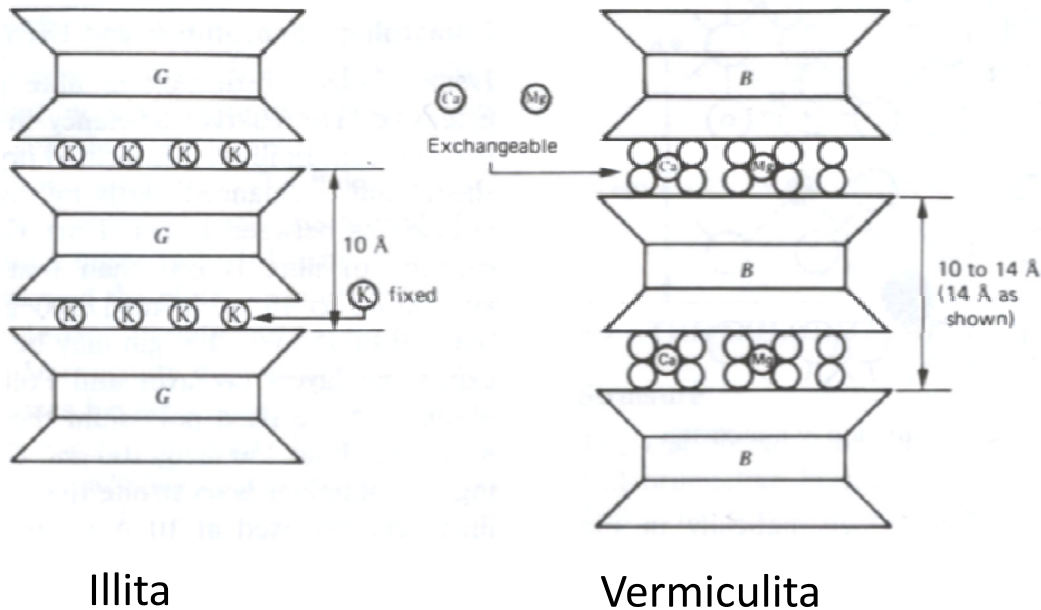


7.5 µm

Trovey, 1971 (apud Mitchell, 1993)

- 25% do Si^{4+} tetraedral é substituído por Al^{3+} , e parte do Al^{3+} octaedral é substituído por Mg^{2+} ou Fe^{2+} , o que gera deficiências de carga.
- Estas deficiências são balanceadas por K^+ entre camadas, que cabe *exatamente* na cavidade hexagonal da lâmina tetraedral, formando uma **ligação forte** entre camadas.
- O espaço basal é fixo em 10 Å, mesmo na presença de líquidos polares (i.e., **nenhuma expansão**)
- Cargas variáveis de aresta quebrada
- Illitas contribuem relativamente pouca ASE e CTC ao solo

Minerais 2:1 – Vermiculitas

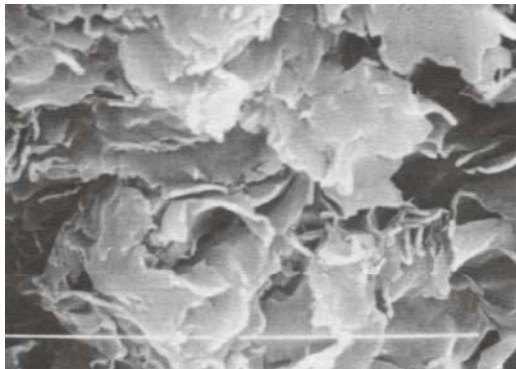
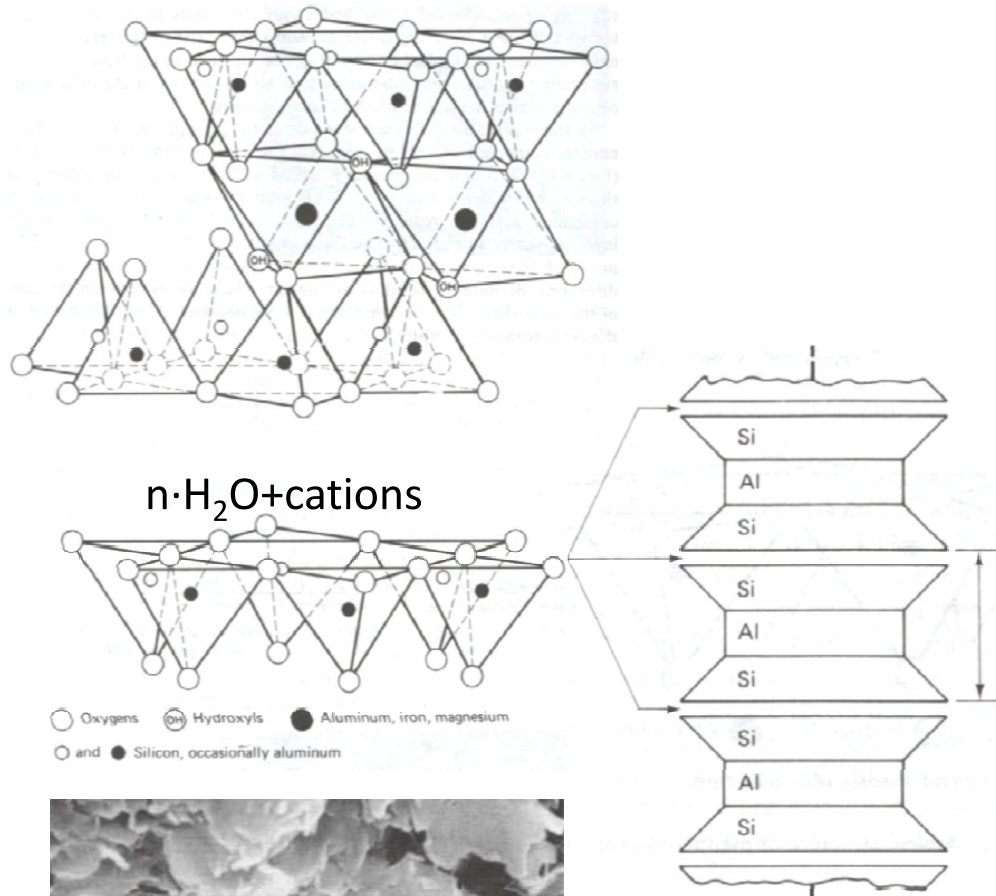


Illita

Vermiculita

- O octaedro é comumente brucita (Mg).
- SI isomórfica menor do que para micas, portanto com menor carga residual, por isso
- Em vez de K⁺ “fixo” entre as camadas, contém cátions como Ca²⁺ e Mg²⁺ e hidratados, portanto
- Permite expansão: camada variável entre 10 Å a 14 Å.
- ASE e CTC similar a esmectitas
- Entre-camada frequente.

Minerais 2:1 - esmectita



(Holtz e Kovacs, 1981)

5 μm

- Cátions e H_2O ocorrem entre camadas, portanto a distância basal vai de 9.6 a 18 Å (muito expansiva).
- Ligação entre camadas: van der Waals e cátions .
- As menores argilas. ASE até $800 \text{ m}^2 \text{ g}^{-1}$, CTC até 162 cmol kg^{-1}
- Em solos tropicais, ocorrem em alguns sedimentos recentes, áreas áridas e/ou mal-drenadas

Gibbsite: $\text{Al}(\text{OH})_3$

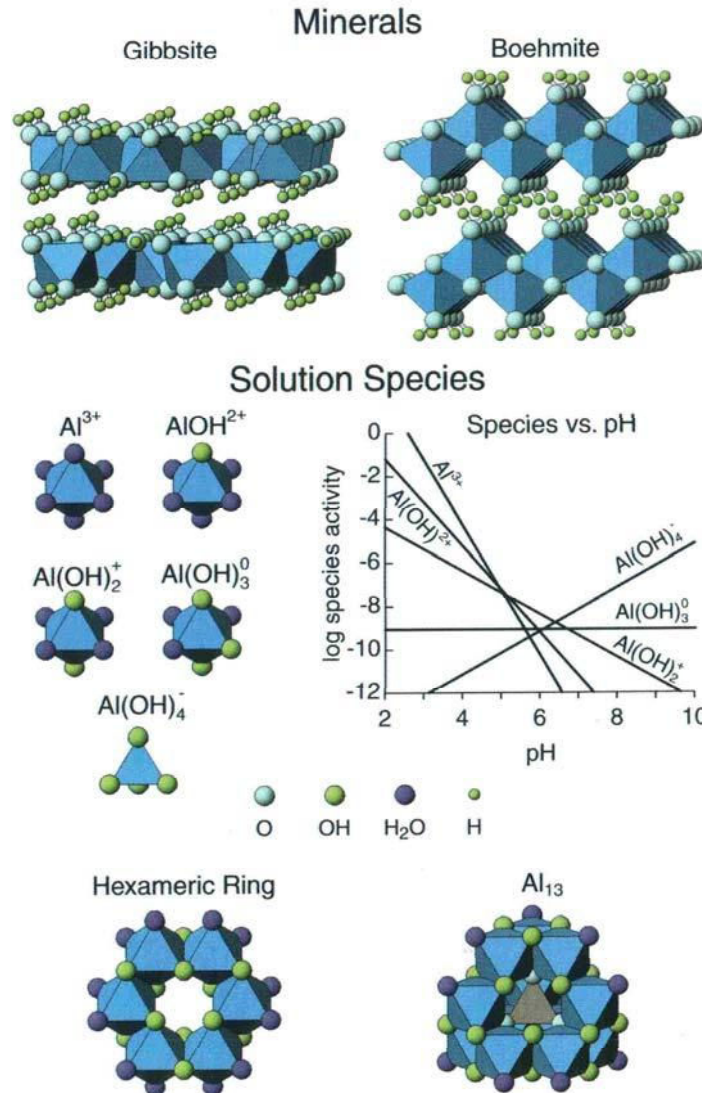


Plate 8-1. Polyhedral models of the crystal structures of gibbsite and boehmite, and of five monomeric and two polymeric Al solution species. The graph shows the distribution of activities of the monomeric solution species as a function of pH, calculated assuming equilibrium with gibbsite and using the stability constants from Bertsch and Parker (1996). The central Al-containing tetrahedron in the Al_{13} molecule is shown in gray for clarity.

- Laminar, praticamente só com carga variável de aresta quebrada
- Muito estável, pouco reativa
- $\text{Al}(\text{OH})_3$ amorfo: **extrema** ASE e capacidade de sorção

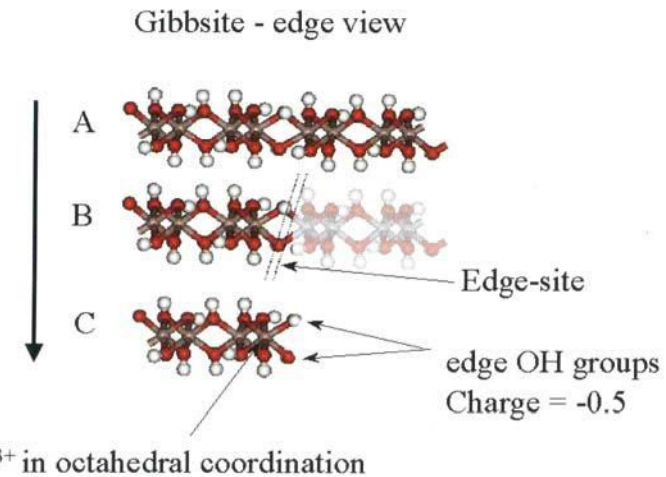


Plate 2-7. Edge sites of gibbsite. The ball-and-stick structure of gibbsite, $\text{Al}(\text{OH})_3$, is shown projected on edge (along the crystallographic b axis) at the top. (A) A larger portion of the crystal; (B) development of an edge-site, leaving two dangling Al-O bonds. (C) In the larger crystal, these bonds were connected to Al atoms with each Al atom providing a charge of +0.5. These dangling bonds are now undercoordinated and will react with water or other solutes in an attempt to complete their coordination sphere.

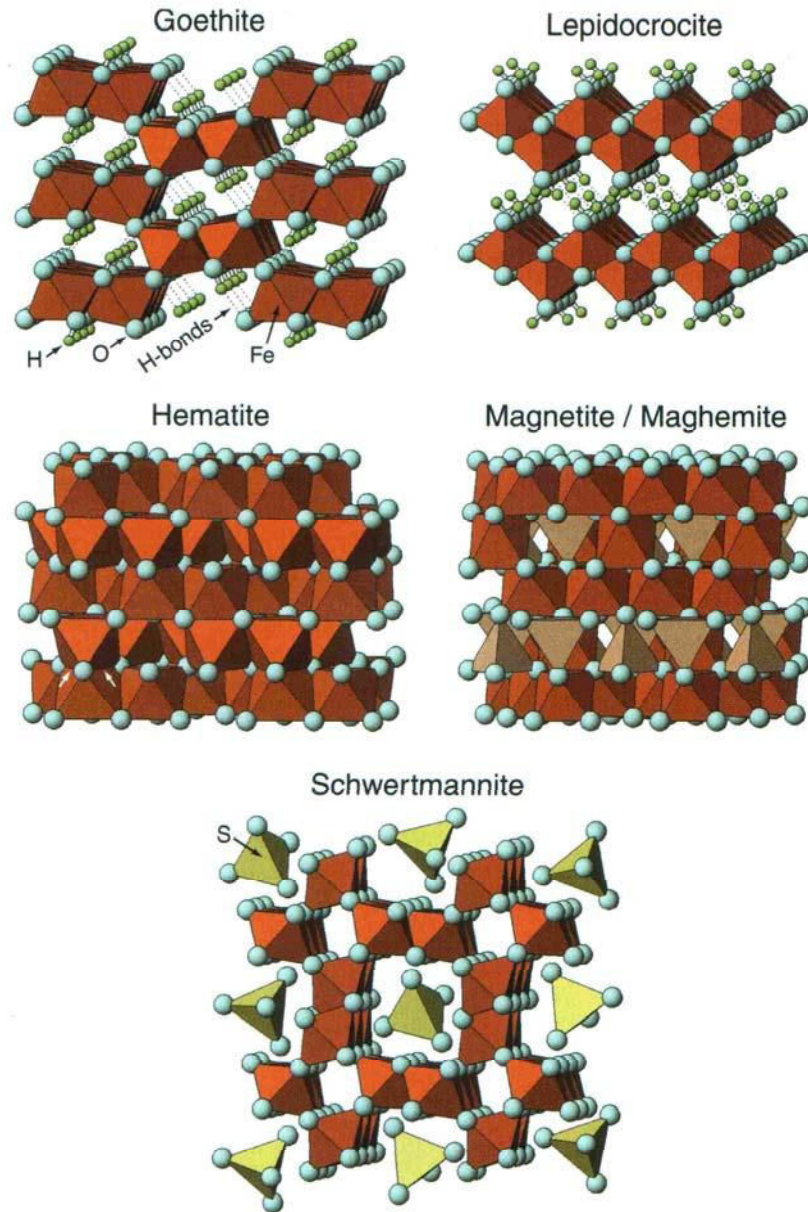


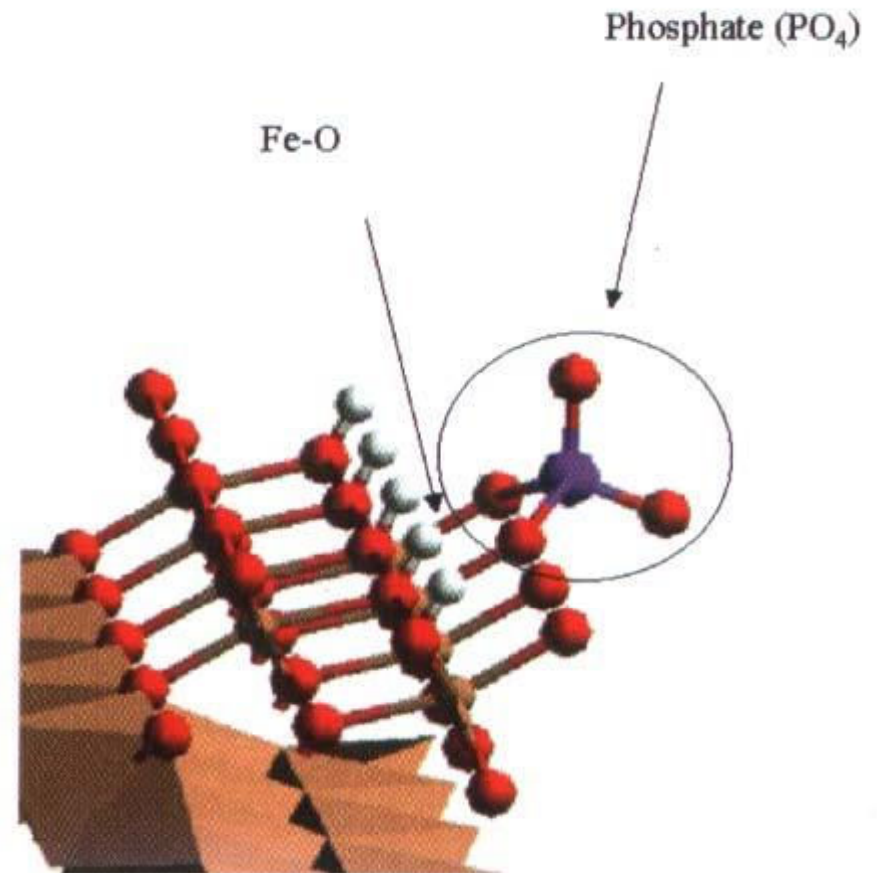
Plate 10-1. Polyhedral structure models for selected Fe oxides. Arrows in the hematite structure point to a shared face between two adjacent octahedra. Iron-containing tetrahedral sites in the magnetite/maghemite structure are drawn slightly lighter for clarity.

Óxidos de Fe

- Existem vários óxidos, oxi-hidróxidos e hidróxidos de Fe
- No solo, ocorrem esp. goethita (FeOOH) e em menor escala, hematita Fe_2O_3
- Todos virtualmente sem SI, i.e. possuem apenas cargas variáveis de aresta. ASE 50-200 $\text{m}^2 \text{g}^{-1}$,
- Goethita presente em quase todos os solos do mundo, mas esp. no trópico úmido
- Bigham et al., 2002

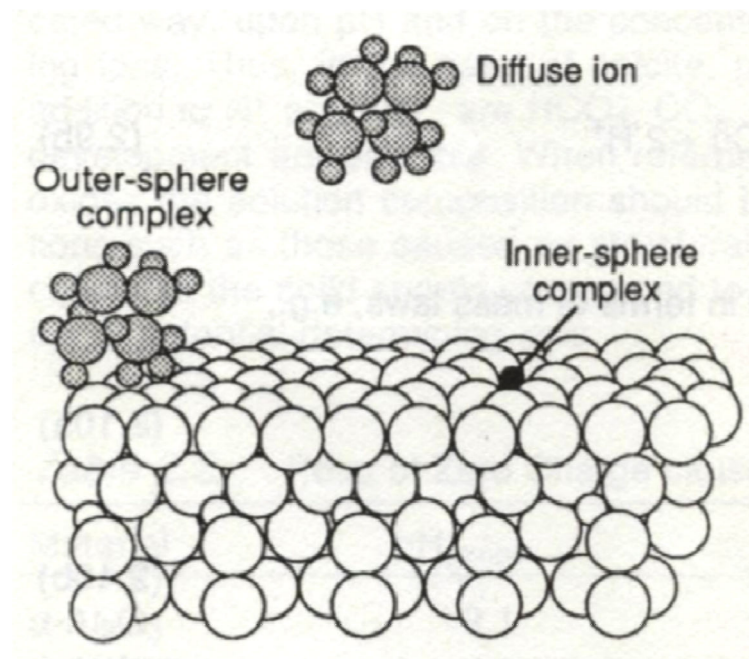
Óxidos de Fe

- As arestas quebradas possuem grande afinidade por diversos cátions hidratados (esp. ETs), mas principalmente por ânions hidratados, como o fosfato, e
- Vários ânions orgânicos
- Ferridrita e óxidos amorfos muito mais ativos e de maior ASE ($800 \text{ m}^2 \text{ g}^{-1}$)

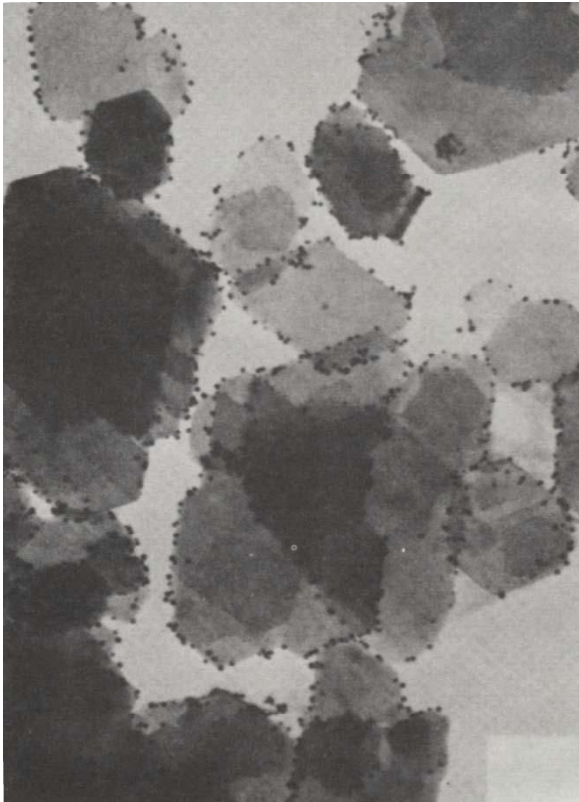


(Ad)sorção catiônica

O contato da argila com o cátion pode ser direto (*inner sphere complex*), ou indireto (*outer sphere*), intermediado pela camada de hidratação .



Ex. Sorção em aresta de caulinita



Kaolinite and negative gold sol

(van Olphen, 1991)

- Caulinita altamente cristalina de depósito geológico (caulim)
- Em pH manipulado, atrai íons de determinada carga, que podem mesmo começar a se polimerizar nas arestas quebradas – por isso são visíveis nesta imagem TEM

Modelos de interação organo-mineral

424

- Ex. Ligado à cadeia de óxido de Fe (Schulten & Leinweber, 2000)
- área ainda pouco explorada fora dos experimentos de laboratório e com óxidos sintéticos

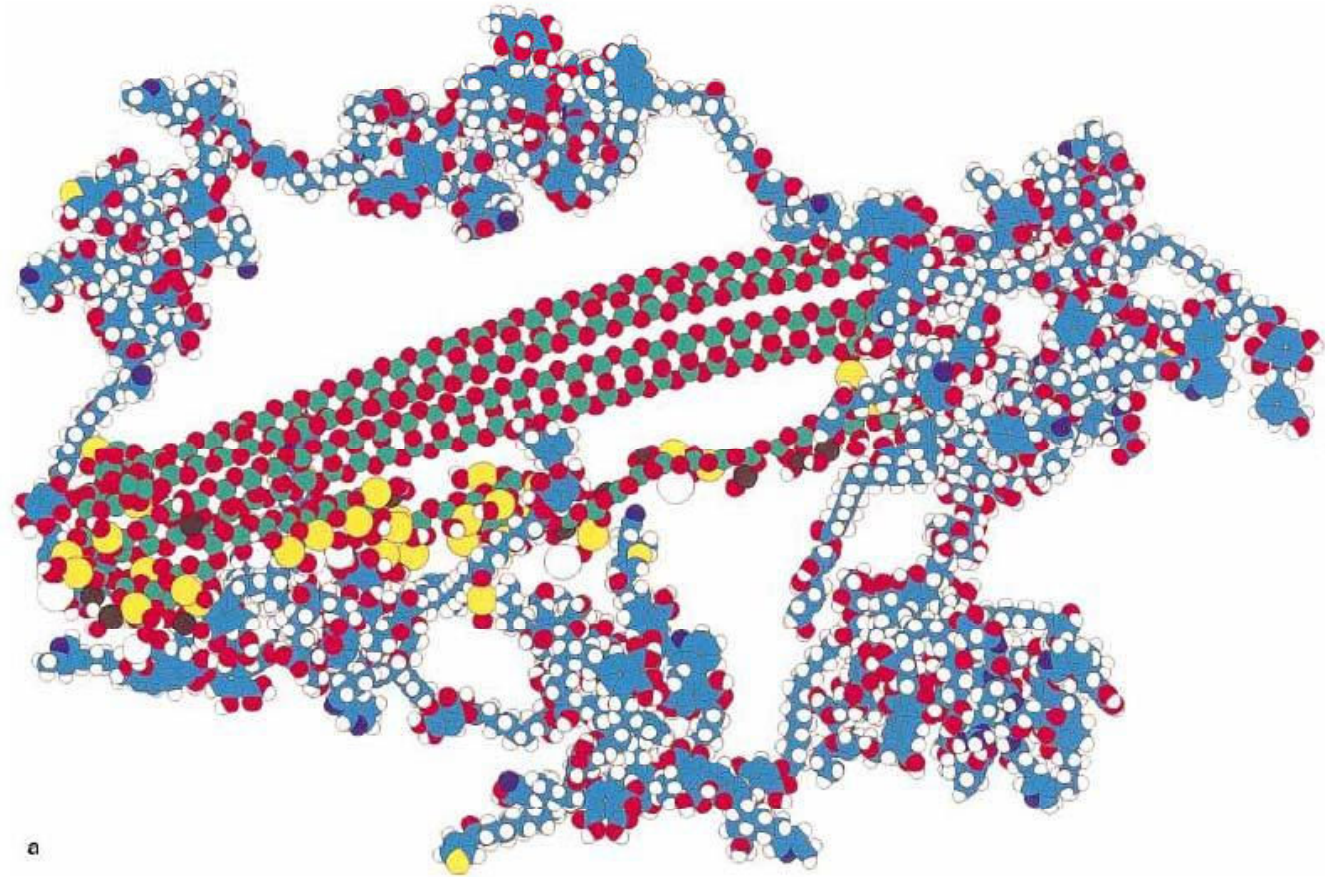
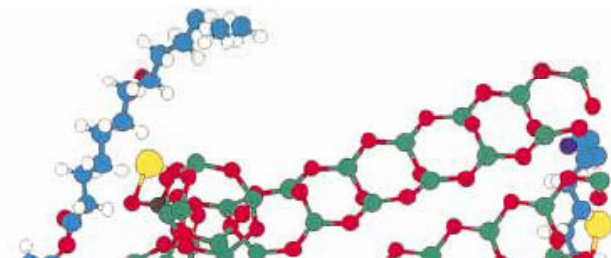


Fig. 13a,b Colour plot of a organic-mineral macromolecule (a) assembled from seven HA subunits, trisaccharides, hexapeptides, three Fe oxide chains, phosphates, and alkali- and heavy metals (part B, see text; seven molecules, 6218 atoms) and enlarged section of the Fe oxide coil entangled with covalent aliphatic chains and aromatic ring systems (b). The element colours are: yellow Al (medium size radius, 0.128 nm); yellow Ca (large radius, 0.18 nm); white K (large radius, 0.22 nm); black Mg (large radius, 0.15 nm); black P (small radius, 0.1 nm); white Na (medium radius, 0.18 nm); for other colours, see Fig. 7



Novas técnicas

- Grande potencial de uso em solos
- Lehmann et al., 2008

LETTERS

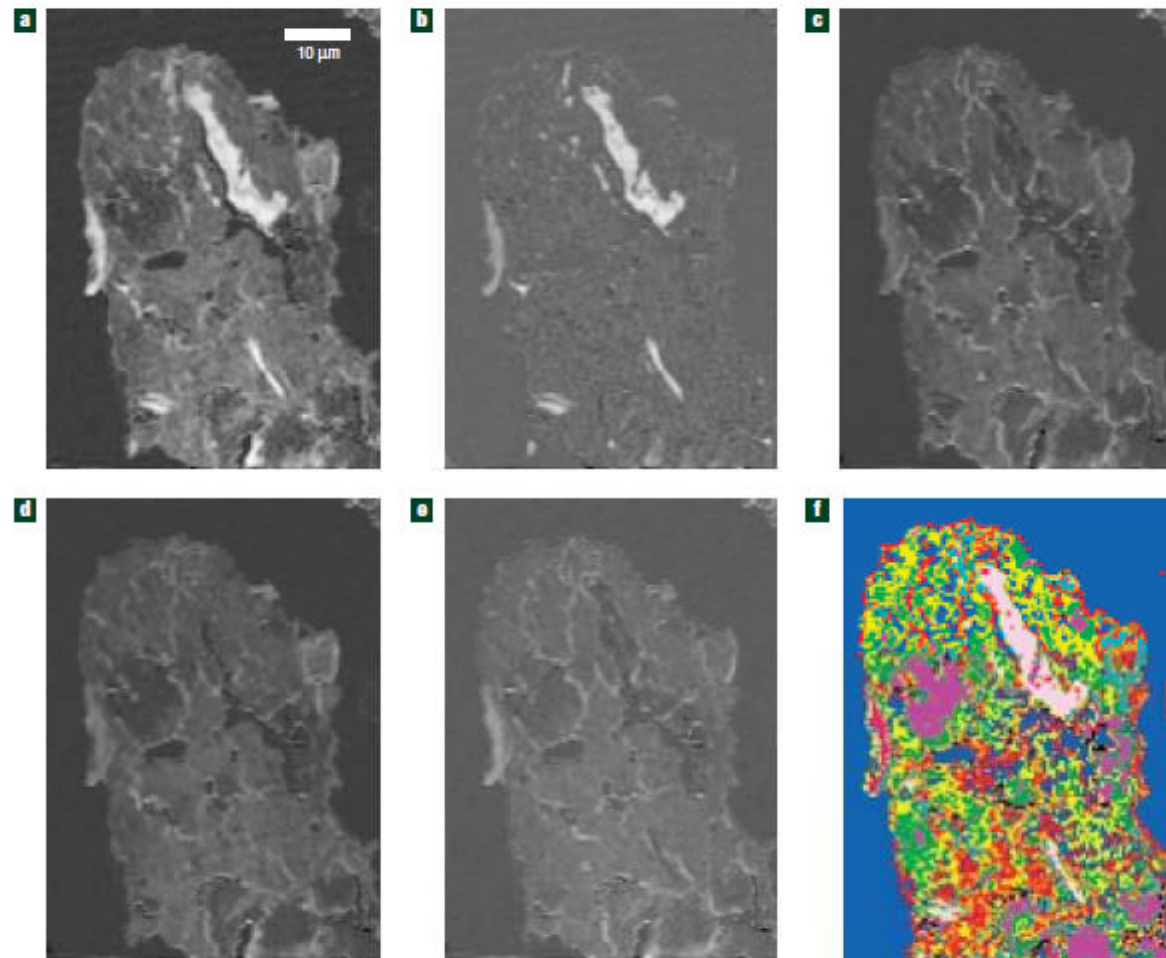


Figure 2 Distribution of carbon contents and molecular forms in a soil microassemblage from Nandi Forest (Kenya) determined by NEXAFS in combination with STXM. **a**, Total carbon (subtraction of energy region at 280–282 eV from 290–292 eV). **b**, Aromatic carbon (subtraction of energy region at 280–282 eV from 284–286 eV). **c**, Aliphatic carbon (subtraction of energy region at 284–286 eV from 287.3–287.8 eV). **d**, Carboxyl carbon (subtraction of energy region at 284–286 eV from 288–289 eV). **e**, Phenolic carbon (subtraction of energy region at 284–286 eV from 286.4–287.4 eV). **f**, Cluster map of carbon forms (clusters are shown separately with their spectra in Fig. 3).

Novas interpretações

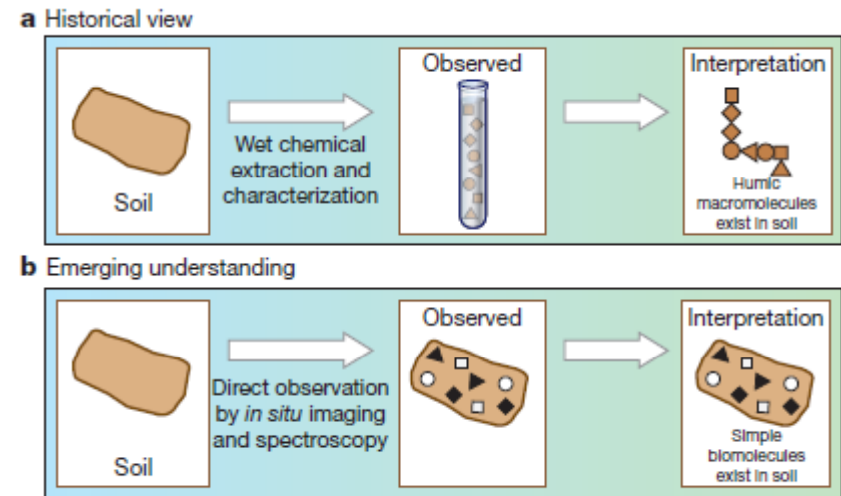


Figure 2 | In soil, the existence of humic substances has not been verified by direct measurements. a, Based on chemical analysis of the extracted materials

doi:10.1038/nature10386

PERSPECTIVE

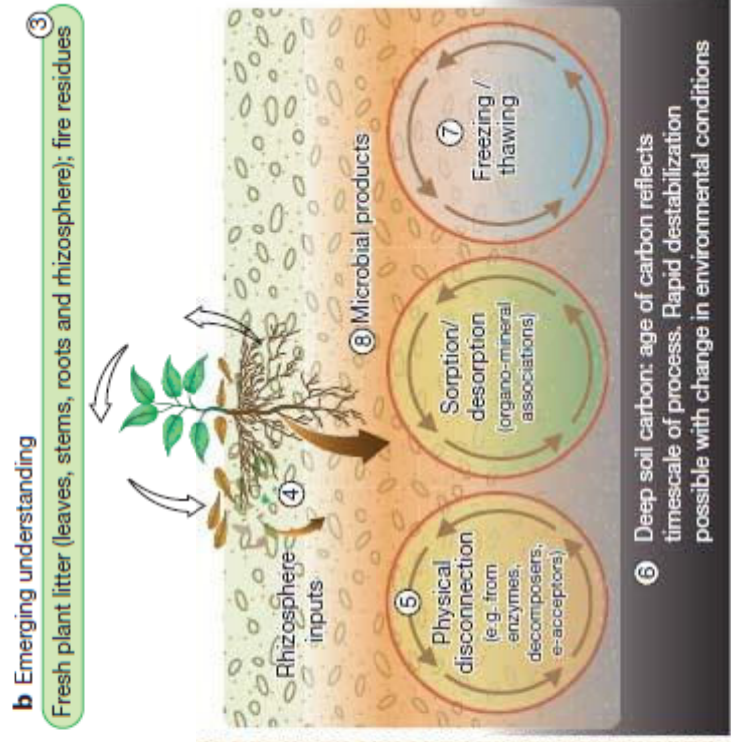
Persistence of soil organic matter as an ecosystem property

Michael W. I. Schmidt^{1*}, Margaret S. Torn^{2,3*}, Samuel Abiven¹, Thorsten Dittmar^{4,5}, Georg Guggenberger⁶, Ivan A. Janssens⁷, Markus Kleber⁸, Ingrid Kögel-Knabner⁹, Johannes Lehmann¹⁰, David A. C. Manning¹¹, Paolo Nannipieri¹², Daniel P. Rasse¹³, Steve Weiner¹⁴ & Susan E. Trumbore¹⁵

Globally, soil organic matter (SOM) contains more than three times as much carbon as either the atmosphere or terrestrial vegetation. Yet it remains largely unknown why some SOM persists for millennia whereas other SOM decomposes readily—and this limits our ability to predict how soils will respond to climate change. Recent analytical and experimental advances have demonstrated that molecular structure alone does not control SOM stability: in fact, environmental and biological controls predominate. Here we propose ways to include this understanding in a new generation of experiments and soil carbon models, thereby improving predictions of the SOM response to global warming.

Table 1 | Representation of soil carbon in ecosystem models and recommendations for potential improvements

Insight	Properties of most published models	Recommendations
1. Molecular structure	Decay rate of all pools keyed to substrate (or texture in CENTURY-type models*) and modified by moisture and temperature as constant Q_{10} above 0 °C.	Model decay rate as function of substrate properties and positions in microenvironment, microbial activity, and soil conditions including pH, temperature and moisture. See 4, 5, 6, 8.
2. Humic substances	Have a cascade of increasing intrinsic recalcitrance due to decomposition and synthesis.	Replace the cascade with cycling of organic matter into and out of microbial biomass. See 1, 8.
3. Fire-derived carbon	Do not include fire-residues as inputs or SOM. Do not represent decay of analogous substrates.	Add input pathway for fire-derived carbon. Add aromatic compounds to SOM types.
4. Roots	Parameterize litter quality with leaf/needle chemistry. Have simplified root and dissolved organic carbon inputs.	Use separate characterizations for below-ground and above-ground inputs. See 6.
5. Physical heterogeneity	Lack physical processes, such as aggregation (some have tillage factor), spatial heterogeneity, or processes that would produce priming effect†.	Non-normal probability distributions, density-dependent terms for organic matter and microbial biomass. Parameters from 3D, fine-resolution models.
6. Soil depth	No change in processes or rate constants with depth of soil or carbon input. Site-level tuning required to reproduce long turnover times.	Representations of mineral associations, root and dissolved organic inputs, and physical disconnections. Explicit depth resolution for decomposition and transport.
7. Permafrost	Lack processes governing permafrost soil carbon cycling. Lack fully coupled methane biogeochemistry.	Add O ₂ limitation and freezing effects on CO ₂ and CH ₄ production. Develop soil columns to represent inundation, permafrost thaw and thermokarst.
8. Soil micro-organisms	Treat microbial biomass as pool of active carbon. Lack effects of microbial community or enzymes on rates and decomposition products.	Create and model microbial functional types, analogous to plant functional types. Introduce full soil nitrogen cycle coupled to carbon cycle.



Lembre-se

- Há diversas superfícies nos diversos minerais do solo
- Cargas não são sempre necessárias para sorção de MOS
- No trópico úmido, embora a mineralogia seja principalmente cau+goe+gib+hem,
- Os teores, cristalinidade e intemperização desses minerais são altamente variáveis
- Espécies acessórias como illita, HIV, esmectitas, óxidos de Mn etc. podem complicar o sistema sortivo