

Electron transfer from interior Fe(II) to edge Fe(III) in reduced nontronite under anoxic conditions

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Interior Fe(II) in reduced Fe-bearing clay minerals represents a large source of electrons upon redox reactions. However, it is mysterious how the electrons are ejected from the physically isolated interior Fe(II). Here we show that electrons from interior Fe(II) in reduced nontronite (rNAu-2) can be slowly transferred to edge Fe(III) due to redox potential gradient from interior to edge. rNAu-2 was specially oxygenated for hours (obtained as “O-rNAu-2”) so that the reactive edge Fe(II) was oxidized but the less reactive interior Fe(II) was retained. Upon anoxic storage of O-rNAu-2 without exogenous electron acceptors, the fraction of edge Fe(II)/Fetot increased prominently with storing time. The rate of Fe(II) oxidation by O₂ and the resultant production of hydroxyl radicals were also boosted after anoxic storage of O-rNAu-2. Characterizations confirmed that anoxic storage altered the coordination of structural Fe(II) and balanced the ratios of Fe(II)/Fe(III) in interior and edge sites. We propose that the redox potential gradient of Fe(III)/Fe(II) from interior to edge in O-rNAu-2 drives the transfer of electrons from interior Fe(II) to edge Fe(III) with the generation of reactive edge Fe(II). The mechanism improves the underpinning of how interior Fe(II) in clay minerals responds to redox perturbations.

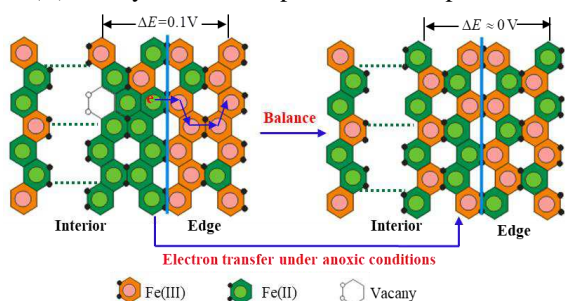


Fig.1 Mechanism of electron transfer from interior Fe(II) to edge surface Fe(III) upon anoxic storage.