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Investigations on structural iron electrochemical properties in layered silicates using massive mica electrodes

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Nuclear waste repositories are being installed in deep excavated rock formations in some places in Europe to isolate and store radioactive waste. In France, the Callovo-Oxfordian formation (COx) is a potential candidate for a nuclear waste repository. The redox reactivity (kinetics and thermodynamic redox potential) of COx clay rock samples are already under study using microscopic, spectrometric and wet analysis techniques. In order to cross and overcome certain limits by improvement in the knowledge, specific electrodes should be constructed and devoted to the deepening of the electrochemical behaviour of the COx system in different situations.

Iron is one of the most common redox species in soils and sedimentary rocks. Iron-bearing phyllosilicates play key roles in various biogeochemical processes. The complexity of the physical and chemical (along with structural) changes involving their structural iron makes the studies of its redox properties challenging. Most of the recent reported efforts were focused on probing Fe redox on finely powdered clay (and often micas) particles, and have been hampered by inadequate interactions between particles and electrodes. Moreover, such experiments usually involve redox probe ions, thus adding supplementary difficulties in the determination of structural iron redox parameters such as redox potential (Eh) and kinetics.

The present study aims at qualitatively investigating the above mentioned phenomena on minerals like iron-bearing micas (Table 1).

Table 1: List of micas, geographic origins, and structural formulas

Specie	Origin	Structural formula	Iron content (% wt)
Biotite ¹	Bancroft, Ontario	$K_{1.74}Na_{0.17}[Fe^{2+}_{2.35}Mg_{3.18}Mn_{0.11}Ti_{0.18}](Si_{5.94}Al_{1.98}Ti_{0.07})O_{20}OH_{1.97}F_{2.04}$	14.42%
Muscovite ¹	Madras	$K_{1.72}Na_{0.19}[Al_{3.84}Fe^{3+}_{0.13}Mg_{0.04}](Si_{6.1}Al_{1.9})O_{20}OH_4$	0.94%
Lepidolite ²	Unknown	$K_2[AlLi]_3(Si_6Al_2)O_{20}(OH,F)_4$	< 0.02%

1: obtained from Ward's Natural Science Establishment: ref 46V1194 (biotite) and ref 46V5474 (muscovite)

2: unknown origin

In the current work, we present initial insights regarding efforts to build a direct electrical interface between solid electrodes and conveniently shaped macroscopic mica crystals in order to investigate the redox properties of structural iron in dry and aqueous environments, in the presence of representative perturbations.

A classical three electrode system has been used for voltammetric measurements. Platinum plate (1cm²) was the counter electrode. Potentials have been measured against either silver-silver chloride electrode (Ag-AgCl/3M KCl) or Saturated Calomel Electrode (SCE/KCl_{sat}) as reference electrodes. Open Circuit Potential (OCP) measurements and Cyclic Voltammetry (CV) were realised as well as Long term OCP measurements, along with pH and other parameters, are also measured. Most of the experiments discussed here have been conducted in unbuffered NaCl or KCl 0.1 M solutions, at 25°C. Anoxic conditions were maintained by first bubbling N₂ and then maintaining a gas layer in the head space of the reactor. Long term measurements showed that in these conditions, pH stays at a value around 8.9

and is stable for several weeks. Experiments realised in buffered solution, at pH 7.5, using 1 mM Piperazine-1,4-bis(2-ethanesulfonic acid) (PIPES) and 2 mM NaOH did not show any observable change. In some experiments, 5 mM ferricyanide ($\text{Fe}(\text{CN})_6^{3-}$) have also been used as a redox probe.

High resistivities previously have been reported for this type of material, ranging from 1010 to 1015 $\Omega\cdot\text{cm}$ at room temperature. Given the current flows detection limit of the apparatus used for measuring ($\sim\text{nA}$), the mm-thick pieces used in first experiments should normally behave like insulating screens on Ag (or maybe Cu-Ag) electrodes, e.g. no current could be measured across the sample with low iron content. OCP measurement consists in measuring the electrode rest potential against a reference electrode, in absence of observable current. It provides a first indication on the type of material present on the support electrode; normally no potential should be measured in absence of an electrically conductive path. Unfortunately, first records showed that OCP can be measured immediately after the immersion of all the first electrodes prepared (Figure 1, left) even on muscovite and lepidolite, clearly indicating the presence of water in the different samples. However, signals obtained for lepidolite and muscovite are less stable and can only be conveniently recorded in absence of external perturbation around the electrode such as vibration or even air movement, whereas signals obtained for the different biotite samples are very stable. Changing parameters in the electrolyte such as pH (figure 1, right) removal of O_2 , or change in Cl^- does not seem to affect the measured OCP of this type of electrode as it stay stable for days. Several week-long monitoring on ten biotite electrodes, dipped in unbuffered NaCl 0.1 M, showed that the OCP slowly decreases and stays stable, at values between 0.1 and 0.14 mV/NHE (data not shown), despite occasional pH oscillation between 4 and 9.

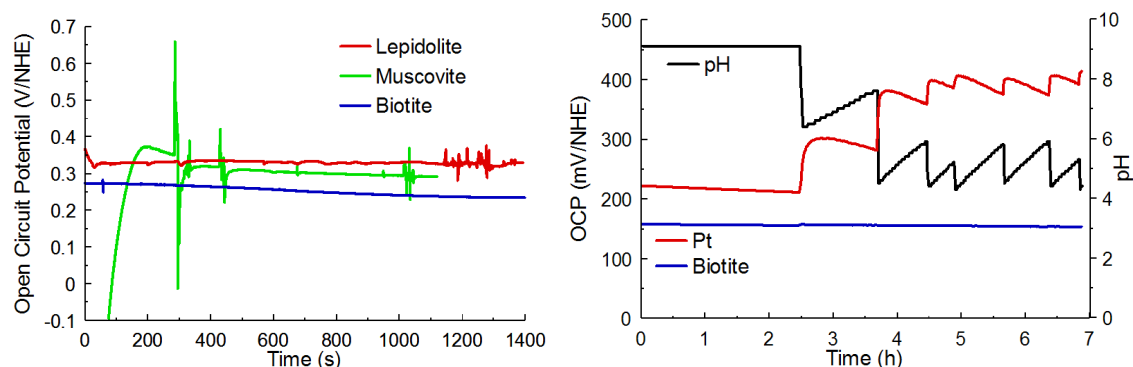


Figure 1: (left) OCP measurements recorded after immersion of various electrodes in NaCl 0.1M (pH 7.5). (right) Effects of HCl 0.1M repeated dropwise addition in the bathing electrolyte on a biotite electrode and on a platinum electrode.

Results of these experiments show that several aspects of the designs of such electrodes have to be improved for further experiments. From these observations, we can't preclude that water might participate in the electrical contact between the support electrode and the solution, but we can still hypothesize that it could be due to interlayer traces of water, offering a poorly electrically conductive path in lepidolite and muscovite, whereas another mechanism might participate in the biotite sample. First, lowering of the water content in the mineral must be realised, using smaller crystals, longer drying and vacuuming time, and using more penetrating and impregnating resins. Platinum plates and evaporated platinum or carbon are envisioned for the inert support electrode. Using thinned slices should reduce electrical resistivity of the whole bulk structure, allowing a more convenient observation of the coupled electrons transfers that might occur between separated crystal surfaces. Hence, more suitable cutting techniques, such as wire sawing, should be planned to obtain thinner slices. More mica samples must also be selected, with higher and lower iron contents than the one used in the present experiments. This first set of experiments in interfacing solid electrodes and conveniently shaped mica crystals offers hope that this will be a valuable technique for probing structural iron.

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