

ESF Short visit Grant – Final report

Applicant: Dr. Caroline Schmidt, Eberhard Karls University Tuebingen, Germany
Host: Dr. Gregory Druschel, University of Vermont, USA

Voltammetric iron measurements in freshwater sediments.

Purpose of the visit

The main goal of the visit to Dr. Gregory Druschel's laboratory at the University of Vermont, USA, was to learn using voltammetric microelectrodes. This technique allows to determine redox active species (i.e. iron, oxygen, sulfide, manganese) in aqueous systems, including profile measurements along geochemical gradients. The intention was to improve the theoretic knowledge of voltammetry, as well as learning the appropriate application of this technique using the analytical measurement system of the company AIS, Newark, USA. In addition the construction, maintenance and repair of the respective electrodes was planned to be part of the training in order to establish the application of voltammetry in the laboratory of the applicant. A major focus was on the detection of dissolved iron redox species, as most of the research projects in the applicant laboratory deal with iron-associated environmental research questions. However, the potential of this technique to measure as well other redox active species offers an excellent method to investigate other components that could be coupled to the iron cycling in geochemically stratified environments/batch systems.

The current expertise of the applicant comprises the use of potentiometric and amperometric microelectrodes. The application of voltammetry broadens the applicant's competence and allows to perform a broad range of high resolution measurements, including pH, redox potential, electron acceptor (i.e. oxygen, sulfide, ferric iron) and donor (i.e., ferrous iron, manganese(II)) concentration. These methods constitute the major techniques that are applied in the applicant's research projects (i.e. geochemical gradients in freshwater sediments, geochemical gradients in rice root systems, substrate diffusion and microbiological location in geochemical gradients). In addition, the application of these techniques is of increasing interest for various research projects in the Geomicrobiology group (applicant's laboratory).

Description of the work carried out during the visit and major results

During the first week of the visit in Dr. Gregory Druschel's laboratory the focus was mainly on the basic principles of voltammetry and the classical use of the respective microelectrodes. For this purpose the electrochemical principles have been discussed and later interpreted by means of obtained voltammograms. First measurements have been performed in lake water (representative for environmental sample with environmental ionic strength) in which iron, manganese and sulfide concentrations have been added and

consequently determined under oxic and anoxic conditions. Extensive calibrations have been performed for the different geochemical compounds in a calibration cell connecting the working, reference, and counter electrode (Figure 1a). In addition interfering physico-chemical conditions, such as pH changes, oxygenation or chemical pollution of the electrode surface (i.e. by sulfides or organic matter) during measurement have been monitored and substantially discussed.

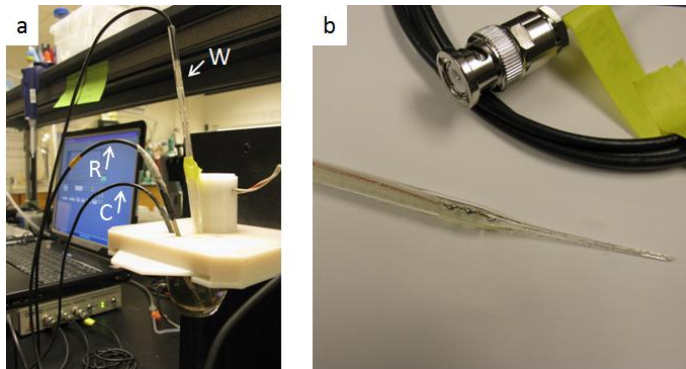


Figure 1. Set-up for voltammetric microelectrode measurement (W: working electrode, R: reference electrode, C: counter electrode) in the calibration cell connected to the potentiostat and the working computer (a). Lab-constructed working electrode for voltammetric measurements (b).

A major goal was to calibrate the electrodes for ferrous iron using the pilot-iron method (Figure 2). As ferrous iron gets oxidized immediately when it gets in contact with oxygen the exact calibration for this compound is rather intricate. For this reason the pilot-iron method has been developed, that allows to use the calibration of manganese(II) (stable in the presence of oxygen during the period of measurements) to convert the voltammetric signal into actual ferrous iron concentration.

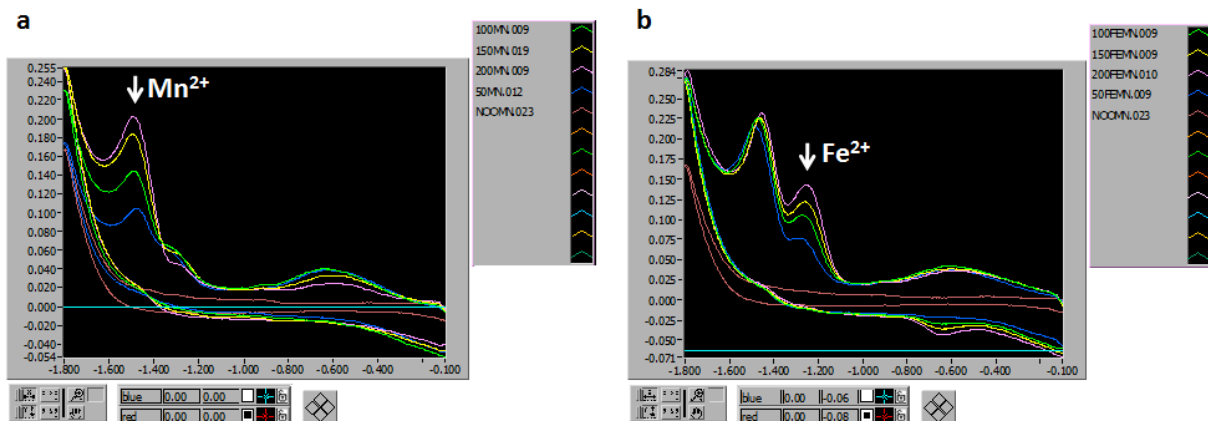


Figure 2. Screenshots of the calibration voltammograms for manganese(II) (a) and ferrous iron (b) running cyclic voltammetry using the AIS analyzing tool. The x-axis represents the potential in V and the y-axis the current in μA , respectively. The increasing peak high represents the increasing concentrations that have been chosen for calibration (0, 50, 100, 150, 200 μM). The calibration of ferrous iron has been done in the degassed fluid where the maximum manganese(II) calibration concentration was present. The comparison between the ferrous iron and manganese(II) calibration will be used for the pilot iron method, in which the more redox-stable manganese(II) can be used to calibrate voltammetric electrodes for ferrous iron).

In an ideal case the regression lines of the manganese(II) and ferrous iron calibration run parallel. Due to geochemical disturbances in the medium slight deviations might occur.

However, the correction function between the two regression lines can be used to calibrate ferrous iron with the manganese(II) signal. This comparison has to be repeated for any new medium in which measurements will be performed. During the laboratory visit the sensitivity of ferrous iron towards oxygen during the voltammetric measurement has been tested. An exact calibration applying the pilot-iron method and the comparison between the ferrous iron and manganese calibration has been performed.

In addition the signals of broken and misconnected electrodes, that mimic trouble shooting during future measurements, have been tested and interpreted with respect to their cause of defect. The data were treated using the analysis program that is provided by the company AIS, Newark, USA. The different settings of the analysis and reading programs were discussed and tested in detail in order to be well prepared for setting up the voltammetric system at the University of Tuebingen.

During the second week voltammetric electrodes were constructed (Figure 1b) and used in different samples that provide the classical media (i.e. sediments, biofilms, agar) in which most measurements in the applicants laboratory will be done. Although, this technique is planned to be mostly applied to determine the iron redox species in any kind of samples in the applicant's laboratory the detection of other redox species (i.e. S-species) has been trained as well in order to exploit the potential of the voltammetric technique and to expand the experimental/technical facilities.

The construction of voltammetric electrodes comprised a number of steps including the connection of a copper and a gold wire that were glued with Epoxy resin into a tapered Pasteur pipette. After drying the electrode surface was sanded and polished to obtain a smooth tip (gold) surface. The gold surface was later plated electrochemically with mercury, in order to create a Au-Hg alloy onto which the electrochemical reactions will take place. The electrodes were tested in oxic lake water without and under addition manganese (II). Oxygen and manganese(II) show distinct signals in the voltammogram which allows to conclude on the quality of the electrode.

Using these electrodes measurements were performed in several samples that contained typical matrices in which voltammetric analysis will be performed in the applicant laboratory. A special focus was on measurements in a freshwater lake sediment (Lake Champlain, USA) that showed a distinct redox stratification. During these measurements the decrease in oxygen and the increase in bioavailable iron fractions were monitored as a function of depth. As soon as oxygen was used up the signal for dissolved ferrous iron appeared and slightly increased in depth until it disappeared again (probably precipitation). The signal of dissolved ferric iron increased in parallel to ferrous iron. As the signal for uncomplexed dissolved ferric iron is only poorly pronounced the question arises whether the distinct peaks that were detected in the sediment samples originate from organic matter complexed ferric iron that might get chelated by microbial activity in the ferric iron reduction zone. In addition pH and redox measurements were performed in the same sediment core using conventional potentiometric microsensors. By means of this set of preliminary data first estimations on the redox zonation (incl. expansion of certain redox zones) was done.

Similar measurements will be repeated in the applicant's laboratory with fresh undisturbed sediment samples from Lake Constance (major research project of the applicant).

As a side project the sulfide redox speciation (as well as pH) was followed in biofilms that reduce elemental sulfur. It could be detected that the major species in the overlying medium was polysulfide rather than elemental sulfur accumulated in the biofilm (increasing amounts with increasing depth in biofilm). Moreover a pH profile was recorded with the same resolution through the biofilm. A slight pH decrease was measured with increasing depth in the biofilm. As this biofilm is as well capable to reduce ferric iron a future project (in collaboration with the host institute) will focus on the geochemical gradients in the biofilms grown on elemental sulfur and ferric iron in separate undisturbed (not shaken) set-ups.

In addition preliminary test measurements have been performed in gradient experiments in which a layered agar matrix contains ferric iron, an electron shuttle and iron reducing bacteria (from bottom to top). Due to long distance electron shuttling between bacteria and ferric iron minerals, iron reduction would occur in the lower layer and an increasing ferrous iron concentration should be measured. The major goal of these first measurements was to understand the functioning of voltammetric electrodes in the different measuring matrices and to detect possible interferences therein. The described test measurements will be repeated in the applicant's laboratory in well preserved/conditioned samples in order to follow precise research questions and to gather a substantial data set for peer-reviewed publication.

Future collaborations with host institution

After this visit it is intended to keep close contact with the host laboratory in order to have exchange on data analysis of obtained voltammograms. The test measurements on the described iron-reducing and sulfur-reducing biofilms provided interesting insights on biofilm geochemistry. A potential future cooperation research project between the host and the applicant laboratory will address geochemical variations/gradients within these biological structures.

Projected publications to result from the grant

This research grant has offered the possibility to learn how to use voltammetric microelectrodes, their technical limits with the goal to establish this technique in the applicant's laboratory. Current research projects in the Geomicrobiology research group require the application of this technique. The expected results of these projects will lead to peer-reviewed publications in which ESF and the FIMIN funding will be acknowledged.

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