

Development of a micro-interdigitated electrode array for use in high precision TIMS-based isotope ratio determinations

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Thermal ionization mass spectrometry (TIMS) remains the method of choice for high precision Pb isotopic measurements, but “silica gel” techniques used to generate thermalized Pb ions have ionization efficiencies of only 10% at best. To improve Pb ionization efficiencies from liquid glass ion emitters and ultimately the precision of U-Pb age determinations we are using electrochemical techniques to increase Pb ionization efficiencies *in situ* in liquid glasses. Our initial work demonstrated that Pb-doped high temperature (~1,300°C) liquid glass can serve as the electrolyte in an electrochemical cell and that Pb metal atoms prevalent in the glass under vacuum conditions can be oxidized to Pb⁺ by the application of ~1V across Pt wire electrodes. To take advantage of this ionization mechanism, we are developing a micro-interdigitated electrode array (IDA) for use as an “electrochemical” ion source. This array consists of a “comb” structure of interleaved tungsten electrode “fingers” sputtered onto a pure silicon wafer. The array fabrication process includes spinning photoresist on an oxidized 275µ thick silicon wafer and exposing the wafer to UV light through a photomask. The DC sputter deposition system applies a 1µ layer of tungsten to the wafer. A photoresist liftoff procedure removes most of the metal layer, leaving the IDA structures on the wafer. The electrode lengths and widths range from 100-200µ and 10-200µ, respectively. There are 1-14 pairs of these electrodes on each IDA, with gap widths of 10-15µ. Our initial results reveal that a Pb-doped silica suspension can be dried and melted on the IDA surface by a metal ribbon resistive heater placed in contact with the electrically non-conducting silicon wafer substrate of the IDA. Our next step will be to install the IDA and heater ribbon in a Finnigan-MAT 261 TIMS, and to connect the assembly to a specially-designed potentiostat that will allow the IDA to float at 10KV while a differential voltage from 0.1 to 10V is applied across the IDA electrodes. This work is currently in progress.

Potential for manganese oxidation in shallow groundwater induced by water table fluctuation

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On-off cycles of production wells, especially in bank filtration settings, cause oscillations in the local water table, which can entrap significant amounts of dissolved oxygen (DO) in the shallow groundwater. Although attempts to quantify air entrapment and transport in groundwater are ongoing, less attention has been paid to the potential geochemical reactions initiated by DO introduction to low-DO groundwater.

The potential for DO introduced in this manner to oxidize manganese (Mn), mediated by the obligate aerobic *Pseudomonas putida* GB-1, was tested in a column of quartz sand with anoxic influent solution and 1.3-m water table changes every 30-50 h. The frequency and amplitude of the oscillations simulated those of a bank filtration site in Berlin, Germany. After a period of filter ripening in the column, 100 µM Mn was rapidly removed during periods of low water table and high dissolved oxygen concentrations. The accumulation of Mn in the column was confirmed by XRF analysis of the sand at the conclusion of the study, and both measured net oxidation rates and XAS-derived speciation suggest microbial oxidation as the dominant process. The addition of Zn, which inhibited GB-1 Mn oxidation but not its growth, interrupted the Mn removal process, but Mn removal recovered within one water table fluctuation. Thus transient DO conditions could support Mn oxidation, and the conditions under which this process could be relevant in shallow groundwater in alluvial sediments will be presented.