

## Voltammetry as a tool for detecting metal sulfide particles and nanoparticles in natural waters

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This paper deals with voltammetric characterization of metal sulfide particles and nanoparticles (PbS, HgS, FeS, CdS, Ag<sub>2</sub>S and CuS) at the Hg and the glassy carbon electrodes in 0.55 M NaCl + 0.03 M NaHCO<sub>3</sub> electrolyte, pH = 8.5. The aim was to investigate a possibility of using voltammetry in the detection of metal-sulfide nanoparticles in natural waters. The proposed electrochemical approach was applied in the detection of metal sulfide particles in two stratified lakes: saline Rogoznica Lake on the eastern Adriatic coast and Lake Pavin, a crater lake in the Central Massif, France.

The results of this work demonstrate that Pb, Hg, Fe, Cd, Ag and Cu sulfides, either as suspended powders or as precipitated nanoparticles, yield cathodic peaks between -0.9 and -1.7 V. Different experimental conditions (i.e. ageing of the particles, deposition potential and accumulation time) can affect shapes and positions of these reduction peaks. In anoxic natural samples, reduction peaks similar to those observed in model solutions were detected suggesting that voltammetry is a promising method for determination of metal sulfide nanoparticles. However, reduction peaks in the same potential range have been observed by other authors, who assigned them to the reduction of multimeric FeS(aq) complexes or clusters. The key findings of this work that other analytes: Cu<sub>2</sub>S, CuS, PbS, HgS, CdS, Ag<sub>2</sub>S nanoparticles, metal sulfide powders and sulfur powder produce similar reduction peaks. Therefore, here, we propose an experimental procedure to clarify the origin of voltammetric peak around -1.1 V in anoxic natural waters.

## Thermodynamic properties and stability of the high-pressure silicate ellenbergerite in natural systems

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Ellenbergerite, [(Ti,Zr)<sub>2</sub>Mg<sub>2</sub>□<sub>2</sub>]Mg<sub>18</sub>Al<sub>18</sub>[Si<sub>24</sub>O<sub>84</sub>(OH)<sub>30</sub>], was first described by Chopin *et al.* (1986) as inclusions in pyrope megacrysts from the Dora-Maira UHP-quartzites of Parigi, western Alps, Italy. Three major endmembers are known: two silicate endmembers (titanian and zirconian ellenbergerite) and an isostructural Mg-phosphate endmember (phosphoellenbergerite), along with the isostructural iron-arsenite ekatite. The upper thermal and the lower-pressure stability limits of Ti-ellenbergerite were determined by Chopin *et al.* (1992) and the limiting lower pressure / lower temperature reaction by Burchard *et al.* (2001). The upper thermal and lower-pressure stability limits of Zr-ellenbergerite were determined by Burchard & Schreyer (1996). Comodi & Zanazzi (1993 a & b) published compressibility and thermal expansion data.

All these data were used to retrieve the entropy and the enthalpy of formation of Zr- and Ti-ellenbergerite at standard conditions ( $H^{\circ}_{f,298,Ell}$ ,  $S^{\circ}_{298,Ell}$ ). The Gibbs free energy of formation of both ellenbergerite endmembers ( $G^{\circ}_{f,T,P,Ell}$ ) was calculated for all experimental brackets from  $G^{\circ}_{f,298}$  of all other involved phases using the datasets of Berman (1988) and Holland & Powell (1990 & 1998). The Cp functions of ellenbergerites, calculated according to Berman & Brown (1985), and the volume data of Comodi & Zanazzi (1993 a & b) were used to extract single values of  $H^{\circ}_{f,298,Ell}$  and  $S^{\circ}_{298,Ell}$  for each experimental bracket. The final values were retrieved by non linear optimization of the single values. The ellenbergerite stability curves calculated from these optimized data are in good agreement with all experimental brackets. Further calculations show that the ellenbergerite stability field is highly sensitive to water activity and bulk iron content of the rock, which may justify the rarity of ellenbergerite in nature.

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