Experimental study of stibnite solubility and antimony complexation in aqueous sulfide solutions from 20 to 95˚C

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Modeling antimony transport and mobility in natural hydrothermal systems and mitigation of stibnite (Sb_2S_3) scaling in geothermal power stations require precise data on changes in stibnite solubility in response to small changes in pH, sulfide concentration, pressure and temperatures between 20˚C and 350˚C. There is some uncertainty in stability and stoichiometry of antimony(III) sulfide and hydrosulfide species (i.e. thioantimonites and oxythoantimonites) at 25˚C and at higher temperatures, the nature of the thioantimony(III) stoichiometry is poorly constrained.

We have conducted flow-through solubility experiments with natural stibnite to detemine the solubility of stibnite in aqueous sulfide solutions from pH 6.1 to 12.7 and sulfide contents from 0.01 to 0.06 molal S_{total} at 22˚C. Higher temperature experiments up to 60˚C have been completed at pH 11.1 and 0.006 molal S_{total} and experiments up to 95˚C and at variable pH are on-going. Our experimental results are similar to the solubilities found at 25˚C by [1]. Krupp(1988) concluded that $H_xSb_2S_4^{2-x}$ species are dominant between pH 3 to 12. We note that for arsenic(III)-sulfide/hydrosulfide interactions, the dominant thioarsenite stoichiometry is apparently as the $As(HS)_3$ moiety [2], [3], [4]. At 60˚C, our solubilities are also similar to solubilities extrapolated to higher pH and temperature from [1] but predict lower solubilities at 90˚C. Our measurements will provide a complete set of stibnite solubility data from 22˚ to 95˚C in reduced, sulfide-containing fluids and permit a new evaluation of the stoichiometry and stability of thioantimonite species over this temperature range.

References

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Regional Erosion Surfaces and Climatic Readjustments, Midwest USA: Clues from late Pleistocene loess and paleosols (OIS 5e-2)

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Background

In the Midwestern, USA, early Wisconsinan time was marked by a series of events that until recently were not clearly linked to post-glacial climatic readjustment on a regional scale. Areas outside the Wisconsinan glacial border and adjacent to major river divides in several Midwestern states were examined in an attempt to locate similar adjacent regions on a scale comparable to continental glaciations.

Studies in the early 20th Century in northeastern Iowa identified an extensive erosion surface [1]. Buried by late Wisconsin loess, this surface cut the entire stratigraphic section from the Wisconsin till to the pre-Illinoian till and thus established its relative age as younger than Wisconsin till and older than late Wisconsin loess deposition. Radiocarbon dates for basal Wisconsinan soils, the uppermost unit truncated by the erosion surface, indicated an age of generally greater than 18000 BP. That age indicates its development was a direct response to shifts in climate associated with glacial retreat.

Wisconsin glaciation extended through much of the upper Midwest but at that time, there was no evidence that the surface in Iowa had parallels in adjacent regions. In the 1980's, we began studies of the Ohio/Wabash stream divides in southeastern Indiana traditionally known as "Illinoian till plain' stratigraphically, late Wisconsin loess overlying Illinoian till. From the investigations, it was determined that although the loess was present in a uniformly continuous blanket across these areas, there was little or no Illinoian till beneath. The late Wisconsin loess lay directly on bedrock, pedisediment, or older tills. Borings on subdued highs revealed that these erosional outliers contained complete stratigraphic sections that had been sequentially truncated by an erosions surface [2, 3]. Hidden beneath loess, this erosion surface had cut the slopes that descend in all directions from the remnant outliers to form the floor of the 'till' plain.

Recent Regional Evidence

The Mississippi/Ohio divide in southern Illinois within the Illinoian drift border and well south of the Wisconsinan drift border were examined most recently. Multiple coring sites and soil pits were located near the divides of tributaries to the Big Muddy River drainage. Here, as in Indiana and Iowa, undisturbed thicknesses of late Wisconsin loess directly overlie bedrock, pedisediment or older drift revealing erosional surfaces. Illinoian till is present only in protected coves of the subsurface landscape.

Conclusions

During the waning phases of the last glaciation in North America, a period of significant subaerial erosion occurred that remained largely unknown and undocumented, in part because of a lack of exposures and the difficulty in developing subsurface stratigraphic landscapes. The relative synchroneity, extent, and number of erosion surfaces outside the Wisconsinan drift border suggest a subaerial response to shifts in climatic events occurring during and immediately following the withdrawal of the last glacial ice sheet.

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