Advanced Electrochemical Studies of Hydrothermal Systems

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Advanced high temperature electrochemical measurements were made by (1) potentiometric techniques and (2) an electrokinetic method.

(1) A recently developed potentiomentric cell has been employed to measure the association constant of HCl(aq) at temperature up to 400°C using an advanced flow-through, yttria-stabilized zirconia pH sensor. The measured association constants are given in the table below.

T, °C	P, bar	ρ, g cm^{-3}	- pK, observed	- pK compilation
320	230	0.699	1.46	1.55
350	230	0.617	2.35	2.39
365	276	0.585	2.87	2.74
380	276	0.543	2.91	3.17
390	281	0.420	4.03	4.10
400	265	0.206	4.59	6.20

Comparison of our experimental data with a compilation, presented as an empirical analytical equation of Lvov et al. (2000), showed that within the uncertainty of our experimental measurements (±0.1 pK units), the data agree with calculated values thereby supporting the validity of this measurement and the reliability of our potentiometric technique.

(2) Another recently developed technique is a high temperature microelectrophoresis cell, which was employed for measurements of zeta potential at the zirconia/aqueous solution interface over a wide range of pH at temperatures up to 200°C. The data obtained allowed us to estimate the isoelectric points of 5.8 at 25°C and 4.8 at 200°C. The obtained zeta potentials can be used for studying the water-rock interactions in hydrothermal conditions. Also, understanding mineral surface and adsorption behavior in hydrothermal systems is necessary to model the transport processes of dissolved species in deep groundwater and in nuclear repository facilities.

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References

Lvov S.N., Zhou X.Y., Ulyanov S.M., and Bandura A.V. (2000), *Chemical Geology*, 167, 105-115.

Sea surface temperature patterns in the Early Holocene: Global Ocean response to insolation forcing

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The early Holocene (before about 5 kyr bp) is often thought of as a time period warmer than the present, and is referred to in terms such as the "Hypsithermal" or "Climatic Optimum". We compile sea surface temperature data (SST) from the published literature which, in agreement with our model results, shows that while there is high latitude warmth, there is broad cooling in low latitudes suggesting that, globally, the Early Holocene was not dramatically warmer than present.

Early Holocene summertime warmth has long been inferred on land in the Northern Hemisphere. Recent high resolution data suggest that SST was warm not only in the high latitude North Atlantic, but in the Antarctic as well. Reconstructions from low latitudes (based on faunal assemblage data, Mg/Ca ratios, and alkenone indices) show slightly cooler SST during the Early Holocene. In addition, the data in the tropical Pacific shows enhanced zonal and meridional SST gradients such as are found during "La Nina" type conditions today.

Modelling studies show that orbitally driven insolation changes result in SST patterns very similar to those inferred from the paleoceanographic data. While changes in precessional forcing dominate the Holocene trends in monsoon activity and continental temperature, the symmetrical SST response (cool tropics, warm poles) reflects the importance of changes in the tilt of the earth's axis in determining the patterns of ocean temperature. The models also show a more "La-Nina" like temperature pattern in the Early Holocene tropical Pacific. While this is most likely a response to changes in seasonality (precession) at low latitudes (e.g. Clement et al., 1999), it reinforces the tropical cooling produced by changes in orbital tilt.

References

Clement, A.C., Seager, R., and Cane, M. (2000), *Paleoceanography*, **15**, 731-741.