pH-Eh diagram of ore-forming elements from first principles molecular dynamics simulations

XIANDONG LIU[12], MICHIEL SPRIK[2], JUN CHENG[2], XIANCAI LU[1] AND RUCHENG WANG[1]

[1] State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210093, P. R. China

[2] Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom

pH-Eh diagram maps out the stable species of an aqueous elecrochemical system with respect to the activity of proton and electron under a certain T-P condition. Such diagram presents the fundamental properties of aqueous species, which is very useful for understanding numerous natural processes, such as transport and enrichment of elements. Research of aqueous speciation has heavily relied on solubility experiments and related thermodynamics calculations. Due to the experimental difficulty in high T-P conditions, first principles molecular dynamics (FPMD) simulations have been attracting more and more attentions.

FPMD based vertical energy gap method was an advanced technique developed recently by our group (Adriaanse *et al*.., 2012; Costanzo *et al*.., 2011), which combines electronic structure calculation, MD and free energy perturbation theory. With this method, one can evaluate the ingredients for making pH-Eh diagrams of aqueous complexes: acidity (p*K*a) and redox potential (pE). In this presentation, we will show the results of important ore-forming elements. The p*K*a case studies include H_2S_n/HS_n^-, Zn^{2+} and Cu^{2+}. The calculated redox couples are Cu^+/Cu^{2+} and Fe^{2+}/Fe^{3+}. Comparisons between the calculated and experimental values indicate a reasonable accuracy. Origins of the error such as density functionals and finite size effects will be discussed.

[1] Adriaanse C., Cheng J., Chau V., Sulpizi M., VandeVondele J. and Sprik M. (2012) Aqueous Redox Chemistry and the Electronic Band Structure of Liquid Water. *Journal of Physical Chemistry Letters* **3**: 3411-3415. [2] Costanzo F., Sulpizi M., Della Valle R.G. and Sprik M. (2011) The oxidation of tyrosine and tryptophan studied by a molecular dynamics normal hydrogen electrode. *Journal of Chemical Physics* **134**.

Roles of NH_4NO_3 and secondary organics in growing > 10 nm new particles to cloud condensation nuclei size in marine atmosphere

XIAOHUAN LIU, YUJIAO, ZHU, HE MENG, GAO HUIWANG AND YAO XIAOHONG

[1] Key Laboratory of Marine Environment and Ecology, Ministry of Education of China, Ocean University of China, Qingdao 266100, China

A Fast Mobility Particle Sizer was used to investigate new particle formation events over the marginal Sea in China during two cruise experiments in the falls of 2010 and 2011. New particles cannot grow over 30 nm in three out of four new particle formation events in 2010. The air quality modeling results showed that formation of secondary organics (SO) occurred through the events, formation of NH_4NO_3 was thermodynamically forbidden. SO was likely the major contributor to the growth of > 10 nm new particles. In one event, new particles grew over 50 nm (the threshold of particle acting as cloud condensation nuclei (CCN)) and the modeling results showed formation of NH_4NO_3 and SO being concurrently with the growth of > 10 nm new particles. However, the formation rate of SO in the event was significantly less than that in one out of the three events. Formation of NH_4NO_3 was proably the key factor in growing > 30 nm new particles to CCN size and formation of SO may play an important role in growing particles <30 nm. In 2011, a regional nucleation event was observed in the marine and coastal atmosphere and formation of NH_4NO_3 was identified from the modeling and was probably the key factor in growing > 30 nm new particles to CCN size.

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