

## The copper deposit of Gaoua, Burkina Faso: A Paleoproterozoic porphyry deposit

E. LE MIGNOT<sup>1,2\*</sup>, L. SIEBENALLER<sup>3</sup>, D. BEZIAT<sup>4</sup>, S.  
SALVI<sup>4</sup>, A.-S. ANDRE-MAYER<sup>1</sup>, L. REISBERG<sup>2</sup>  
AND G. VELASQUEZ<sup>4</sup>

<sup>1</sup> GéoRessources, Université de Lorraine, BP239, 54506  
Vandoeuvre-lès-Nancy, France

(\*correspondence: elodie.le-mignot@univ-lorraine.fr)

<sup>2</sup> CRPG/CNRS, 54501 Vandoeuvre-lès-Nancy, France

<sup>3</sup> IRD GET, 31400 Toulouse, France

<sup>4</sup> GET, Université Paul Sabatier, 31400 Toulouse, France

The copper occurrence of Gaoua is located in the Boromo-Goren greenstone belt, southern Burkina Faso. In this deposit, copper mineralization is predominantly present in the form of chalcopyrite and is hosted in Paleoproterozoic volcanic and plutonic rocks of andesitic to dioritic composition.

Geochemical analyses of the host diorite and andesite suggest an island arc setting for the formation of these rocks. Brecciation is widespread, accompanied by abundant chalcopyrite ± anhydrite in the matrix, as are quartz ± carbonate veins, which commonly form stockwerk-like networks. Microthermometric analyses of fluid inclusions indicate high temperature (>400°C) and high salinity fluids (>30% wt% eq. NaCl), related to hydrothermal fluid circulation contemporaneous to diorite intrusion and andesitic volcanism. The above data suggest that the copper mineralization formed in a porphyry-type context.

Pyrites and molybdenites associated with the porphyry mineralization were dated by the Re-Os method. The resulting isochron yields an age of 2170 ± 40 Ma, corresponding to a pre-Eburnean magmatic accretion event. Paleoproterozoic porphyry deposits are very rare since they form at shallow depths and, therefore, are very sensitive to erosion. Nevertheless, the high Re and radiogenic Os contents, together with the low common Os contents of the dated pyrites and molybdenites, argue for the reliability of the data.

## FT-ICR Mass Spectrometric and Density Functional Theory studies of Solvated Cerium Chloride Clusters

KONO H. LEMKE<sup>1</sup> AND YIN ZHAO<sup>1</sup>

<sup>1</sup>Department of Earth Sciences, University of Hong Kong,  
Pokfulam Road, Hong Kong, SAR, China (kono@hku.hk)

The molecular-scale speciation of cerium in aqueous fluids (bulk liquid and vapor phase) is a primary field of interest with important implications for our understanding of the transport and deposition of REE's in the Earth's crust. Mass spectrometric and quantum chemical studies of cerium chloride solutions can provide important insight into the composition, structure and energetic properties of molecular cerium species, and as such, deliver new information with respect to the distribution and abundance of such materials in aqueous fluids.

Here we present results from electrospray ionization (ESI) Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometric experiments of cerium chloride complexes and clusters in the gas-phase, in particular, clusters of the general form  $[\text{Ce}_m\text{X}_n]^+$  ( $\text{X}=\text{Cl}, \text{OH}, \text{O}$ ) and corresponding micro-solvated species. We also report equilibrium geometries and associated energetic properties using M06/cc-pVXZ-PP ( $\text{X}=\text{D}, \text{T}$ ) level theory in combination with quasi-relativistic effective core potentials for Ce. Ion cluster experiments have been conducted on a custom-modified Bruker-Daltonics 7T FT-ICR mass spectrometer with temperature-control, ESI capability and pulsing valves facilitating ion-solvent reactions. Molecular species identified upon electrospray ionization of aqueous  $\text{CeCl}_3$  include a)  $[\text{CeCl}_2]^+(\text{H}_2\text{O})_n$ ,  $[\text{CeClOH}]^+(\text{H}_2\text{O})_n$  and  $[\text{Ce}(\text{OH})_2]^+(\text{H}_2\text{O})_n$  with  $n=0-4$ ; b) polynuclear  $[\text{Ce}_m\text{Cl}_{3m-j}]^+(\text{H}_2\text{O})_n$  with  $m=1-5$  and  $n=0-4$  c) mixed polynuclear  $[\text{Ce}_m\text{Cl}_{3m-2}\text{OH}]^+$  and  $[\text{Ce}_m\text{Cl}_{3m-3}\text{O}]^+$  with  $m=1-5$  and d) larger solvated clusters of the general form  $[\text{Ce}_m\text{Cl}_{3m-4}\text{O}]^{+2}(\text{H}_2\text{O})_n$  and  $[\text{Ce}_m\text{Cl}_{3m-4}\text{O}]^{+2}(\text{H}_2\text{O})_n$  with  $m\leq 6$  and up to six water molecules. We also conducted mass spectrometric experiments in which the concentration-dependence (1-20mM; pH 5.2-6.9) of the cerium cluster distribution was probed. Results from these concentration-dependent experiments demonstrate that cerium chloride clustering increases with  $\text{CeCl}_3$  concentration, in other words, at higher  $\text{CeCl}_3$  concentrations (lower pH) more cerium chloride is present as polynuclear chlorocerate. With respect to solution pH, it is likely that the emergence of clusters with bridging hydroxo groups, e.g.  $[\text{Ce}_m\text{Cl}_{3m-2}\text{OH}]^+$  arises as a consequence of the partial hydrolysis of  $[\text{Ce}_m\text{Cl}_{3m-j}]^+$  clusters, in particular, in the acidic pH range. Last but not least, the observed correlation between ion mass spectra and solution content appears to demonstrate that dinuclear clusters are intermediates on the way from the  $[\text{CeCl}_2]^+$  complex to the formation of larger "bulk-like" chlorocerate clusters. In conclusion, results from our ESI mass spectrometric and DFT study strongly point toward molecular clustering being an important factor in understanding Ce speciation in aqueous fluids.