Study on adsorption of submicrometer gold on kaolinite by quantum chemistry calculations

HONG HANLIE,1,2,* MIN XINMIN,2 AND FU ZHENGYI2

1The Center for Materials Testing and Research, Wuhan University of Technology, Wuhan, Hubei 430070, P.R. China
2National Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, Hubei 430070, P.R. China

ABSTRACT
The electronic structure and energies of Au atoms adsorbed on an atomic cluster of kaolinite were calculated using the self-consistent-field Discrete Variational (DV) method. A hexagonal ring of SiO4 tetrahedra and three AlO2(OH)4 octahedra, comprising 38 atoms, was used to model the kaolinite crystal flake. An Au atom was used to model the submicrometer Au. Calculations were performed with Au atoms adsorbed at different sites. The systems with lower total energy are those with Au adsorbed on the edge surfaces. The adsorption of Au atoms on the edges is more stable than Au atoms adsorbed on the basal plane. Bond order calculations suggest that significant shifting of atomic charge and overlap of electron clouds between Au and the surface atoms of kaolinite takes place in the systems with Au adsorbed on the edges, especially at sites near Al octahedra.

INTRODUCTION
The intimate association of clay minerals and submicrometer Au has been recognized since the Carlin deposit was found in the 1970s. Foster (1970) pointed out that most of the Carlin Au is related to the clay minerals kaolinite and hydromica; in the oxidized zone, clay minerals play an important role in Au accumulation during Au mineralization process (Boyle 1979); recently, Transmission Electron Microscopy (TEM) investigation showed submicrometer Au adsorbed on the edges of kaolinite and illite (Ye et al. 1994; Hong and Ye 1998; Hong et al. 1999).

It is well known that kaolinite has a heterogeneous surface charge, and the basal surface is believed to carry a constant structural negative charge, which is attributed to the isomorphous substitution of Si4+ by Al3+. The charge on the edges is due to the protonation/deprotonation of surface hydroxyl groups and this depends on the solution pH (Zhou and Gunter 1992). Zhang et al. (1994) pointed out that at the edges, especially at sites near Al octahedra. Qian et al. (1986) found submicrometer Au particles associated with clay minerals and inferred that they were electrostatically adsorbed onto the crystal edges of kaolinite, but the interaction force of adsorption between Au and kaolinite is similar to that of interstitial atoms in a compound. Adsorption of heavy metals onto kaolinite has been investigated in some detail (Angove et al. 1998); the results show that adsorption involves complexion of adsorbing ions with aluminol, and perhaps silanol, groups which reside predominately on the crystal edges. Rosliyakov (1990) proposed that Au is adsorbed on the crystal surface of clay minerals, however, there is an adequately strong adsorption bond between Au and clay minerals, and hence it is a type of chemical adsorption. Boyle (1979) pointed out that, in clay minerals, most of the Au is combined as complexes. However, there is some controversy as to whether the Au is present in a chemical combination with the clay minerals or whether the Au occurs as a colloidal adsorbate. Using the Self-Consistent Field Discrete Variational Xα (SCF-Xα-DV) quantum chemistry calculation method, we have calculated the energetics of models of Au adsorption onto kaolinite surfaces. The data obtained about the manner of adsorption provides a scientific basis for understanding the close association of Au and clay minerals and hence the mechanism for Au mineralization in submicrometer Au deposits.

THEORETICAL APPROACH

Calculation method
Self-Consistent-Field Discrete Variational Xα (SCF-Xα-DV), proposed by Eills and Painter in 1970, has commonly been used to understand chemistry at the level of atoms and molecules (Ellis and Guenzburger 1997). Electronic energy levels and charge density of atoms in a solid system are calculated, and therefore it is possible to explore the properties of systems on the basis of the semi-quantitative chemical bond data obtained from the model calculation.

* E-mail: honghl@public.wh.hb.cn