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Rational *ab initio* modeling for low energy hydrogen-bonded phyllosilicate polytypes

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Abstract: In a series of recent papers implementing *ab initio* DFT modeling with VASP, we have explored the kaolin system at zero pressure, kaolinite under pressure up to 60 GPa and the known kaolin phases under moderate pressure at 10 GPa. We summarize here the concepts, conclusions and falsifiable predictions printed in this series of papers, stressing independent and recent experimental results. A new rationalization of the kaolin system results, clarifying its stability diagram, its diagenesis and its solid-state phase transformations. The existence at moderate pressure of two new translations –a/3 and (a + b)/3, not possible at zero or low pressure, leading to five-fold coordination for Si was correctly predicted. Two newly and independently observed kaolinite polytypes (kaolinite II and III) were also correctly predicted. The existence of a still unobserved (SU) kaolinite IV phase is predicted at a pressure not higher than 60 GPa. Finally, transformations of dickite II into SU dickite III and nacrite into SU nacrite II are predicted to occur around 10 GPa. Optimized crystal structures predicted by *ab initio* modeling for the most likely low enthalpy polytypes are printed, which should simplify their identification when they will be observed, as they did for kaolinite II and III. Concepts developed here for kaolin minerals are generally applicable to hydrogen-bonded phyllosilicate polytypes or other hydrogen-bonded layered systems. This series of papers then implements a new way of expanding knowledge about experimentally difficult systems: inexpensive and relatively fast quantum computations can bring support to experimental results when conflicting reports exist in the literature, as well as produce predictions that are easily falsifiable experimentally, thus pointing to fruitful directions for new experiments. This loop of quantum computation followed by critical experiments results in faster and cheaper scientific progress as seen here on the kaolin system.

Key-words: kaolin system, kaolinite, dickite, nacrite, solid-state phase transformations, diagenesis, phyllosilicate polytypes, hydrogen-bonded, layered systems, *ab initio* modeling.

1. Introduction

The energy intensity and environmental impact of the exploitation for oil of the Alberta oil sands have been a research topic at the NRC-ICPET and elsewhere for many years now. From this research, it has become clear that many processing problems in the extraction of bitumen from the sands arise from the presence of clay minerals and clay-organic interactions (*e.g.*, Kotlyar *et al.*, 1987, 1993, 1998; Kasongo *et al.*, 2000; Sparks *et al.*, 2003; Liu *et al.*, 2004; Omotoso & Mikula, 2004; Tu *et al.*, 2005; Jiang *et al.*, 2008; Mercier *et al.*, 2008; Gray *et al.*, 2009; Dongbao *et al.*, 2010). The source of many of those processing problems related to clays resides at the atomic level in the relative adsorption energy of water and organic molecules (from bitumen, solvents, humic matter, etc.) on the surface of various clay minerals. As corresponding measurements are very difficult to perform, we are exploring quantum modeling as an alternative or complement to measurement in assessing the fate of clay minerals in multiphase oil sands processes for bitumen extraction and upgrading.

Ab initio DFT software does not parallelize very well due to fairly random access to vast amounts of computer memory, limiting the usefulness of fast cache memory and to fiber optics interconnects that are fast, but not fast enough for the job at hand. As a result, quantum software currently runs very slowly for systems with more than about 150 atoms. This number is sufficient to model accurately the clay minerals themselves, but not their surface chemistry nor their interfaces with water and/or organic molecules. Just a few years ago, this limiting number was more like 30 atoms. Here, we discuss recent applications of *ab initio* DFT methods to kaolin-group polytypes first at zero pressure in Mercier & Le Page (2008) (MLP08), then kaolinite under pressure up to 60 GPa in Mercier & Le Page (2009) (MLP09), and finally all observed kaolin phases under moderate pressure at 10 GPa in Mercier *et al.* (2010) (MLPD10). The present article stems from our oral presentation in session MC102 at IMA2010 in

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