Effect of lactate, glycine, and citrate on the kinetics of montmorillonite dissolution

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ABSTRACT

The montmorillonite dissolution in saline solutions that mimic synthetic lung fluids (SLF) was investigated to gain knowledge on the clearance mechanisms of inhaled clay particles. Dissolution rates were measured at pH 4 (macrophages) and 7.5 (interstitial fluids) at 37 °C in flow-through reactors. The effect of organic acids was investigated through the addition of lactate, citrate, and glycine (0.15, 1.5, and 15 mmol/L). Lactate or glycine does not markedly affect the montmorillonite dissolution rates at pH 4, but at pH 7.5 there exists a slight inhibitory effect of lactate on the dissolution, probably due to a reduction in the number of reactive surface sites caused by lactate adsorption. Citrate enhances the dissolution rate by 0.5 order of magnitude at pH 4 and more than 1 order of magnitude at pH 7.5, thus indicating the prevalence of the ligand-promoted over the proton-promoted dissolution mechanism under these experimental conditions. The kinetic data were used to estimate the reduction in size of an inhaled clay particle. At pH 7.5, a particle 500 nm in diameter could be reduced 25% in the presence of citrate, whereas the reduction in saline solution would only be 10% after 10 years.

Ligand adsorption was measured in batch experiments at pH 2–11 and EQ3NR was used to model the capacity of the ligands to form soluble species of Al. Citrate, glycine, and lactate adsorb onto montmorillonite under acidic conditions, up to 23, 26, and 60 µmol/g, respectively. However, only citrate can complex the released aqueous Al at pH 4 and 7.5, which contributes to enhance dissolution rate and prevents precipitation of gibbsite at pH 7.5.

The enhancement of the dissolution rate in acidic citrate solution very likely comes from the formation of surface complexes between the ligand and the edge surface of montmorillonite. In neutral conditions the effect may be also due to the decrease of the activity of Al3+ by formation of aqueous Al-citrate complexes.

Keywords: Montmorillonite, dissolution rate, organic ligands, adsorption

INTRODUCTION

After decades of research, a substantial and growing understanding of the important role played by geochemical processes on the health effects of biodurable minerals has been gained. Although the precise mechanism to induce disease in an organism has not been fully clarified yet, the initial contact between the organism and the mineral is via the mineral surface in an aqueous medium. The interaction of surface reactive groups (sites with acid-base properties, active sites for cation exchange, surface charge, hydrophilicity or hydrophobicity of the surface, production or adsorption of oxygen-free radicals, etc.) with the biological medium may induce the mineral toxicity (Fubini and Fenoglio 2007). Thus, it is important to see how the surface interaction occurs to understand the pathogenesis of minerals. This understanding requires a mineralogical and geochemical surface characterization. There are very few studies on mineral dissolution in a biologic medium and they are mainly focused on highly toxic asbestos and silica (Scholze and Conradt 1987; Humé and Rimstidt 1992; Werner et al. 1995; Gunter and Wood 2000; Oze and Solt 2010), as well as talc (Jurinski and Rimstidt 2001).

Smectite, kaolin, and illite constitute the main part of the fine and ultrafine fraction in soils and sediments. Therefore, they are the main compounds of suspended dusts formed by mechanical and chemical weathering processes. Human beings are constantly exposed to mineral dust. However, very few studies exist on the toxicity of smectite and clays in general. The World Health Organization indicated the dire need to tackle research on this matter in its report “Environmental Health Criteria on Bentonites and Kaolins” (WHO 2005).

Smectite dissolution has not been investigated using similar physical and chemical conditions to those found in the lung. However, this reaction has been extensively studied under Earth surface conditions for decades (Zysset and Schindler 1996; Bauer and Berger 1998; Cama et al. 2000; Huertas et al. 2001; Amram and Ganor 2005; Metz et al. 2005; Golubev et al. 2006; Rozalén et al. 2008, 2009b). The dissolution reaction is produced in specific active sites on the surface, and is controlled by several factors including temperature, pH, and the presence of organic ligands and inhibitors. Most studies agree that under the same pH conditions the dissolution rate is faster in the presence of organic ligands than that without organic ligand (Zutic and Stumm 1984; Furrer and Stumm 1986; Carroll-Webb and...