

ABSTRACT

As the 21st century approaches, the National Aeronautics and Space Administration (NASA) is considering extending permanent human presence beyond low Earth orbit. Among the missions being considered by NASA are human exploration of Mars and its satellites, establishment of a manned lunar outpost, and evolutionary expansion of humans into our inner solar system. A permanent human outpost on the moon will be a staging area for launching manned missions to other planets and is therefore a necessary first step to achieving NASA's goals. Due to the exorbitant costs of transporting food and resources to a lunar base, it will be essential to establish a regenerative life support system (RLSS). The RLSS will depend upon green plant photosynthesis to provide food, potable water, and oxygen and to remove wastes and carbon dioxide. Lunar soils will play an essential role in the development of lunar based agriculture. Therefore, the study of how lunar soils will react when exposed to a terrestrial environment is important to the success of a manned lunar outpost.

Lunar soils are similar to terrestrial analogs. However, they are devoid of water and are extremely reduced. Additionally, they contain potentially toxic concentrations of Cr and Ni. NASA has only a limited supply of lunar soils retrieved from the Apollo missions and these are considered a national treasure. Lunar simulants have been developed by NASA to be used as a first step in understanding the reactivity of lunar materials and establish research protocols that may be used with actual lunar soils. In this study we examined the long-term dissolution kinetics and

mechanisms of a basalt and glass simulant under conditions that may be encountered in a plant root rhizosphere. Mineral surfaces were examined with transmission and scanning electron microscopy and the microscopic analyses support mechanisms determined from dissolution data. Additionally, we investigated the sorption kinetics and mechanisms of chromate, arsenate, and Ni on potential lunar soil secondary weathering products employing an array of sophisticated atomic-resolution techniques and a pressure-jump relaxation kinetic technique for studying rapid kinetic reactions .

Long term dissolution studies were conducted, using both lunar simulants at pH values of 3, 5, and 7 and in the presence of citric and oxalic acid. At pH 3 and 5, dissolution of the lunar glass simulant followed a two stage process. The first stage involved the parabolic release of Ca, Mg, Al, and Fe and the linear release of Si. Dissolution was incongruent resulting in a leached layer rich in Si and Ti that was verified by transmission electron microscopy. During the second stage, the release of Ca, Mg, Al, and Fe was linear, which was attributed to the repolymerization of a Si-rich leached layer. The Si-rich leached layer scavenged Si from solution and created a porous network that was no longer a diffusional barrier to the release of cations. During this second stage, hydrolysis of the bulk glass, not diffusion through the leached layer, was the rate-limiting step. In the presence of the organic acids, the dissolution of the synthetic lunar glass proceeded by a one stage process. The release of Ca, Mg, Al, and Fe followed a parabolic relationship, while the release of Si was initially linear and eventually approached a steady state. The rate-limiting step was the diffusion of cations through the Si/Ti rich leached layer which was observed with transmission electron microscopic analysis. A two-step mechanism was proposed involving the initial surface adsorption of the organic ligand followed by hydrolysis of the surface and chelation of cations in solution.

For the basalt simulant, the rate of dissolution for all experiments followed a two-stage process. During the first stage, the rate of dissolution for all elements was rapid, followed by a slower, more linear rate during the second stage. The first stage was attributed to the dissolution of ultrafine particles created during the sample grinding process. During the second stage, dissolution proceeded on the larger mineral surfaces at higher energy sites such as dislocations, twinning planes, fluid inclusions, etc. The order of cation release was related to the stabilities of the minerals present in the MLS-1 basalt. For the pH experiments, it was proposed that H^+ ions dissolved the minerals present in the basalt through a combination of diffusion, exchange with structural cations and protonation of the surface. In the organic acid experiments, a two step mechanism was proposed involving the initial surface adsorption of the organic ligand followed by hydrolysis of the surface and chelation of cations in solution.

The kinetics and mechanism of chromate and arsenate adsorption was investigated using a pressure-jump relaxation kinetic technique and X-ray absorption fine structure (XAFS) spectroscopy. Pressure-jump relaxation experiments indicated that both arsenate and chromate formed inner-sphere bidentate surface complexes with goethite. This occurred via the formation of an intermediate inner-sphere monodenate surface complex. For both oxyanions, the rate-limiting step was the reaction proceeding from the mono- to the bidentate surface complex. Rate information indicated that arsenate more favorably formed an inner-sphere bidentate surface complex on goethite than chromate. This is consistent with XAFS spectroscopy and the finding that chromate is the more mobile of the two oxyanions in the vadose zone.

The surface structure of Ni(II) sorbed on kaolinite was investigated using XAFS and transmission electron microscopy (TEM). XAFS along with

crystallographic considerations indicated that a bidentate binuclear surface complex formed at all surface site occupancies followed by Ni-hydroxide nucleation. TEM was used to examine the spatial resolution of the precipitate and indicated that Ni-hydroxide formed discrete islands or clusters over the kaolinite surface.