**08:45 a.m.** Sharp, Thomas G.                                          № **7376**

## LATTICE-RESOLUTION IMAGING OF MICA (001) SURFACES WITH ATOMIC FORCE MICROSCOPY

SHARP, Thomas G. and BUSECK, Peter R., Departments of Geology and Chemistry, Arizona State University, Tempe AZ, 85287
Atomic force microscopy (AFM) is a scanning probe technique for characterizing microtopography and structure of either conducting or nonconducting surfaces. It uses the repulsive or attractive forces between a sharp tip and a sample surface to create three-dimensional topographic images on the micrometer to atomic scale. Lattice resolution has been demonstrated in vacuum, air, and in fluids and has been applied to surface reconstruction, relaxation and sorption processes. To interpret structural details of complex surfaces, one needs to be aware that the image appearance is influenced by the operating conditions. Mica (001) surfaces are standards for the demonstration of lattice resolution with AFM because they are relatively easy to prepare and image. We have imaged the (001) surfaces of various muscovite samples to explore the sensitivity of AFM and the variation in observed structures.

Lattice images of Li-bearing muscovite display a variation in surface structure ranging from nearly hexagonal arrays of holes, corresponding to empty interlayer sites, to lower symmetry structures that suggest buckling of the tetrahedral sheet. Pits ranging from 5 to 10 nm across occur with continuous tetrahedral-sheet structure, indicating that the surface mica layer is locally indented. A series of experiments was undertaken to investigate the force dependence of observed structures. Images obtained with a repulsive contact force ranging from 1.6 to 24 nN vary greatly in apparent structure but not systematically with the applied force. These variations may result from changes in tip shape during the experiments. Lattice resolution has also been obtained using attractive forces between 6.0 to 0 nN with results similar to those obtained using repulsive forces.

**09:00 a.m.** Swope, R. J.                                          № **7880**

CRYSTAL STRUCTURE REFINEMENT OF Cl-RICH 1M BIOTITE.
SWOPE,R.J., SMYTH,J.R., MUNOZ,J.L.,Dept. Geol. Sci., Univ of Colo., Boulder,CO,80309, GUNDERSEN,L.C.S. U.S. Geol. Surv.,MS 939, Lakewood,CO 80225
High-grade metamorphic biotites commonly contain 1-3% Cl. Thermodynamic modeling of Cl=OH exchange requires knowledge of the location of Cl in the biotite structure; because Cl is a significantly larger anion than OH (1.81 vs. 1.38 Å) it has been suggested that ideal OH=Cl substitution might not apply. To resolve this question we refined the structure of a Cl-rich (1.5%) 1M biotite from a granulite-facies quartz-feldspar-biotite-garnet gneiss from the Reading Prong (Rocky Hill, Warwick, NY).

A single crystal of the Rocky Hill biotite was mounted on a Siemens 4-circle diffractometer equipped with a rotating anode. The structure was refined from 1094 independent reflections with F>6.0 σ(F) out to sinθ/λ = 1.19 with an R of 3.41%. The unit cell determined from higher angle data was a=5.339(2), b=9.252(2), c=10.171(2), β= 100.20(2). The approximate position of Cl was recognized from the difference-Fourier map as being close to the hydroxyl (04) site. The refined position of Cl is shifted away from 04 toward the K (interlayer) site by 0.56 Å. at x=0.114(1), y=0.50000, z=0.345(2).

The observed c dimension of the Rocky Hill biotite is significantly shorter than would be predicted on the basis of the Fe/(Fe+Mg) ratio (0.46). This contraction may be explained by electrostatic attraction between K and Cl (K-Cl = 3.45 Å; cf. K-Cl = 3.145 Å in sylvite). Therefore, thermodynamic models that assume ideal Cl-OH exchange in biotite are most likely in error.

**09:15 a.m.** Guggenheim, Stephen                                  № **32130**

## THE CRYSTAL STRUCTURE OF PARSETTENSITE BY ELECTRON-OPTICAL METHODS AND COMPARISONS TO STILPNOMELANE.
EGGLETON, R.A., Dept. of Geology, Australian National University, Canberra, Australia; GUGGENHEIM, Stephen, Dept. of Geol. Sci., Univ. of Illinois at Chicago, Chicago, Illinois 60680.

The crystal structure of parsettensite, ideally $M^+_{7.5}$ (Mn, Mg)$_{49}$ $(Si_{64.5}Al_{7.5})_{\Sigma = 72}O_{168}(OH)_{50}$ where $M^+$ are exchangeable cations, was solved by trial-and-error methods based on high-resolution electron-optical images, and by using electron-optical diffraction data. Dynamical-diffraction effects were minimized by using very thin grains and because superlattice reflections streaked parallel to Z* by stacking disorder were not affected significantly by orientation changes near the (001). Derived

models of a single layer projected down Z were compared to hk Fourier transforms. The technique was sufficient to discriminate between two reasonable models. The ideal three-dimensional model conforms to C2/m symmetry with cell parameters of a = 39.2(2) Å, b = 22.79 (4) Å, c = 18.0(1) Å, $d_{001}$ = 12.55 Å and β = 135.8(4)°.

Parsettensite is a modulated 2:1 layer silicate. It consists of a continuous Mn-rich octahedral sheet coordinated by silicate tetrahedral rings forming islands three tetrahedral rings wide. Islands are linked by inverted and partially tilted four-ring tetrahedral connectors, with junctions of three islands forming also twelve-ring connectors. Layers are cross-linked through two sets of four-ring connectors. Although the tetrahedral island connectors are different from stilpnomelane, the tetrahedral islands are similar, which explains the similarities in the diffraction patterns of the two minerals as noted by earlier workers.

**09:30 a.m.** Guthrie, G. D., Jr.                                  № **25854**

**REFINEMENT OF THE TURQUOISE STRUCTURE AND DETERMINATION OF THE HYDROGEN POSITIONS**
GUTHRIE, G. D., JR. and BISH, D. L., Geology/Geochem., MS D469, Los Alamos National Laboratory, Los Alamos, NM 87545
The structure of turquoise, $CuAl_6(PO_4)_4(OH)_8 \cdot 4H_2O$, was solved in 1965 by Cid-Dresdner (Z. Krist., 121:87) using single-crystal X-ray diffraction data and material from Lynch Station, VA, the only locality known to possess single crystals large enough for single-crystal work. The proposed structure has several intriguing features, including: (1) two roughly equivalent sites, only one of which is filled by Cu; and, (2) O-H bond lengths spanning an abnormally large range (0.66–1.05 Å). We have used powder diffraction data and Rietveld analysis to examine these observations on a more commonly encountered form of turquoise from Altar, Chile.

Our turquoise sample was extremely pure, as judged by light microscopy, scanning and transmission electron microscopies, and X-ray diffraction. Seven g of powder were obtained from 13 turquoise nuggets. Wet chemical analysis gave the following composition: CuO (7.45%), ZnO (0.22%), CaO (<0.008%), FeO (0.52%), MnO (0.008%), MgO (0.16%), Na₂O (0.06%), K₂O (0.014%), P₂O₅ (34.2%), SiO₂ (0.72%), Al₂O₃ (37.5%), Fe₂O₃ (0.40%), H₂O⁺ (18.07%).

In order to determine site occupancies and hydrogen positions, both X-ray (Cu $K\alpha$ and Fe $K\alpha$ radiation) and neutron (constant-wavelength [1.552 Å, as refined] and time-of-flight ) data were used. Refinement was done using the Rietveld program GSAS and the non-hydrogen atom positions of Cid-Dresdner (1965) as a starting model. Hydrogen positions were predicted using an ionic modeling technique (Guthrie et al., 1991), and difference-Fourier maps were calculated in the vicinity of the predicted positions using the neutron data. Negative peaks were found at each of the 8 predicted positions, and these were added to the model. Refinement proceeded using all data sets. Finally, Fe was added to the model in an amount consistent with the chemical analysis. The occupancies of Fe and Al were varied and constrained to a full occupancy of each site

The basic aspects of the Cid-Dresdner model were confirmed in this sample. Lattice parameters were **a** = 7.4100(2) Å; b = 7.6356(2) Å; c = 9.9052(3) Å; α = 68.652(1)°; β = 69.639(1)°; γ = 65.034(1)°. No evidence was found for significant occupancy of the "empty Cu-site," and no evidence was found for appreciable ordering of Fe in the octahedral sites. The hydrogen positions deviated slightly from those reported by Cid-Dresdner, and the O-H bond lengths were more reasonable. All hydrogen sites were strongly anisotropic, but an attempted refinement of anisotropic temperature factors was unsuccessful. The occupancy of each hydrogen site was also varied to evaluate the extent to which each site was occupied. The hydrogen sites associated with the Cu sites were examined closely, since a complete occupancy of these sites would result in overbonded oxygens. However, these sites appeared to be filled completely.

**09:45 a.m.** Burnham, C. W.                                  № **25853**

**PARAMETERIZED MEG-DERIVED SHORT-RANGE REPULSIVE POTENTIALS FOR OXYGEN–OXYGEN AND CATION–OXYGEN INTERACTIONS**
GUTHRIE, G. D., Jr., MS D469, Los Alamos Nat'l. Lab., Los Alamos, NM 87545; BURNHAM, C. W., Dept. of Earth and Plan. Sci., Harvard University, Cambridge, MA 02138; BISH, D. L., MS D469, Los Alamos Nat'l. Lab., Los Alamos, NM 87545.
Ionic modeling of mineral structures relies upon an accurate description of the short-range interactions between atoms. The MEG-approach has proven to be a successful method for determining short-range energies. Using this approach, energies are calculated as a function of separation, and the data can be fit to an exponential expression (i.e., parameterized in terms of atom separation). The method can further accommodate isotropic crystal-field effects on the electron density of atoms by placing a charged shell (the Watson sphere) around each nucleus. The potential of the shell is set to the site potential at the atomic site by adjusting the radius of the shell. These effects are only significant for anions.

We have calculated MEG energies for oxygen–oxygen and cation–oxygen interactions using shell-stabilized oxygens. Energies were calculated for interactions involving the following cations: Li⁺, Be²⁺, B³⁺, C⁴⁺, N⁵⁺, Na⁺, Mg²⁺, Al³⁺, Si⁴⁺, P⁵⁺, S⁶⁺, K⁺, Ca²⁺, Sc³⁺, Ti⁴⁺, Rb⁺. Our calculations spanned a large range in atom separations and in radius of the Watson sphere around oxygen. We formulated the short-range interaction as a Buckingham potential ($W_{ij} = \lambda exp[-r_{ij}\rho^{-1}] - Cr^{-6}$). The constants ($\lambda$, $\rho$, and C) were parameterized in terms of oxygen shell radius (i.e., oxygen site potential). Values of $R^2$ for the fits to the energy-separation data and the $\lambda$,$\rho$-shell radius data were greater than 0.9999, those for the fits to the C-shell radius data ranged from 0.989–1.000. Hence, MEG-derived short-range energies can be determined easily for most conditions of geological interest. Furthermore, the potentials can be incorporated into standard energy-minimization routines (e.g., WMIN). By calculating the site potentials and redetermining $\lambda$, $\rho$, and C during minimization, potential-induced breathing can be simulated.

We have tested these potentials in numerous structures, and the ionic model appears to work well for many minerals. For some structures (e.g., TiO₂ polymorphs, forsterite), the incorporation of isotropic effects to the electron density of oxygen only slightly changes the minimum-energy structure. Other structures (e.g., diopside) appear to be highly sensitive to this effect. A simple ionic model, using MEG-derived short-range potentials (static Watson sphere) and Coulomb interactions, is insufficient to describe the structure of diopside. However, our current procedure, using a dynamic Watson sphere, models the structure of diopside as well as more complicated models that use several empirical potentials.