

AQUEOUS CHEMICAL WEATHERING OF A MARS ANALOG LITHOLOGY: KINETIC MODELING FOR A FERRAR DOLERITE COMPOSITION. A. C. McAdam¹, M. Yu. Zolotov¹, M. V. Mironenko², L. A. Leshin³, and T. G. Sharp¹, ¹Dept. of Geological Sciences, Arizona State University, Box 871404, Tempe, AZ 85287-1404, amcadam@asu.edu, ² Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., Moscow 119991, Russia, ³Sciences and Exploration Directorate, NASA Goddard Space Flight Center, Greenbelt, MD 20771.

Introduction: The cold, dry soils of the Antarctic can serve as relevant analogs to martian soils. Soils formed from weathering of the Ferrar Dolerite (diabase) are especially useful, since this dolerite is itself a good analog to shergottite (basaltic martian meteorite) lithologies. Previously, we have presented the results of (ongoing) analytical studies of the mineralogies in a sample of the Ferrar Dolerite and associated soil from Lewis Cliff in the Central Transantarctic Mountains [e.g. 1,2]. We are studying these analog samples to investigate weathering products and processes, and thereby to gain insight into Mars-like weathering mechanisms.

Chemical weathering processes can also be explored by theoretical modeling. Several authors have carried out equilibrium thermodynamic modeling to explore water-rock and gas-rock interactions on Mars [e.g. 3-5]. However, these models can only provide the final results of weathering reactions and reveal reaction trends. To investigate weathering in a system in which many reactions have not reached equilibrium (likely for many reactions occurring under low temperature (T) and low water/rock conditions), kinetic data, such as mineral dissolution rates, need to be incorporated into weathering models.

Here, we report on our initial results in investigating martian weathering processes through application of a kinetic weathering model to a Ferrar Dolerite composition.

Approach: The ultimate goal is to investigate temporal changes in the mineral assemblages and fluids produced during weathering, and the relationship to changes in initial amounts and compositions of solutions and rocks, T, pH, and activities of dissolved gases. Our first objective is to investigate the weathering of a Ferrar Dolerite mineralogy under open system conditions in which solution is constantly flowing through the rock. Modeling results can then be compared to the mineral assemblage produced by natural weathering, to gain insight into the alteration conditions involved. We evaluated temporal changes in the amounts of remaining and dissolved material, under different T and pH conditions and parent rock/soil properties. Although this initial model is not directly representative of the Antarctic environment, which is not exposed to constant flowing water, this simple system is a logical starting place for understanding the effect of model parameters on weathering. Also, an estimation of dissolution behavior with less water involved can be made by scaling the results to longer dissolution times.

Low temperature (0°C) chemical weathering is modeled to occur in 1 kg of sand of a simplified Ferrar Dolerite composition consisting of 50 vol % diopside and 50 vol % labradorite. The dissolution of each mineral,

presented as sphere particles, is considered separately. The variables are starting mineral, initial amount of mineral, initial grain diameter, T, pH, and time increment. Changing grain size allows us to change the amount of surface area exposed to solution.

Dissolution rates for 0°C were calculated from published rate data at 25°C [e.g., 6-8] using the Arrhenius equation and activation energies (E_a) for diopside and labradorite, which represented pyroxene and plagioclase in the dolerite. Although the dolerite pyroxenes are actually dominated by augite and pigeonite, dissolution rates are not available for pigeonite and augite data is only available for low pH. Diopside kinetic parameters were therefore used to represent the pyroxene. Future work will incorporate the small amounts of magnetite, quartz, and K-feldspar that are present in the rock. Differing values of E_a have been reported in the literature. We used 14 kcal/mol for labradorite [9] and ~13 kcal/mol for diopside [10]. The calculated rates are shown vs. pH in Fig. 1.

Results: Our calculations show that pH and grain size have a sizable influence on dissolution. Both diopside and labradorite show an increase in dissolution rates as the pH is lowered from neutral, but they exhibit opposite behavior as pH is raised from neutral, with diopside showing a decrease and labradorite an increase (Fig. 1). At 25°C, rates are approximately an order of magnitude higher, but a similar pattern of variation with pH is still observed.

Changes in pH have an interesting affect on the relative volume of minerals left in the system after a period of dissolution, as shown in Figure 2. Between pH values of ~4 and ~10, labradorite dominates, as diopside dissolves preferentially. In acidic solutions, labradorite dissolves preferentially and diopside dominates. The volume of diopside left will be greater than that of labradorite above a pH of ~10. These general patterns are observed for all three dissolution times shown in Fig. 2, but as dissolution times are increased, deviation of the plagioclase/pyroxene ratio from 1 increases, for a given pH.

Figure 3 shows how grain diameter decreases with time at a given pH (pH 5) and given starting grain diameter. For both minerals, grain diameters decrease with time more quickly with decreasing grain size. The decrease in the total surface area of the mineral grains shows a similar pattern with respect to time (not shown). For a given grain size, labradorite grains dissolve more slowly at this pH.

Discussion: At this stage, some preliminary qualitative comparisons can be made to the results of weathering observed in the Antarctic samples, and to potential martian weathering. Changes in the plagioclase/pyroxene

ratio with pH (Fig. 2) support the idea that dissolution kinetics, in solutions of pH ~4-10, can lead to an enhancement in the apparent plagioclase content of a weathered basaltic rock or soil. This may suggest that the Antarctic soil and rock we have studied were altered by solutions with average pH values of ~4-10. In fact, because the soil contains more plagioclase than pyroxene and the parent rock shows more dissolution of pyroxenes. This may also be used to draw tentative conclusions about possible martian weathering processes. TES data indicate that the global surface spectral type 2 (ST2) composition, interpreted as andesitic or as partially altered basalt [11], is more plagioclase-rich than surface type 1 (basaltic) [12]. Larger amounts of plagioclase in ST2 compositions could be due in part to preferential chemical weathering of pyroxenes vs. plagioclase in basaltic materials, at low temperature and pH ~4-10 solution conditions.

Also, the Antarctic soil has abundant sulfate salts, which have an oxygen isotope signature consistent with some of the salts being formed by interactions of acidic aerosols with the soil [e.g. 13]. This may suggest that the average weathering fluid was of sub-neutral pH. At pHs below neutral (7) and above 4, pyroxene is preferentially dissolved. The action of acid aerosols, integral to Martian "acid fog" models [e.g. 14], could similarly lead to sub-neutral weathering solutions in which pyroxene is more readily dissolved than plagioclase. Elevated plagioclase/pyroxene ratios observed in some martian surface materials [e.g. 15] may indicate low pH weathering.

When making these preliminary comparisons, several caveats must be kept in mind. One is that a simplified dolerite composition was used. Another is that this is an open system model, in which there is a constant flow of solution. This is very different than the Antarctic and Mars environments. For example, Lewis Cliff receives a yearly average of ~10g of water equivalent precipitation/cm², as snow, and only a small amount melts [16]. Despite this, many of the trends in mineral dissolution with time resulting from this model can be scaled to an approximate Antarctic time frame. For example, the pattern observed in Fig. 3 will be similar with less water available, but the amount of time over which grains dissolve would increase by several orders of magnitude. Also, it is widely observed that natural weathering rates are slower than experimental rates, complicating the use of these rates to try to understand natural weathering. However, when starting materials are identical, the discrepancy between lab and field rates is generally ~1-2 orders of magnitude and can be due to a variety of factors [10].

The next step will be to use a thermodynamic model to see what minerals precipitate from the fluids in which minerals in this open system dissolved. These secondary minerals can then also be compared to minerals produced during natural weathering.

In summary, applying an open system kinetic weathering model to a basaltic mineralogy has revealed interesting trends in changes in grain size and plagioclase/pyroxene

ratios with changes in pH and dissolution time. The initial model results suggest that plagioclase/pyroxene ratios in martian materials and analogous Antarctic soils can be used to constrain the pH and timing of weathering.

References: [1] McAdam A.C. et al. (2005) *LPS XXXVI*, Abst. #2041. [2] McAdam A.C. et al. (2005), *EOS Trans. AGU* 86, Fall Meet. Suppl., Abst. P51D-0957. [3] Gooding J.L. (1978) *Icarus*, 33, 483. [4] Gooding J.L. et al. (1992) *Mars*, U. Ariz. Press, 626. [5] Sidorov Yu. I. and Zolotov M. Yu. (1986) *Chem. Phys. Terr. Plan., Adv. In Phys. Geochem.*, vol. 6, 191. [6] Knauss K.G. et al. (1993) *GCA*, 57, 285. [7] Sverdrup H.U. (1990) *Kinetics of Base Cation Release due to Chem. Weath.*, Lund. Univ. Press, 246. [8] Brady P.V. and Walther J.V. (1989) *GCA*, 53, 2823. [9] Blum A.E. and Stillings L.L. (1995) In *Chem. Weath. Rates of Silicate Min.*, p. 291, Min. Soc. Am. [10] Brantley S.L. (2004) In *Treatise on Geochemistry*, vol. 5, 73. [11] Wyatt M.B. et al. (2004) *Geology*, 32, 645. [12] Bandfield J.L. et al. (2000) *Science*, 287, 1626. [13] Bao H. et al. (2000) *Nature*, 407, 499. [14] Banin A. et al. (1997) *JGR*, 102, 13,341. [15] Rogers A.D. et al. (2005) *JGR*, 1109, doi: 10.1029/2003JE002399. [16] Claridge G.G.C. and Campbell I. (1987) *Antarctica*, Elsevier, 368.

