

THE EFFECTS OF SUBTLE CRYSTAL CHEMICAL MINERAL CHARACTERISTICS ON DISSOLUTION PROCESSES; NEW EXPERIMENTS ON MINERALS REACTED IN MARS AQUEOUS LABORATORY SIMULATIONS. H. E. Newsom¹, C. K. Shearer¹, N. L. Lanza¹, A. M. Ollila¹, M. J. Nelson¹, M. A. Bullock², J. M. Moore³, and M. N. Spilde¹. ¹Institute of Meteoritics, University of New Mexico, Albuquerque 87131. MEL14@unm.edu., ²South-west Research Institute, 1050 Walnut St. Suite 426, Boulder, CO 80302, ³NASA Ames Research Center, Space Sciences Division, M/S 245-3, Moffett Field, CA 94035

Introduction: Long duration experimental alteration runs in a martian simulation apparatus (Fig. 1) are being conducted at NASA Ames Research Center to determine the nature of alteration processes on the martian surface under different aqueous conditions. An early set of experiments was conducted minerals common in martian basalts (silicates, phosphates, sulfates) and glass were allowed to react in experimental vessels with acidic solutions simulating what may have been an earlier Mars atmosphere [1, 2]. The early experiments involved crushed mineral grains (generally 1-3mm) that were introduced into the experimental chambers in proportions similar to SNC basaltic meteorites. We now present the preliminary results of individual mineral experiments in which large (>.5cm) polished mineral grains and basaltic glass were reacted individually for a full year. Some results of the early 3 month pull were discussed by Nelson et al. [3]. Several specimens of each mineral type were included and subsequently removed from the system at 3 months, 6 months and one year. The second set of experiments were conducted using acidic solutions with the same compositions used in the first set of experiments, but mineral grains were polished instead of acid washed, and each mineral grain is reacted individually.

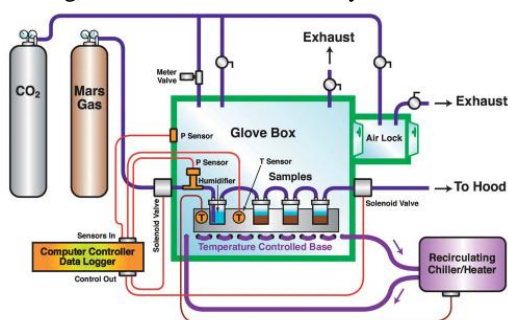


Fig. 1. NASA AMES Mars chamber experimental setup.

Experimental conditions – Minerals of the new set of experiments were cut and polished before introduction into sample holders for placement in the experimental chambers. The samples were held in the apparatus using Teflon screws to ensure that the polished surface would be exposed to the fluids. The minerals discussed in this abstract are apatite and olivine.

The minerals in their holders were put in 250 ml sample chambers with 100 ml water, and a headspace containing CO₂, about 100 ppm each of SO₂ and HCl,

and about 10 ppm NO₂ was maintained throughout the run. The sample chambers were held within a CO₂-filled glove box and maintained at a constant temperature of 25°C throughout the duration of the experiment.

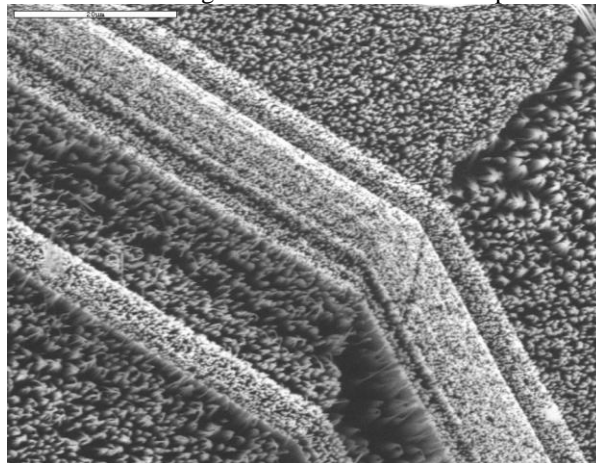


Fig. 2. SEM backscatter image of an apatite crystal (AP18) run for one year under simulated martian conditions. Note the remarkable etched pattern, with preferential reaction of compositionally distinct growth zones in the apatite with martian solutions. Scale bar is 20 microns.

Preliminary results – The samples were analyzed at the University of New Mexico using a JEOL SEM and JEOL 8200 electron microprobe. The most spectacular results from the preliminary examination of the experimental samples is for the apatite (Figs. 2, 3). Apatite (Ca₅(PO₄)₃(OH,F,Cl)) is a common accessory mineral in martian rocks and is important as a carrier of trace elements such as REE, Th, U. The Ca site may be occupied by divalent cations such as Sr, Fe and Mn, trivalent cations such as the REE and Y and monovalent ions such as Na. The P-site may accommodate Si, As, S and C. Due to differences in cation valence state, coupled substitution is required to maintain charge balance. The coupled substitution could involve on the Ca-site: $2Ca^{2+} \leftrightarrow Na^{+} + REE^{3+}$ or both the Ca- and P-sites: $Ca^{2+} + P^{5+} \leftrightarrow REE^{3+} + Si^{4+}$. The apatite used in this experimental study exhibited oscillatory zoning of F, Cl, Na, and REE (Fig. 4). The correlations among these elements implies the above coupled substitutions are important in this apatite. It is anticipated that both Th and U will exhibit similar oscillatory zoning and this will be confirmed via ion microprobe analyses.

The sample run for one year (AP18) shows the preferential dissolution of the apatite that is closely tied to distinct compositional zoning within the apatite (Figs. 2, 3). The dissolution morphology forms a remarkable texture of remnant pillars (Fig. 2). The pillars vary in height and size depending on the zoning pattern of the mineral. In addition to the formation of pillars, some pits have also formed on the surface exposed to the fluids (Fig. 3) that are not related to the zoning. There must be a control on the nature of the dissolution due to the different composition or structural state in the different mineral zones. Zones of higher atomic number composition dissolved more slowly than those zones of lower atomic number. This illustrates the crystal chemical control over both the extent of apatite dissolution and the incorporation of trace elements into the fluid during dissolution.

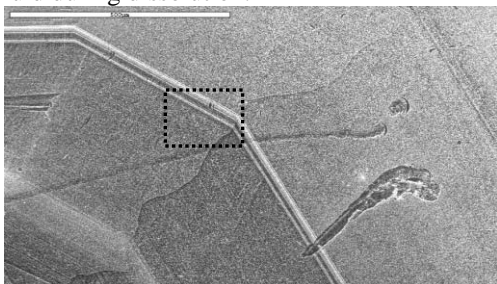


Fig. 3 SEM backscatter map for apatite sample AP18. Notice the dissolution pit. The area of Fig. 2 is outlined and the scale bar is 500 microns.

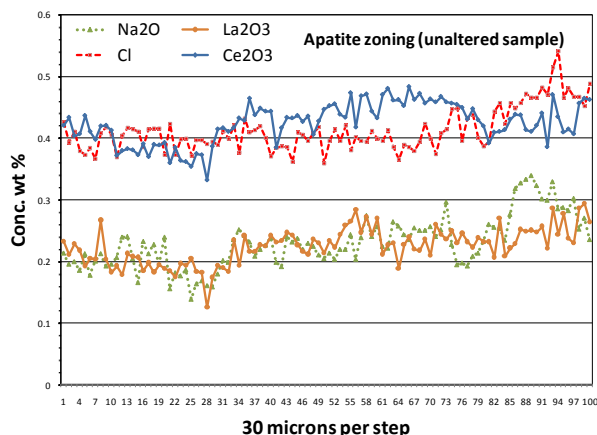


Fig. 4. Step scan microprobe analyses across an unaltered piece of the apatite mineral used in the experiments. Note the coupled variations in Na_2O , with La_2O_3 , and Ce_2O_3 due to charge balance.

The olivine samples also showed evidence of dissolution during the experiments. The observed etching on the surface of both samples resembles etching due to weathering described by Velbel [5] in olivine minerals from Hawai'i. He found that pits began at points and

then opened into cone-shapes. This cone shape is attributed to the development of pits at the tip of the cone from preexisting dislocations. Awad et al. [6] performed a study of alteration textures on another San Carlos olivine composition (Fo_{91}), and found quite different textures than were observed by Velbel (2006) and in this study. Awad et al. (1999) found much more linear features, apparently initiating as round pits. However, this may be the result of the experimental parameters; small grains were constantly washed with acidic water, in contrast to Velbel (2006), which used olivine preweathered in terrestrial seawater, and this study, in which large grains lay in still acidic brine.

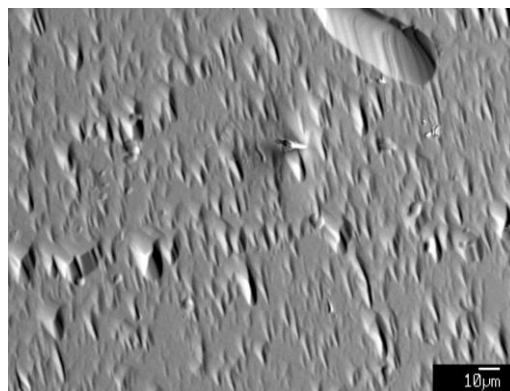


Fig. 5. Close up image in SE of Olivine-5. Cone-shaped pits cover the surface, and appear to have an orientation preference. Scale bar is 10 microns.

Conclusions – Long duration experiments show that substantial changes occur to minerals exposed to fluids under martian conditions. These results suggest that subtle differences in mineral crystal chemistry will strongly impact dissolution rate and morphology. In the case of the olivine and apatite, the results show that dissolution of these phases could lead to the release and mobilization of trace elements including REE, and Ni. The release of Ni due to alteration could help explain the high Ni contents of the martian soil [7]. Alteration of apatite can affect the behavior of the REE with implications for age dating. Detailed analysis of the experiments is just beginning.

References - [1] Bullock, M.A. et al., (2004) *Icarus*, 170, 404-423. [2] Bullock, M.A., and Moore, J.M (2004) *Geophys. Res. Letters*, 31, L14701, doi: 10.1029. [3] Nelson et al. (2007) *7th Mars*, #3089. [4] Velbel, M.A. (2006) *Lunar Planet. Sci.* XXXVII, #1807. [5] Awad, A., et al. (2000) *Geochimica et Cosmochimica Acta* 64, 10, 1765-1772. [6] Newsom et al. (2005) *Lunar Planet. Sci.* XXXVI, #1142, [5] Newsom, (2006) *Nature* 438 570-571. [6] Nelson et al., 2005. *Geochim. et Cosmochim.* 69 no10 2701-2711. Acknowledgments- Funding was provided by NASA P.G.&G. and MFRP (Moore, Bullock) and MFRP (NNG04GE87G, Newsom).