ALBITE DISSOLUTION IN HIGH SALINITY BRINES INDICATES LIMITED AQUEOUS ALTERATION ON POST-NOACHIAN MARS M.E. Elwood Madden[1], C. M. Phillips-Lander[1], and J. L. Miller[1,2] [1]School of Geology and Geophysics, University of Oklahoma, Norman, OK, USA, (melwood@ou.edu), [2] Earth and Planetary Sciencts, Johns Hopkins University.

Introduction: Plagioclase feldspars with diverse compositions have been reported by rovers and orbiters on Mars [1,2,3,4]. Orbital spectra suggest sodic plagioclase occur alongside clays at Mawrth Vallis, which have originated either as tuff or distal detrital clastic sediments [2]. MER Spirit investigations observed basaltic plagioclase (An_{18-36}) Crater [1]. X-ray diffraction and ChemMin data from MSL also indicate a broad diversity of plagioclase feldspars, including (~An_{57}) in Rocknest aeolian deposits at Gale Crater [3] and $An_{\sim 25-35}$ in the Shaler outcrop [4].

Sulfate and chloride salts have also been reported by MSL, MER Spirit and Opportunity, and CRISM on Mars [5]. These salts stabilize liquid water in the cold, dry environments on Mars' surface by depressing the solution freezing point, slowing evaporation by decreasing vapor pressure, and retaining water via hygroscopicity [5,6]. Mg and Ca sulfate salts have been observed in diverse environments on Mars including ~20 to 40 weight percent of Eagle crater outcrop in Meridiani Planum [7], 1-2% in late-stage diagenetic sulfate veins [8] and layered sulfate deposits on Aeolis Mons, Gale Crater [9]. Chloride salts have been reported in the southern highlands of Mars [10]. Due to low surface temperatures and pressures, post-Noachian aqueous alteration likely occurred in high salinity solutions that are stable or metastable at modern surface conditions.

Previous research has shown that mineral dissolution rates decrease in brines [11,12,13,14,15,16,17]. However, solution compositions also influence dissolution rates for carbonates [15], pyroxene [17], and quartz [18,19]. Feldspar dissolution rates are known to be influenced by pH, temperature, and fluid saturation state [20,21,22, 23]. The purpose of this study is to assess feldspar dissolution in low pH, high salinity brines to determine how solution composition and activity of water influence dissolution rates and mineral lifetimes in Mars-relevant brines.

Methods: A sample of Amelia Albite (An~10) obtained from Wards Scientific (#460234) was characterized using electron microprobe and XRD. Albite was micronized, sonicated and washed to clean mineral surfaces prior to reaction, and air-dried. BET analysis yielded a surface area of 2.1 m^2/g.

Batch dissolution experiments were conducted at pH 2 in duplicates with a ratio of 1g albite/L solution using 18 MΩ ultra-pure water (UPW) adjusted to pH 2 with H_2SO_4 (sulfate salt experiments) or HCl (chloride salt experimentes) plus 2.7 M $MgSO_4$ brine (a_w=0.92), 1.24 M $MgCl_2$ (a_w=0.92), 2.9 M $MgCl_2$ brine (a_w=0.75) and near-saturated 5.85 M $MgCl_2$ (a_w=0.33) brine at 25°C. We chose Mg-salts to avoid cations found in the albite, remove the potential influence of different cations on dissolution rates, and focus solely on anion chemistry and activtity of water.

All experimental batch reactors were placed on a shaker table operating at 150 rpm for 30 days. Solution + mineral slurry amples were taken at intervals of ~5 days. We split the sample and used 2 ml for pH measurements. The remaining slurry was syringe-filtered. UV-Vis measurements of Si and atomic adsorption spectrometry (AAS) of Na were utilized to calculate dissolution rates for each solution by plotting aqueous data and fitting with a linear trend line; the 1st-derivative of the trend determined the initial dissolution rate. These rates were normalized using BET derived surface area and used to calculate mineral lifetimes using a shrinking sphere model [11,24].

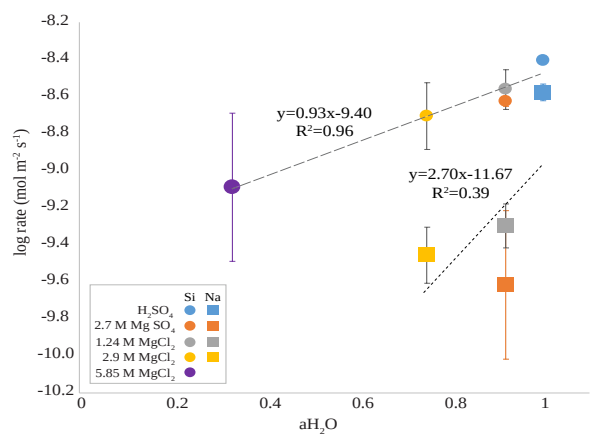

Figure 1: Albite dissolution rates in brine based on Si (circles) and Na (squares). H_2SO_4 (blue), 1.24 M $MgCl_2$ (grey), 2.7 M $MgSO_4$ (orange), 2.9 M $MgCl_2$ (yellow) and 5.85 M $MgCl_2$ (purple). Error bars are smaller than the data point if not visible.

Results: Log albite dissolution rates decrease with decreasing activity of water (Figure 1). Si-based log dissolution rates decrease from -8.41 in H_2SO_4 (aw=1) to -9.09 mol m^{-2} sec^{-1} in 5.85 M $MgCl_2$ (aw=0.33). Measured log dissolution rates for 2.7 M $MgSO_4$ (-8.63) and 1.24 M $MgCl_2$ (-8.56) are within error and have similar activities of water (a_w=0.92), suggesting anion chemistry does not significantly influence albite dissolution. Log dissolution rates in 2.9 M $MgCl_2$ brine (a_w=0.75) were slightly slower than the less concentrated brines (-8.71), as expected given decreasing activity of water.

Na-based log albite dissolution rates in brines are approximately an order of magnitude slower than Si-based rates.

Discussion: Albite dissolution rates decrease with decreasing activity of water. Si-based dissolution rates are significantly faster than reported dissolution rates in UPW adjusted to pH 2 with HCl [20,22,25]. Na-based dissolution rates are approximately an order of magnitude faster than UPW adjusted to pH 2 with HCl [20,22,25], with the exception of H_2SO_4. However, Si-based albite dissolution rates are similar to dissolution rates in pH 3 solutions of oxalic acid and acetate [26].

observed decrease in dissolution rates with decreasing activity of water mirrors trends observed for other silicates including nontronite [14] and olivine [12], as well as jarosite, a ferric sulfate phase. The linear trend through the log Na rate data has a slope (2.7) which is slightly lower, but within error of Steiner et al. (3.3-3.9)'s trend for jarosite, nontronite, and olivine dissolution experiments [14] conducted at pH 1-4. This suggests there may be a universal rate relationship between decreasing dissolution rate and activity of water.

Effect of solution composition and pH: Anion composition did not appear to influence dissolution rates, as both 2.7 M $MgSO_4$ and 1.24 M $MgCl_2$ brines produced similar rates at similar activity of water (a_w~0.92). This contrasts with previous brine dissolution studies on quartz [18,19], carbonates [15], and pyroxene [17] conducted at circumneutral pH. However, other brine dissolution studies conducted at acid pH (<4) [11,12,14] also did not did not vary significantly due to changing anion chemistry. Therefore, anion composition effects may be most significant at circumneutral pH, where dissolution rates are minimized.

Albite lifetimes under Mars relevant conditions: Mineral lifetimes for a hypothetical 0.001 m albite grain increase by an order of magnitude (from 10s to 100s of years) as a_w decreases from 1 to 0.33. These data indicate that even if high salinity brines were in contact with albite grains on Mars surface, high-salinity brines would have minimal impact on albite dissolution unless they were active over relatively long time periods. Therefore, the persistence of albite on Mars' surface at Meridiani Planum and Gale Crater, both of which show evidence for periods of aqueous alteration under acidic conditions [27-29], suggests that post-Noachian aqueous alteration was limited in duration and/or extent.

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