

**FLUIDS, EVAPORATION AND PRECIPITATES AT GALE CRATER, MARS.** S.P. Schwenzer<sup>1</sup>, J.C. Bridges<sup>2</sup>, R. Leveille<sup>3</sup>, R.C. Wiens<sup>4</sup>, N. Mangold<sup>5</sup>, A. McAdam<sup>6</sup>, P. Conrad<sup>6</sup>, S. P. Kelley<sup>1</sup>, F. Westall<sup>7</sup>, J. Martín-Torres<sup>8,9</sup> and M-P. Zorzano<sup>10</sup>. <sup>1</sup>Dept. of Physical Sciences, CEPSAR, Open University, Milton Keynes UK; susanne.schwenzer@open.ac.uk; <sup>2</sup>Space Research Centre, Dept. of Physics and Astronomy, University of Leicester, UK; j.bridges@le.ac.uk; <sup>3</sup>Canadian Space Agency, St-Hubert, QC, J3Y 8Y9, Canada; <sup>4</sup>Space Remote Sensing, Los Alamos National Laboratory, Los Alamos, , USA; <sup>5</sup>Laboratoire Planétologie et Géodynamique de Nantes, LPGN/CNRS and Université de Nantes, , France; <sup>6</sup>NASA Goddard Space Flight Center, Greenbelt, MD, USA; <sup>7</sup>Centre de Biophysique Moléculaire, CNRS, Rue Charles Sadron, 45071 Orléans Cedex 2, France; <sup>8</sup>Instituto Andaluz de Ciencias de la Tierra, Spain, <sup>9</sup>Division of Space Technology, Luleå University of Technology, Kiruna, Sweden, <sup>10</sup>Centro de Astrobiología (INTA-CSIC), Spain.

The Mars Science Laboratory (MSL) mission landed in Gale Crater, Mars, on 6<sup>th</sup> August 2012, and has explored the Yellowknife Bay area [1]. The detailed mineralogical and sedimentological studies provide a unique opportunity to characterise the secondary fluids associated with this habitable environment.

#### Clay mineral formation at Gale Crater, Mars:

The Yellowknife Bay formation is a sedimentary lake bed and fan deposit sequence [1] that consists of conglomerates [2], and fine grained sediments including mudstones [3]. Within this sequence a complex set of diagenetic features is observed. The sequence begins with the early deposition of the sediment, followed by clay mineral formation and a variety of contemporaneous or later diagenetic events [4], including ‘raised’ ridges alongside clays, voids, sulfate-filled voids and late sulfate veins [5-7]. We have modeled the conditions necessary to form the observed clay minerals [3] from the Portage host rock composition present at the Gale site and concluded that dissolution of 70 % Portage amorphous phase, 20 % olivine, and 10 % Portage whole rock can form clays of the observed composition [8]. Here we present the fluids that are in equilibrium with the newly forming minerals and investigate, whether those fluids are capable of forming the observed sulfate veins.

**Methods:** We use CHIM-XPT [9] to model alteration mineral formation conditions from rocks at Gale crater. We use titration models (details in [8]). For the model presented here we calculated reactions of 70 % Portage amorphous component [10,11], 20 % olivine, and 10 % Portage whole rock [12] at 10 °C. We extracted the mineral forming fluid at W/R of 1000 and 100. Here W/R is mass of initial fluid over reacted rock.

**Fluids:** Clay formation reactions [8] produce clays as observed at the Gale site at a model W/R between 1000 and 100. Fluids in contact with the newly forming minerals are generally dilute, but at 100 are more concentrated than at 1000 for most species (Fig. 1). They are of Na-Cl nature with S-species, SiO<sub>2</sub>(aq), K and Ca being the next most abundant dissolved solids.

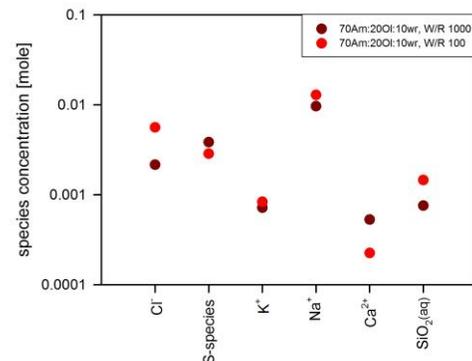


Fig. 1. Species concentrations in the fluid accompanying clay formation during incongruent dissolution of Portage soil (70 % amorphous component, 20 % olivine, 10 % whole rock) at 10 °C.

**Evaporation:** We modeled the evaporation of this fluid (Fig. 2). The initial deposit is SiO<sub>2</sub>, followed by sulfate species and at the highest concentrations rock salt. Sulfate species transition from gypsum to anhydrite with decreasing water activity in the system. Carbonate precipitation is minor, because the initial model assumed separation from the surface and atmosphere, and only minor amounts of dissolved CO<sub>2</sub>.

**Carbonates?** The precipitation of minor carbonate is in accordance with the non-detection of carbonates in the clay-rich sediments [3]. However, a lake in contact with the atmosphere could take up CO<sub>2</sub> depending on CO<sub>2</sub> partial pressure, which would in today’s Mars atmosphere lead to a CO<sub>2</sub>-concentration of 0.02 mmol/L and potentially some carbonate precipitation in a well mixed lake.

**Gypsum or anhydrite?** The hydration state of the observed sulfate is not necessarily the same as upon precipitation. Experiments have shown that the initial precipitate at low temperatures is almost always gypsum, but that a transition to bassanite or anhydrite may occur as early as within hours after the initial precipitation [13, 14]. With a low partial pressure of H<sub>2</sub>O in the current Martian atmosphere [15], some of the dehydration might have occurred as recently as during drilling.

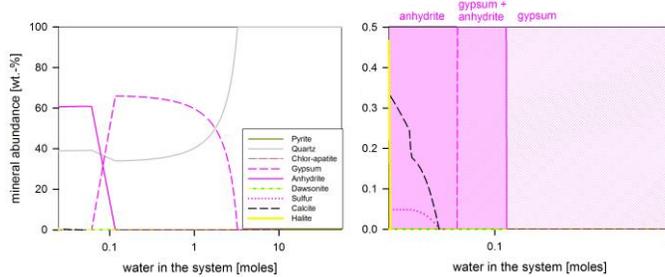


Fig. 2. Evaporation of the fluid forming clay minerals at 10 °C from incongruent dissolution of Portage soil.

Left: Full range of water activities, Right: Mineral precipitates when the system approaches dryness.

**Amounts of silica and sulfate.** Mass balance calculations show that it is possible to explain the high SiO<sub>2</sub> areas by precipitation of SiO<sub>2</sub> from the fluid that formed the clays either in a fractionated precipitation event or during re-dissolution of previously precipitated sulfates. Only minor evaporation is needed, if a fluid from clay formation at W/R 1000 evaporates. This means one kg of fluid contains 10 g of dissolved host rock, which precipitates 7.6x10<sup>-4</sup> moles (or 0.013 mg) SiO<sub>2</sub>. The same amount of dissolved host rock can precipitate as much as 5.2 x10<sup>-4</sup> moles - or 0.004 mg - CaSO<sub>4</sub>.

**Scenarios for Gale Crater:** From our models, two scenarios of the vein-forming stage of diagenesis are possible: 1) If the fluids reached the fractures and evaporated in place, a ‘dirty’ sulfate precipitate would result, with the sulfate vein containing some silica and halite (Fig. 3). Depending on fluid flow in the vein and evaporation, fractionation of the ascending fluid might occur and the precipitate might become more pure sulfate over time and/or space.

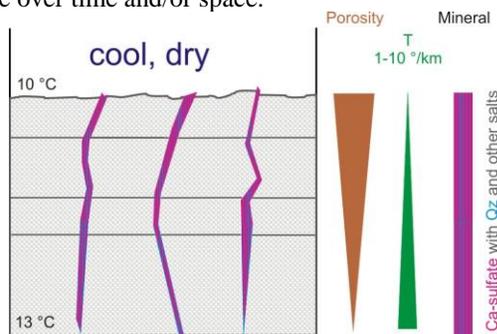


Fig. 3. Scenario of vein formation directly from the clay forming fluid.

2) In analogy to the Watchett Bay site (Upper Triassic, UK, [16]), a two step process seems plausible. The initial fluid evaporates, e.g. in the shallow subsurface or from a ground water-fed lake. Such a lake could receive water from the subsurface diagenetic fluids (groundwater) and from surface runoff (as seen by the conglomerates [2]). Evaporation of this water – with ions derived from the basaltic-composition rocks of the wider Gale area – results in a layer of ‘dirty’ sulfates during a dry period [1]. After burial of that layer by more (lake) sediments upwelling fluids preferentially dissolve the sulfates in the initial layer and deposit this

refined sulfate in the veins (Fig. 4). The second scenario is in line with the observation of pure Ca-sulfate and the complex nature of sedimentation and diagenetic processes observed at Yellowknife Bay [1-7].

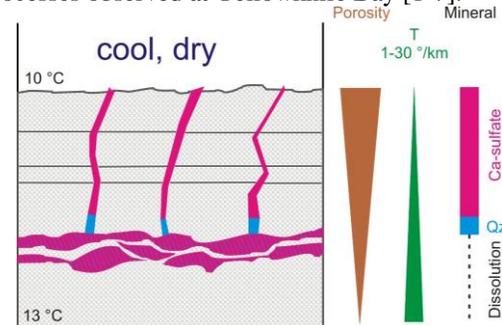


Fig. 4. Scenario in analogy of the Watchett Bay site (Upper Triassic, UK, [16]): a first layer of ‘dirty’ sulfate is deposited and later re-dissolved, which produces pure sulfate veins - as observed at Gale.

**Outlook:** Sulfates have been observed in several layers along the traverse, most recently at Pahrump. From orbit, higher concentrations of sulfates have been observed in the layers within Mt. Sharp above the current location [17]. Evaporation of a brine derived from alteration of basaltic rock compositions could explain such concentration, especially if repeated evaporation and re-filling of a lake occurred.

**References:** [1] Grotzinger, J. P., et al. (2014) *Science*, 343: DOI: 10.1126/science.1242777. [2] Williams et al. (2013) *Science*, DOI: 10.1126/science.1239505. [3] Vaniman D. T. et al. (2014) *Science*, 343: 10.1126/science.1243480. [4] McLennan, S. M. et al. (2013) *Science*, 343: doi: 10.1126/science.1244734. [5] Leveille, R. J. et al. (2014) *JGR Planets*, DOI: 10.1002/2014JE004620. [6] Siebach, K. L. et al. (2014) *JGR*, DOI: 10.1002/2014JE004623. [7] Stack, K. M. (2014) *JGR*, DOI: 10.1002/2014JE004617. [8] Bridges et al. (2014) *JGR*, DOI: 10.1002/2014JE004757. [9] Reed, M.H. et al. (2010) User Guide for CHIM-XPT: A Program for Computing Reaction Processes in Aqueous-Mineral-Gas Systems and Minplot Guide. University of Oregon, Eugene, Oregon. [10] Morris, R.V. et al. (2013) 44th LPSC, abstr. #1653; Houston. [11] Morris, R.V. (2014) 45th LPSC abstr. #1319; Houston. [12] Gellert, R. (2013) 44th LPSC Abst. #1432, Houston. [13] Ossorio et al. (2014) *Chemical Geology*, 386: 16–21. [14] Carbone et al. (2008) *Eur. J. Mineral.* 20: 621–627. [15] Bish, et al. (2003), *Icarus* 164: 96–103. [16] Philipp, S. L. (2008) *Geological Magazine*, 145 (6), 831–844. [16] Thomson B.J. et al. (2011) *Icarus*, 214, 413.