**THE ALTERAION HISTORY OF CLOVIS CLASS ROCKS IN GUSEV CRATER AS DETERMINED BY Ti-NORMALZED MASS BALANCE ANALYSIS.** B. Sutter<sup>1</sup>, D.W. Ming<sup>2</sup>, P.B. Niles<sup>2</sup>, D.C. Golden<sup>1</sup>. <sup>1</sup>Jacobs ESCG, 2224 Bay Area Blvd. Houston, TX 77058, <u>brad.sutter-2@nasa.gov</u>, <sup>2</sup>NASA-Johnson Space Center, Houston, TX 77058.

Introduction: The West Spur Clovis class rocks in Gusev Crater are some of the most altered rocks in Gusev Crater and likely contain a mixed sulfate and phyllosilicate mineralogy [1,2]. The high S and Cl content of the Clovis rocks suggests that acidic vapors or fluids of H<sub>2</sub>SO<sub>4</sub> and HCl reacted with the Clovis parent rock to form Ca, Mg,- sulfates, iron-oxyhydroxides and secondary aluminosilicates (~60 wt.%) of a poorly crystalline nature (e.g., allophane) [1]. Up to 14-17 wt.% phyllosilicates (e.g., kaolinite, chlorite, serpentine) are hypothesized to exist in the Clovis materials suggesting that Clovis parent materials while possibly exposed to acidic pHs were likely neutralized by basalt dissolution which resulted in mildly acidic pHs (4-6) [1, 2]. This work proposes that subsequent to the alteration of the Clovis rocks, alteration fluids became concentrated in ions resulting in the addition of silicate and salts. The objective of this work is to utilize Tinormalized mass balance analysis to evaluate (1) mineral gains and losses and (2) elemental gains and losses in the Clovis rocks. Results of this work will be used evaluate the nature of geochemical conditions that affect phyllosilicate and sulfate formation at Gusev crater.

**Materials and Methods:** The chemical and mineralogical gains and losses of altered Clovis rocks Plano, Ebenezer, and Uchben rocks were evaluated relative to the less altered Wooly Patch rocks (Sabre and Mastodon). The Wooly Patch and Clovis rocks are considered to be derived from similar parent rock and thus, Wooly Patch can serve as an intermediately altered parent material.

Titanium mass-balance analysis terms include mass transport ( $\tau_{jw}$ ) of an element or mineral (j) in the weathered soil or altered rock (w) (e.g., Clovis) compared to its parent material (p) (e.g, Wooly Patch) and is calculated relative to an immobile element (i), where C is the concentration of the respective elements and/or minerals:

$$\tau_{jw} = (C_{jw}/C_{iw} // C_{jp}/C_{ip}) - 1$$
(1)

The gain or loss of an element or mineral is determined by referencing the mobile element or mineral to an immobile element (e.g., Ti). When  $\tau_{jw}$  is 0, the element is immobile; negative values indicate the element was removed or the mineral dissolved from the weathered material, and positive values indicate the element or mineral was added from a source other than the parent material. For example, when  $\tau_{jw} = -0.30$ , 30% of that element has been lost from weathered material relative to that element's starting concentration in the parent material.

Sometimes a large positive or negative  $\tau_{jw}$  may be misleading in an absolute sense because there was such a small amount of that element in the parent material. Absolute gain or loss can be calculated (equation 2) where  $\alpha_{jw}$  (mmoles/100g) indicates the amount of an element or mineral in the altered material that was either added or removed from the parent material.

 $\alpha_{jw} = C_{jw} - C_{jp} \times (C_{iw}/C_{ip})$ 

**Results/Discussion:** The chemical mass balance results demonstrate that relative to the Wooly Patch rocks the Clovis rocks (Plano, Ebenezer, and Uchben) received fractional additions of Mg, Ca, K, Mn, S and Cl (Fig. 1). Fractional additions and errors were for K were very high. Fractional changes in Fe, Al, and Si were low compared to the other elements. The high fractional addition of Mn suggests reducing conditions at one time, which may have resulted in elevated Fe additions as well. Fe may have been previously lost and the most recent aqueous activity added Fe back to the Clovis rocks resulting in minimal net gain or loss in Fe (Fig. 1).



Fig. 1. Fractional elemental gain and loss for Plano, Ebenezer, and Uchben rocks.

The fractional losses of Na and Al while low suggested feldspar dissolution (Fig. 1). The addition of Na in Plano suggested that more Na was added back into Plano, probably as NaCl subsequent to losses that



Fig. 2. Absolute gain and loss of elements  $(\alpha_{j_W}:mmole/100g)$  from Plano, Ebenezer and Uchben rocks.

occurred previously. Fractional losses of P were low which suggested that minor amounts of phosphate minerals were dissolved.

While the fractional levels of Si additions were low, they along with Mg were the highest absolute additions to the Clovis Rocks (Fig. 2). This suggested that Mg rich olivine or pyroxene material was weathred elsewhere and its Mg and Si products were deposited in the Clovis rocks. These Mg and Si bearing solutions may have possessed some Fe from the corresponding olivine or pyroxene that added Fe back to the Clovis rocks as discussed above. Similar absolute molar amounts of Ca and S were added to the Clovis rocks (Fig. 2) indicating that the weathering solutions also supplied Ca and S to the Clovis rocks. The absolute amounts of Cl did not correspond with absolute additions of Na which suggests that HCl containing fluids or aerosols could have added Cl to the Clovis rocks (Fig. 2).

Mineral mass balance indicates that between 20 and 65 % of the pyroxene and feldspar were lost from Clovis rocks (Fig 3). The dissolution of pyroxene and feldspar released likely resulted in the leaching away of base cations. Chemical mass balance indicates low amounts of some elements (e.g., Na, Al, ) were leached away while others were added (e.g., Mg, Ca, Si, K, S, Cl) (Figs. 1 and 2). One plausible scenario is that the pyroxene and feldspar dissolved, which resulted in the leaching away of base forming cations like Ca, Mg, and Na, and allowed for secondary aluminosilicate formation in the Clovis rocks [1,2].

The chemical mass balance signature with its additions of Mg, Si, Ca, K, S, and Cl demonstrates that subsequent to dissolution of pyroxene and feldspar the



Fig. 3. Fractional loss of feldspar (F) and pyroxene (Px) for Plano, Ebenezer, and Uchben materials. Numbers below bars represent absolute loss of minerals ( $\alpha_{iw}$ :mmole/100g)

leaching fluids became more concentrated in Mg, Ca, K, Si, S, and Cl which allowed for additions to occur when these fluids evaporated.

Conclusions: Chemical and mineralogical mass balance analysis demonstrate an evolving sequence of aqueous alteration of the Clovis materials. Mineralogical mass balance indicates that the first stage of alteration of the Clovis materials likely involved dissolution of pyroxene and feldspar which resulted in the leaching away of base cations and the formation of secondary aluminosilicates [1,2]. Following this first stage of mineral dissolution, alteration fluid ion concentrations increased resulting in the additions of Mg, Si, Ca, S, and Cl. The additions were likely derived from fluids that leached other nearby rocks and minerals of their constituent ions. Cl additions may have involved additions from HCl vapors and possibly some NaCl dissolution (e.g., Plano). Gusev Crater was likely exposed to periods of relatively higher aqueous activity that dissolved minerals and was followed by periods of lower aqueous activity that allowed ion additions. Future work will combine amounts of mineral loss with mineral dissolution rates to estimate duration of aqueous alteration.

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