

TITANIUM MASS-BALANCE ANALYSIS OF PASO ROBLES SOILS: ELEMENTAL GAINS AND LOSSES AS AFFECTED BY ACID ALTERATION FLUIDS. B. Sutter¹ and D.W. Ming², ¹Jacobs ESCG, 2224 Bay Area Blvd. Houston, TX 77058, brad.sutter-2@nasa.gov, ²NASA-Johnson Space Center, Houston, TX 77058.

Introduction: The Columbia Hills soils have been exposed to aqueous alteration in alkaline [1] as well as acid conditions [2,3]. The Paso Robles class soils are bright soils that possess the highest S concentration of any soil measured on Mars [2]. Ferric-sulfate detection by Mössbauer analysis indicated that acid solutions were involved in forming these soils [4]. These soils are proposed to have formed by alteration of nearby rock by volcanic hydrothermal or fumarolic activity. The Paso Robles soils consist of the original Paso Robles-disturbed-Pasadena (PR-dist), Paso Robles-PasoLight (PR-PL), Arad-Samra, Arad-Hula, Tyrone-Berker Island1 and Tyrone-MountDarwin [2,3]. Chemical characteristics indicate that the PR-dist and PR-PL soils could be derived from acid weathering of local Wishstone rocks while the Samra and Hula soils are likely derived from local Algonquin-Iroquet rock [3]. The Paso Robles soils were exposed to acidic sulfur bearing fluids; however, little else is known about the chemistry of the alteration fluid and its effects on the alteration of the proposed parent materials. The objectives of this work are to conduct a titanium normalized mass-balance analysis to 1) assess elemental gains and losses from the parent materials in the formation of the Paso Robles soils and 2) utilize this information to indicate the chemical nature of the alteration fluids.

Methods: The titanium mass-balance approach (equation 1) [5,6] was employed to determine elemental gains and losses from the Paso Robles soils relative to proposed parent materials discussed above.

Titanium mass-balance analysis terms include mass transport (τ_{jw}) of an element (j) in the weathered soil or altered rock (w) compared to its parent material (p) is calculated relative to an immobile element (i), where C is concentration of the respective elements:

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

The gain or loss of mobile elements is determined by referencing the mobile element to an immobile element (e.g., Ti, Zr, Nb). When τ_{jw} is 0, the element is immobile; negative values indicate the element was removed from the weathered material, and positive values indicate the element 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. Ti was used as the im-

mobile element because it was the only immobile element measured by the APXS.

Sometimes a large positive or negative τ_{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 α_{jw} (moles/100g) indicates the amount of an element in the altered material that was either added or removed from the parent material.

$$\alpha_{jw} = C_{jw} - C_{jp} \times (C_{iw}/C_{ip}) \quad (2)$$

The τ_{jw} and α_{jw} plotted values for the PR-dist and PR-PL soils were averages of all the calculations relative to the chemical composition of ground holes by the Rock Abrasion Tool (RAT) of Wishstone and Champagne materials. The Samra and Hula τ_{jw} and α_{jw} plots were relative to only the Algonquin-Iroquet RAT brushed material.

Results and Discussion: The PR-dist and PR-PL soils both had high S τ_{jw} which agrees with previous work [2,3] that indicates that these soils were exposed to sulfuric acid solutions (Fig. 1ab). The origin of the S acidity has been attributed to magma degassing and/or oxidation of an iron sulfide deposit [3]. Additions of other elements were indicated by high τ_{jw} values of Fe, Mn, Ni, Zn, Ca, Mg, P, Cl and Br. The largest absolute gains (α_{jw}) were attributed to S, Fe, with relatively moderate gains attributed to Mg, Ca, P, and Si. Absolute gains in Mn, Ni, and Zn were very low. These gains suggest that open system dissolution occurred where acid fluids dissolved olivine, pyroxene and calcium phosphate bearing rock releasing Mg, Ca, Fe, Si and P. The solute bearing acid S fluid percolated through rock/soil and deposited its constituents forming the PR-dist and PR-PL soils. The rock that was leached of its olivine, pyroxene and calcium phosphate could be nearby Wishstone like material or some other rock with similar mineralogy. The low Al τ_{jw} and α_{jw} indicates very little gain or loss of Al. Olivine and pyroxene tend to be more easily weathered than Na-feldspar. This indicates not enough dissolution time had elapsed to allow significant dissolution of feldspar and is likely why so little Al was added to these soils.

The Samra soil and Hula clod both had S gains but where Hula had gains in Ca, Mg, Fe, and Si, Samra had losses in these elements (Fig. 2ab). The Hula τ_{jw} gains of Cl, Br, Cr and Ni while significant did not have large α_{jw} values. This indicated the Cl, Br, Cr and Ni absolute gains were small relative to Ca, Mg, Fe,

and Si. Similar to the PR-dist and PR-PL soils the Hula gains in Fe, Mg, Si, and Ca were derived from acid fluids dissolving olivine and pyroxene elsewhere. The lack of Hula Al gains indicates dissolution times were not sufficient to release enough Al from more stable Na-feldspar. Unlike Hula, Samra had losses in Mg, Ca, and some loss in Si and Fe. One potential hypothesis is that Samra is a soil that overlies Hula. Sulfur acid fluids leached Samra Ca, Mg, Si, and Fe and deposited them into Hula as indicated by gains in these same elements (Fig. 2ab).

Conclusion: Calculated gains in PR-dist, PR-PL, and Hula soils were derived from open system dissolution. Sulfur acid fluids moved through nearby materials dissolving easily weathered olivine, Ca-phosphate (PR-dist, PR-PL only) and possibly pyroxene. Dissolution times were relatively short because weather resistant Na-feldspar did not provide significant Al to these soils.

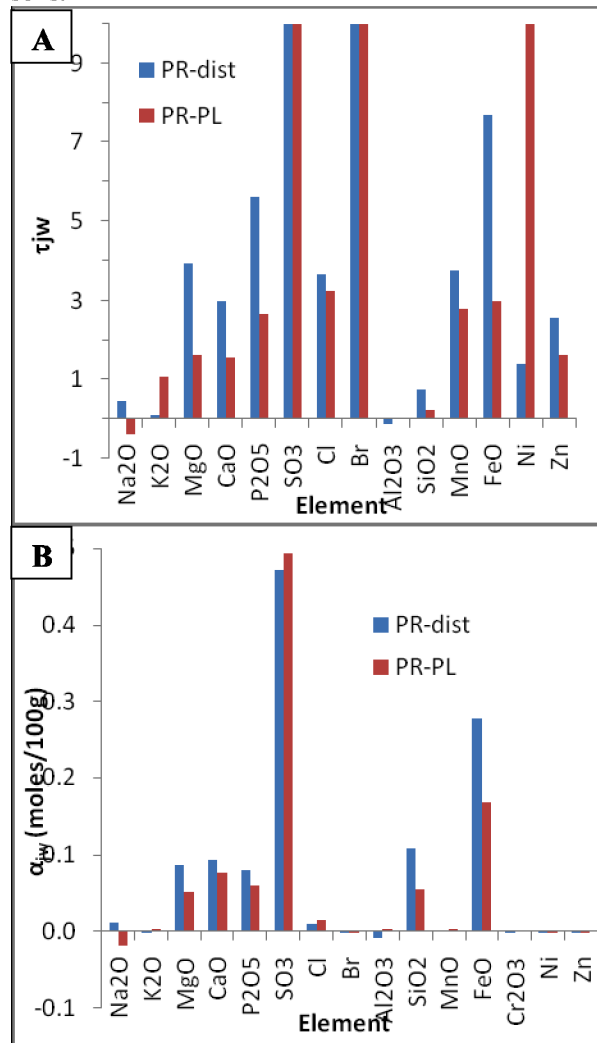


Fig 1 a. τ_{jw} and b). α_{jw} for Paso Robles-disturbed (PR-dist) and Paso Robles-PasoLight (PR-PL) soils.

Samra despite its accumulation of sulfate, could have supplied elements to Hula. The next step in this work is to determine the amount of olivine and pyroxene dissolution in the Samra soil. Mineral losses can then be coupled with mineral dissolution rates to estimate the time of aqueous activity under acid conditions and elevated hydrothermal temperatures.

References: [1] Clark et al. (2007) *JGR*, 112, doi:10.1029/2006JE002756. [2] Ming et al. (2006) *JGR*, 111, doi:10.1029/2005JE002560. [3] Yen et al. (2008) *JGR*, 113, doi:1029/2007JE002978. Morris et al., (2006) *JGR*, 111, doi:10.1029/2005JE002584. [5] Nesbitt, H.W. (1979), *Nature*, 279, 206. [6] Chadwick, O.A. et al., (1990) *Geomorph.*, 3, 369.

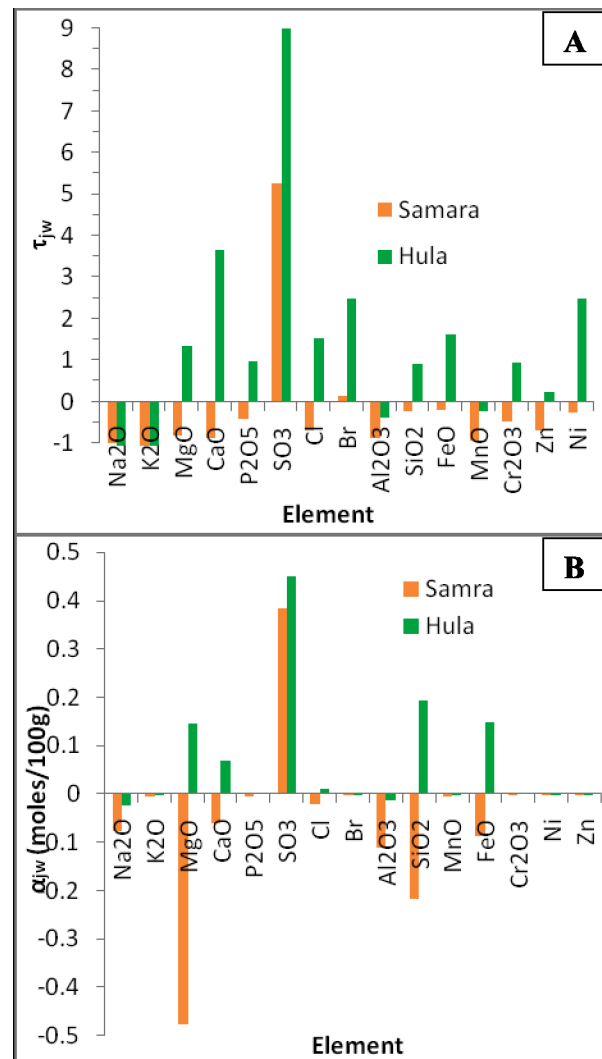


Fig 2 a. τ_{jw} and b). α_{jw} for Samra soil and Hula clod.