ACCOUNTING FOR SALT DILUTION IN THE CHEMICAL INDEX OF ALTERATION: APPLICATIONS TO DON JUAN BASIN, ANTARCTICA, AND MARS. A. Foerder[1], P. Englert[1], C. Koeberl[2], J. L. Bishop[3], E. K. Gibson[4], [1]University of Hawai'i at Mānoa, Honolulu, HI 96822; afoerder@hawaii.edu, penglert@hawaii.edu), [2]Department of Lithospheric Research, University of Vienna, 1090 Vienna, Austria; [3]SETI Institute, Mountain View, CA 94043 USA, [4]NASA Johnson Space Center, Houston, TX 77058, USA

Introduction: This study aims to modify the Chemical Index of Alteration (CIA) equation by accounting for attenuation caused by the dilution of Ca, Na, K, and Mg-sulfate salts, in addition to locally abundant Ca and Na-chloride salts. The modification promises a more accurate understanding of the degree of chemical alteration. This will also allow us to develop a strategy for assessing chemical alteration on Mars. The CIA was developed as a quantitative method to measure the degree to which a rock has undergone chemical alteration [1]. The CIA is based on the ratio of Al to the comparatively mobile cations Ca, Na, and K. It has been applied to various terrestrial environments as well as landscapes beyond the boundaries of Earth, such as Mars [e.g., 2, 3, 4].

CIA values indicate different degrees of chemical alteration of rock, with higher values indicating more alteration. Unaltered mafic sources typically have CIA values of around 30-35. Values above 40 suggest some influence from chemical alteration, and values above 50 provide strong evidence for chemical weathering. For example, in the McMurdo Dry Valleys (MDV), our region of investigation, CIA values for unaltered geologic members range from 42 to 65 [5]. (Figure 1).
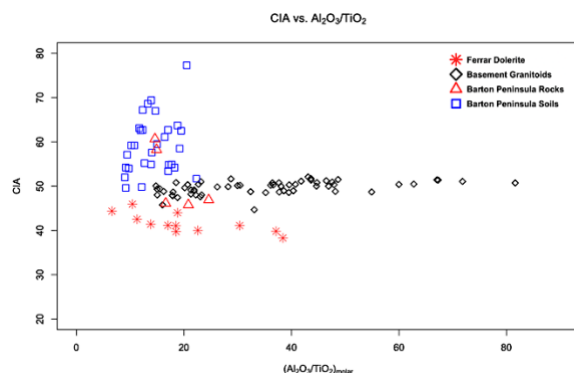

Figure 1: *CIA data of ADV primary geologic constituents "Basement Granitoids" [6, 7]), "Ferrar Dolerite" [8, 9], and Barton Peninsula Rocks and Soils [10]. Barton Penisula soils show varying degrees of chemical alteration.*

The CIA was developed for terrestrial rocks, and values are calculated with the concentration of calcium in silicate minerals. Cations present in non-silicate minerals are not considered. The assumption is that in regular, non-arid environments, salts do not accumulate and chemically-altered ions will be transported out of the sample. CIA values calculated for samples with secondary minerals—such as sulfates—are likely reduced, making the rock appear less weathered than it is.

Efforts have been made to address what could be hypothesized as a "dilution effect" [e.g., 11, 12, 13] by secondary minerals and retained as various salts (e.g. gypsum, bassanite, anhydrite), however, obstacles remain. Additional barriers include cations binding to more than just sulfate, and sulfate binding to more than just one cation. It would be useful to quantify chemical alteration in the hyperarid MDV if the effect of accumulated non-mobilized salts can be accounted for.

Methods: Investigations of surface and subsurface processes in the MDV, an established martian analog environment, have revealed strong evidence of past and present chemical alteration, notably through the presence of aqueously-derived sulfate salts and clays. Select samples from Don Juan Basin (DJB) of the South Fork of Wright Valley, MDV, exhibit very low CIA values that most likely result from salt dilution.

The original CIA is defined as CIA = Al_2O_3/Al_2O_3 + CaO^* + Na_2O + K_2O (molar basis). CaO^* is the amount of CaO in the silicate fraction of the samples [1]. Our modification assumes that measured SO_3 and Cl^- are present as Ca, K_2, Mg $(SO_4)_2$, and NaCl, or $CaCl_2$. The order of the sulfate and chloride species follows their preference of precipitation per their respective K_{sp} values (solubility constant product). The following steps are taken to modify the CIA: 1) Convert CaO, K_2O, Na_2O, and MgO % to mole fraction. MgO is included to address its presence on Mars (kieserite), 2) Multiply oxide moles by the molecular weight of each in its sulfate form to attain % sulfate and chloride: Ca, K_2, Mg $(SO_4)_2$, and NaCl, or $CaCl_2$, 3) Subtract Ca, K_2, Mg $(SO_4)_2$, and NaCl, or $CaCl_2$ % from each oxide's original % abundance, 4) Insert the new value of oxide % into CIA equation to determine the undiluted CIA value. If after subtracting Ca, K_2, Mg $(SO_4)_2$, and NaCl, or $CaCl_2$ % from each oxide's original % abundance, the value returned is negative, the oxide is assumed to be completely consumed by SO_3 or Cl^- to form the oxide's sulfate or chloride form. In this instance, CaO, K_2O, Na_2O, and MgO are inserted into the CIA equation as "0". An equation for this could appear as:

$$CIA_{Salt} = 100 \cdot \frac{Al_2O_3}{Al_2O_3 + [CaO^*]_{SC} + [Na_2O]_{SC} + [K_2O]_S + [MgO]_S} \ (molar)$$

Where subscripts *S* and *C* are the oxide abundances after subtracting respective sulfate and chloride abundances. This equation should provide a qualitative (and

quantitative) means to establish the degree of chemical alteration in the soils analyzed.

Results and Discussion: We applied this modified CIA technique in our investigation of three sediment cores taken from the center of Don Juan Pond, DJB [14]: core 2074, taken in the center of the pond; core 33, taken 150 m southwest, and core 39, taken 300 m southwest. Core 2074 is from approximately 116 m above sea level (asl), while cores 33 and 39 are at approximately 116.4 m elevation. Major, minor, and trace element abundances were measured using X-ray fluorescence (XRF). Sulfur measurements were conducted using LECO combustion. Overall, there is an increase in the abundance of diagnostic oxides Al_2O_3 and TiO_2, elements K and Na, the ratio Th/U, and a decrease in sulfate mineralogy with distance from Core 2074.

Calculated unmodified CIA values show an increasing gradient (see Figure 2) with Core 2074 exhibiting the lowest values (15 and 23) and Core 33 (34 to 40) and 39 (36 to 48) exhibiting a higher range of values. The trend contradicts all other chemical alteration indicators. We hypothesize that salt dilution is responsible for this trend.

Application of the salt dilution modification to the DJB cores resulted in Core 2074 CIA_{Salt} values of 100, indicating fully chemically-altered samples. This is expected and is likely the result of the highest reported total salts (sum of salts reported by XRD) of all samples investigated. CIA_{Salt} values for Core 33 show significant alteration in most samples. Values changed from 35 to 47; 38 to 60; 35 to 100; and 37 to 82. As expected, Core 39 CIA_{Salt} values are the least affected. Original and CIA_{Salt} values are plotted against the molar ratio Al_2O_3/TiO_2 (Figure 2). Application of the salt modification to the CIA reversed the chemical alteration gradient and aligns it with all other chemical alteration indicators. Results show that the proposed/derived adjustment process could be valid, at least as a first approximation.

Implications: As with Mars, DJB remains an extremely cold, dry, and igneous environment, with the added presence of hypersaline, and stable surface water. Widespread martian jarosite, gypsum, and anhydrite have been interpreted as a sign that transient, chemically-altering fluids were active on Mars [e.g., 15, 16]. Though void of jarosite, sulfate mineralogy in DJB is predominantly expressed as aqueously-derived anhydrite and gypsum with comparable abundances to those measured on Mars. The scarcity of Na^+ and K^+, and the relative abundance of Ca^{2+} at the martian surface [17] means that the salt-modified CIA only modifies CaO abundance for the presence of $CaCl_2$ and $CaSO_4^{2-}$, not $(Na_2, K_2) \cdot SO_4^2$. Martian soil samples that exhibit approximately twice the sulfate abundance of the rocks may be underestimating the modified CIA.
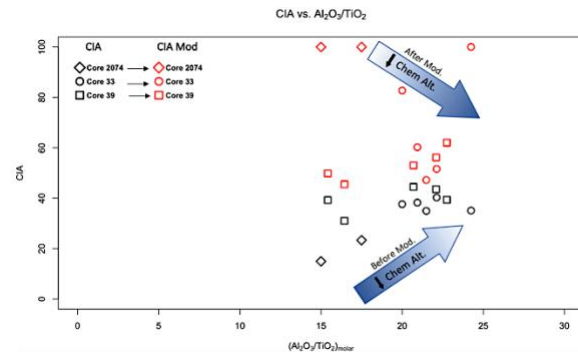

Figure 2: Comparison of unmodified (black points) and salt-modified (red points) CIA values for samples contained in Cores 2074, 33, and 39 in Don Juan Basin. Al_2O_3/TiO_2 values remain the same for original and modified CIA values. Alteration gradient reverses after salt modification of CIA.

Kieserite ($MgSO_4 \cdot H_2O$) is abundant on the martian surface [18], but is not accounted for in the original or our modified CIA equation. This may lead to an underestimation of salt dilution and an inaccurate portrayal of chemical alteration taking place on Mars.

Based on the CIA salt modification results, which align with the other chemical alteration indicators, it can be concluded that this method has successfully explained the chemical alteration trend in DJB. Future implementation of the CIA on Mars should look to account for the disproportionately large abundance of Ca^{2+}, lack of Na^+ and K^+, and the presence of Mg as kieserite.

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