RE-EVALUATING THE CIA PALEOCLIMATE PROXY ON MARS AT CURIOSITY'S DRILL SITES.

K. L. Siebach[1] and S. M. McLennan[2], [1]Rice University, Houston, TX (ksiebach@rice.edu), [2]Stony Brook University, Stony Brook, NY.

Introduction: The Chemical Index of Alteration (CIA) is a paleoclimate proxy based on feldspar alteration (ratio of Al to labile cations Ca, Na, K). This ratio is based on well-established chemical trends as rocks become more chemically weathered, following the chemical breakdown of feldspars as cations are flushed out of the system or incorporated into secondary salts. It was developed by Nesbitt and Young and has been tested and used in a variety of places on Earth and Mars to track paleoclimate changes [1-7].

CIA values for unaltered mafic sources are typically ~30-35, values above 40 suggest some influence from chemical weathering, and values above 50 are compelling evidence for chemical weathering. As developed, the proxy only includes Ca in silicate minerals; Ca (or Na, or K) from non-silicate minerals is subtracted. On Mars, we usually only have geochemical data, and so we cannot correct for cations that are not bound into silicate minerals. Uncorrected CIA values represent the minimum CIA value; including excess CaO or K_2O from secondary minerals makes the rocks appear to be less weathered than they really are, hence giving us a conservative estimate for weathering on Mars [6, 7].

Corrections, e.g. for secondary calcium sulfate, have been considered, but significant problems remain, including: (1) the implications of an arbitrarily-corrected weathering estimate are much less clear than the implications of a conservative estimate. (2) While we may know that there is, e.g., some calcium sulfate in the observed sample, we also know that calcium is also bound with other anions (e.g., phosphate), and that sulfate on Mars is frequently bound with other cations, such as Mg or Fe, which would not register in the CIA calculation at all. The presence of other cations and other anions means that estimating how much of the CaO is bound with nonsilicate anions is largely guesswork without a significant number of samples to compare.

In Yellowknife Bay, at the Sheepbed mudstone, as an example, Curiosity analyzed a sufficient number of geochemical samples with very similar baseline chemistry to be able to show when sulfur addition affected CIA. Figure 3 of McLennan 2014 [6] shows that, for the Sheepbed mudstone, when the amount of sulfate is plotted against the calculated (uncorrected) CIA value, the CIA values are constant until $SO_3 > 8$ wt%, then decrease with additional SO_3. The lack of change in CIA despite sulfate ranging from 1 to 8 wt% implies that in the Sheepbed mudstone, 8 wt% sulfate can be incorporated in the rock without any correlation to CaO. This brings us to a third reason to be cautious with CIA corrections: (3) the presence of significant XRD amorphous material in all the samples means that some elements are present in each sample that are not bound into either crystalline silicates or salt minerals. For example, minor amounts of sub-crystalline sulfide in Mars dust could dramatically alter perceived CIA values if all sulfur was assumed to be bound as calcium sulfate.

While arbitrarily selected corrections to the CIA may introduce excess error, it would of course be useful to have a better approximation for the Martian paleoclimate. Here, we use the combination of geochemical and mineralogical data obtained by Curiosity at ten drill/scoop target sites to better constrain the influence of secondary minerals on Martian CIA values.

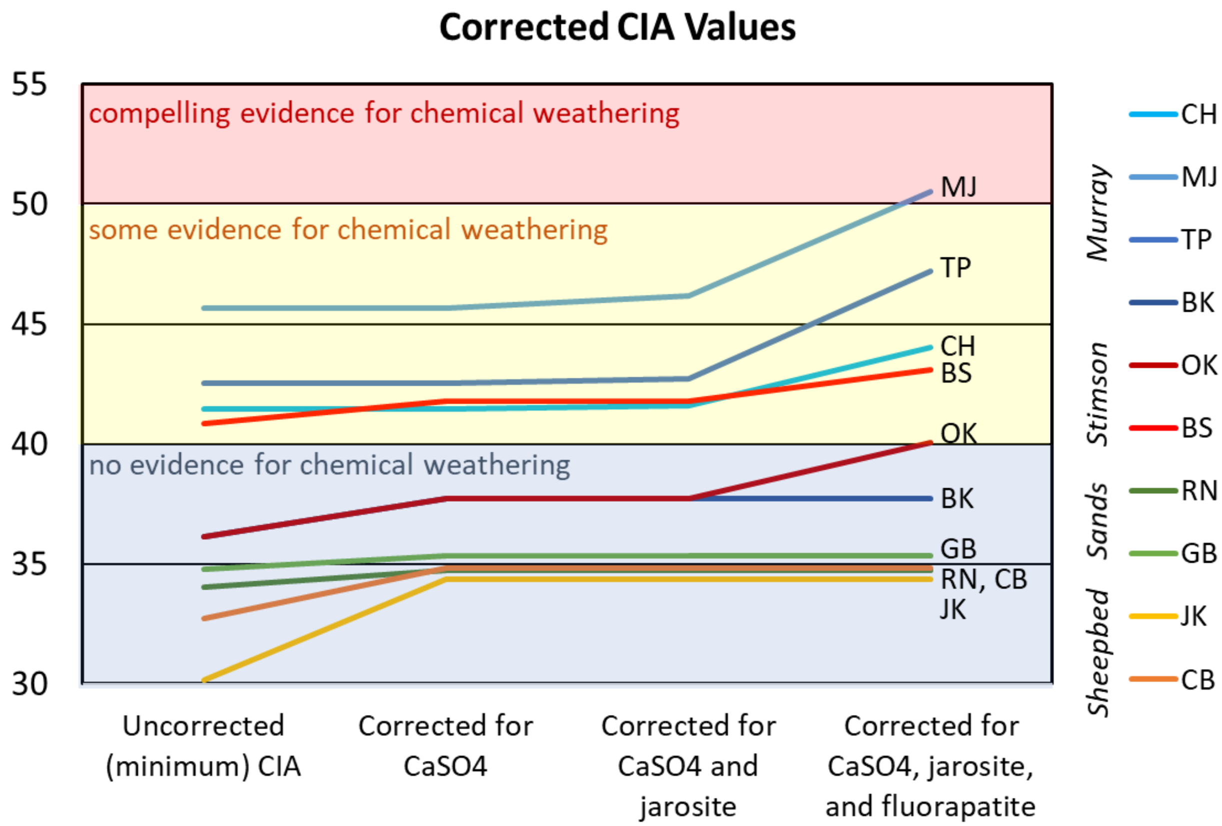
Targets: Ten targets were selected because they have APXS geochemistry data and CheMin XRD mineralogy data, and the crystal chemistry of the mineral phases within these targets were recently published in [8]. Targets include two sediment samples (RN, from an inactive sand shadow, and GB, from an active sand dune), two Sheepbed mudstone samples (JK and CB), four Murray mudstone samples (CH, MJ, TP, and BK), and two Stimson sandstone samples (BS and OK).

Methods: For each of the targets, the weight-percent-based elemental chemistry was converted into molar amounts, and then the amount of each element present in each crystal phase was calculated using the crystal chemistry results from Morrison et al. [8]. The CIA values for the bulk geochemistry and various corrected geochemistries were calculated based on subtracting CaO or K_2O in crystalline non-silicate minerals, including CaO in gysum, K_2O in jarosite, and CaO in fluorapatite, as reported in Figure 1, using molar proportions input into the following equation:

$$\mathrm{CIA} = \frac{\mathrm{Al_2O_3}}{\mathrm{Al_2O_3} + \mathrm{CaO^*} + \mathrm{Na_2O} + \mathrm{K_2O^*}}$$

In this equation, CaO* and K_2O* are corrected by subtracting CaO and K_2O in crystalline non-silicate minerals from the bulk values.

It is important to note that at this stage, no correction has been made for amorphous CaO, Na_2O, or K_2O, which could be primary or secondary. This is ongoing work, for which a key step is separating cations bound in phyllosilicates, which are silicate minerals for CIA calculations, and cations in non-silicate amorphous materials—these two categories are typically reported together as x-ray amorphous material.



Results and Discussion: CIA values corrected for CaO and K_2O in non-silicate minerals increased by an average of 2.6 units, with a range from 0.6 to 4.8 units. These small differences in CIA values do slightly increase the probability that the samples have been chemically weathered, but the overall sample interpretation remains much the same.

Sediments: Minerals contained within windblown sediments on Mars appear to have experienced minimal chemical weathering, and these targets contain almost no secondary minerals, so the sediments have CIA values very similar to unaltered basalts.

Sheepbed: The drilled samples in the Sheepbed mudstone contained some excess calcium sulfate minerals, as observed from visible inspection of the drill sites [9], but correcting CIA values for the crystalline calcium sulfate left the CIA just under 35 for both samples, consistent with previous results indicating a lack of evidence for chemical weathering in this unit [6, 7].

Stimson: The Stimson sandstone shows more evidence for chemical weathering than the modern basaltic sands, which may reflect a slightly more weathered source for the sediments or alteration that occurred during lithification and diagenesis [10].

Murray: The Murray mudstone shows the most evidence for chemical weathering of any of the units observed by Curiosity so far in Gale crater [11, 12], and this evidence becomes more clear when the CIA values are corrected to subtract non-silicate minerals found in the lake, particularly flourapatite. Buckskin (BK) is a high-Si sample with distinctive chemistry that has very low Al_2O_3 and low CIA values.

Summary: CIA remains a useful paleoclimate indicator for Earth and Mars. Reporting the minimum (uncorrected) CIA value for Martian sediments is preferable to correcting the CIA without mineralogical information, but as a first-order estimate, CIA values corrected for non-silicate minerals are likely to be about 2-3 units higher than uncorrected values.

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