

USING CURIOSITY DRILL SITES TO TEST THE CHEMICAL INDEX OF ALTERATION.

K. L. Siebach¹, C. N. Achilles², R. J. Smith³, S. M. McLennan³, E. Dehouck⁴. ¹Rice University, Houston, TX (ksiebach@rice.edu), ²NASA Goddard Spaceflight Center, Greenbelt, MD, ³Stony Brook University, Stony Brook, NY, ⁴LGL-TPE, Université de Lyon, France.

Introduction: The Chemical Index of Alteration (CIA) is a paleoclimate proxy based on feldspar alteration (oxide molar ratio of Al to the sum of Al and labile cations Ca, Na, K). This ratio is based on well-established thermodynamics; as rocks become more chemically weathered, igneous minerals break down and release cations, allowing those cations to be flushed out of the system or incorporated into secondary salts. As chemical weathering advances and cations are lost, CIA increases from igneous proportions. In sedimentary rocks, CIA values represent the time-integrated history of weathering from source rock to surface exposure. The ratio was developed by Nesbitt and Young and has been tested 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 of chemical weathering, and values above 50 are compelling evidence for chemical weathering. The equation for CIA is:

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

CIA Corrections: Note the asterisks on the cations: as developed, the proxy only includes cations present in silicate minerals, including both primary igneous minerals and phyllosilicates. The addition of cations from fluids, e.g. as precipitates or secondary salts, would otherwise artificially decrease CIA values, because it adds cations into the system that were not originally present in the igneous detritus. This is commonly referred to as the correction to CIA values; any Ca, Na, or K from non-silicate minerals or secondary salts, is subtracted [1,4]. Correcting CIA values adds a complication because the mineral hosts for the cations must be known.

On Mars, we typically only have geochemical data, and so correcting for cations that are not bound in silicate minerals is challenging. Uncorrected CIA values represent minimum CIA values; including excess cations from secondary minerals makes the rocks appear to be less weathered than they really are, therefore giving a conservative estimate for weathering on Mars [6, 7]. Different studies have sought to use different approximations for corrections to martian CIA values based on bulk geochemistry, for example, one could assume that all sulfate is bound to CaO. This is problematic for multiple reasons: (1) Sulfur is not always bound to CaO; indeed we have identified Mg- and Fe- sulfates [8, 9], so sulfate may be unrelated to

CIA. (2) Detrital igneous minerals that contain CaO are present in every sample analyzed with the CheMin X-ray diffractometer (XRD), so at least some of the calcium is not secondary [9]. (3) The implications of an arbitrarily or potentially over-corrected CIA value are poorly defined and not conservative. An uncorrected CIA value will give a minimum estimate for the degree of weathering in Mars's ancient past, but one that is over-corrected will indicate weathering that has not occurred. Without mineralogy, estimating how much of the CaO is bound with nonsilicate anions is largely guesswork, so without additional data, CIA values should not be corrected. Instead, uncorrected values should be considered minimum estimates of paleoweathering.

While imperfect corrections to the CIA may introduce excessive errors, it would of course be useful to have a better approximation for the Martian paleoclimate. In this work, we update our previous work [10] using the combination of bulk geochemical and mineralogical data obtained by Curiosity at now 18 drill/scoop target sites to better constrain the influence of secondary minerals on martian CIA values.

Data and methods: Eighteen targets were selected with both APXS geochemistry data and CheMin XRD mineralogy data [9-12]. 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), two Stimson sandstone samples (BS and OK), and twelve Murray mudstone samples (CH, MJ, TP, BK, OU, MB, QL, SB, DU, ST, HF, RH).

For each of the targets, the 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 [9,11,12]. CIA values were calculated for the bulk geochemistry (uncorrected) and corrected geochemistry of each sample. Corrected geochemistries were calculated by subtracting cations in crystalline non-silicate minerals, specifically CaO in gypsum, anhydrite, and bassanite, K₂O in jarosite, CaO in fluorapatite, and Na₂O in halite.

We compared the “uncorrected CIA” to the “corrected CIA and simply subtracted to show the amount of change in CIA that resulted from correcting for secondary minerals. In figure 1, we compare the amount of change in CIA to the uncorrected measured CIA value and to the wt% SO₃ in the sample in order to

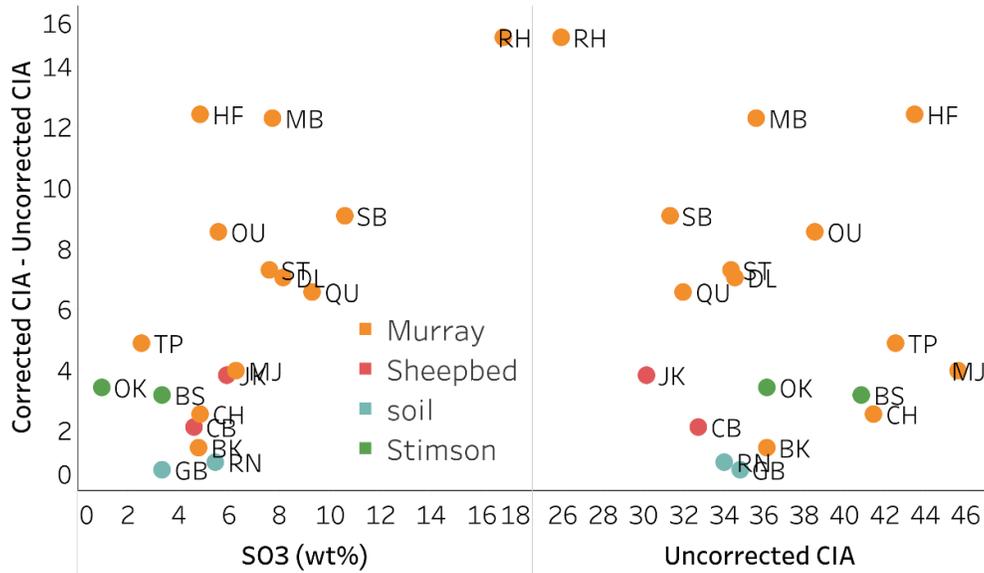


Figure 1. The difference between corrected and uncorrected CIA values are plotted against the sulfate content of the samples and the uncorrected CIA values. While high amounts of sulfate do predict the presence of some secondary salts, there is not a simple rule-of-thumb for predicting the correction to CIA values. We advise using uncorrected minimum estimates.

check whether there is a simple rule to predict when CIA values are accurate upon initial measurement.

It is important to note that at this stage, we do not correct for amorphous CaO, Na₂O, or K₂O, which could be primary or secondary. Cations bound in phyllosilicate minerals should be included as silicates for the CIA calculation, but it is difficult to accurately estimate the abundance and likely cation content of phyllosilicates compared to the amorphous material. At this stage, we are just using the best estimates of the amount of amorphous and clay materials from work by Achilles et al. and Smith et al., this conference [13-14].

Results and Discussion: The CIA values, corrected and uncorrected, for martian samples in Gale crater, based on APXS, are generally quite low, reflecting minor chemical weathering. The CIA values are higher in the Murray mudstone than in all other measured units, and have been broadly increasing with elevation [15]. The maximum “corrected” CIA value observed in the Murray mudstone was 56, which indicates chemical weathering that was comparable to the weathering occurring in Iceland today [16].

Correcting CIA values for cation additions in secondary salts changed the CIA value of most samples by less than 5, although the amount of salt, and therefore the amount of change to CIA, was much higher in the most recent Vera Rubin Ridge samples (e.g., the Rock Hall RH sample CIA increased by nearly 15). The amount of sulfate is not always a good predictor of the amount of secondary cations; broadly, if the target has more than 7 wt% SO₃, there will likely be some secondary salts affecting the CIA by at least ~6 units.

However, some targets with low SO₃ are also strongly affected by added salts (e.g., Highfield, HF).

Summary: Further study of each stratigraphic group of targets is required to establish when CIA is likely affected by secondary salt addition. In the absence of mineralogical information, there is not at present a clear way to estimate the amount of CaO, K₂O, and Na₂O bound to secondary salts in martian samples, especially Murray mudstone samples. At this point, we suggest, in the absence of quantitative mineralogical data, using uncorrected CIA values and reporting them as minimum estimates of paleoweathering rather than making any assumptions about the salt content.

References: [1] Nesbitt, H.W. and Young G.M. (1984) *Geochim. Cosmochim. Acta*, 48(7), 1523-1534. [2] Nesbitt, H.W. and Wilson R.E. (1992) *Am. J. of Science*, 292(10), 740-777. [3] Nesbitt, H.W. et al. (1996) *J. Geol.*, 104(5), 525-542. [4] Fedo, C.M. et al. (1997) *Precamb. Res.*, 86(3-4), 201-223. [5] Young, G.M. and Nesbitt, H.W. (1999) *Geol. Soc. Am. Bull.*, 111(2), 264-274. [6] McLennan, S.M. et al. (2014) *Science*, 343(6169). [7] Siebach, K.L. et al., (2017) *JGR*, 122(2), 295-328. [8] Rapin, W., et al. (2019) *Nature* 12, 889-895. [9] Morrison, S.M. et al. (2018) *Am. Min.*, 103 (6): 857-871. [10] Siebach, K. L. and McLennan, S.M. (2018) 49th LPSC, Abs. 2694 [11] Bristow, T. F., et al. (2018) *Science Adv.* 4(6) eaar3330. [12] Rampe, E. B., et al. (this meeting). [13] Achilles, C. A., et al. (this meeting). [14] Smith, R. J., et al. (this meeting). [15] Mangold, N., et al., (2019) *Icarus* 321 619-631. [16] Thorpe, M. T., et al. (2019), *Geochim. Cosmochim. Acta*, 263, 140-166.