

# Basalt weathering rates on Earth and the duration of liquid water on the plains of Gusev Crater, Mars

E.M. Hausrath<sup>1,2\*</sup>

A.K. Navarre-Sitchler<sup>2</sup>

P.B. Sak<sup>3</sup>

C. Steefel<sup>4</sup>

S.L. Brantley<sup>2</sup>

<sup>1</sup>Department of Geosciences, Penn State University, University Park, PA 16802

<sup>2</sup>Johnson Space Center, Houston, TX 77058

<sup>3</sup>Department of Geology, Dickinson College, Carlisle, PA 17013

<sup>4</sup>Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

\*Corresponding author: [Elisabeth.M.Hausrath@nasa.gov](mailto:Elisabeth.M.Hausrath@nasa.gov)

## ABSTRACT

Where Martian rocks have been exposed to liquid water, chemistry versus depth profiles could elucidate both Martian climate history and potential for life. The persistence of primary minerals in weathered profiles constrains the exposure time to liquid water: on Earth, mineral persistence times range from ~10 ka (olivine) to ~250 ka (glass) to ~1Ma (pyroxene) to ~5Ma (plagioclase). Such persistence times suggest mineral persistence minima on Mars. However, Martian solutions may have been more acidic than on Earth. Relative mineral weathering rates observed for basalt in Svalbard (Norway) and Costa Rica demonstrate that laboratory pH trends can be used to estimate exposure to liquid water both qualitatively (mineral absence or presence) and quantitatively (using reactive transport models). Qualitatively, if the Martian solution pH > ~2, glass should persist longer than olivine; therefore, persistence of glass may be a pH-indicator. With evidence for the pH of weathering, the reactive transport code CrunchFlow can quantitatively calculate the minimum duration of exposure to liquid water consistent with a chemical profile. For the profile measured on the surface of Humphrey in Gusev Crater, the minimum exposure time is 22 ka. If correct, this estimate is consistent with short-term, episodic alteration accompanied by ongoing surface erosion. More of these depth profiles should be measured to illuminate the weathering history of Mars.

**Keywords:** Mars, basalt, weathering, reactive transport modeling, rind, pH

## INTRODUCTION

To understand whether life could have existed or still exists on Mars, we need to be able to use data such as that from the Mars Exploration Rovers (Herkenhoff et al., 2004; Squyres et al., 2004; Haskin et al., 2005), the Mars Express satellite (Poulet et al., 2005; Bibring et al., 2006), and meteorites (Gooding et al., 1991; Treiman et al., 1993; Treiman, 2005) to constrain the duration and distribution of liquid water. Such data document the presence of primary silicates such as olivine (Hoefen et al., 2003), pyroxene (Mustard et al., 1997), plagioclase (Bandfield, 2002) and glass (Bandfield et al., 2000; Ruff et al., 2006) that may have weathered to secondary minerals (Christensen et al., 2000; Poulet et al., 2005; Bibring et al., 2006). Here, we

use both qualitative (mineral absence or presence) and quantitative (reactive transport modeling) approaches to interpret basalt weathering on Earth and on Mars.

### **Mineral Persistence**

Minerals persist for different lengths of time in terrestrial weathering environments (Goldich, 1938). To quantify how long a mineral persists before it is solubilized (mineral persistence time) on Earth, we examined the lengths of time that minerals persist in dated soils and chronosequences (Fig. 1; Appendix 1). We observed that persistence times varied from ~10ka (olivine) to ~250ka (glass) to ~1Ma (pyroxene) to ~5Ma (plagioclase), consistent with Goldich. The relative order of these mineral persistences is largely consistent with dissolution experiments (Fig. 2) at pH ~5.5–7. Mineral composition affects the observed persistence times: for example, relative persistence times for plagioclase in Figure 1 which includes all compositions are longer than in Figure 2, where only bytownite is represented.

Given the higher water fluxes, erosion rates, and tectonic activity on Earth, mineral persistence times depicted in Figure 1 are probably minimum estimates of Martian mineral persistence. However, such extrapolations depend upon the pH of weathering (Fig. 2) and such pH is poorly constrained on Mars: weathering pH may have been very acidic (Elwood Madden et al., 2004; Klingelhofer et al., 2004; Tosca et al., 2004; Hurowitz et al., 2006) or close to neutral (Poulet et al., 2005; Bibring et al., 2006). The pH of a weathering solution strongly affects relative mineral persistences (Fig. 2). For example, at extremely low pH, laboratory experiments (Fig. 2) predict dissolution rates of basalt glass > olivine. For  $2 < \text{pH} < 8$ , however, olivine dissolves more quickly than basalt glass.

Persistence times of diopside and bytownite should also be lower than glass at low pH but roughly the same at pH ~4–6. Plagioclase dissolution rates increase with increasing Ca content (Blum and Stillings, 1995), but reported rates for pyroxene do not vary strongly with composition.

To determine if a diagram such as Figure 2 is useful to predict Martian basalt weathering, we first compare its predictions to basalt weathering in Costa Rica and Svalbard. In Costa Rica pyroxene alters before plagioclase, which is consistent with the measured pH of porewaters (~4.7) (Fig. 2). On weathered surfaces in Svalbard, Na-containing glass is weathered to depths of ~250  $\mu\text{m}$  (Figs. 3, 4). Olivine phenocrysts intersecting the surface do not protrude significantly nor show embayment (Fig. 3b). Smoothing of ~20–40  $\mu\text{m}$  of the phenocryst roughness at the rock surface yields a minimum estimate of the weathering advance distance due to free-face dissolution. The observation that glass is dissolving deeper (more quickly) than olivine is consistent with the measured porefluid pH range for Svalbard (~7–9) (Fig. 2).

Since relative mineral weathering in Costa Rica and Svalbard follows pH trends documented by dissolution experiments, extrapolation of these trends to the Martian surface should reveal pH conditions of Martian weathering. Mineral compositions on Mars range from intermediate to ferroan olivine (McSween et al., 2006) and intermediate to calcic plagioclase (Bandfield, 2002; McSween et al., 2004). Both high and low Ca pyroxenes have been detected (Mustard et al., 1997; Hamilton et al., 2003; Bibring et al., 2005; McSween et al., 2006). Glass of a basaltic andesite composition, documented in a Martian meteorite (Greshake et al., 2004), would dissolve only slightly more slowly than the basalt glass dissolution line on Figure 2. The diopside dissolution line represents a good estimate for dissolution of Martian pyroxenes. The plagioclase dissolution rate may be up to one order of magnitude lower than the plotted line for

bytownite. At the low pH values suggested for Mars, relative weathering of glass and olivine may yield constraints on pH. For example, Mangold et al. (2007) propose that relatively unaltered olivine may be found with altered glass in the Nili Fossae region of Mars. Such dissolution of glass without alteration of olivine is consistent (Fig. 2) with either very low or high pH

### Reactive Transport Modeling

Where concentration-depth data is available such as on the rock Humphrey in Gusev Crater on Mars (Gellert et al., 2006), it is possible to calculate weathering duration using reactive transport codes. We used CrunchFlow (Maher et al., 2006) to forward model weathering rinds from Costa Rica, Svalbard, and Humphrey (Fig. 4) in one dimension using laboratory rates and diffusivities (Appendix 1). For the Costa Rica basalt, dissolution of plagioclase and pyroxene and precipitation of Fe and Al oxides in the reaction front were modeled (Fig. 4a). The weathering rock was modeled as 66% plagioclase + 26% pyroxene+2.6%quartz +1.8%alkali feldspar +1% magnetite +1.5%ilmenite + 1% porosity. Secondary minerals allowed to precipitate include kaolinite, Fe(OH)<sub>3</sub>, gibbsite, and siderite. CrunchFlow was similarly used to fit dissolution of Na-containing glass in Svalbard where the weathering rock was modeled as 25% glass + 73% inert mineral + 2% porosity because only glass was observed to dissolve (Appendix 1). No secondary minerals were included since few were observed. This implicitly assumes that while olivine dissolves by free-face dissolution at the surface, its dissolution rate within the rock is negligible relative to glass. The model fit to the glass dissolution is consistent with an inferred surface retreat of ~0.4 mm (Fig. 4b), consistent with petrographic observations of spalling (Appendix 1).

The Alpha Particle X-ray Spectrometers on the Mars Exploration Rovers have measured chemistry with depth in drilled holes for many rocks (Gellert et al., 2006). When profiles are normalized to Ti, negative values of the dimensionless mass-element-transfer coefficient  $\tau_{Ti,j}$  (Appendix 1) for elements such as Mg, Fe, Ca and P are observed. Mg and Fe loss from the inferred weathering rind on Mars rock Humphrey is consistent with olivine loss (Hurowitz et al., 2006). Humphrey is inferred to contain plagioclase, pyroxene, and Fo52 with up to 10% high-silica glass (Ruff et al., 2006). The weathering rind on Humphrey (McSween et al., 2004; Gellert et al., 2006) (Fig. 3) is modeled here because abrasion reached unaltered parent (Gellert et al., 2006), and forward modeling relies upon knowledge of parent material.

All Fe and Mg loss was attributed to olivine dissolution, similar to our earlier assumption of Na loss due to glass dissolution for Svalbard. Fe and Mg (McSween et al., 2004) were assigned to Fo84 and Fo25, the two probable end members of zoning in Humphrey (McSween et al., 2006). The olivine is probably zoned; this simplification facilitates modeling. The assumption of Fo84 (14%) and Fo25(11%) results in a rock that is 25% olivine (McSween et al., 2004; McSween et al., 2006). Following our approach to Svalbard, the rest of the rock (72%) is assumed to be inert.

The shortest time that allowed a fit to the reaction front was 22 ka with a modeled weathering advance rate of  $10^{-8}$  m yr<sup>-1</sup>. In contrast to Svalbard, the front was fit without surface retreat. However, Mars experiences physical erosion at rates of  $0.04 \times 10^{-9}$  (Golombek and Bridges, 2000) to  $3 \times 10^{-3}$  m yr<sup>-1</sup> (Sagan, 1973). Since the chemical weathering advance rate is within the range of physical erosion rates, the profile could represent steady-state thickness

(weathering rate = erosion rate). In any case, it is likely that erosion removed some of the surface of Humphrey, implying that the calculated 22 ka is a minimum weathering duration.

This 22ka weathering duration is within a factor of ~10 of the olivine persistence times in terrestrial and laboratory environments (Fig. 1), as well as the time estimates by Stopar et al. (2006) for similar conditions on Mars (1.6–1.9 ka). 22 ka is much shorter than the age of the Adirondack rocks in Gusev Crater, suggesting that the presence of water in this location was extremely brief, or that physical weathering is occurring at close to the same rates as chemical weathering. The 22ka time of weathering may also represent summation of sporadic wet time periods interspersed with much longer dry periods as inferred for meteorites (e.g. Treiman et al., 1993). Such shortlived and episodic alteration may be more consistent with alteration such as that resulting from impacts, rather than more long-lived aqueous alteration such as surface oceans. The weathering duration inferred for diffusion-dominated transport used in our model is also consistent with low water-rock ratios inferred for Adirondack rocks in Gusev crater such as acid-sulfate weathering or thin films of water under snow or frost (Hurowitz et al., 2006).

The hole on Humphrey is one of the shallowest drilled by the Spirit Rover (Arvidson et al., 2006). A number of studies (Ming et al., 2006; Morris et al., 2006) have found that while the Adirondack rocks (which include Humphrey), are minimally weathered, weathering in Columbia Hills was much more intensive. Satellite data document phyllosilicates (Poulet et al., 2005; Bibring et al., 2006), hematite and sulfate (Christensen et al., 2000; Bandfield, 2002; Gendrin et al., 2005). Depth profiles in such areas might yield more information regarding the aqueous history of Mars.

## CONCLUSIONS

Terrestrial mineral persistence data suggest minimum persistence times for olivine (10ka), glass (250 ka), pyroxene (~1Ma), plagioclase (~5Ma) on Mars. These relative mineral weathering rates and relative mineral weathering rates in Svalbard (Norway) and Costa Rica are consistent with pH values of weathering solutions. This suggests that relative persistences on Mars (particularly olivine and glass) may be used to constrain the pH of the weathering fluid. The successful use of reactive transport modeling to match reaction fronts in basalts on Earth lends confidence to the utility of using reactive transport modeling for Mars. The CrunchFlow fit of the weathering rind on Humphrey requires 22 ka of weathering, and could represent steady-state thickness (weathering rate = erosion rate). In any case, the 22ka is a minimum time of exposure to liquid water for this Mars rock due to the presence of physical weathering, and suggests short-term and episodic aqueous alteration in this location. This interpretation of weathering profiles on Mars suggests the type of depth profiles that could be collected to further interpret the aqueous history of Mars.

## ACKNOWLEDGMENTS

We thank J. Moore, J. Bandstra, M. Angelone, J. Cantolina, D. Egglar, J. Mustard, AMASE, WUN, BRIE (NSF IGERT grant DGE-9972759), PSARC, NASA NNG05GN72G, an NAI Research Fellowship, and NSF Graduate Research Fellowship (EMH). We appreciate thoughtful reviews by J. Bandfield, T. Lyons, H. McSween, and J. Taylor. This work was supported in part by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 to Lawrence Berkeley National Laboratory.

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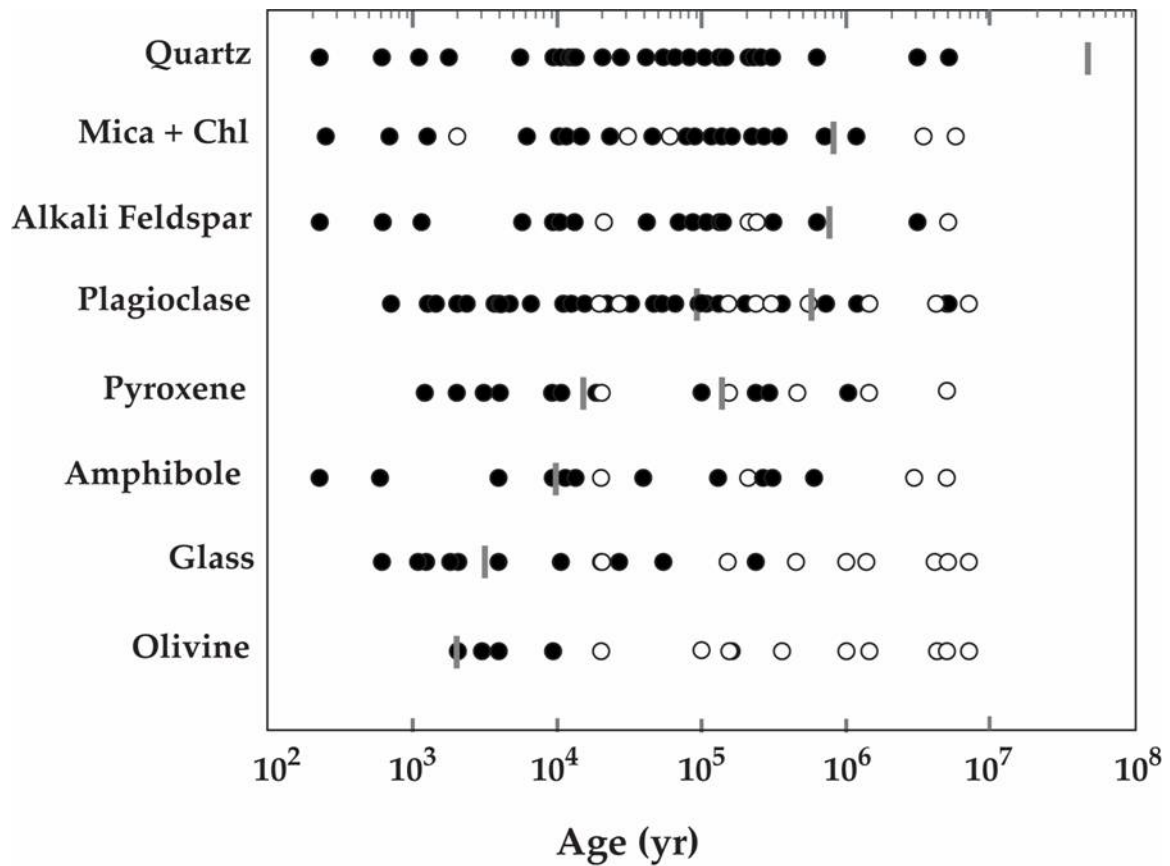


Figure 1. Mineral persistence times defined by  $\geq 2\%$  abundance (closed symbols) of silicates in A and B horizons of modern, dated soils and weathering rinds versus soil age. Open symbols = phase is no longer present within a chronosequence. Gray bars = lifetimes of 1mm silicate spheres calculated from laboratory rate laws at pH = 5; pairs of gray bars = end member compositions. Data compilation described in Appendix 1.



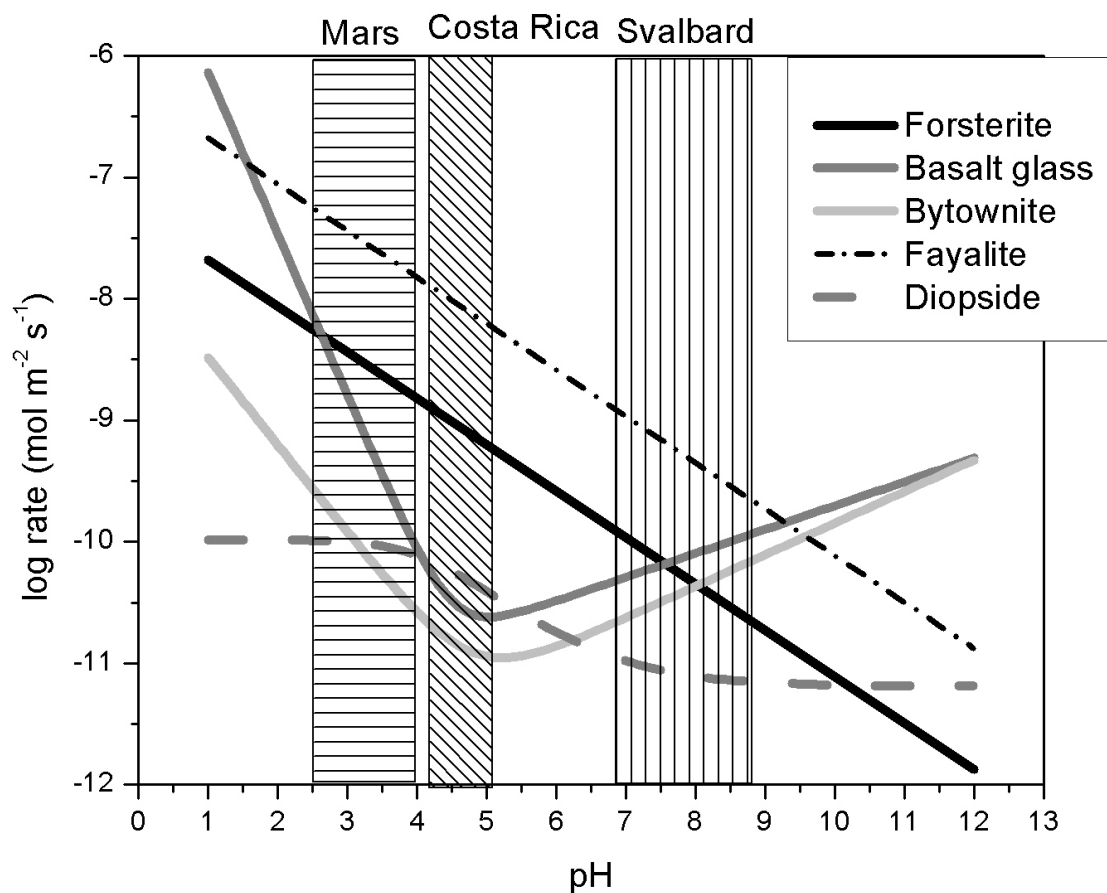


Figure 2. Log dissolution rates of silicates versus pH. Forsterite, basalt glass, and diopside rates from Bandstra and Brantley (in press). Bytownite is estimated from albite, and fayalite from forsterite (Bandstra and Brantley, in press) (Appendix 1). Ranges labeled Svalbard, Costa Rica and Mars represent estimated pH from soil measurements (Svalbard and Costa Rica) or the stability field of jarosite (Mars; Elwood Madden et al., 2004).

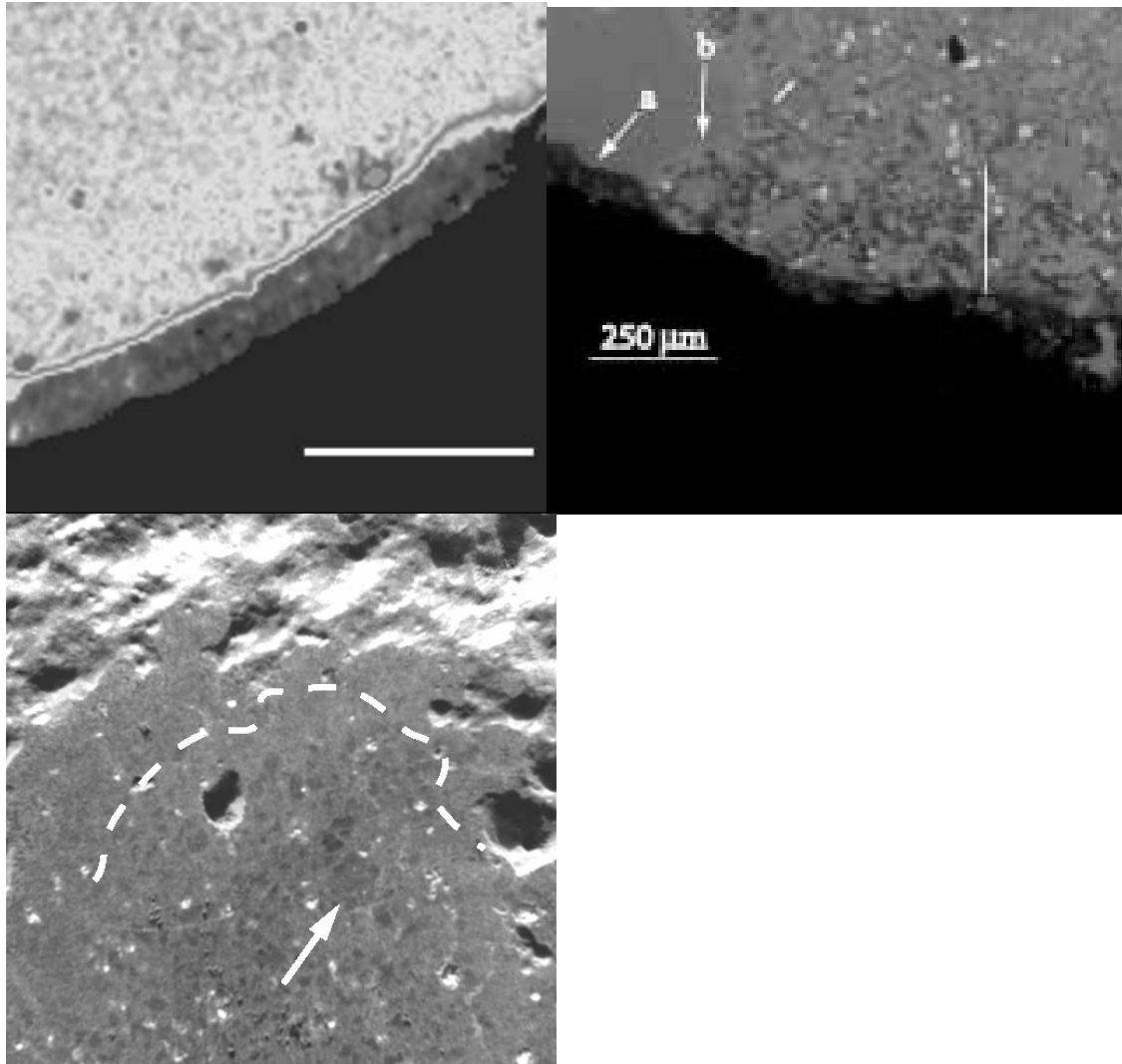


Figure 3. Weathering rinds on basalt samples from a) Costa Rica b) Svalbard and c) Mars. Figure 3a is a computed tomography image of a 1.2 cm-thick weathering rind developed over 35ka on a basalt clast in Costa Rica (Sak et al., 2004). Unweathered core (gray) is rimmed with Fe and Al oxides of the weathering rind (dark material). Weathering increases porosity (black areas). The large olivine grain imaged by back-scattered electron micrography in Figure 3b displays a smoothed outer surface (letter a) without a zoned rim (letter b) (see text). Black areas present to  $\sim 250 \mu\text{m}$  (white line) are pore space created by glass dissolution. The double headed arrow indicates an example of a mineral aggregate used to estimate surface area (Appendix 1). Figure 3c is a Microscopic Image of an inferred weathering rind (dashed white line (McSween et al., 2004)) on abraded rock Humphrey on Mars. ([http://marsrovers.jpl.nasa.gov/gallery/all/spirit\\_p060.html](http://marsrovers.jpl.nasa.gov/gallery/all/spirit_p060.html)). The arrow indicates an inferred olivine grain (McSween et al. (2006)). Figure 3c is  $\sim 2\text{cm}$  across.

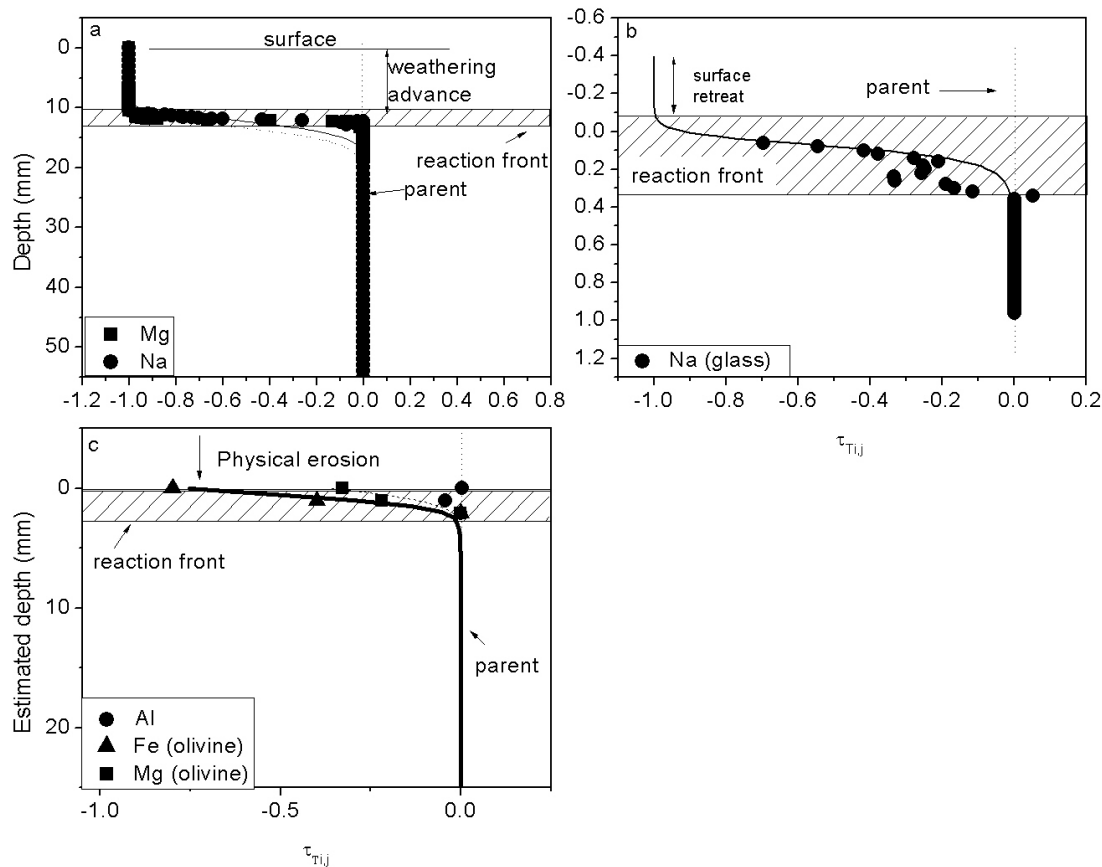


Figure 4. Plots of the dimensionless element-mass-transfer coefficient  $\tau_{Tij}$  ( $= 0$  for average parent,  $= -1$  for 100% depletion) versus depth for weathered basalt from a) Costa Rica b) Svalbard, and c) Mars (Humphrey; Gellert et al., 2006). Profiles are normalized to Ti and except for c) represent the average of 9 or more profiles. Data symbols shown with CrunchFlow model output lines. Data in Figures 4a and 4b are smoothed with a 3-point and 5-point moving average respectively, and parent materials represent average compositions. In Figure 4a Na is in plagioclase, and Mg in pyroxene, and parent and rind analyses are extended for effect. In Figure 4b Na is in glass. In Figure 4c, Mg and Fe are in olivine. The Mars profile was first corrected for dust (Appendix 1). The weathering advance distance for the Costa Rican weathering rind is easily interpreted because, protected in deep soil, it has not eroded (Sak et al., 2004). In contrast, the  $\sim 0.3$  mm of glass dissolved on the basalt weathered in Svalbard is only an apparent distance because the surface has retreated due to erosion.

<sup>1</sup>GSA Data Repository item 2007xxx, supplementary methods and description, is available online at [www.geosociety.org/pubs/ft2007.htm](http://www.geosociety.org/pubs/ft2007.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.