PARTIALLY WEATHERED BASALTIC GLASS - A MARTIAN SOIL ANALOG

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Introduction. The Viking x-ray fluorescence spectrometer (XRFS) provided bulk elemental analyses of Martian surface fines at two different landing sites. In one geochemical interpretation, Toulmin et al. (1) proposed that a mixture of iron-rich smectite clays constitutes the bulk of the fines and noted that such clays are commonly produced on Earth by the weathering of basaltic glass. Gooding and Keil (2) found theoretically that glass weathering on Mars might also be conducive to clay formation. We report here initial results for a study of weathered materials from a variety of terrestrial source rocks and weathering environments, some of which may be applicable to the surface of Mars.

Icelandic Palagonites. Pristine and altered basaltic glass samples from six Pleistocene subglacial eruption centers in Iceland were analyzed by electron microprobe, optical and scanning electron microscopy, and x-ray diffraction techniques. Initial compositions, ages and inferred weathering conditions are approximately the same for all samples. The bulk of each sample is composed of sideromelane fragments approximately 0.1-2 mm in size and displaying curving surfaces characteristic of shattered vesicle walls. The low crystal content of the glass, not more than a few per cent by volume, indicates quenching in a matter of seconds.

Weathering products (hereafter called "palagonite") occur in three distinctive forms: (a) various amounts (up to 30% of the sample volume) of a discontinuous, fine-grained matrix between the glass particles, (b) essentially continuous layers which line the interiors of all but the smallest vesicles, and (c) coatings on the surfaces of individual glass particles (Fig. 1). These coatings may be up to 100 microns thick, although most are within the 30-50 micron range. All three forms of palagonite have similar bulk chemical compositions.

Mineralogy. From the small amount of published work on attempted phase identifications of palagonite (3-6), it appears that mineralogy varies with sample locality. For Icelandic palagonites, our XRD results suggest substantial amounts of zeolites accompanied by oxides and possibly phyllosilicates. Further work is in progress on identification of the clay-sized fraction but, at present, smectites are neither confirmed nor eliminated.

Geochemistry. Microprobe analyses of our palagonites, expressed in oxide form, total to only about 65-90% by weight, with the remainder thought to be water (chemically bound and adsorbed varieties). Although they tend to conceal compositional zonation within layers, recalculated water-free palagonite compositions are useful for glass/palagonite comparisons and demonstrate the large compositional changes which occur during palagonitization (Table 1). The most marked changes are the almost total loss of Na and the sharp decrease in Ca with concomitant increases in K and Fe abundances. Ti and Mg segregate into distinctive bands within the palagonite layers, whereas Si and Al generally maintain their pre-weathering abundances.

According to field observations at Surtsey (6), Icelandic palagonitization probably proceeds by deuteric or hydrothermal alteration of congealed basaltic glass which was initially erupted subaerially or subglacially. Given the saline and CO_2-rich nature of Icelandic geothermal water (7), several important features of hydrothermal palagonitization become apparent. First, potential clay mineral derivatives should exhibit a wide range of thermal stabilities (Fig. 2). Nontronite is predicted to be particularly unstable, especially below $200^{\circ}C$. Secondly, reaction with CO_2 should favor the decomposition of smectites to kaolinite and iron oxides/hydroxides. Finally, carbonate dissolution should increase with fluid salinity, although sudden loss of CO_2 could lead to carbonate precipitation. Zeolite formation could result in the observed differential retention of large cations (e.g., K^+ vs. Na^+ or Ca^{++}).

Application to Mars. When recalculated to a S- and Cl-free basis, the composition of the Martian surface fines (8) compares favorably with that of Icelandic palagonite for all elements except Al (Table 1). In this regard, our results provide some new insights on the possible palagonite component in Martian fines. The first major point is that palagonites of the Icelandic subglacial variety are not isochemical equivalents of their respective basalt progenitors. Consequently, similar geochemical fractionations should be considered in attempts to deduce Martian source-rock compositions from palagonite models of Martian fines. For example, the concentration of component i in the source rock (r) can be related to that of its palagonite derivative (p) as $C(i,r) = C(i,p)F(i)$, where $F(i)$ is a fractionation factor. Using palagonite $F(i)$ values $F(i) = C(i,glass)/C(i,p)$ from Table 1 and taking Viking results for Martian fines (Table 1) as a set of $C(i,p)$ values, we calculate the following composition (weight %) for the hypothetical Martian source rock: 51.4 SiO_2, 0.88 TiO_2, 6.6 Al_2O_3, 14.9 FeO, 11.0 MgO, 14.3 CaO, <0.2 K_2O. However, this recalculation assumes that the oxide-total deficits in both the Icelandic palagonites and the Martian fines analyses are attributable to the same (undetermined) elements. In fact, allowance for an arbitrary 1% CO_2 (as $CaCO_3$) in the 8% deficit in the original Viking XRFS analytical total (8), assignment of the 3.1% S in Martian fines (8) to $MgSO_4$, and estimation of Na abundance as $C(Na,r;Mars) = C(K,p;Mars)C(Na,glass)F(K)/C(K,glass)$ yields the following revised composition for the Martian source rock: 56.0 SiO_2, 0.99 TiO_2, 7.1 Al_2O_3, 16.2 FeO, 6.3 MgO, 11.9 CaO, <1.4 Na_2O, <0.2 K_2O. Other compositions can be calculated by making further allowance for nonisochemical weathering effects.

The second major point to be emphasized here is that the true bulk composition of the Martian fines might be camouflaged if the fines were composed of surficially weathered glass fragments similar to those in Icelandic palagonites. Although significant (>0.25 microns thick) coatings of iron oxide on silicate particles have been rejected as a source of serious compositional aberration in the Viking XRFS results (8), the 30-50 micron thick coatings on palagonitized Icelandic basaltic glass approach or exceed the sample excitation depths of the Viking XRFS (9). We note that particle size compatibility with the apparently silt-sized Martian fines (10) would require extensive weathering of the silicates. Nonetheless, the interpretation of Martian surface fines as partially weathered glass particles should not be excluded.

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PARTIALLY WEATHERED BASALTIC GLASS ...

Allen, C. C., et al.

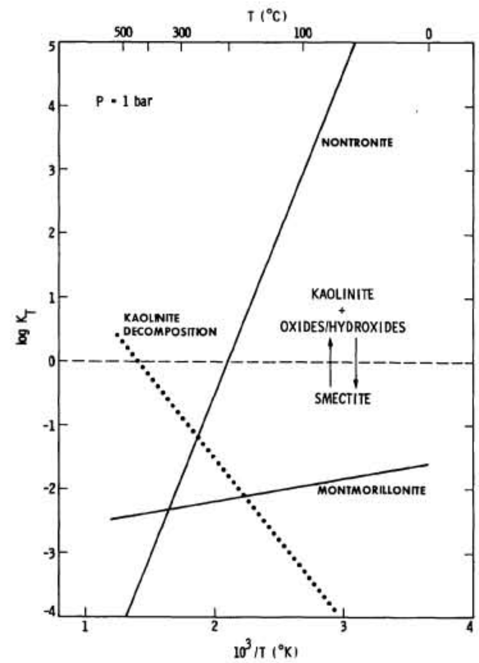

Fig. 1 Sideromelane grains coated by layers of palagonite (arrows). Transmitted light photomicrograph. Scale bar indicates 500 microns.

Fig. 1 Calculated variation of reaction constant (K_T) with temperature (T) for thermal decomposition of clay minerals. Decomposition (favored for log K_T > 0) should be further enhanced by reaction of clays with CO_2 (11).

Table 1

	Glass (mean of 33)	Palagonite (mean of 45)	($\pm$ 1 std dev)	Viking SI Sample (8) (analysis)	(error)
SiO_2	49.6	52.7	49.8- 55.5	54.6	48.1-61.1
TiO_2	2.23	2.53	.48- 4.6	1.1	.7- 1.5
Al_2O_3	14.4	15.3	12.0- 18.7	7.0	4.9- 9.0
FeO*	12.3	16.5	12.8- 20.2	19.9	16.7-23.1
MgO	7.1	6.6	2.02-11.1	10.1	5.1-15.1
CaO	11.6	5.5	1.92- 9.1	6.8	5.5- 8.2
Na_2O	2.46	.19	.05- .32	n.d.	
K_2O	.27	.69	.26- 1.11	<.4	
Total	100.0	100.0		99.9	

*All Fe calculated as FeO   n.d. not determined by Viking