

AN EXPERIMENTAL STUDY OF PHYLLOSILICATE MODIFICATION IN COMETS DURING PERIHELION COULD BE RELEVANT TO FERRIC IRON-RICH LAYER SILICATE FORMATION AT THE MARTIAN SURFACE. Frans J. M. Rietmeijer¹ and Klaus Thiel², ¹Department of Earth and Planetary Sciences, MSC03-2040, University of New Mexico, Albuquerque, NM 87131-0001, USA; fransjmr@unm.edu, ²Department of Nuclear Chemistry, University of Köln, D-50674 Köln, Germany (klaus.thiel@uni-koeln.de).

Introduction: The variety of layer silicates identified at the Martian surface [1] prompted us to introduce the notion that exposure to solar radiation could be an agent for chemical modification of phyllosilicates during weathering of a wide variety of rock types exposed at the Martian surface and of phyllosilicates in permafrost-like soils leading to formation of Fe-rich layer silicates and lower K₂O contents in micas.

The KOSI team applied periods of simulated insolation to dust-ice mixtures of natural Mg-rich silicates, including “olivine” and “montmorillonite” fractions, graphite, charcoal, water and CO₂ ices at -196°C to simulate the physical processes at the surface of an active comet nucleus during perihelion, *e.g.* dust production rates and size distributions, by [2,3]. A transmission electron microscope study of the KOSI-2 experiment found an abundance of Fe-rich layer silicates that were not present in the starting material [4] suggesting hydrocryogenic dust modification. Iron for the chemically modified layer silicates was probably extracted from low-iron layer silicates in the starting material via $(\text{Fe}^{2+} + \text{OH}^-) = (\text{Fe}^{3+} + \text{O}^{2-}) + \frac{1}{2}\text{H}_2$ [4]. Layer silicates on Mars occur in regions characterized by (1) Fe/Mg-smectite (no montmorillonite), (2) Fe-rich clays, *incl.* nontronite (Fe-smectite) and chamosite (Fe-rich chlorite) and (3) montmorillonite [1]. Smectite and chlorite as the products of chemical weathering may have formed in a globally homogenous dust layer on Mars [5]. The surprising chemical reactivity observed in the Viking Lander biology experiments could have been due to catalytic action by smectite-illite clay minerals [6].

KOSI-2 Observations: A mixture of ~10% minerals (Table 1) and ~90% water ice was exposed to simulated sunlight to create the conditions during four perihelion passages (Fig. 1). The 002-basal spacing

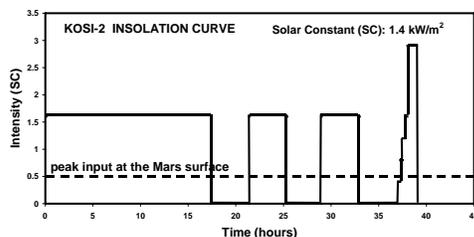


Figure 1: Energy input for four simulated perihelion passages of a comet in the KOSI-2 experiment [7].

Table 1: Mineral impurities in “olivine” and “montmorillonite” fractions of the KOSI-2 experiment (water ice only). The silicate fraction was a mixture of ~90% “olivine” and ~10% “montmorillonite” [7]. Silicates of the starting material in bold italics were found in the TEM study [4].

| “Olivine fraction” | |
|----------------------------|---------------------------------|
| 84-91 % | <i>Forsterite (Fo94)</i> |
| 5-11 % | <i>Enstatite (Fs94)</i> |
| 1.7-2.2 % | <i>Chlorite</i> |
| 1.0-1.5 % | <i>Serpentine</i> |
| 0.1-0.4 % | Talc |
| 0.5 % | Spinel |
| “Montmorillonite fraction” | |
| 93 % | <i>Montmorillonite</i> |
| 3 % | <i>Feldspar</i> |
| 2 % | Muscovite |
| 1 % | <i>Quartz</i> |
| 1 % | Cristobalite |

values [4] and chemical compositions indicate that Fe³⁺ is the only iron species in the layer silicates. Phyllosilicates in the starting materials have low Fe₂O₃ contents for both Mg-rich and Mg-poor compositions (Fig 2a; black dots), including natural mica (red open circles).

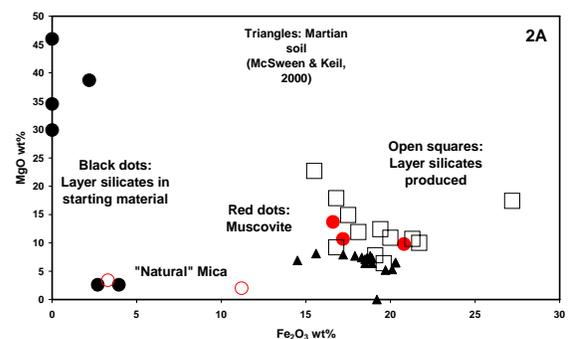


Figure 2A: Fe₂O₃ vs. MgO (wt%) in KOSI starting material (black dots) and modified layer silicates (open squares). KOSI-2 muscovite (solid red dots) is presumably Fe-enriched muscovite from the starting material by comparison with “natural” mica compositions (open red circles). Martian soil compositions [5] are for reference only (solid triangles).

The KOSI-2 Fe-rich muscovite (red dots) suggests it is chemically modified muscovite. This seems plausible as they are among the cluster of Fe-rich chlorite and smectite but we cannot be entirely sure yet. The Fe_2O_3 content of modified KOSI phyllosilicates and the Martian soil are similar. The MgO contents of the Martian soil overlap with the former. The Al_2O_3 content of the modified layer silicates is higher than the Martian soil (Fig. 2b).

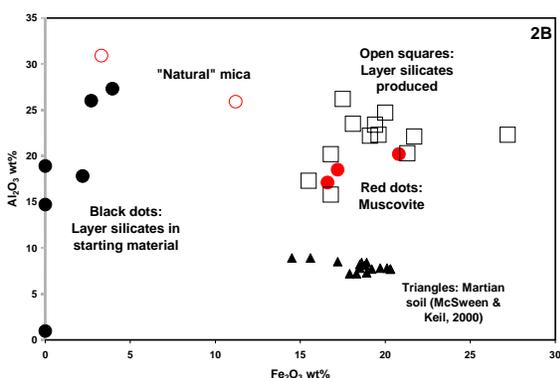


Figure 2B: Fe_2O_3 vs. Al_2O_3 (wt%); same symbols as [2A].

This difference is certainly related to the high Al_2O_3 content of the KOSI-2 starting materials but not inconsistent with “illite” in EETA79001 [6] that suggests that high- K_2O phyllosilicates (mica) existed near the Martian surface. The KOSI-2 starting material included muscovite (Table 1) that is significantly more Fe-rich than typical terrestrial mica. The K_2O contents of “natural” mica and KOSI-2 muscovite are comparable (Fig. 3). The decreasing K_2O values in this KOSI-2 muscovite show a trend consistent with the smectite-illite model [6] to Fe-rich K-bearing smectite and chamosite (Fig. 3; open squares).

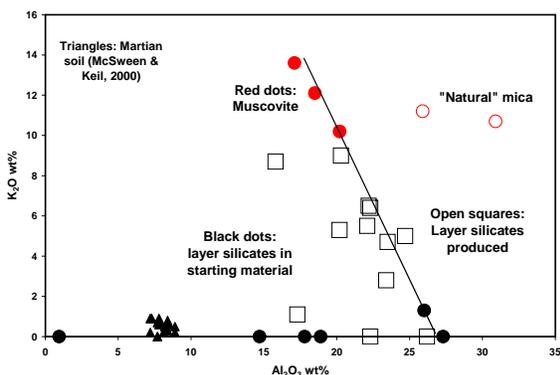


Figure 3: Al_2O_3 vs. K_2O (wt%) in KOSI starting and modified layer silicates, *incl.* KOSI-2 muscovite, and “natural” mica and Martian soil compositions. Symbols are identical to those used in Figure 2. The solid line could be a mixing line between muscovite and montmorillonite and beidel-

lite in the starting materials for the trend of KOSI-produced Fe-rich phyllosilicates, *incl.* chamosite (Fe-chlorite).

Periods of simulated solar radiation caused iron oxidation and iron enrichment in chlorite (chamosite), smectite (nontronite) and muscovite (mica), and concomitant changes in the $(\text{OH}^-)/\text{O}^{2-}$ ratios. It is unclear whether dehydroxylation [4] involved chemical transport at hydrocryogenic conditions or whether it was an entirely intra-crystalline process. As magnesium from layer silicates in the starting material had to be removed probably in solution it seems plausible that hydrocryogenic conditions existed, but so far we have not found pure-MgO or other Mg-rich precipitates in the KOSI-2 experiment.

The processes involved coupled substitutions:

- (1) $\text{Fe}^{3+}(\text{vi}) + 2\text{Al}^{3+}(\text{iv}) + \text{K}^+(\text{interlayer}) = 3\text{Mg}^{2+}(\text{vi}) + \text{Si}^{4+}(\text{iv})$, and for decreasing K_2O contents
- (2) $\text{Fe}^{3+}(\text{vi}) + \text{Al}^{3+}(\text{iv}) = 2\text{K}^+(\text{interlayer}) + \text{Si}^{4+}(\text{iv})$.

Discussion and Conclusions: KOSI-2 showed that a non-traditional geological process caused chemical modification of phyllosilicates in a dirty-ice mixture. What are the implications for layer silicates on Mars assuming solar radiation is an effective process:

- (1) Fe oxidation and Fe enrichment of layer silicates,
- (2) Mg-mobilization,
- (3) Decreasing K-contents from mica to chamosite
- (4) Potentially IR-detectable variability in $(\text{OH}^-)/\text{O}^{2-}$ ratios and correlated increases in the Fe^{3+} content to trace aging of Fe-rich phyllosilicates,
- (5) Dehydroxylation leading to amorphous serpentine [8] and smectite dehydroxylates that are common metastable compounds [9], and
- (6) Geological processing at the Martian surface of these metastable compounds with the basic metal-oxide/ SiO_2 ratios of phyllosilicate minerals [10].

We discussed the KOSI results in a ‘Martian context’ but with an understanding that lower solar radiation as a cause of chemical modification of phyllosilicates at Martian surface conditions throughout time remains to be fully assessed by future controlled experiments.

References: [1] Poulet F. et al. (2005) *Nature*, 438, 623-627. [2] Thiel K. et al. (1991) *Geophys. Res. Lett.*, 18, 281-284. [3] Grün E. et al., (1993) *Geophys. Res. Lett.*, 98, 15091-15104. [4] Rietmeijer F. J. M. and Thiel K. (1995) *LPS XXVI*, 1167-1168. [5] McSween, Jr. H. Y. and Keil K. (2000) *Geochim Cosmochim. Acta*, 64, 2155-2166. [6] Gooding J. L. (1992) *Icarus*, 99, 28-41. [7] Thiel K. et al. (1990) *Proc. LPSC*, 20, 389-399. [8] MacKenzie K. J. D. and Meinhold R. H. (1994) *Amer. Mineral.*, 79, 43-50. [9] Rietmeijer F.J.M. et al. (2004) *Meteoritics Planetary Science*, 39, 723-746. [10] Rietmeijer F. J. M. et al. (2007) on-line doi:10.1016/j.icarus.2007.11.022