

MINERALOGICAL ANALYSIS OF DESERT VARNISH BY DTA/GC:
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Differential thermal analysis (DTA) coupled with gas chromatography (GC) is an analytical technique that is suitable for mineralogical analysis on landed missions to Mars. We have analyzed a variety of substances important to exobiology using DTA/GC. The substances tested included organic compounds (proteins, amino acids), evaporites (NO_3^- , CO_3^{2-} , and NO_2^- salts), clays (montmorillonite, kaolinite, nontronite), Fe-enriched clays [1,2], non-clays (palagonite), and various mixtures of these substances. In addition, we have analyzed samples collected from ecosystems ranging from Antarctic endolithic rocks, evaporitic deposits occurring near thermal alkaline and acid springs in Yellowstone National Park, Wyoming, to gypsum halite evaporitic crusts that form along the intertidal. We compared the DTA/GC with several other techniques and found it to be the most appropriate as a flight instrument for the *in situ* determination of the mineralogy of the Martian surface material [3].

Desert varnish, a coating of manganese and iron oxides held in a clay matrix on the surface of rocks, is widespread on Earth's deserts. Its formation is thought to involve weathering processes acting in conjunction with microbial activity. Consequently, if desert varnish similar to that found on earth is found on Mars, then the probability for life to have arisen on Mars increases.

Data from a typical analysis of a sample of desert varnish is depicted in figure 1. Analyses were conducted using 30 mg of aluminum oxide as the reference material, and 30 mg of sample. Samples were removed from rocks covered with varnish with aluminum oxide grit (this does not give a DTA thermal signature when Al_2O_3 is used as the reference, nor does it react with the varnish). Samples were analyzed under vacuum using a Dupont model 1600 high temperature DTA oven equipped with a model 910 cell base. The heating rate was $10\text{ }^\circ\text{C min}^{-1}$. The system is controlled by a Sun Sparc II workstation. The system was tested and calibrated with pure samples of the suspected unknown minerals in the sample, as well as mixtures of these minerals. Gas evolution during sample heating is sensed by a pressure sensor which triggers a valve allowing the evolved gas to expand from the oven chamber into a GC sample loop.

The first endotherm ($\sim 100\text{ }^\circ\text{C}$) depicted in figure 1 is accompanied by the production of water vapor and can be attributed to the vaporization of water adsorbed to the sample, while the second ($\sim 120\text{-}130\text{ }^\circ\text{C}$) is due to illite. The exotherms and endotherms occurring between 140 and $320\text{ }^\circ\text{C}$ are most likely due to the oxidation and transformations of oxides and oxyhydroxides of manganese. The exothermic peak observed between $320\text{ }^\circ\text{C}$ and $360\text{ }^\circ\text{C}$ is due to the transition of magnetite (Fe_3O_4) to maghemite ($\gamma\text{-Fe}_2\text{O}_3$). The endotherm centered around $400\text{ }^\circ\text{C}$ is accompanied by the formation of water and is due to the oxidation of goethite ($\alpha\text{-FeOOH}$) to hematite ($\alpha\text{-Fe}_2\text{O}_3$). This exotherm may be due to the transition of $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$. The next thermal event is a large exotherm between 420 and $560\text{ }^\circ\text{C}$ and can be attributed to the transition of $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$. This exotherm is followed immediately by what appears to be two overlapping endotherms that are accompanied by the formation of water and are probably due to dehydroxylation of the illite and kaolinite. Usually clay dehydroxylation endotherms are much broader, but in this case they are being somewhat masked by the $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$ exotherm. The next thermal event ($\sim 640\text{ }^\circ\text{C}$) is a small endotherm that is probably due to a change in the magnetic properties of hematite [4]. The endotherm occurring between 690 and $725\text{ }^\circ\text{C}$ is accompanied by the formation of water and is due to the dehydroxylation of montmorillonite. The next three thermal events represent the high temperature transition reactions of montmorillonite, illite and kaolinite respectively.

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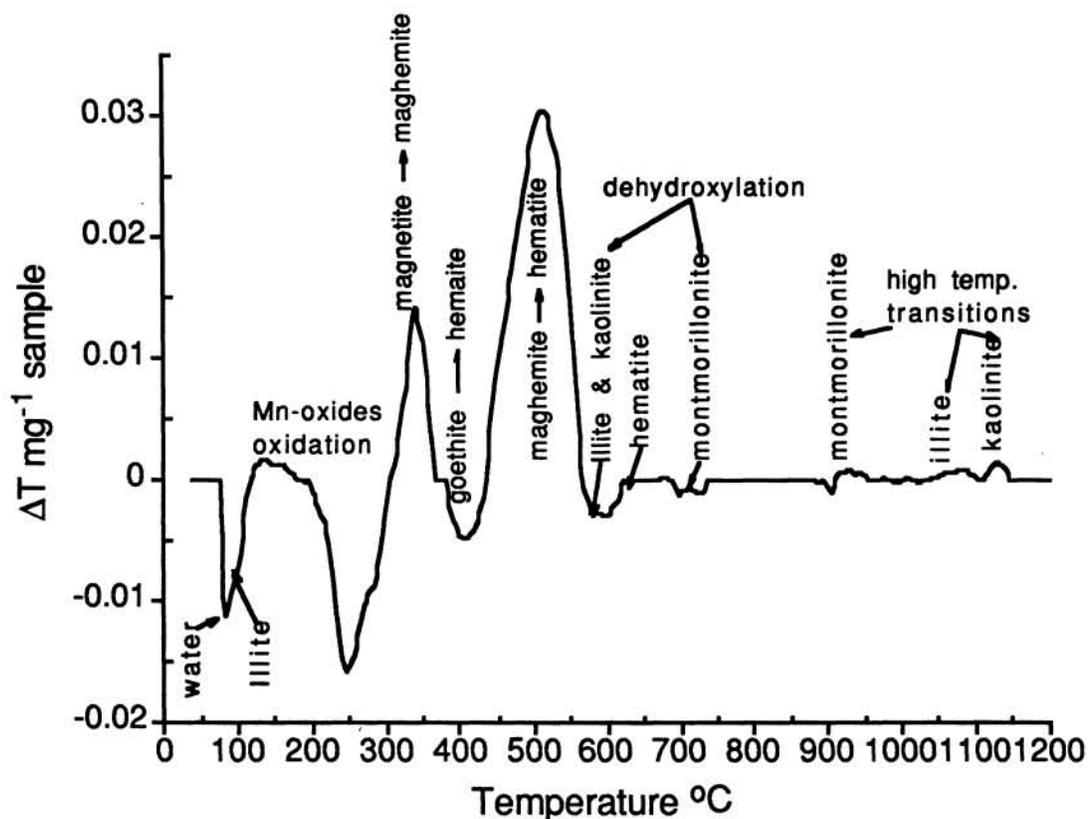


Figure 1. Results of analysis of 30 mg of desert varnish collected from Reno, Nevada by DTA. 30 mg of Aluminum oxide was used as the reference. The samples and reference were heated at $10^{\circ}\text{C min}^{-1}$. The endotherms and exotherms are labeled as to the minerals and reactions that gave rise to each.

References

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