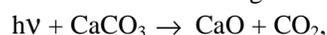


**ON THE PROBLEM OF THE “MISSING CARBONATES” ON MARS.** S. Fonti<sup>1</sup>, A. Blanco<sup>1</sup>, M. I. Blecka<sup>2</sup>, A. Jurewicz<sup>2</sup>, and V. Orofino<sup>1</sup>, <sup>1</sup> Physics Department, University of Lecce, Via per Arnesano, C.P. 193, 73100 Lecce, Italy (fonti@le.infn.it), <sup>2</sup> Polish Academy of Sciences, Space Research Centre, ul.Bartycka 18a, 00-716 Warsaw, Poland.

**Introduction:** The discovery of carbonate deposits on Mars could be very important for a realistic reconstruction of the paleoclimate of the planet [1] and may have interesting implications on the possibility that life developed there in the past [2]. In this respect the messages reaching us from Mars are definitely contradictory. On one hand, many images of the Martian surface show a complex hydrological structure, suggesting the past existence of bodies of standing water, where the carbonate precipitation should have been highly probable. On the other hand, no instrument orbiting around Mars has ever made a definite identification of carbonates in the strikingly homogeneous fines covering the Martian surface, in spite of the fact that the characteristic spectral features typical of such minerals fell within the observed spectral range. Nevertheless, carbonates have been found in the SNC meteorites, which are considered to be of Martian origin, while the possible spectroscopic detection of the presence of carbonates comes from two different observations made from Earth [3], [4]. All this makes the essence of the so-called "missing carbonates" issue, one of the major enigma in Martian science [5].

In the present work, we address this subject, paying the due attention to the reported identifications of carbonates. First, we discuss the effectiveness of the photodecomposition process of  $\text{CaCO}_3$ , suggested by Mukhin et al. [6], taking also into account the reverse reaction (chemisorption of  $\text{CO}_2$  by calcium oxide). Along this direction we then address the role the temperature of the surface of Mars can play in the detectability of carbonates. Finally, some discussion and conclusion are presented.

**Photodecomposition of carbonates:** Assessments of the amount of carbonates present nowadays on the Martian surface should base upon the analysis of various physico-chemical processes. An important example of such a process is the photolysis of calcium carbonate by UV solar radiation through the reaction



quantitatively studied in a laboratory experiment by Mukhin et al. [6]. The authors extrapolated their results to Martian conditions, suggesting that the surface layer on Mars could be effectively depleted of carbonates and completely converted into calcium oxide because of photodecomposition.

The reverse gas-solid reaction (i.e. the adsorption of carbon dioxide on calcium oxide surfaces) has been thoroughly and quantitatively analysed by several authors (see for example [7]). The outcome of the study is that the process in question has to be qualified as chemisorption leading, through the reverse reaction



to unidentate and bidentate carbonate complexes, showing their characteristic features in the IR absorption spectra. The data reported in the literature seem insufficient to have a complete evaluation of the kinetics of the two competing processes. An assessment of their balance, indicative of the importance of chemisorption, can nevertheless be performed.

In the experiment of Mukhin et al. [6] the photoreleased  $\text{CO}_2$  was pumped out of the experimental chamber. Therefore the balance between photolysis and chemisorption had to adjust itself continuously to the lowering pressure, with the consequence that both the rate of adsorption and the amount of superficial carbonate to undergo photodecomposition became lower and lower during the process.

In order to apply the discussion to Martian conditions, let us note that the flux of UV solar photons at the surface of Mars is  $\sim 2 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$  [8]. Such flux, according to the experimental results of Mukhin et al. [6], will give rise to the photorelease of  $\sim 1.3 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$  carbon dioxide molecules from a pure  $\text{CaCO}_3$  surface. However, with a temperature of  $\sim 250 \text{ K}$  and a  $\text{CO}_2$  pressure of  $\sim 6 \text{ mbar}$ , we will have  $\sim 1.6 \times 10^{21} \text{ cm}^{-2} \text{ s}^{-1}$  carbon dioxide molecules hitting the same surface. We note therefore that, even with a sticking probability of  $\sim 10^{-10}$ , chemisorption will still be more effective than photodecomposition. At present, preliminary estimates seem to suggest a sticking probability in the range  $10^{-6} \div 10^{-7}$ . In this case, unlike in the experiment of Mukhin et al. [6], the exchange of  $\text{CO}_2$  between the surface and the atmosphere proceeds under almost constant pressure. This conclusion agrees with the results of Booth and Kieffer [9] who, simulating the growth of carbonates in a "Marslike environment", did not find any appreciable influence of UV radiation.

**Importance of the surface temperature:** If the foregoing conclusions are correct, the reasons for the failure of the identification of carbonates in the Martian spectra should be sought elsewhere, before con-

cluding that the favorable conditions in the Martian paleoclimate did not last long enough for an abundant sedimentation of carbonate materials. For instance it is possible that the detection of the spectral features of carbonates requires an amount of such minerals larger than it is usually thought. This point has been already raised in a recent paper by Orofino et al. [10], where the dependence of the spectral contrast on the size of the carbonate particles is discussed.

However it is important to understand why the only claims of identification are connected with earth-based observations [3], [4], while carbonate characteristic bands have never been observed by spectrometers orbiting around Mars. In fact, in such observations, the size of the observed Martian region is certainly much larger than in observations carried out with orbiting instruments. This seems clearly contradicting the widely accepted statement that carbonates should be more easily detected in well-localized patches of the Martian surface [10]. In this respect it might be noted that the energy coming from the wide region of Mars, seen through the telescope, can almost totally come from a relatively small hot spot around the subsolar point [11], when the subsolar point is within the field of view, as in the case of the mentioned observations.

It is therefore extremely important to assess clearly the influence of the surface temperature on the visibility of the characteristic infrared features of the carbonates in the measured spectra. In order to do this, we have calculated synthetic spectra, in the region between 5 and 20  $\mu\text{m}$ , for different surface temperatures and using a composite surface with different carbonate mass percentages. We have calculated the total emissivity using a linear combination of the albedo of the two components, properly weighted according to the chosen concentration. We assumed an average size of 100  $\mu\text{m}$  for the surface grains and used calcite, as a possible representative of the carbonate materials, and palagonite, as a possible representative of the main constituent of the Martian regolith. For both materials it is possible to find reliable values of the optical constants in the literature [12], [13].

We performed our simulations for three different surface temperature (200, 250 and 300 K) chosen with the purpose of allowing for extreme conditions, as far as high temperatures are concerned. For each temperature, a pure calcite and a pure palagonite surface were considered for comparison. We then determined the minimum calcite concentration still allowing to recognize both characteristic carbonate bands around 7 and 11  $\mu\text{m}$ . The values we have found should represent a good approximation of the possible concentra-

tion of carbonates on the surface of Mars we might expect to detect, as a function of the surface temperature. The preliminary result is that even in the case of a very warm surface, the amount of carbonates is very high (between 40 and 50 %) and might be detected only in very favorable conditions.

**Discussion and conclusions:** We can say that much care has to be taken when trying to assess an upper limit for the carbonate component in the Martian regolith and that the detection of such component by means of an orbiting spectrometer could be extremely difficult. In fact, the possible identification of Martian carbonates would not only imply a careful choice of the most favorable sites, not covered by other materials [10], but it would also require peculiar conditions, such as the observation of the chosen spot when it is very close to the subsolar point. We must admit, however, that the claimed identification of carbonates with earth-based observations cannot be explained simply by assuming that they have been done when the subsolar point coincided with a site particularly rich in carbonates. In fact, the number of independent observations is already high enough to state that the statistical probability of such an occurrence is extremely low.

A possible solution is that the carbonate bands at 7 and 11  $\mu\text{m}$  have to be attributed to a warm atmospheric carbonate dust component. This hypothesis, if confirmed, could readdress the search for Martian carbonates from the surface regolith to the atmospheric dust. Work is already in progress in order to update our calculations with the introduction of an adequate airborne dust component.

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