Revision 1

Highlights and Breakthroughs article for Thomas Bristow David Bish et al.,:The origin and implications of clay minerals from Yellowknife Bay, Gale crater, Mars.

Title (if needed): Clays are messy - also on Mars

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Abstract

The Curiosity rover on Mars, landed in 2012, is capable of mineralogical investigation using X-ray diffraction, complementing the abundant infrared remote sensing data already available on clay minerals. We can, however, expect that the in situ X-ray diffraction information will convey a more complex picture than that inferred from infrared spectroscopy alone.

CheMin has landed

Curiosity is the first planetary probe equipped with and X-ray diffraction (XRD) apparatus. This feat has taken place 117 years after the discovery of X-rays and exactly 100 after the first X-ray diffraction experiment. If we think of the size and requirements of the diffractometers we use in our laboratories, we can see better the technical achievement that this represents. From the scientific point of view, the step is also very important because XRD is the basic tool of the mineralogist. Mineral identification on Mars has been relying mainly on infrared remote sensing. The shortcomings of this approach are obvious: some minerals have no or very weak infrared signature, some minerals share spectral features, the reflection/absorption of infrared radiation on the surface of rock and regolith is a complex phenomenon that affects the spectral shape, and there are atmospheric effects to deal with. Fortunately for clay investigation, clay and other hydrated minerals have a strong infrared signature. An important advantage of the reliance on infrared data in Mars studies is that the interpretation of spectral features has progressed considerably and we can read a good deal into the spectra. In order to progress in this direction, complementary XRD and infrared analyses are essential. However, the shortcomings of XRD analysis on Mars are also obvious. The number of studies will be very small and spatially limited. For clay investigation, the articles by Bristow et al. (this issue) and Vaniman et al. (2014), the very first ones to investigate extraterrestrial clay minerals in situ, highlight the interpretation problems that are faced: why do two clay materials that were collected 2.5 m apart and appear to have the same mineralogy and chemistry have different interlayer expansion behaviour? These problems are typically solved in Earth studies using a variety of physical and chemical treatments before XRD analysis, which are not available for Curiosity. And yet, the issue is crucial, because the measured d-spacing of the *00l* peaks contains information about layer interstratification as well as inorganic and organic intercalation, all of which are very important for deciphering the very nature of the clay, formation conditions, later processes and organic presence. The latter, however, would require such concentrations to affect measurably the expansion behaviour of clays that it is not contemplated at the moment as a likely possibility on Mars. CheMin, the diffractometer on board Curiosity, will allow helpful but limited comparison between XRD and infrared data that will help the interpretation of the wider infrared database from Mars. Such comparison can be completed carrying out similar investigations with Earth analogues, where the infrared spectral features of fully characterized mineral suits are compared with martian spectra.

How much water?

Before Curiosity landed on Mars it was known that Mount Sharp, at the center of Gale Crater, contains strata with Fe/Mg-rich smectite. Curiosity's investigation on site has found what appear to be fluvio-lacustrine materials on the floor of the crater which contain clay (Bristow et al., this issue). This is a welcome discovery suggesting the existence of abundant clay easily accessible below a thin layer of sediment on Mars' surface, and providing further evidence for protracted interaction between water and the martian rocks. Bristow et al. (this isssue) interpret that the clay-containing material was formed in situ, rather than transported and sedimented, because the overall rock chemical composition is similar to that of the average martian crust. If such is the case, the results from Bristow et al. provide important information about water activity and timing on Mars' surface. First of all, the investigated rocks formed after the Noachian era, later than the generally accepted time limit for formation of phyllosilicates of the Fe-Mg composition (Ehlmann et al., 2011), thus potentially pushing forward this limit. Second, the mineralogical composition of the studied samples, including plagioclase, olivine and pyroxene as major phases (Vaniman et al., 2014), indicates incomplete alteration of the original rock and points toward limited liquid water availability. Liquid water is not the only possible agent of clay formation on Mars' surface as ice has also been proposed (Michalski et al., 2013), but the rock morphology indicating a standing water body makes the latter a more likely candidate here. The composition of the clay, an Fe-containing saponite, also points towards limited water availability. On Earth, microscopic saponite is found as a product of in-situ alteration of mineral or glass grains in basalt, while further alteration ussually produces montmorillonite. Saponite formation in macroscopic amounts typically requires high Mg activity. Thus, the investigated rocks on Mars suggest that the water:rock ratio during the alteration reaction was low and that the fluids were in near equilibrium with the basalt. Interestingly, however, the composition of clay in strata at the base of Mount Sharp, detected by infrared remote sensing, is different and consists of nontronite. There is the uncertainty about the authigenic or detrital origin of such clay but if the nontronite formed in situ, the different chemistry may indicate that enough water was available to produce chemical differentiation in the corresponding altered rocks. The future investigation of these rocks by Curiosity, as it makes its way up Mount Sharp, can provide further clues about the mass of water involved in the alteration processes at different locations.

Is all hydrated clay smectite?

The article by Bristow et al. also provides important information about relative humidity conditions on Mars' surface, the hydration state of clays and their spectral identification. Relative humidity measurements by Curiosity in Gale crater (Figure 1 in Bristow et al., this issue) shows sharp daily and seasonal variations. Averaged values have reached 80% relative humidity. According to these results, it is expected that smectite retains hydration water, even if it undergoes cycles of hydration and drying. The spectral identification of smectite is based on the position and shape of the hydroxyl infrared vibration bands and the existence of the molecular water vibration band at ~1.9 µm. According to Curiosity's measurements of relative humidity such identification is validated. However, submarine Fe-rich hydrothermal talc of low crystal order has been described with near-infrared spectra similar to that of the Mg/Fe-smectite identified on Mars (Michalski et al., 2014). The molecular water in this talc is not located in the interlayer space, as in smectite, but seemingly trapped within the hexagonal cavity of the tetrahedral sheet and is more difficult to release (Cuadros et al., 2013). Talc with such form of molecular water retention is a possibility on Mars and an alternative to automatically linking hydration water in clay with smectite. Further investigation and improved interpretation of spectral features may shed light on the possible presence of hydrated clay phases other than smectite.

One final thought. Clay investigation in Earth studies is challenging even though we can use a whole array of analytical tools. There is no reason to expect that clay on Mars is any less messy. We should not be surprised if, at the first stage, XRD of martian clay complicates rather than simplifies the picture that we have generated with infrared remote sensing.

References

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