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Formation of titanium oxide (TiO_2) polymorphs in an emerged submarine volcano environment: Implications for Mars.

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Abstract

The study of terrestrial Martian analogues is crucial for the knowledge of the mineralogy and the formation mechanisms that occur in Mars. This work is focused on the study of titanium oxide polymorphs found in the same volcanic emplacement (a 100 million years old submarine volcano), as their formation need different environmental conditions. The three most common phases (rutile, brookite and anatase) were identified in the same samples by means of Raman spectroscopy, a technique that will be implemented in the next ESA Exomars2020 mission.

1. Introduction

The landing site of the Exomars2020 mission could be a sedimentary terrain fractured with volcanic events, formed in a submarine environment. The analysis of such a terrestrial environment is a fundamental step to understand the geological processes that could have happened in Mars. For that purpose, the Meñakoz outcrop (Biscay, northern Spain) is being currently studied and proposed as a terrestrial Martian analogue. It represents a 100 million submarine volcano scenario that erupted at 800-1000 m in depth through sea sediments; the pillow lavas together with the sedimentary units emerged 60 million years ago [1]. Among others, titanium dioxides are commonly found in this kind of emplacements.

On Earth, titanium occurs mainly in oxide or mixed oxide forms. Main polymorphs of TiO_2 are rutile (the most thermodynamically stable phase) brookite and anatase (both metastable and can be transformed into rutile irreversibly at high temperatures) [2] Rutile is the high-pressure and high-temperature polymorph that can be formed, among other reasons, because of hydrothermal alterations [3]. On the other hand, brookite and anatase are the low-temperature polymorphs, being the latter the one with the lowest formation temperature. Brookite is the rarest of the natural TiO_2 polymorphs due to its lowest stability, although both brookite and anatase are stable even at 700ºC. Above this temperature, brookite is converted into rutile while, in some cases, anatase could begin its transition to rutile at ~600ºC [4].

2. Sample description

The analysed samples were extracted from the cliff on the Meñakoz outcrop with the help of a hammer. Samples were sliced and polished until the surface was free of deformations using progressively finer abrasive grit.

3. Materials and methods

For the proper characterization of the titanium oxide polymorphs, Raman spectroscopy was employed. The instrument used was an InVia confocal micro-Raman spectrometer (Renishaw, UK), provided with a 532 nm excitation laser, working in both point by point and Raman image mode using laser power filters to avoid thermal transformations.

4. Results and discussion

Rutile (Figure 1) with its main Raman bands at 447 (weak, w) and 610 (medium, m) cm^{-1} was detected in the inner part of the samples. In order to clearly see the band at 447 cm^{-1}, a band decomposition procedure was performed.

As the high-pressure and temperature polymorph, it can be stated that rutile was formed during the eruption of the volcano, when the pressure and the temperature reached high enough values. Due to its stability, it is still present nowadays inside the rocks.

Brookite (Figure 2, black) was identified also in the inner part of the sample with Raman bands at 154 (strong, s), 214 (w), 248 (w), 284 (w), 322 (m), 366 (w), 410 (very weak, vw), 501 (vw), 543 (vw) and 640 (vw) cm^{-1}. Regarding anatase (Figure 2, blue), it was detected both in the inner part and on the surface of the samples. Its Raman bands are 143 (very strong, vs), 198 (vw), 397 (m), 514 (w) and 637 (m) cm^{-1}.

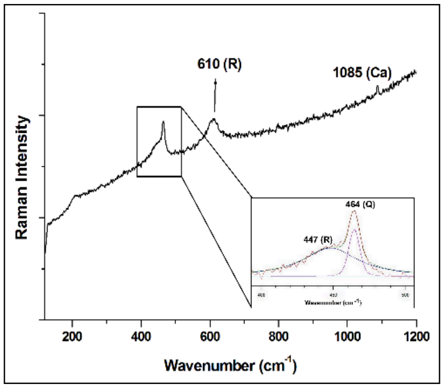

Figure 1. Raman spectrum of rutile (R) together with quartz (Q) and calcite (Ca). The decomposition of the band at 447 cm^{-1} is presented.

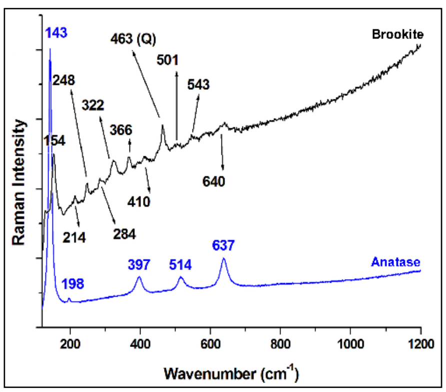

Figure 2. Raman spectra of brookite (together with quartz, Q) and anatase.

Formation mechanism of brookite is still unclear. It is an accessory mineral in igneous rocks and it may be formed under hydrothermal conditions [5], but also during the cooling process of the lava. Anatase arises as an alteration product of Ti-rich minerals such as ilmetite ($FeTiO_3$), which is common in volcanic rocks; the formation of this TiO_2 polymorph suggest a hydrothermal like origin [6], which could happen in Meñakoz, due to its submarine volcanic nature.

5. Conclusions

The identification of titanium oxides is very helpful in the comprehension of the formation mechanisms in Mars. The differences related to the temperature or pressure for their formation could provide clues to establish different formation environments and thus, to understand the environmental and geological history of Martian rocks. The presence of rutile indicates that there was an episode where the temperature and pressure were high, probably during the eruption of the volcano. The other polimorphs (brookite and anatase) arise from alteration processes indicating their later formation.

Acknowledgements

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