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RAMAN STUDY OF SECONDARY MINERALS IN A RECENT LAVA TUBE.

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Introduction: Extreme conditions are all around the world. From the atomic scale (where new technological applications constrain more and more materials) to the macroscopic scale (where environment is sometimes hostile for humans).In this later case, risk management requiresobtaining quick and reliable information on the physics and chemistry involved in these hostile area that are volcanic eruption, nuclear accident and so on.

Precisely, in the frame ofunderstanding and management of volcanoes hazard, non entirely cooled post-eruptive lava flow is a dynamic system with hot spots, heat, fluid and ionic transfers.In this unstable and dangerous environment, lava tubes act like natural drilling allowing to probe inside the lava layers. Inside lava tube one can find secondary minerals resulting from the physical and chemical activity inside the lava flow. Thus, these secondary minerals are like undirect witnesses of the chemical processes withinthe lava layer and direct witnesses of the recent past of the environment in the lava tube.

These volcanic secondary minerals are seldomstudied [1,2] and a site of great interest is a recent lava tube from the 2007 eruption of the *Piton de la Fournaise* volcano (La Réunion island, Indian Ocean, France). This lava flow is more than 60 meters deep [3], still hoton some spots and presents varied fumarolic and secondary mineralsinside lava tubes (Fig. 1).

The CEMHTI group (Orléans, France) has a great experience of *in situ* Raman measurements and for the study presented here, we adapted a laboratory *in situ* spectrometer [4,5] for field measurements.

In this paper, we present first the technical adaptations made for a field use of the laboratory *in situ* spectrometer, its capabilities and limits as well.Secondly, we present identification of secondary mineral phases growing in the lava tube with a particular emphasis on the study of whitespeleothems and dendrites by mean of XRD, SEM-EDX and Raman spectroscopy.

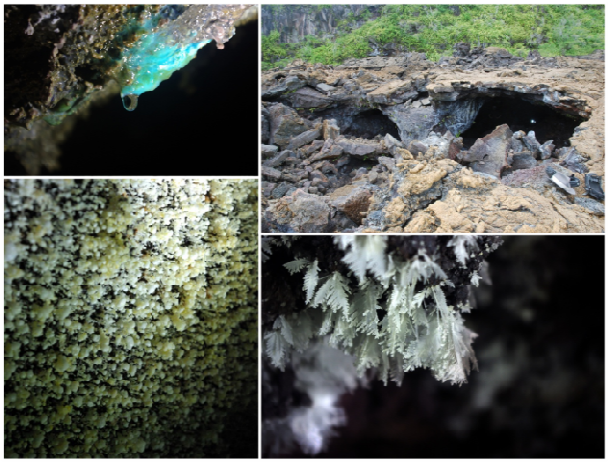

Figure 1: Entrance of the lava tube (up right) Exemples of secondary minerals found in the lava tube (left and bottom right)

Experimental Methods: The volcanic speleothem was characterized at various length scales: the composition, the morphology and the atomic structure were probed by mean of MEB-EDX, XRD and Raman spectroscopy. All these techniques were additionallyperformed at CEMHTI laboratory after the field Raman campaign.Instruments are ESEM XL40 (FEI), D8 Advance diffractometer (BRUKER AXS), and for Raman, an InviaReflex Renishaw Spectrometer for the lab setup and a RA100 Renishaw spectrometer for the field setup. Figure 2 shows one of us (AC) working at the adjustment of the field Raman probehead.

Figure 2: Experimentalist at work in a lava tube with the field Raman setup.

Preliminaryresults and discussion: Figure 4 presents two typical uncorrected Raman spectra acquired with the field setup from the white volcanic speleothem shown on Figure 3. Top spectrum is Thenardite (V) and bottom spectrum that of up to now unidentified vanadate mineral. One immediately can remark the presence of water with Thenardite, the incredible flatness of the background and the narrowness of the main peaks: HWHM = 5 cm^{-1} (the resolution of the spectrometer is ≈ 1 cm^{-1}). All this elements being the signatures of high crystalline quality probed by mean of a high quality instrument.

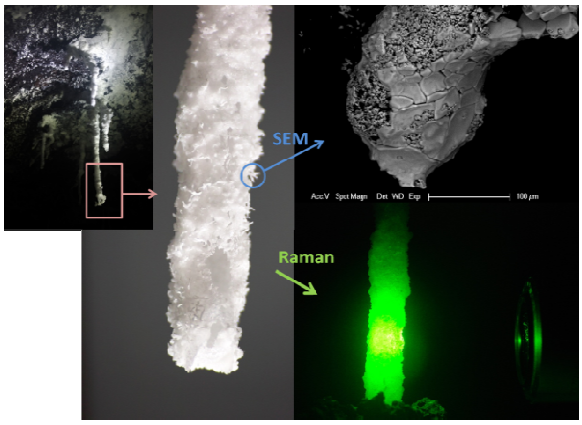

Figure 3 : White speleothem growing hanging to the lava tube ceiling (top left). At right are pictured SEM imaging (top) and Ramancharacterization (bottom) of it.

Among the minerogenetic mechanisms listed by Forti*et al.* [3] our study deals mainly with intermediate temperature mechanisms (400 ÷ 0 °C) that are ions exchange, substitution of atoms, supersaturation, deposition from aerosols and vapors, evaporation, oxidation/reduction and hydration/dehydration. The richness of processes is a nice reflection of the richness of information about the physical-chemistry dynamic of the lava flow that should give such studies: Among others classical secondary mineral phases, we observed the *in situ*transition from sulfate hydrate (mirabilite) to thenardite, the presence of various Na_2SO_4metastable phases and unidentified vanadates phases …

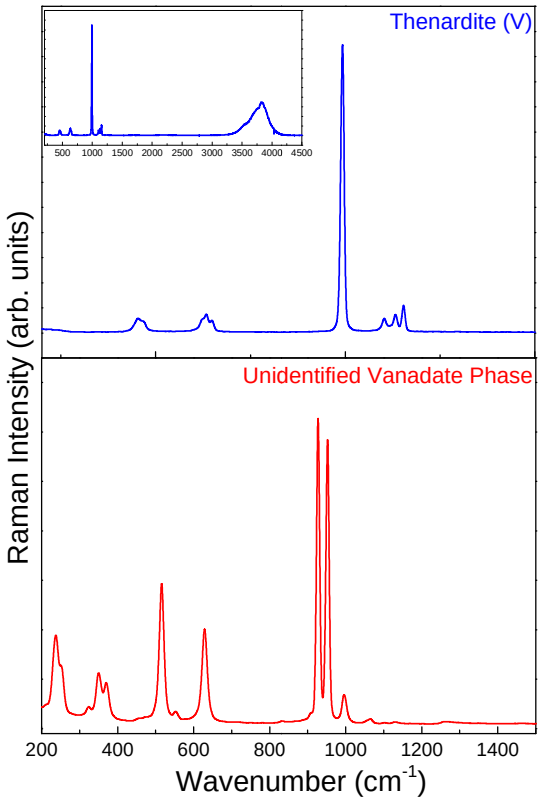

Figure 4 : Uncorrected Raman spectra acquired with the field Raman setup.

Partial Conclusion: Three months after the field campaign on the volcano, the environmental conditions of the lava tube evolved very quickly and all the speleothems disappeared.

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