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Nanoscale Investigation of Belgian Chocolate by Atom Probe Tomography.

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The recent trend in food science is to study the structure and its influence on functionality. One of the main challenges for this is the complexity of food systems. As an example, the relevant length scales in food systems extend from the macroscale (typically cm) to the nanoscale. Drastically different structures are observable at different scales, but are all important in the food processing and preparation. In the case of our sample, it is indeed known that cocoa butter can present six different crystallographic structures with their own melting points and densities. These influence the chocolate properties, such as the fat bloom formation, and induce different sensory perception [1]. In the case of chocolate, experiments have been performed to determine the microstructure and crystallinity of dark, mild and white chocolates so as to study phase separation, phase transition and polymorphism, as well as emulsifying and rheological properties. For this, a wide range of microscopy and microanalysis techniques have been used such as light microscopy, X-ray microtomography, X-ray scattering, X-ray diffraction, scanning electron microscopy and atomic force microscopy [2-5]. In this work, we used Atom Probe Tomography (APT) to analyse dark chocolate. APT is a powerful technique for the characterization of both the composition and the 3D structure of materials at the atomic-scale. The versatility of the most recent APT instruments allows the study of samples that were not possible only a few years ago: minerals, biominerals and geological samples, or even biological samples such as bacteria [6].

The structure of most chocolate consists of a suspension of sucrose, milk and solid cocoa particles embedded in a continuous semi-solid 'fat phase' [7-8]. Therefore, the sample preparation and analysis remains challenging. Due to the structure of chocolate, a modified lift-out method has been used to produce APT samples where a micromanipulator needle is used as a hook to lift the materials (Figure 1.a), which is then transferred to the APT coupon. The material is sharpened and then any voids filled with Pt-weld in the FIB system so as to ensure the structural stability of the tip. APT Experiments were performed in a LEAP 4000X HR system with conditions of acquisition: 30-100 pJ, 25-100 kHz, 50 K, DR: 0.1-2%.

One of the first observations made during the experiments is the presence of a rather large tail on the MS peaks, even when the laser energy is decreased. It has to be noted that, with the heterogeneous structure of the sample and the presence of some porosity, the detection rate has to stay low to avoid sample's fracture. The mass spectra contain mainly peaks that can be assigned to C-based materials, up to C_5. A more detailed analysis of the peak remains challenging. Is it well known that chocolate bars contains elements such as Fe, Zn, Ca, K, Na and Mg with a concentration ranging from 10 to 1000 μg/g. Even though the elemental sensitivity of the APT allows detecting species down to 1 ppm, the relatively high background noise and the presence of tails does not allow the quantification of these minor elements. In the case of successful experiments, two different phases can be observed: the first one consists in mainly carbon-based materials (> 70%) with some Ga and Pt from the sample preparation process. The content in Pt (< 5%) is far smaller than the usual Pt content in Pt-weld (≈ 30% in these experimental conditions), implying that it is representative of the original sample. The composition of the second phase involves mainly the presence of CO and CO_2. These differences are likely to be due to different phases of the chocolate suspension (see Figure 1b).

As a conclusion, our experiments showed that dark chocolate bars can be analyzed by APT as any other hard matter systems. Further experiments are required to unravel the details of the composition as well as to explore the possibility of observing crystallography on chocolate samples [9].

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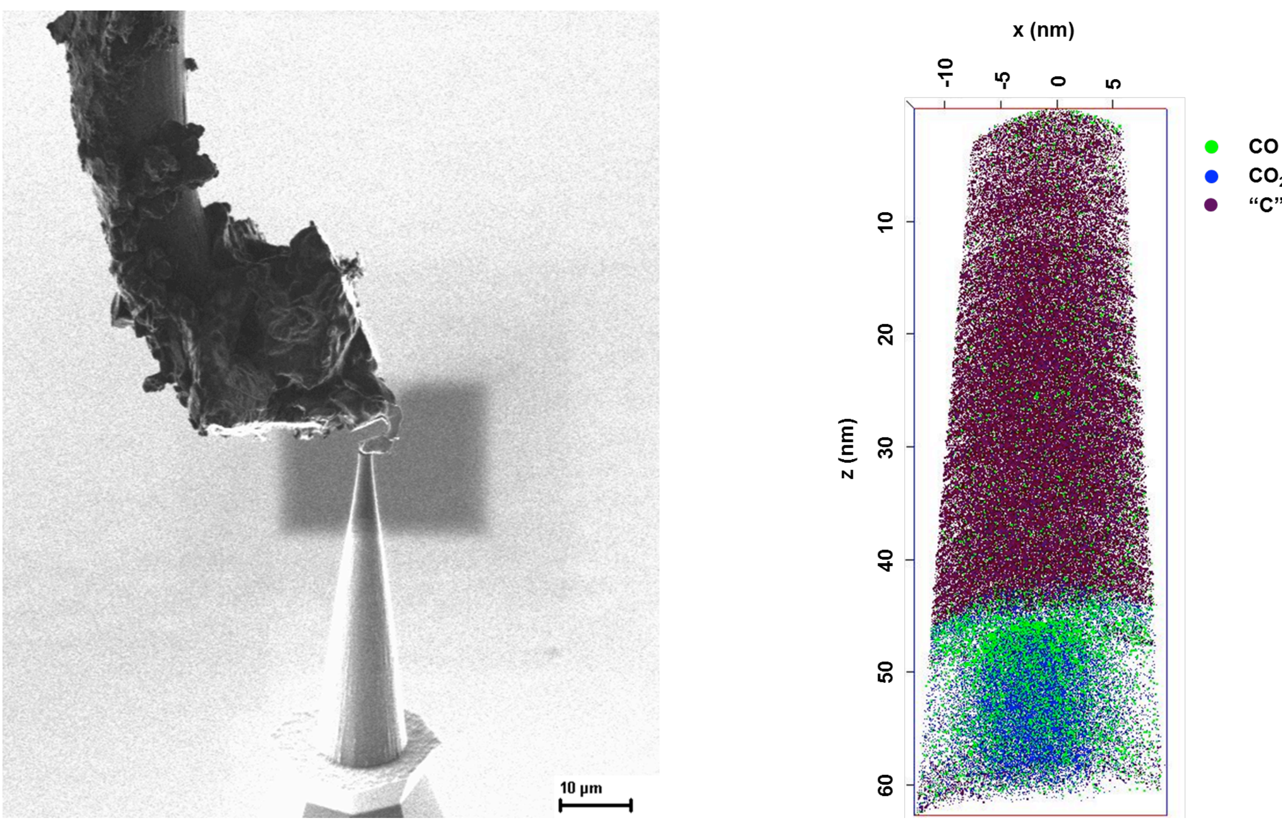

Figure 1. a) Sample preparation with the chocolate-covered micromanipulator needle - **b)** 3D reconstruction of a chocolate tip with the presence of two main phases: the top phase corresponds to C-based materials (**purple** dots / from C_1 to C_5). The bottom phase involves mainly CO and CO_2 species (CO are represented as **green** dots and CO_2 as **blue** dots).

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