

# On the porous mesostructure of milk chocolate viewed with atomic force microscopy

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## Abstract

The surface structure of commercial milk chocolate is examined using atomic force microscopy. It is shown that its surface topography is complex, comprising a finely mottled, yet irregular texture with most structural elements measuring  $<3\mu\text{m}$  in size. It is also demonstrated that a large number of microscopic pores exists at the surface. The morphology of these pores is highly variable, with observed cavities generally being conical in nature with irregularly shaped openings. Typical pore depths range from 1 to  $3\mu\text{m}$  and are randomly distributed on the surface of milk chocolate, without any defining features in their vicinity to suggest their existence. In the past, it has been postulated that such pores are opening to channels; these being responsible for liquefied cocoa butter transport and subsequent promotion of fat bloom formation. To shed light on any such relationship, milk chocolate is subjected to multiple (6, 12 and 24) temperature cycles (each from 25 to 27 °C and 25 °C over 2 h). Results show that following many cycles, there is crystal growth around some pores, but that the pores themselves are not appreciably altered. This suggests that, under these experimental conditions, they are not directly involved in bloom mediation or liquefied fat transport in milk chocolate. © 2005 Published by Elsevier Ltd. on behalf of Swiss Society of Food Science and Technology.

*Keywords:* Milk chocolate; Atomic force microscopy; Pore; Pits; Fat crystals; Crystal growth; Bloom formation

## 1. Introduction

From a materials science perspective, milk chocolate is a complex substance produced from numerous ingredients using many processing steps. The organoleptic attributes of milk chocolate are strongly dependent on the proportions and spatial distribution of the cocoa mass, milk solids and sugar particles, and on the crystal properties of the continuous cocoa butter (CB) fat phase. The basic processing steps necessary to develop the correct texture, flavour and CB fat crystal habit are: (i) bulk ingredient mixing, (ii) refining, (iii) conching, (iv) tempering and (v) cooling. While responsible for the snap, gloss and sharp melting profile of chocolate at body temperature, CB is also the culprit in fat bloom, a defect that afflicts all chocolates, and in

particular soft-centre and dark chocolates. The three main sources of fat bloom in chocolate are related to composition, processing and storage, with the latter being the least controllable of these parameters, particularly once the chocolate is in the hands of the consumer. Higher storage temperatures ( $>30\text{ °C}$ ), compounded by temperature fluctuations, can dramatically increase bloom formation (Lonchampt & Hartel, 2004).

Previous atomic force microscopy (AFM) investigations by our group (Hodge & Rousseau, 2002) have shown that the surface of properly tempered milk chocolate is complex in its topography, consisting of a finely mottled, yet irregular texture with structural elements measuring  $<3\text{--}4\mu\text{m}$  in size. Bloomed chocolate, identified by a beige-white, powdery coating on the surface of the chocolate, is characterized by the presence of large protruding CB fat crystals (upwards of  $5\mu\text{m}$ ) and hence, a comparatively rougher surface vis-à-vis unbloomed chocolate. It is hypothesized that these

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crystals are formed as a result of molten and migrating lipid species that (re)crystallize at the surface of chocolate into the larger  $\beta$ VI crystals that are responsible for CB fat bloom.

Within this context, it has been shown that fat bloom in chocolate is often ascribed to the migration of liquefied fat to the surface via diffusion or capillary action, though neither mechanism precludes the other. Using mercury porosimetry, the notable contribution of Loisel, Lecq, Ponchel, Keller, and Ollivon (1997) demonstrated that chocolate has a porous structure. Over-tempered chocolate containing 32% CB had a porosity of 4% while well-tempered chocolate had cavities accounting for 1% of the chocolate volume. Their results did not allow determination of pore properties, namely diameter, morphologies and depths, but did hint that chocolate does not necessarily have a well-developed pores network.

The objectives of the present research are two-pronged. The initial objective is to provide phenomenological insight regarding the surface morphology of milk chocolate, with particular attention paid to the mesostructure of pores. Secondly, through temperature cycling, the role of pores on CB crystal growth and fat bloom initiation and development is ascertained.

## 2. Materials and methods

Milk chocolate wafers (38 mm  $\times$  38 mm  $\times$  1.5 mm), purchased from a local supplier and stored at 8–10 °C until required, consisted of 34.7% fat [a mixture of CB some milkfat (MF)] and 14% milk solids. A Bioscope atomic force microscope (AFM) with Nanoscope IIIa controller (Digital Instruments, Santa Barbara, CA, USA) was used in tapping mode to image 50  $\mu$ m  $\times$  50  $\mu$ m to 5  $\mu$ m  $\times$  5  $\mu$ m areas of the milk chocolate surface topography. No sample preparation was required for this technique. The AFM tips used had a cantilever spring constant of 40 N/m and were oscillated at  $\sim$ 350 kHz. The tips had an end-point radius of  $\sim$ 10 nm and a body angle of 30°.

Crystal growth was induced by cycling the chocolate from 25 to 27 °C and back to 25 °C over a 2-h period, using a Peltier temperature-controlled microscope stage (TS-60 stage, Instec Inc., CO, USA). The temperature during the heating portion of the cycle was ramped up at 1 °C/min. The temperature was then held for 1 h before cooling, at 1 °C/min to 25 °C. Samples were subjected to 6, 12 or 24 cycles. By minimizing vibrations and maintaining the tip–sample spatial relationship, the same field was examined for each sample throughout the experiments. Furthermore, the thickness of the sample ( $\sim$ 1.5 mm) ensured that the heat transfer through the sample was rapid. Numerous in situ scans

of all samples were taken and the series of cycles shown represents the typical evolution seen on the chocolate.

Solid fat content (SFC) in the milk chocolate was determined using a Bruker Minispec Mq pulsed nuclear magnetic resonance (pNMR) unit (Bruker Canada, Milton, ON, Canada). A Rigaku Geigerflex (Danvers, MA, USA) X-ray diffraction (XRD) unit ( $\lambda = 1.79$  Å) was used to determine powder diffractograms of the polymorphic forms of the CB in the chocolate after 0 and 24 cycles. Scans from 3° to 30°  $2\theta$  were performed. For both of these analyses, the fat phase from the samples was removed, according to the method of Cebula and Ziegler (1993). Samples were chopped with a knife and then sifted to obtain particle sizes less than 0.5 mm. This powder was then mixed with 500 ml of cold water, shaken and allowed to stand at room temperature for 4 h. The insoluble material including the CB fat was recovered by vacuum filtration.

## 3. Results and discussion

The pores found in milk chocolate showed varied and complex mesostructures. Fig. 1 shows a two-dimensional (2-D) surface scan (A) of chocolate showing numerous pores scattered throughout the surface. An analysis of the cross section (B) of one of the pores is illustrated, indicating a depth of  $\sim$ 3  $\mu$ m and a mouth diameter of  $\sim$ 6  $\mu$ m. The 3-D isometric representation (C) of the scan shows the irregular nature of the surface and the dramatic appearance of the pore. The surrounding surface morphology of this sample was of uniform roughness with the surface being no different in the immediate vicinity of the pores from the rest of the sample.

The pore examined in Fig. 2 contrasts dramatically with those found in Fig. 1, lying adjacent to a large, flat protruding crystal-like structure. The pore in this case has a measured depth of  $\sim$ 0.9  $\mu$ m. This crystal may be a developing bloom crystal aided in its formation by the adjacent pore, although there is no proof of this. Fig. 3 shows a pore in close proximity to large smooth features, which may be possible bloom formation in progress (Smith & Dahlman, 2005). This pore has a measured depth of  $\sim$ 2  $\mu$ m and an orifice dimension of 4  $\mu$ m. The above results are contrary to Loisel et al. (1997) who stated that chocolate does not contain pores with diameters larger than 0.4  $\mu$ m at the surface. Divergences in our respective results may be due to at least two factors: (i) the different techniques used (AFM vs. porosimetry) or (ii) chocolates of different origins and/or processed under dissimilar conditions. Nevertheless, the present results indicate that pores with surface diameters up to 15 times larger than those mentioned by Loisel et al. (1997) are present on the surface of milk chocolate. Numerous scans also indicate

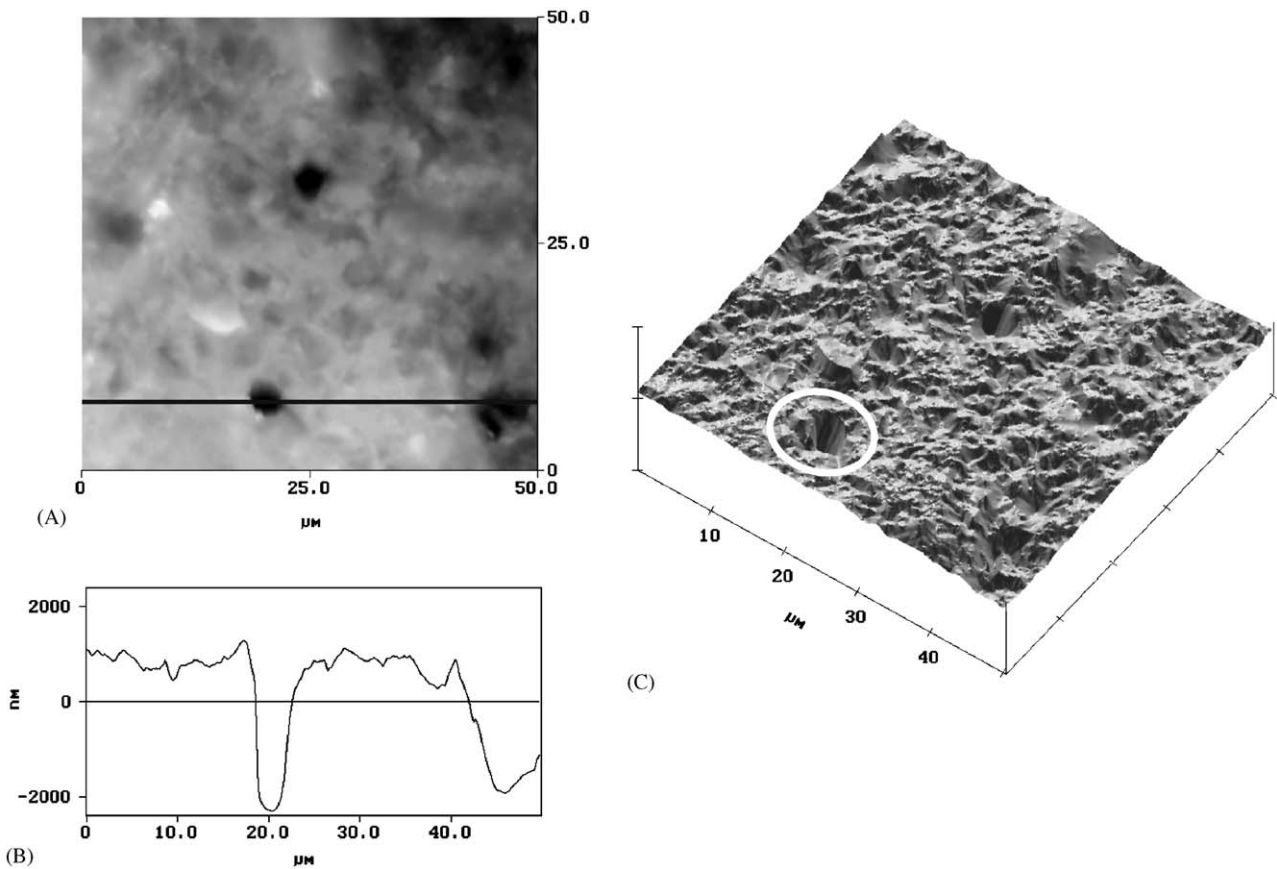


Fig. 1. Scan ( $50\ \mu\text{m} \times 50\ \mu\text{m}$ ) of chocolate surface representing height by grey shading (A); cross section corresponding to the dark line (B); and isometric representation (C). The  $z$ -axis scale is  $4.4\ \mu\text{m}$ . The circle in the isometric representation corresponds to the pore shown in the cross section.

that pores likely number in the hundreds per  $\text{cm}^2$ , with these being randomly distributed on the surface of milk chocolate.

It is generally assumed that the formation of these pores is a processing artefact. During chocolate manufacture, a key step is tempering, which ultimately results in the contraction of the chocolate and, de facto, the generation of pores and hairline cracks. Too fast a cooling rate may introduce these attributes on the chocolate, which in turn, may promote bloom formation. Kleinert (1962) mentioned that homogeneous heat release, resulting from even cooling, reduced temperature gradients between the various layers of the chocolate, and consequently delayed blooming. A second possibility is that these pores are in fact small air bubbles. Though there is no conclusive evidence against these pores being bubbles, the great variability in morphology and locations (e.g., beside a crystal) does not lend itself to this hypothesis. Furthermore, the cavities are not hemispherical, as one would likely expect with bubbles.

In examining the visual appearance of the surface, the true origin of these cavities remains debatable. As mentioned, Loisel et al. (1997) believed that chocolate

does not consist of a well-developed interconnected porous network, and if it did, the existing pores were probably filled with liquid CB (if the chocolate is at room temperature). Following this hypothesis, if these features are channels partially filled with CB, and thus appear as pits, there should be changes in their morphology as molten CB travels through towards or away from the surface. Within this context, Adenier, Ollivon, Perron, and Chaveron (1975) found that covering chocolate with aluminium foil prevented bloom formation, arguing the foil prevented oil migration by minimizing the pressure difference at the surface of chocolate when exposed to air. A second possibility not envisaged by these authors is that a foil cover may reduce temperature fluctuations at the chocolate's surface, thereby slowing down any structural modifications. Complicating the elucidation of pore structure is the instrumental limit of the AFM itself, which generally has a  $z$ -axis deflection limit of  $\sim 10\ \mu\text{m}$ , depending on instrument, tip and sample properties. This restricts imaging of structural feature (i.e., channels or pores) deeper than a few microns. Nevertheless, until a more definite answer is provided, these mesostructural features are hereafter referred to as pores.

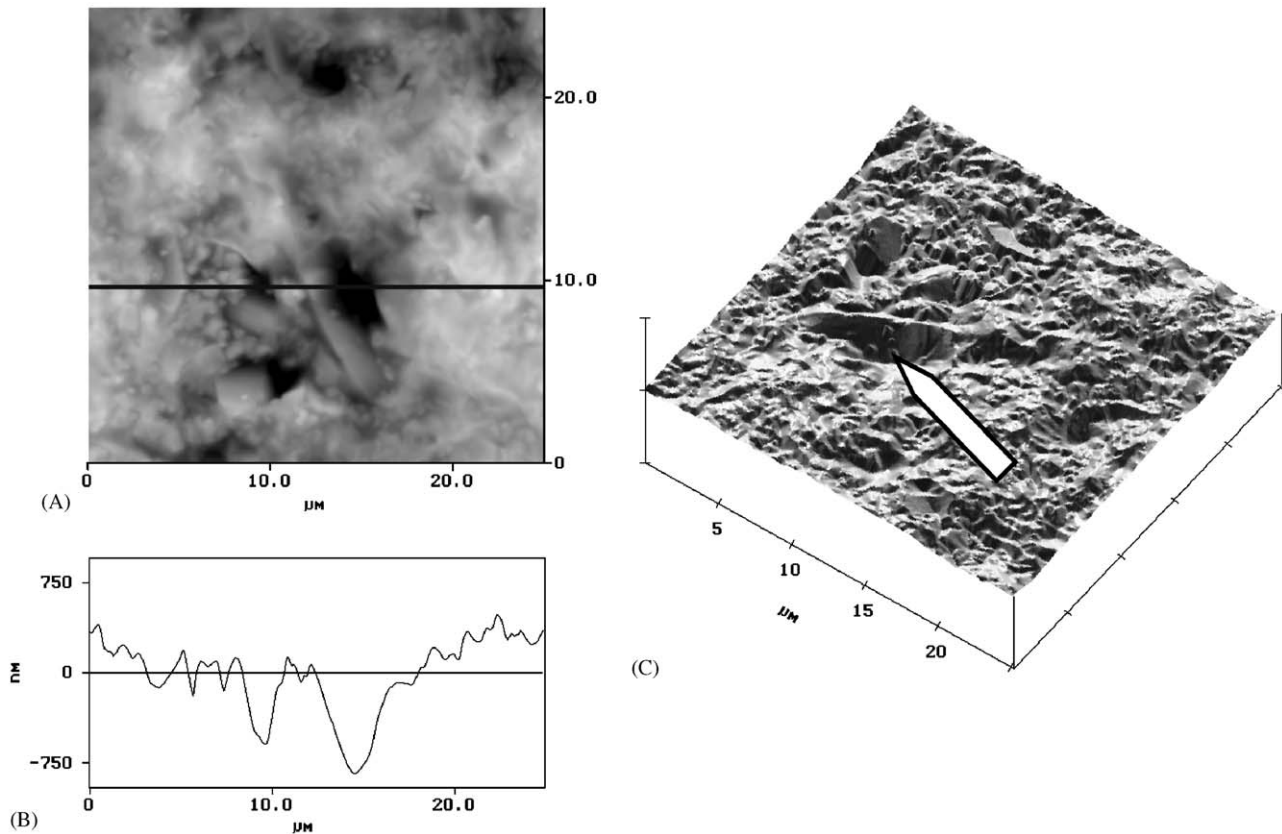


Fig. 2. Scan (25  $\mu\text{m} \times 25 \mu\text{m}$ ) showing a shallow pore adjacent to a flat jutting crystal; height by grey shading (A); cross section corresponding to the dark line (B); and isometric representation (C). The z-axis scale is 1.75  $\mu\text{m}$ . The arrow in the isometric representation identifies the deepest cavity shown in the cross section.

Temperature cycling has been used to induce changes in crystal structure, often in pharmaceutical applications and, to a lesser extent, in food products. With respect to chocolate, many groups have used this method to accelerate bloom albeit with substantially larger temperature gradients than in the present study (Ali, Selamat, CheMan, & Sunia, 2001; Bricknell & Hartel, 1998; Hachiya, Koyano, & Sato, 1989a, b). In order to assess whether pores influence crystal and bloom formation, milk chocolate was cycled between 25 and 27 °C repeatedly (up to 24 times) in order to gradually induce structural change in the chocolate, but not modify its structure too rapidly, particularly as we were interested in examining evolution in the same field of interest. Attempts with larger temperature gradients (e.g., 25–30 °C) resulted in ‘tectonic’ surface shifts, which prevented examination of the same field during cycling. Thus, during the course of in situ scans, the surface of the chocolate would move preventing measurements of the same field of view. These findings imply that a slight variability in the storage temperature of chocolate (> 3 °C) redistributes structural elements at the chocolate’s surface, and likely within the interior as well (though with AFM, this could not be assessed). The

probable cause of this structural shift is CB fat crystal liquefaction and (re)solidification.

In order to determine if pores present on the surface were involved in the development of surface crystal growth, the height data, and cross section across the middle of a pore were examined as a function of the number of cycles to assess any changes in morphology or dimensions of the pore (Fig. 4). Prior to any cycling (0 cycles), the chevron-like pore present at centre was  $\sim 3 \mu\text{m}$  deep with a breadth of  $\sim 7 \mu\text{m}$ . A crystal at top right was visible only after 12 and 24 cycles. Most importantly, however, was the lack of change in mesostructure of the pore itself, indicating that it was likely not involved in the crystal growth process, or if it was, the changes generated were in the sub-micron range and not visible at this scale.

Fig. 5 shows the evolution in surface structure in the vicinity of this pore as a function of the number of cycles. At 0 cycles, the 2-D (illumination mode)  $15 \mu\text{m} \times 15 \mu\text{m}$  image (A) reveals the presence of the pore whereas the 3-D (isometric) image (C) provides a clearer picture of its morphology. After 6 cycles, there was little change in structure, except for perhaps a slight smoothing of the surface and the presence of a small

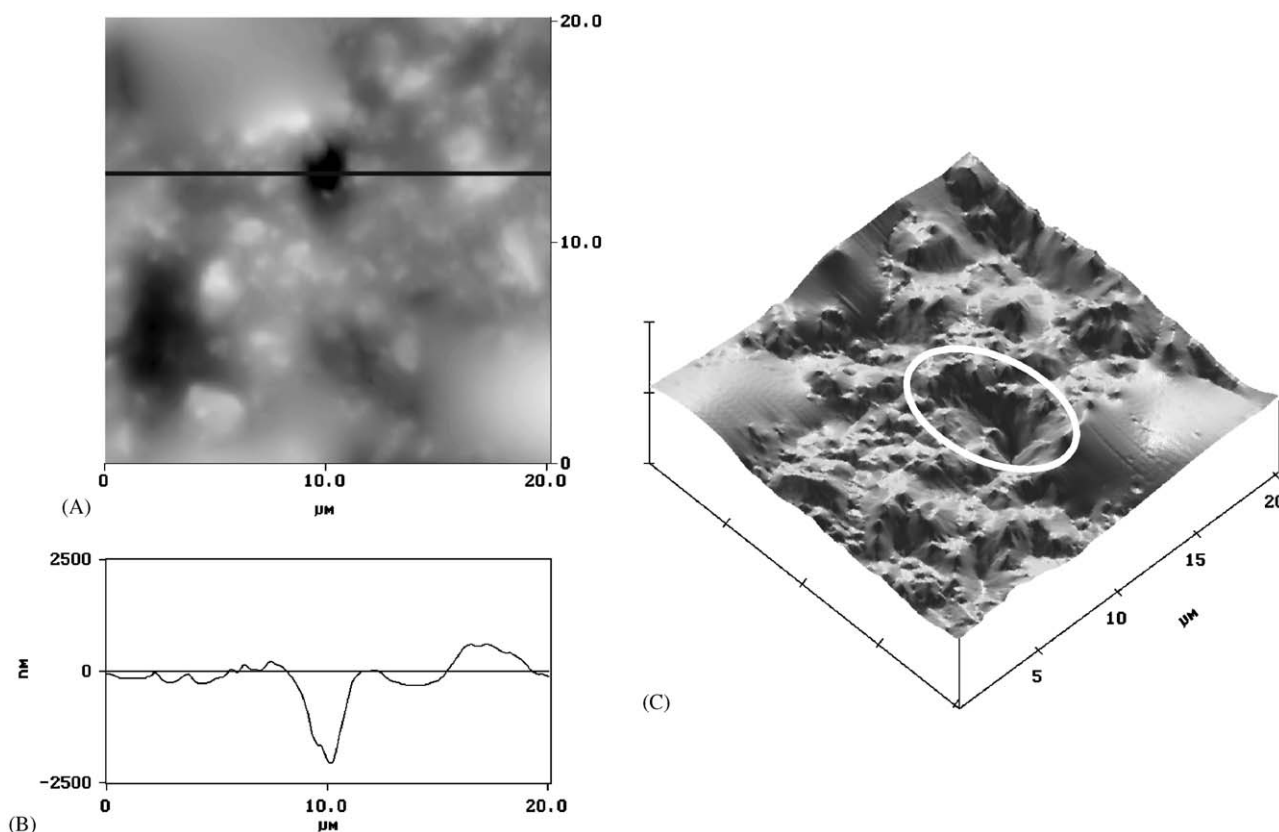


Fig. 3. Scan ( $20\ \mu\text{m} \times 20\ \mu\text{m}$ ) showing a pore adjacent to an area possibly undergoing bloom; height by grey shading (A); cross section corresponding to the dark line (B); and isometric representation (C). The  $z$ -axis scale is  $5\ \mu\text{m}$ . The pore shown in the cross section is identified by the circle in the isometric representation.

crystal that had grown, at top right (visible in both A and C). A cross-sectional representation revealed the crystal growth (B). After 12 and 24 cycles, the crystal was readily visible in the surface map of the sample. The 3-D and cross-sectional views of the sample confirmed the growth. After 24 cycles, the visible portion of the crystal measured  $\sim 2.5\ \mu\text{m} \times 3.0\ \mu\text{m}$  and protruded  $\sim 2\ \mu\text{m}$  from the surface of the chocolate. It was at a distance of  $< 5\ \mu\text{m}$  from the mouth of the cavity.

The use of temperature cycling from  $25$  to  $27\ ^\circ\text{C}$  was enough to induce notable crystal growth on the surface of the chocolate. Furthermore, given that the samples used were wafers  $< 2\ \text{mm}$  thick, the temperature gradients within the samples were small. However, none of the cycled samples demonstrated any bloom visible to the naked eye. Generally, crystals must be at least  $5\ \mu\text{m}$  in length and be present in sufficient numbers to alter chocolate's visual appearance by diffusing light. During this study, a large number of samples were cycled in an effort to determine the role of pores, if any, on fat migration and fat bloom. In many cases, there was crystal growth visible on the surface of the milk chocolate, even in the absence of pores. Fig. 6A shows the surface of milk chocolate following 18 cycles where Fig. 6B shows crystals after 54 cycles. In the former, a

crystal at the surface measuring  $\sim 5\ \mu\text{m}$  in length is visible (identified with the arrow). In the latter, the two arrows point to the extensive crystal growth that has taken place. Visible are a  $\sim 10\ \mu\text{m}$  portion of a crystal and second smaller perpendicular crystal measuring  $\sim 5\ \mu\text{m}$  nearby. Both crystals are partially embedded within the chocolate mass. As pointed out by Jewell (1972), bloom formation occurs both within and at the surface of chocolate, although internal bloom crystals are smaller and more irregularly shaped.

Before any cycling, the CB crystals in the milk chocolate existed in the  $\beta\text{V}$  form. Following 24 cycles, crystals were primarily in the  $\beta\text{V}$  polymorph with a slight amount of  $\beta\text{VI}$  crystals. From our previous work (Hodge & Rousseau, 2002), larger temperature variations in storage temperatures (i.e., greater than  $10\ ^\circ\text{C}$ ) substantially accelerate the  $\beta\text{V}$ – $\beta\text{VI}$  polymorphic transition, particularly when such transitions and/or triacylglycerol (TAG) melting points are included within the temperature range of a fluctuation.

There was a change in SFC of  $\sim 1.8\%$  between samples stored at  $25$  and  $27\ ^\circ\text{C}$ , where SFCs were  $83.1\%$  and  $81.3\%$ , respectively. Though this change is quite small, these repeated fluctuations in SFC were sufficient to induce structural changes within the chocolate, not

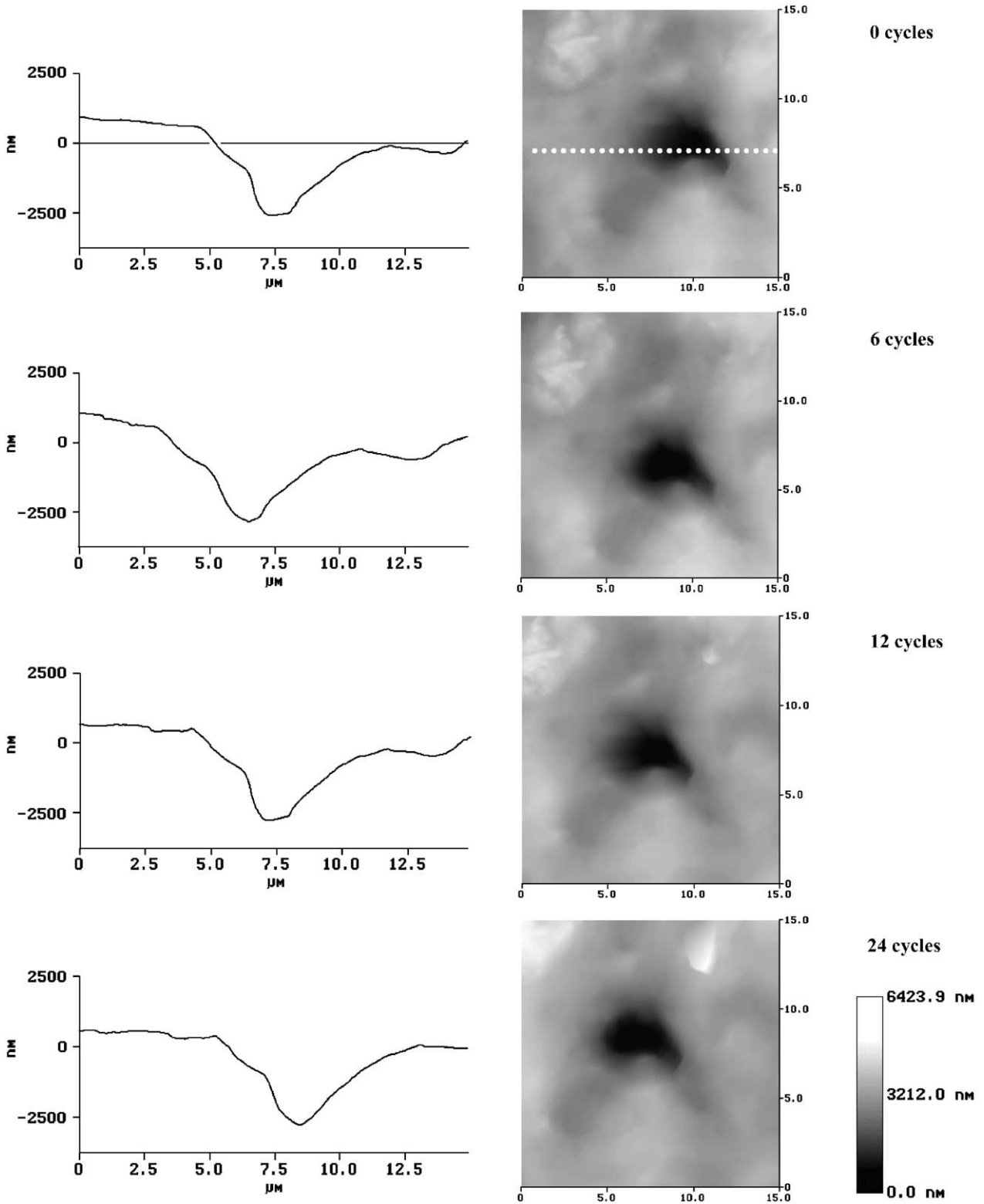


Fig. 4. Surface scans ( $15\ \mu\text{m} \times 15\ \mu\text{m}$  scans) of the vicinity of a pore as a function of the number of cycles from 0 to 24. The 2-D (illumination mode) (left side) and 3-D (isometric mode) (right side) images are provided. To maintain clarity, the dotted line identifying the cross section is only shown for 0 cycles. The z-scale at bottom right ranges from the lowest (black) to highest (white) point.

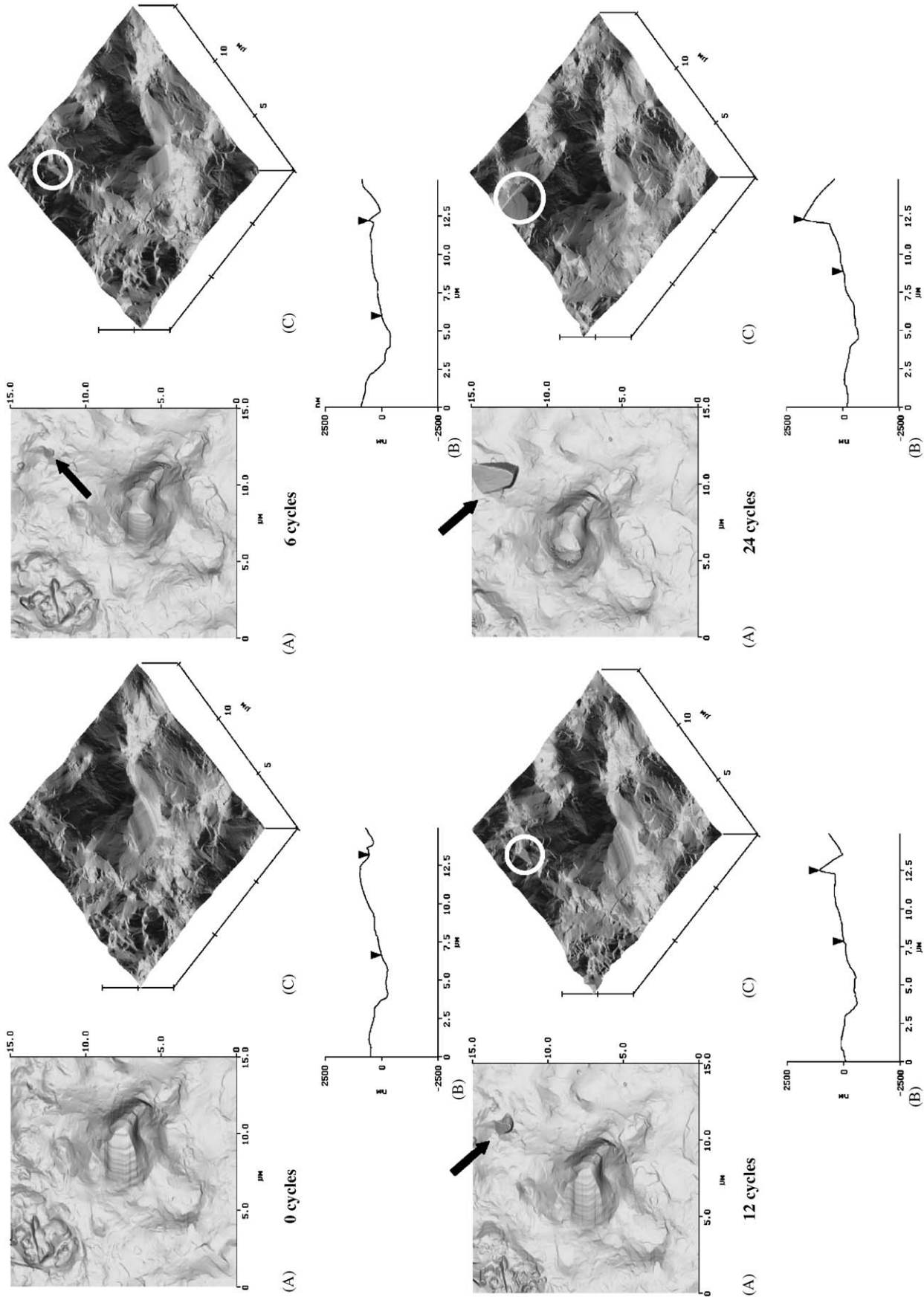


Fig. 5. Height data and cross section across the middle of the pore examined as a function of the number of cycles; height by grey shading (A); cross section corresponding to the dark line (B); and isometric representation (C) is same for each set of cycles. The z-axis scale is 5 μm. Dark arrows in (A) and white circles in (C) at each set of cycles identify location of growing crystal.

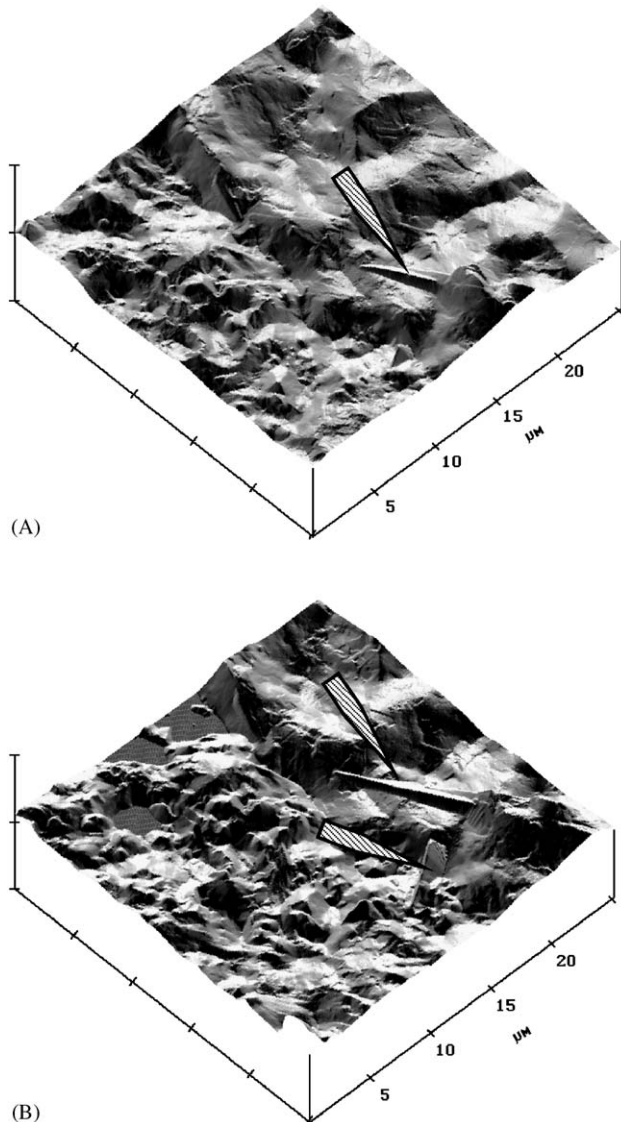


Fig. 6. Cocoa butter fat crystal growth on the surface of milk chocolate (scale:  $25\ \mu\text{m} \times 25\ \mu\text{m} \times 5\ \mu\text{m}$ ). Fig. 6A shows the surface of milk chocolate after 18 cycles. Fig. 6B shows crystals after 54 cycles. Arrows identify crystals that have grown.

only in terms of microstructure, but also in terms of polymorphic transitions. Of note, the cycling temperatures ( $25\text{--}27\ ^\circ\text{C}$ ) were well below the melting point of the  $\beta\text{V}$  polymorph ( $\sim 34\ ^\circ\text{C}$ ) (Hodge & Rousseau, 2002), indicating that the  $\beta\text{V} \rightarrow \beta\text{VI}$  transition observed was promoted by the temperature fluctuations, though it was not melt-mediated. During extended storage, the  $\beta\text{V} \rightarrow \beta\text{VI}$  transition will usually occur via a solid-state transformation. Within this context, Hettich (1966) noted a difference in bloom formation between chocolate stored at  $24\ ^\circ\text{C}$  precisely or at  $24 \pm 1\ ^\circ\text{C}$ , with temperature fluctuations leading to an increase in the rate of bloom formation. These findings imply that in order to prevent the loss of chocolate's acceptable

organoleptic properties, it is important to minimize temperature fluctuations during storage.

From a phenomenological perspective, it is likely that if a porous network does exist in milk chocolate, the pores must in fact be channels partially filled with fat, at least based on the mesostructure observed. However, given that the pores are not appreciably altered with this temperature cycling regime ( $25\text{--}27\text{--}25\ ^\circ\text{C}$ ), yet there is obvious crystal growth, they are not involved in liquefied fat migration. Secondly, our numerous surface scans show that crystal growth can occur without any pores nearby, further indicating that pores are not a necessary element of bloom formation in solid milk chocolate. What mechanism is responsible for bloom formation, then? The key point to consider is the repeated dissolution and (re)crystallization of some TAGs in the fat phase present under the influence of temperature cycling. When increasing the temperature from  $25$  to  $27\ ^\circ\text{C}$ , a small proportion of less-stable crystals will (partially) melt and be able to feed larger crystals that are still present at the higher temperature. Existing crystals will grow in size upon cooling as they act as a template for re-crystallizing CB (or perhaps MF) TAGs upon cooling from  $27$  to  $25\ ^\circ\text{C}$  (Ziegler, Shetty, & Ananteswaran, 2004). The second element to consider is the exothermic nature of recrystallization and associated polymorphic transitions, which may liquefy some of the surrounding fat around the crystals. Both scenarios will result in accrued liquid fat in the immediate vicinity of existing fat crystals, leading to an acceleration of polymorphic transitions and evolution in microstructure. In neither case is pore-mediated transport required. Within this context, Aguilera, Michel, and Mayor (2004) mentioned that both diffusion and capillary forces might play an important role in liquid fat transport. The lack of change in pore morphology may indicate that only diffusion, and not capillary action, is occurring under these experimental conditions. Lastly, it is important to consider that few, if any, existing crystals will fully melt and dissolve given the small change in SFC. Thus, the crystals that jut at the surface of the milk chocolate probably already exist within the chocolate.

There are obvious limitations of the study. With AFM, we are strictly examining the surface structure and not the interior of the chocolate. When cycled chocolate samples were snapped in half with the intent of examining the internal structure of the cycled chocolate, the interior was too rough for proper AFM examination. However, one may postulate that the structure of the crystals within the body of the chocolate is altered by the dense particle network.

In conclusion, smooth and rough areas as well as defined pores are regular features of the surface of properly tempered milk chocolate. From our analyses, most pores in milk chocolate measure  $3\text{--}6\ \mu\text{m}$  in

diameter with depths of 1–3  $\mu\text{m}$ . Pore morphology, however, is highly variable (circular, chevron-like, oval, etc.) and typically pore location on the surface does not appear associated with any specific structural feature(s). When subjected to multiple (6, 12 and 24) mild temperature cycles (25–27–25  $^{\circ}\text{C}$  over 2 h), crystal growth can take place around pre-existing pores, but the pores themselves are not appreciably altered, suggesting they are not necessarily involved in liquefied fat transport and/or bloom formation under these experimental conditions.

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