Chemically oscillating reactions in the formation of botryoidal malachite

DOMINIC PAPINEAU$^{1,2,3,*}$

$^1$London Centre for Nanotechnology, University College London, London, WC1H 0AH, U.K.
$^2$Department of Earth Sciences, University College London, London, WC1H 0AH, U.K.
$^3$Centre for Planetary Sciences, University College London and Birkbeck College London, London, WC1H 0AH, U.K.

ABSTRACT

The origin of banding patterns in malachite [Cu$_2$CO$_3$(OH)$_2$] is an enduring problem in geology. While the bright green, vivid colors of this mineral have been attributed to the presence of Cu, no specific process has been proposed that can explain the perfect circularly concentric banding and geometrical shapes in botryoidal malachite. These patterns of concentric equidistant laminations are comparable to those arising from chemically oscillating experiments using the classical reactants of the Belousov-Zhabotinsky (B-Z) reaction. Through optical microscopy and micro-Raman imaging, this contribution documents that the geometric centers of the self-similar geometric patterns are often composed of organic matter. Carbon isotopes and trace elements further suggest that non-biological decarboxylation reactions of biological organic matter took place during diagenesis. Hence, the morphological and chemical characteristics of chemically oscillating reactions offer a plausible explanation for the formation of botryoidal malachite and abiogenic environmental decarboxylation reactions.

Keywords: Malachite, botryoids, Belousov-Zhabotinsky reaction, organic matter, Raman, decarboxylation; Earth in Five Reactions: A Deep Carbon Perspective

INTRODUCTION

Mineral banding is a common feature of mineral overgrowth during precipitation from aqueous solutions and microbial growth. Episodic growth leads to single crystals with concentric euhedral layers representing the age and composition of each generation of fluids, such as metamorphic zircons. However, this process does not predict that crystal habits or banding should have circularly concentric and radial geometries, such as in botryoidal malachite. The geometric shape of malachite can be modeled as a “surface normal growth” phenomenon, based on a nonlinear equation that plots cusps between smooth spheroids (Jettsetuen et al. 2006). It has also been suggested that such geometric patterns grow heterogeneously, as a function of time and influenced by some external processes triggering nucleation (Jamtveit and Hammer 2012). While mathematical models can make progress, the enigma of the natural process leading to malachite banding and its occurrence as bunches of grapes is an enduring puzzle. This phenomenon is also relevant for biosignatures because stromatolite-like botryoidal growths commonly occur in malachite, yet their occurrence in nature is generally inconsistent with photic environments required for a photosynthetic microbial origin. In fact, botryoidal malachite generally occurs as crusts inside cavities in country rocks affected by supergene, briny, and Cu-rich fluids. Indeed, malachite is usually thought to be hydrothermal alteration or a secondary mineral developed from the weathering of other minerals. Yet, no theory fully explains the origin and shape of its distinct and notable banding.

At the start of the twentieth century, new diffusion experiments in silica gels showed the development of periodic layering due to diffusion; a pattern referred to as Liesegang banding (Liesegang 1910, 1915). The original idea put forward to explain the periodic color layering was due to metal cation impurities diffusing in silica gel, which creates color gradients in objects like agate geodes (Liesegang 1910). This phenomenon was subsequently proposed to explain banding in malachite (Hartman et al. 1934). Indeed, the appearance of Liesegang bands in silica gel is similar to some patterns exhibited by natural agates and chalcedony in geodes from volcanic terrains (Götze 2011). However, most patterns in malachite and geodes are rounded as opposed to linear such as in Liesegang banding, hence this type of diffusion does not explain the geometry of botryoids. Therefore, current explanations for the origin of banding in malachite are incomplete.

The Belousov-Zhabotinsky reaction (B-Z reaction from hereon) is spontaneous under standard conditions and involves the oxidation of carboxylic acids (such as malonic acid, C$_3$H$_4$O$_4$) by a strong oxidizer and its corresponding halide salt (such as the oxidized halogen bromate and its halide salt bromide), as well as a strong acid (such as sulfuric acid; Belmonte et al. 1997; Orbán et al. 2001). When using metal-bearing redox-sensitive dye, such as ferroin (phenanthroline ferrous sulfate, C$_{12}$H$_8$FeN$_2$O$_4$S), this decarboxylation reaction becomes notable and unique as it produces characteristic self-similar patterns of circularly concentric chemical waves (Zaikin and Zhabotinsky 1970). Over minute time scales, these chemical waves are displayed as blue-purple, circular, concentric, and equidistant waves that propagate radially and periodically from randomly located spots in the orange-colored solution. Bubbles of CO$_2$ eventually form...