



Full paper/Mémoire

## Urolithiasis: What can we learn from a Nature which dysfunctions?



Dominique Bazin <sup>a, b, \*</sup>, David Portehault <sup>b</sup>, Frederik Tielens <sup>a</sup>, Jacques Livage <sup>a</sup>, Christian Bonhomme <sup>a</sup>, Laure Bonhomme <sup>a</sup>, Jean-Philippe Haymann <sup>c, d</sup>, Ali Abou-Hassan <sup>e</sup>, Guillaume Laffite <sup>a, e</sup>, Vincent Frochot <sup>c, d</sup>, Emmanuel Letavernier <sup>c, d</sup>, Michel Daudon <sup>c, d</sup>

<sup>a</sup> Sorbonne Universités, UPMC Univ Paris 06, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, 11, place Marcelin-Berthelot, 75005 Paris, France

<sup>b</sup> CNRS, Laboratoire de Physique des Solides, 91405 Orsay, France

<sup>c</sup> AP-HP, Hôpital Tenon, Service d'Explorations Fonctionnelles Multidisciplinaires, 75970 Paris cedex 20, France

<sup>d</sup> INSERM, UMR S, 1155, Hôpital Tenon, 75020 Paris, France

<sup>e</sup> Sorbonne Universités, UPMC Université Paris 06, UMR 8234, Laboratoire de Physico-chimie des Électrolytes, Nanosystèmes Interfaciaux, 4, place Jussieu, case 51, 75252 Paris cedex 05, France

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### ABSTRACT

Learning from Mother Nature constitutes a major intellectual movement encompassing music, architecture and chemistry. In this contribution, we would like to assess the symmetry and the interface present in pathological calcifications in order to propose a bio-inspired approach. We present an overview on the observations made on kidney stone growth at the macroscopic scale. The results are discussed at the molecular scale and examples are proposed to implement the biological asymmetrical growth in pathological calcifications in biomimetic strategies such as in *in vitro* microfluidic experiments.

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## 1. Introduction

Learning from Mother Nature is not a specificity of materials science [1–3]. In the music of Olivier Messiaen (1908–1992), one of the most important composers of the twentieth century, birdsongs are considered as a section of music. A birdsong can be short with repetitive features but, more commonly, it is melodic and more elaborate than a simple call [4]. Another example can be related to the work of an architect, Otto Frei (1925–2015) who passed away recently. He wanted his buildings to contribute to improve everyone's living conditions. He tried to make as little impact as possible on nature and to learn from natural

design, i.e. from the structures of crab shells, birds' skulls or spider webs [5,6].

Biomimetalisation processes constitute an exciting research field in which we have already learned a lot from Mother Nature [7–9]. In this contribution, we review a range of research outputs we have obtained regarding pathological calcifications [10–14], in order to show that it is possible to propose at least one example of a bioinspired approach to the field based on kidney physiology. Because the chemistry of the kidney is quite a wide subject, and one hundred chemical phases have been identified in kidney stones (Ks), here we decided to focus on biological entities, which can be considered as Janus particles. The concept of Janus particles was first proposed by De Gennes [15] 20 years ago in his Nobel Prize lecture, following the results obtained by C. Casagrande and M. Veyssié [16,17]. As

\* Corresponding author.

E-mail address: [dominique.bazin@u-psud.fr](mailto:dominique.bazin@u-psud.fr) (D. Bazin).

defined by M.D. McConnell et al. [18], Janus particles are traditionally composed of two chemically distinct regions, making them suitable for applications as biological sensors, nanomotors, antireflection coatings, optical sensing devices, and two-phase stabilizers, as well as for fundamental studies in asymmetric particle assembly. As an illustration of Janus particles, a schematic representation of such entities has been provided in Fig. 1. For the sake of clarity, we only consider here metallic Janus particles [18–20]. As can be seen in the following figures (Fig. 1A–C), Janus particles may display distinct morphologies. In the case of nanotubes (Fig. 1D1 and D2), peculiar distributions of the second metal (in black) can lead to the construction of two enantiomers, leading to helimagnetism (in the case where the first metal is Pt and the second Co, for example) or enantioselective catalysis [21].

Following the definition provided by M.D. McConnell et al. [18], we start this contribution with a description of KSs at the macroscopic scale, in which at least two chemical phases have been identified. Details at the mesoscopic scale are then provided through observations performed using a latest generation scanning electron microscope (Field Emission Scanning Electron Microscope, or F.E.-S.E.M.). We will see that pathological calcifications exhibit peculiar mineral/organic ratios as well as crystal/amorphous interfaces. To the best of our knowledge, such a kind of interface is not used to generate Janus particles. Finally, we would like to propose that a chemical process based on the pathogenesis of Randall's plaque (RP) generates a deposit made of calcium phosphate apatite (CA) at the origin of a calcium oxalate KS.

## 2. Observations at the macroscopic scale

Regarding most of the KS samples, several chemical phases are identified. In the case of the KS made of calcium

oxalate monohydrate (COM), (Fig. 2A), the presence of a whitish deposit termed RP [22–27], generally made of CA in a local hollow point on the surface of COM KS induces the dissymmetry. Actually, RP serves as a nucleus of the kidney stone and constitutes today a major public health problem in western countries. More complex structures exist, however, and the presence of more than one hundred chemical compounds has been identified in KSs. Fig. 2B shows a typical KS made of COM and calcium oxalate dihydrate (COD) on which a RP made of CA is present.

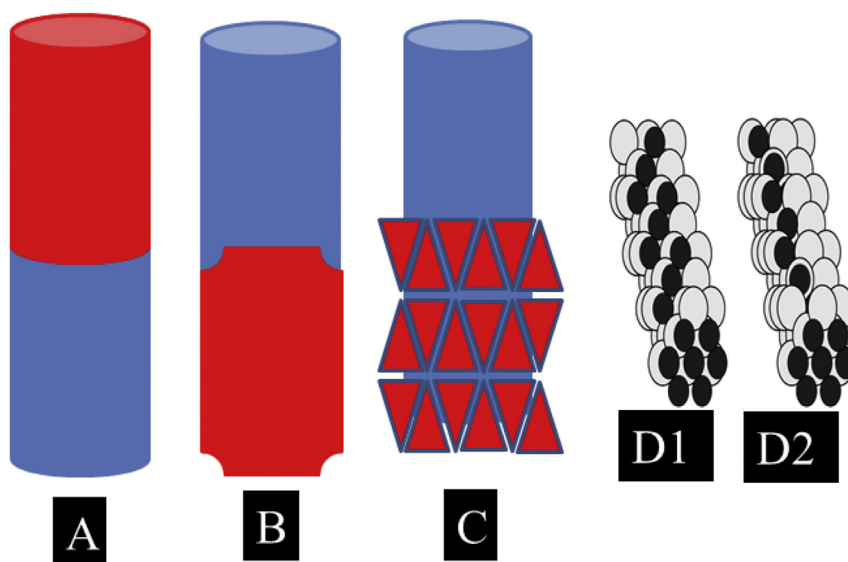
## 3. Dissymmetry at the mesoscopic scale

Observations through FE-SEM underline that the complexity of pathological calcifications (Fig. 3A) exists also at the mesoscopic scales (Fig. 3B). For example, in the case of RP, observations (Fig. 3B) show that these calcifications are composed of a mixture of tubules with calcified walls and tubules obstructed by calcium phosphate plugs. Thus, the lack of centrosymmetry can be induced by the chemistry and the structure at the macroscopic and mesoscopic scales. In some cases, RP is made of sodium hydrogen urate monohydrate (UrNa) mixed with plates of COM (Fig. 2C).

The final illustration is crystals present in urine [28,29]. For these biological entities, the lack of centrosymmetry may be due to the morphology as well as the chemistry. In Fig. 4A we can see calcite crystals at the corners of a crystal made of COD, whereas in Fig. 4B the photograph shows weddellite crystals deposited on the surface of anhydrous uric acid.

## 4. Chemistry at the interface

A precise understanding of the pathogenesis of calcifications lies in the description of the interface. The



**Fig. 1.** Schematic representation of metallic Janus particles. The lack of centrosymmetry may come from the chemistry (A) but also from both the chemistry and the structure (B and C). In some cases, peculiar Janus particles may be related to enantiomers (D1 and D2).

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