

## Comments on the article "Descriptive human pathological mineralogy"

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### Introduction

As a research team comprising a geologist and a urologist, we welcome this opportunity to review the article, "Descriptive Human Pathological Mineralogy," by Gibson (1974). Because the article emphasizes our primary interests, urinary calculi, we shall restrict our comments to that aspect of the article.

We believe that Gibson (1974) has overstated and seriously underdocumented the complexity of urinary stone disease. In particular, eight minerals were included by Gibson (see Table 1) which have been rarely reported and only tentatively identified as true *in situ* stone components (Herring, 1962; Sutor and Scheidt, 1968; Prien and Prien, 1968). On the other hand, well-documented urinary stones composed of uric acid, urate salts, cystine, xanthane, and matrix concretions were excluded because they are not minerals, *sensu strictu*; these organic components are found in about 15 to 20 percent of all analyzed urinary stones (Prien, 1963; and Hesse *et al.*, 1972).

Our examination of approximately 14,000 surgically-removed as well as spontaneously-passed urinary stones has revealed a large variety of artifacts which on proper documentation were indeed shown to have originated outside the human urinary tract (see also Herring, 1962). Such artifacts were not mentioned in the article by Gibson (1974).

Finally, there appear to be some errors in the discussion of the optical mineralogy of apatite and in the chemistry and significance of newberyite.

In summary, the article by Gibson (1974) seems to have added confusion rather than clarification to the understanding of urinary stones and stone disease. Herein we shall attempt to clarify some of the confusion.

### Stone composition

Any stone received by a crystallographer for analysis and reportedly derived from the human urinary tract may, in fact, have (1) originated in the human urinary tract as reported, (2) undergone a metamorphosis or decomposition after removal from the urinary tract, or (3) originated outside the urinary tract and thus be an artifact. Additionally, the crystallographer must be alert for mislabeled stones, such as those from animals and organ systems other than the urinary tract.

The published literature indicates that the vast majority of human urinary calculi comprise a rather limited number of crystalline species. These species include (1) calcium oxalates—weddellite and whewellite, (2) certain phosphates—brushite, carbonate-apatite, hydroxyapatite, newberyite, octacalcium phosphate, struvite, and whitlockite, (3) uric acid and derivate salts—uric acid, uric acid dihydrate, ammonium acid urate, monosodium urate, and disodium urate monohydrate, and (4) other organic compounds—cystine and xanthane. Our analyses of over 14,000 urinary stones support the earlier reports (*e.g.*, Prien and Frondel, 1947; Herring, 1962; Sutor and Scheidt, 1968; and King, 1971) of a limited number of crystalline species originally in human urine.

From time to time the very rare occurrence of a previously unobserved constituent of a urinary stone is reported in the literature; see for example, Mulvaney *et al.* (1972), Hesse *et al.* (1973), and Joekes *et al.* (1973). However, Gibson (1974) has described eight crystalline substances, listed in Table 1, either not hitherto reported or known only to occur as minor constituents in fewer than one stone per thousand. Because of their extremely rare occurrence in the urinary system, it would have been most useful if the *in situ* origin, optical properties, and X-ray diffraction pattern had been thoroughly documented for monetite, hannayite, halite, gypsum, hexahydrate, vaterite, calcite, and aragonite. Furthermore, clinical judgment dictates detailed case histories to document

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TABLE 1. Rarely reported minerals in human urinary calculi

MINERAL <sup>1</sup>	COMPOSITION	CRYSTAL SYSTEM	OCCURRENCE PER 15,000 STONES (Gibson, 1974)	PREVIOUS REPORTS <sup>2</sup>
Aragonite	CaCO <sub>3</sub>	Orthorhombic	Included in Calcite	Lagergren, 1962 <sup>3</sup> Beck and Bender, 1969
Calcite	CaCO <sub>3</sub>	Hexagonal	4	None
Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	Monoclinic	3	Lagergren, 1956
Halite	NaCl	Cubic	2	None
Hannayite	Mg <sub>3</sub> (NH <sub>4</sub> ) <sub>2</sub> (HPO <sub>4</sub> ) <sub>4</sub> ·8H <sub>2</sub> O	Triclinic	5	None
Hexahydrate	MgSO <sub>4</sub> ·6H <sub>2</sub> O	Monoclinic	1	None
Monetite	CaHPO <sub>4</sub>	Triclinic	3	Beck, Mulvaney, Rhamy and Gibson, 1974
Vaterite	CaCO <sub>3</sub>	Hexagonal	Included in Calcite	None

<sup>1</sup>These minerals have rarely been reported as *in situ* components of human urinary stones (see Herring, 1962; Sutor and Scheidt, 1968; and Prien and Prien, 1968); however, several of these minerals are common in human gall stones (Sutor and Wooley, 1969; and Lonsdale and Sutor, 1972) and in urinary stones in other animals (Sutor and Wooley, 1970).

<sup>2</sup>Included here are only reports based on x-ray diffraction or microscopic studies. Infrared analyses, such as those by Otsuji, *et al.*, (1968), Haux and Natelson (1970), and Takasaki (1975) have been excluded because whereas specific radical groups (e.g., PO<sub>4</sub><sup>=</sup> and CO<sub>3</sub><sup>=</sup>) are identifiable, the exact species (calcite + hydroxyapatite versus carbonate-apatite) can not be determined. Similarly chemical analyses are also not included.

<sup>3</sup>Lagergren (1962) has not directly observed a calcium carbonate calculus but includes these three references to aragonite; Loeper and Cartier (1951), Barraud (1952), and Boissier (1952).

whether an unusual mineral is an artifact or a "new disease."

An example of the need for careful documentation of the *in situ* origin of a stone can be found in the alleged calcite/aragonite stones mentioned by Gibson (1974) and reported in an earlier article by Beck and Bender (1969). The patient, a 33 year old female, passed four stones, six were then irrigated from the bladder, and four more were subsequently evacuated; the stones were angular and rarely exceeded 5mm maximum diameter (Beck and Bender, 1969). Because all the stones were either passed or removed *without* surgery, the critical question remains, "did the patient insert the stones into her own bladder?" Sutor (oral communication, 1972) discussed a female patient with recurrent calcite rhombs in the bladder. When the patient was confronted with evidence that her urethra was easily distendable and the probable inorganic origin of the stones, she subsequently reported no recurrence of the stones (Sutor and O'Flynn, 1973). Furthermore, LeGeros (1965) found that at 100°C the ratio of carbonate to phosphate in

aqueous solution must exceed 40 if aragonite is to precipitate, otherwise the only precipitate is carbonate-apatite. Since Beck and Bender (1969) reported no accompanying apatite, the *in situ* origin of the calcite/aragonite stones is further clouded.

This discussion of calcite/aragonite has not been an effort to refute the report of Beck and Bender (1969), but rather is an illustration of the extreme care and precision needed to document the *in situ* pathogenic origin of rare minerals.

### Organic stone-forming components

Uric acid, its various hydrates and salts, along with cystine and proteinacious gels (matrix) account for up to 20 percent of urinary stones (Hesse *et al.*, 1972; also see Lonsdale and Mason, 1966). Frank *et al.* (1970) have reported an uncommonly high, 34.6 percent, occurrence of uric-acid-bearing stones among a group of 622 patients studied over a 12 year period. Thus to exclude compounds which are not minerals *sensu strictu* from a discussion of human pathological

stone disease omits a large portion of pathogenic stones.

Additionally, most organic compounds common to urinary stones are crystalline substances (Lonsdale and Sutor, 1972) with fixed physical, optical, and atomic properties; thus their identification can be accomplished using standard mineralogical techniques.

### Artifacts

These items are not the result of *in situ* crystallization or precipitation and generally account for about one percent of all analyzed stones (Herring, 1962; and Brien *et al.*, 1974). Some of the more common artifacts we have observed, many of which were also reported by Herring (1962), include: quartzite, quartzo-feldspathic siltstone, limestone (some with asphalt), calcite, chert, jasper, metallic shot, blood clots, sutures, prostatic tissue, catheter fragments, bone fragments, and one struvite-encrusted ball of petrochemical jelly (gas chromatograph data).

There are several likely origins for artifacts. Some possibilities include (1) retrieval from a urinal of material erroneously thought to have been passed spontaneously, (2) post-surgical remnants, (3) catheter fragmentation, (4) intentional effort by the patient to gain attention either by bringing a stone to a urologist or by self-implantation, and (5) unique biological accidents.

The urologist, confronted with an artifact, must carefully weight the probable sources and develop an appropriate course of treatment (see also Prien, 1963). Thus a careful analysis and identification of such artifacts is mandatory.

A case of exceptionally sophisticated deception was reported by Sharon and Diamond (1974). During a 23-day hospitalization of a 21 year old female nurse, five uric acid stones were removed by cystoscopy from her bladder. After a search of her hospital room revealed a cache of uric acid stones, it was concluded that she had implanted the stones in her own bladder.

### Apatite

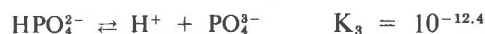
In his discussion of the mineralogy and optical properties of apatite Gibson (1974) notes that "laminations of this material occur on spherulites about one micron across, which give *uniaxial optic figures without the aid of condensers or a Bertrand lens*" (emphasis ours). This interpretation is inconsistent with the theory of interference figures as discussed by Kamb (1958) and Bloss (1961, p. 92-122). Surely a

condensing lens and either a Bertrand lens or the removal of an eyepiece is required. The notation that the "figures" occur in presumably concentrically layered stones implies that black-cross, or simultaneous N-S and E-W extinctions were, in fact, observed. This black-cross extinction, which mimics a centered uniaxial optic-axis figure, is common to concentrically layered as well as radially crystallized substances when viewed with crossed nicols; for example, chert, feldspathic spherulites, and many zeolite nodules.

We also consider it unfortunate that carbonate-apatite and hydroxy-apatite were lumped under the heading 'apatite' rather than separated. Sutor *et al.* (1974) studied collections of urinary stones from Great Britain and Northern Ireland; they reported that "hydroxyapatite is the form which almost invariably crystallizes with the calcium oxalates, and . . . carbonate-apatite is usually laid down with struvite." Independent observations by Griffith and Musher (1975) have led them to speculate that carbonate-apatite is most commonly associated with urinary stones resulting from the hydrolysis of urea by urease which in turn is related to *Proteus* infection; the predominant mineral would be struvite.

### Newberyite

According to Gibson (1974) it is "a mineralogic enigma . . . an acid phosphate . . . frequently associated with struvite" which itself crystallizes only in alkaline urine. To the contrary, newberyite,  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ , should not be considered an acid phosphate, and it is not likely a product of direct precipitation from acidic urine because, in dilute solutions,  $\text{HPO}_4^{2-}$  is the dominant phosphate radical only between pH 7.2 and 12.4. Krauskopf (1967, p. 88) gives the following dissociation, or equilibrium, constants for phosphoric acid in water:



These data indicate that the predominant phosphate phase in solution is  $\text{H}_3\text{PO}_4$  at pH less than 2.1,  $\text{H}_2\text{PO}_4^-$  between pH 2.1 and 7.2,  $\text{HPO}_4^{2-}$  between pH 7.2 and 12.4, and  $\text{PO}_4^{3-}$  at pH greater than 12.4. At present, there exists no definite experimental evidence or theoretical determination for the necessary conditions to precipitate newberyite from the complex chemical system, urine. It should be noted, however, that Sücker (1963) achieved the complete conversion

of struvite to newberyite by immersion in 0.01 N HCl for 62 hours.

Sutor (1968) has called to question the pathological significance of newberyite. She reported newberyite from 17 percent of the calculi studies; it was associated with struvite; and all the stones were at least 20 years old—some dating to the 18th century. Furthermore, Whitaker (1968) showed that struvite can begin to decompose to newberyite in about six days. The physicochemical basis and the clinical significance of newberyite are thus in question.

### Summary

Whereas the article by Gibson (1974) could have familiarized geologists with the fascinating field of human urinary stones, it falls short due to omissions and incompletely documented postulates.

Numerous rarely observed minerals were listed without (a) adequate mineralogical identification, (b) documentation of their human *in situ* origin, or (c) appropriate discussion of their clinical significance. Approximately 15 to 20 percent of all stones were not discussed because only minerals *sensu strictu* were considered, thus excluding all organic concretions. Artifacts, which originate outside the urinary tract, were not mentioned, yet crystallographic analysis is a reliable method of identifying these objects. We believe Gibson's (1974) discussion of the optical properties of radially crystallized and concentrically layered apatite was confusing and perhaps erroneous. Newberyite,  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ , was identified as a precipitate in acidic urine, whereas, in fact,  $\text{HPO}_4^{2-}$  is the dominant phosphate radical in alkaline dilute aqueous solutions, pH between 7.2 and 12.4. The bibliography and documentation were in our opinion deficient.

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