

Study of calcium oxalate monohydrate of kidney stones by X-ray diffraction

M. T. D. Orlando, L. Kuplich, D. O. de Souza, H. Belich, J. B. Depianti, C. G. P. Orlando, E. F. Medeiros, and P. C. M. da Cruz

Universidade Federal do Espírito Santo (UFES), Av. Fernando Ferrari 514, 29075-910 Vitória, Espírito Santo, Brasil

L. G. Martinez

Instituto de Pesquisas Energéticas e Nucleares (IPEN), Campus Universidade de São Paulo (USP), 05508-900 São Paulo, São Paulo, Brasil

H. P. S. Corrêa

Universidade Federal de Mato Grosso do Sul (UFMS), 79070-900 Campo Grande, Mato Grosso do Sul, Brasil

R. Ortiz

Escola de Artes, Ciências e Humanidades (EACH), Universidade de São Paulo (USP), Avenue Arlindo Bettio 1000, 03828-000 São Paulo, São Paulo, Brasil

(Received 16 May 2007; accepted 28 February 2008)

X-ray powder diffraction was used to study the phase composition of human renal calculi. The stones were collected from 56 donors in Vitória, Espírito Santo state, southeastern Brazil. An XRD phase quantification revealed that 61% of the studied renal stones were composed exclusively of calcium oxalate [34% formed only by calcium oxalate monohydrate (COM) and 27% presents both monohydrate and dihydrate calcium oxalate]. The 39% multi-composed calculi have various other phases such as uric acid and calcium phosphate. Rietveld refinement of XRD data of one apparent monophasic (COM) renal calculus revealed the presence of a small amount of hydroxyapatite. The presence of this second phase and the morphology of the stone (ellipsoidal) indicated that this calculus can be classified as non-papillary type and its nucleation process developed in closed kidney cavities. In order to show some advantages of the X-ray powder diffraction technique, a study of the phase transformation of monohydrate calcium oxalate into calcium carbonate (CaCO_3) was carried out by annealing of a monophasic COM calculi at 200, 300, and 400 °C for 48 h in a N_2 gas atmosphere. The results of the XRD for the heat treated samples is in good agreement with the thermogravimetric analysis found in the literature and shows that X-ray powder diffraction can be used as a suitable technique to study the composition and phase diagram of renal calculi. © 2008 International Centre for Diffraction Data. [DOI: 10.1154/1.2903738]

Key words: kidney stones, calcium oxalate, calcium oxalate monohydrated, X-ray diffraction

I. INTRODUCTION

Urolithiasis has been described as the third most common affliction of human urinary tract, estimated to occur in approximately 5% of the population of any industrial country. In addition, statistics have shown a recurrence rate of 2.5%, affecting mainly adults 20 to 60 years of age (Asokan *et al.*, 2004). The renal calculi are formed as a result of a biological maladjustment of the urine and are often heterogeneous containing mainly oxalate, phosphate, and uric acid crystals (Koide *et al.*, 1986; Grases *et al.*, 1998).

Although urinary calculi can be easily removed in most cases, it is not possible to prevent their recurrence even after the stone's removal, either by invasive or non-invasive clinical or surgical procedures (Coe *et al.*, 1992; Singh *et al.*, 1999). The nucleation process of the crystal is an important factor during the initial stage of the calculi genesis. Once the heterogeneous nucleation starts, the stone continues to grow because of the deposition of either original or different composition substances on the original substrate. The potential risk of recurrence, with consequent degradation of the renal

function along the expected lifetime (especially in children), justifies an investigation of urinary calculi composition, nucleation, and its associated pathologies.

The formation of renal calculi based on calcium oxalate crystals has been widely reported since 1985, but researchers have paid little attention to its nucleation process (Koide *et al.*, 1986). According to schematically kidney morphology proposed by Söhnel and Grases (1995), calcium oxalate monohydrate calculi ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ or COM) can be classified in two groups: (I) COM papillary calculi and (II) non-papillary COM calculi (Grases *et al.*, 1998).

The first group (I), COM papillary calculi, is associated with COM renal stones, which appear attached to papillae. This group presents a conical morphology and is formed by a core, or stone nucleus, situated in the urolith interior and a shell in its outer part grown out from the core (Söhnel and Grases, 1995). Grases *et al.* (1998) point out the existence of four different types of papillary calculi core upon which the crystal growth occurs. Furthermore, the same authors remark that the fixation process of the nucleus on the papilla has been overlooked in previous studies.



Figure 1. (Color online) Calculus #30 (II-a morphology) from a local resident in Vitória, Brazil (measurement in cm).

The second group (II), non-papillary COM calculi, presents typically ellipsoidal morphology, which is clearly different from the papillary calculi (type I). It grows in renal closed cavities and can be broadly classified into two main groups: (II-a) and (II-b). The II-a type renal calculi contain no core and their inner structures resemble the random patterns exhibited by sedimentary rocks. In this type of kidney stone, the material is distributed irregularly on the inner part and may occasionally contain small spheres of hydroxyapatite. On the other hand, the II-b calculi contain a core that is mainly organic matter that functions as a seed for the development of the stone body. Most of the bodies of this type of stone are constituted by columnar COM crystals emerging from the core and, because of the absence of an attachment to the epithelium, are found in renal cavities. Moreover, Elliot (1973) points out that these stones can be initiated by a small papillary stone detached accidentally from the papilla and trapped in the kidney cavities.

There are many useful techniques that can be used to obtain the urinary calculi composition, including chemical analysis (Hodgkinson, 1971; Westbury and Omenogor, 1970), infrared spectroscopy (Bellanato *et al.*, 1973; Takasaki, 1971), X-ray powder diffraction (Gibson, 1974; Lonsdale *et al.*, 1968), electron microscopy (Spector *et al.*, 1978), and atomic absorption spectroscopy. XRD analysis, used to study the composition of calculi, provides the identification of its phases and their type and quantities, allowing for the discovery of the origin of the calculi.

Renal calculi with calcium oxalates are represented by the general formula $\text{CaC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, where x is the number of bonded-water molecules, which can vary from 1 to 2. It can be formed on crystalline seed particles of organic or inorganic compounds that work as a nucleating substrate. Therefore, the H_2O molecule might be bound or free, depending on if the H_2O molecule belongs to the crystal structure or the organic compound among them. Some of the characterization techniques commonly used are not suitable to give the structural information about the H_2O molecule. For instance, chemical, infrared spectroscopy, and thermogravimetric analysis (TGA) cannot define by themselves whether the H_2O molecule is structural or interstitial. On the other hand, the X-ray powder diffraction technique (Gibson, 1974; Lonsdale *et al.*, 1968) associated with a Rietveld refinement of the

TABLE I. Composition of calculi.

| Calculi phase | N (%) |
|---|--------|
| $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ | 19(34) |
| $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} + \text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ | 15(27) |
| $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} + \text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + \text{phosphate}$ | 7(12) |
| L-Cistina | 2(4) |
| Mixed | 13(23) |

data can define the position of the H_2O molecule and, as a consequence, can help to determine the $\text{CaC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ phase present in renal calculi. Therefore, the analysis of the crystalline phases and the determination of the morphological characteristics of renal calculi are important tools for the etiological diagnosis of this disease. Another advantage of the X-ray powder diffraction technique is that the powder can be characterized without a surgical procedure by analyzing the fragmented crystals collected from the urine, which follows the extra-corporeal shock wave lithotripsy (ECSWL). Our research group has already reported a preliminary XRD data analysis on urinary calculi fragments collected from 25 donors submitted to ECSWL procedures in Vitória, Brazil (Azevedo, 2002). In that work, a semi-quantitative analysis of the calculi composition revealed that they consisted of a combination of calcium oxalate monohydrate, calcium oxalate dihydrate, uric acid, and calcium phosphate. Among the 25 stones, 36% had calcium oxalate monohydrate type ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) as the main phase and 60% exhibited calcium oxalate dihydrate ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) as the main component.

II. EXPERIMENTAL

A. Samples

Renal calculi of 56 donors from the inhabitants of Vitória and surrounding areas were collected for this study. It is important to note that all kidney stones in this work were expelled naturally or obtained by surgical procedures (Kuplich, 2004).

First, all collected calculi were dried in a dissector filled with nitrogen gas at room temperature for 2 weeks. Second, the dry calculi were photographed and classified according to the criteria proposed by Grases *et al.* (1998). Figure 1 represents a typical calculus fragment. After this procedure, the calculi were crushed in an agate mortar in order to obtain a fine mesh powder ($57 \mu\text{m}$ in size).

TABLE II. Composition of calculi by gender.

| Calculi phase | Male (%) | Female (%) |
|---|----------|------------|
| $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ | 11(31) | 8(40) |
| $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} + \text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ | 12(33) | 3(15) |
| $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} + \text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + \text{phosphate}$ | 5(14) | 2(10) |
| L-Cistina | — | 2(10) |
| Mixed | 8(22) | 5(25) |

TABLE III. Results of Rietveld refinement and the reliability factors for Sample #25.

| | |
|------------------------------------|--|
| Phase | CaC ₂ O ₄ ·H ₂ O (Calcium carbonate monohydrate) |
| Crystal system | Monoclinic |
| Space group | <i>P</i> 121/ <i>c</i> 1 |
| Unit cell dimensions | <i>a</i> =6.2952(2) Å, <i>b</i> =14.5951(4) Å, <i>c</i> =10.1185(3) Å, <i>β</i> =109.46(0)° |
| Cell volume | 876.56(4) Å ³ |
| Density | 1.996 g/cm ³ |
| χ^2 | 2.203 |
| <i>R</i> (<i>F</i>) ² | 0.0554 |
| <i>wRp</i> | 0.0999 |
| <i>Rp</i> | 0.0770 |

B. X-ray diffraction and refinement

X-ray diffraction patterns of the samples were measured in order to obtain the phase composition of the renal calculi. The XRD measurements were performed with a Rigaku Multiflex laboratory diffractometer, using a Cu *Kα* sealed tube working at 40 kV, 30 mA, a scintillation counter, and a diffracted beam graphite monochromator. The diffraction patterns were recorded in the step scan mode at 0.02 steps and at a measurement rate of 2 s/step. The divergence, receiving, and scatter slits used were 1/2°, 0.3 mm, and 1/2° respectively. The diffraction patterns were registered within the angle range from 4 to 120° 2θ. Some of the samples had their diffraction data collected using the X-ray Powder Diffraction (D10B–XPD) beamline (Ferreira *et al.*, 2006) of the National Synchrotron Light Laboratory (LNLS), Campinas, Brazil. The wavelength used was 1.19197(3) Å and selected by a double-bounce Si(111) monochromator, with the first crystal water cooled and the second one bent for sagittal focusing (Giles *et al.*, 2003) using an Na(Tl)I scintillation counter.

In both cases, the instrumental parameters were obtained from the refinement of standards samples of LaB₆ and Al₂O₃ (NIST, 2000, 2005). The Powder Diffraction File database was used for phase identification. The identified phases were calcium oxalate monohydrate (COM) (PDF 20-0231), calcium carbonate (PDF 05-0586), calcium oxalate dihydrate (COD) (PDF 17-0541), and uric acid (PDF 28-2016) (ICDD, 2005). The Rietveld refinement of the X-ray diffraction data was performed using the GSAS and EXPGUI package (Larson and Von Dreele, 2000; Toby, 2001).

C. Thermal treatment

A partial phase diagram study of CaC₂O₄·H₂O was carried out, submitting the calculi to heat treatments performed with a computer controlled furnace under an inert nitrogen (99.9% N₂) atmosphere controlled by a mechanical flux meter, in order to remove the bonded H₂O molecule. The study was carried out on two calculi containing only the calcium oxalate monohydrate phases (labeled here as #45 and #25), which were divided in four equal weight samples. Three samples of the same stone were submitted to heat treatments for 48 h at 200, 300, and 400 °C, whereas the fourth sample was held at room temperature (N₂ atmosphere) in order to compare with the treated samples. After each thermal treatment, the sample was submitted for an X-ray diffraction measurement under a nitrogen atmosphere.

This process allows for the determination of the true phase transformation, but TGA can only determine the temperature at which the loss-of-mass occurs, regardless if it is attributable to interstitial water or bonded H₂O molecule.

III. RESULTS AND DISCUSSION

A. X-ray diffraction and Rietveld analysis

The quantitative analysis was done using the integrated area method both for the laboratory and synchrotron diffraction data (Table I). The gender phase composition of the 56 calculi is presented in Table II. As it can be seen in Table I,

TABLE IV. Results of Rietveld refinement and the reliability factors for Sample #30.

| Phase | CaC ₂ O ₄ ·H ₂ O (Calcium carbonate monohydrate) | Ca ₁₀ (PO ₄) ₆ (OH) ₂ (Hydroxiapatite) |
|------------------------------------|---|--|
| Crystal system | Monoclinic | Monoclinic |
| Space group | <i>P</i> 121/ <i>c</i> 1 | <i>P</i> 1121/ <i>b</i> |
| Unit cell dimensions | <i>a</i> =6.2945(1) Å, <i>b</i> =14.5961(3) Å, <i>c</i> =10.1177(2) Å, <i>β</i> =109.46(0) | <i>a</i> =9.479(5) Å, <i>b</i> =18.883(9) Å, <i>c</i> =6.8888(9) Å, <i>γ</i> =120.45(3) Å |
| Cell volume | 876.56(4) Å ³ | 1062.98(70) Å ³ |
| Density | 2.125 g/cm ³ | 3.063 g/cm ³ |
| χ^2 | | 1.826 |
| <i>R</i> (<i>F</i>) ² | | 0.0244 |
| <i>wRp</i> | | 0.0827 |
| <i>Rp</i> | | 0.0629 |

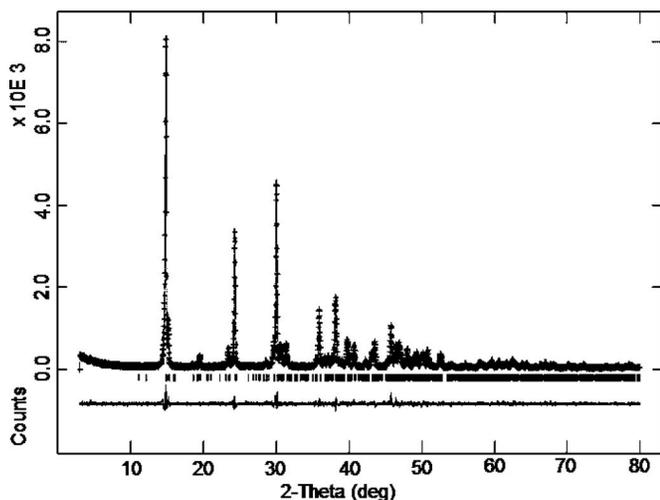


Figure 2. Final Rietveld refinement (line) of Sample #25, data experimental (circle), and difference between both.

the results are in good agreement with the results reported by Ansari *et al.* (2005), in which calcium oxalate monohydrate is the calculi major phase.

In order to get an improvement on the calculi phase analysis, a Rietveld refinement of two apparently monophasic COM calculi (labeled here as #25 and #30) was performed. Table III presents the main results of the refinements for Sample #25, with the goodness-of-fit.

Thompson-Cox-Hastings pseudo-Voigt modified profile function in the Rietveld refinements was used, and the starting crystal structure data for the refinements were taken from the ICSD database: 30-782 for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (COM), 34-457 for hydroxyapatite, and 30-783 for $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (COD) (FIZ and NIST, 2006). The Rietveld analysis of Sample #25 showed that the sample is monophasic, i.e., $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (COM). On the other hand, the Rietveld refinement of the calculus #30 indicated the presence of 15.1% weight fraction of hydroxyapatite and 84.9% weight fraction of COM (Table IV). The χ^2 , $R(F)^2$, wRp , and Rp indicate the quality of the

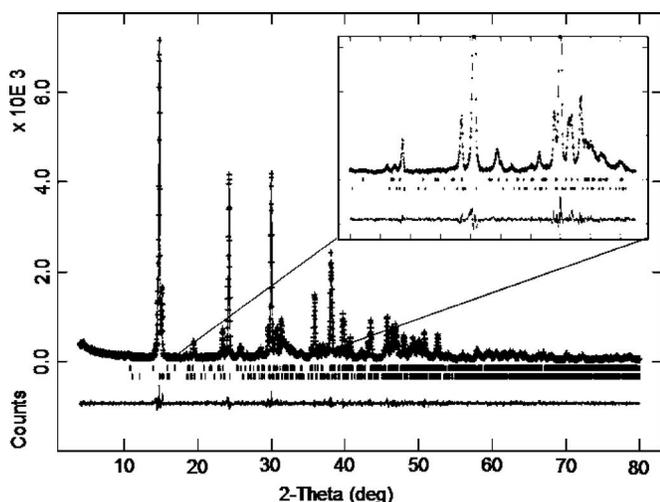


Figure 3. Final Rietveld refinement (line) of Sample #30, data experimental (circle), and difference between both. The first phase is $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (COM) and the second is $\text{Ca}_{4.87}\text{HO}_{12.56}\text{P}_3$ (hydroxyapatite).

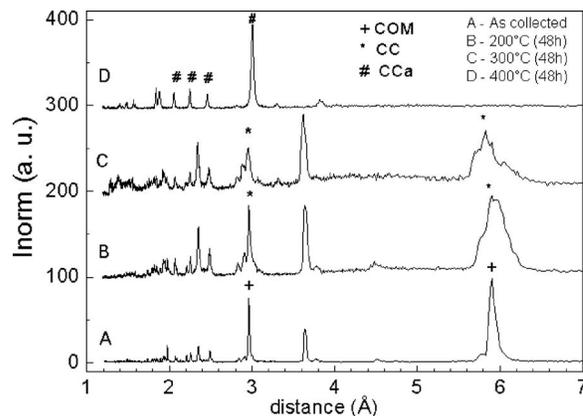


Figure 4. Thermal treatment of Sample #45: (a) as collected, (b) 200 °C, (c) 300 °C, and (d) 400 °C. It was detected as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (COM) with a consequent phase transition to CaC_2O_4 (CO) and CaCO_3 (CCa).

fit for the whole set of powder diffraction data, regardless of the number of phases. Figures 2 and 3 show the Rietveld refinement plots.

B. Phase transition

By means of the heat treatments followed by XRD analysis, presented in Figures 4 and 5, it was possible to verify the temperature dependence of the phase transformation of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (COM) into CaC_2O_4 (calcium oxalate-anhydrous-CO) and CaCO_3 (calcium carbonate-CCa) or, in other words, to establish a partial phase diagram of this transformation. It was investigated at which temperature the bonded H_2O molecules were removed from $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (COM) with the subsequent phase transition to CaC_2O_4 (CO) and CaCO_3 (CCa).

In Figures 4 and 5, the phase evolutions of the renal calculi #45 and #25, respectively, as a function of the annealing temperature treatment is shown. The intensity of the peak at 3.67 Å in Figure 4 shows how the amount of anhydrous calcium oxalate CaC_2O_4 (CO) increased steadily from 25 °C (as collected) up to 200 °C. The broadening of the peak at ≈ 6 Å can also be observed, which can be associated to the crystallite size reduction of the $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ phase, caused

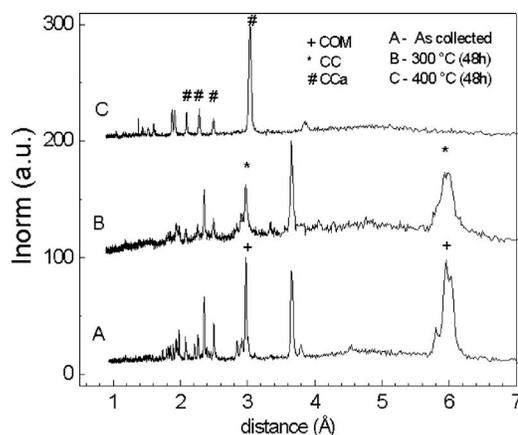


Figure 5. Thermal treatment of Sample #25: (a) as collected, (b) 300 °C, and (c) 400 °C. It was detected as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (COM) with a consequent phase transition to CaC_2O_4 (CO) and CaCO_3 (CCa).

by the removal of the bonded H₂O, with subsequent transformation into CaC₂O₄. The XRD features of the latter treatment (400 °C) reveal that CaC₂O₄ (CO) was transformed to CaCO₃ (CCa).

The crystalline-to-amorphous phase transition has not been observed to occur, as can be seen following the peak ≈3.7 Å. The test of repeatability shown in Figure 5, carried out on calculus #45, also illustrates the same behavior. These results show that the bonded H₂O molecule leaves the CaC₂O₄·H₂O below 200 °C. This behavior is in good agreement with Kaloustian *et al.* (2002, 2003) studies using thermogravimetric analysis, which indicate that the bonded H₂O molecule, in calcium oxalate urinary calculi, was removed at about 180 °C. Moreover, observing the thermal evolution of the ≈2.96 Å peak (COM), the calcium oxalate (CO) was completely transformed into calcium carbonate (CCa) after the heat treatment at 400 °C for 48 h, which is confirmed by the non-existence of the CaC₂O₄ (CO) peak at 3.67 Å after the heat treatment at 400 °C. These results are also in good agreement with thermogravimetric analysis results reported by Kaloustian *et al.* (2002, 2003), which shows the phase transition CaC₂O₄→CaCO₃+CO after annealing CaC₂O₄·H₂O at temperatures of 450 to 550 °C. These findings also show that X-ray powder diffraction can be used as a suitable technique to study the composition and phase equilibrium of renal calculi.

IV. CONCLUSION

X-ray powder diffraction was used as a suitable technique to study the phase composition of renal calculi expelled naturally or obtained by surgical procedure. The stones were collected from 56 donors in Vitória, Espírito Santo state, southeastern Brazil. The XRD phase quantification revealed that 61% of the renal stones were composed exclusively by calcium oxalate, being 34% formed only by calcium oxalate monohydrate (COM), whereas the remaining 27% presents both monohydrate and dihydrate calcium oxalate. The 39% non-exclusive calcium oxalate calculi presented other phases like uric acid and calcium phosphate. Two calcium oxalate renal calculi samples were analyzed by Rietveld refinement with the results confirming that these samples presented CaC₂O₄·H₂O as the main phase. However, for one of the samples (#30), the refinement has shown the presence of 15 vol % hydroxyapatite. Considering this result and the Grases *et al.* (1998) model, Sample #30 has grown upon a hydroxyapatite core. In addition, Sample #30 may be classified as non-papillary type II-a calculus.

In order to show the versatility of the XRD technique, we have also studied the phase transformations from monohydrate calcium oxalate (CaC₂O₄·H₂O) to anhydrous calcium oxalate (CaC₂O₄) and to calcium carbonate (CaCO₃), when COM calculi were heat treated for 48 h at 200, 300, and 400 °C in a N₂ gas atmosphere. Using only XRPD we have confirmed that there exists a phase transition CaC₂O₄→CaCO₃+CO after an annealing at 400 °C for 48 h. The results, obtained by X-ray powder diffraction technique, are in good agreement with those from a TGA reported in the literature, and indicate that X-ray powder diffraction can be used as a suitable technique to study the composition and phase diagram of renal calculi.

ACKNOWLEDGMENTS

The authors thank the Brazilian national scientific agencies CNPq (Projects CNPq 504578/2004-9 and CNPq 471536/2004-0) and CAPES for financial support. We also thank *Companhia Vale do Rio Doce* (CVRD) and *Companhia Siderúrgica de Tubarão* (CST), and gratefully acknowledge the LNLS (Project XPD-4742).

- Ansari, M. S., Gupta, N. P., Hemal, A. K., Dogra, P. N., Seth, A., Aron, M., and Singh, T. P. (2005). "Spectrum of stone composition: Structural analysis of 1050 upper urinary tract calculi from northern India," *Int. J. Urol.* **12**, 12–16.
- Asokan, D., Kalaiselvi, P., Farooq, S. M., and Varalakshmi, P. (2004). "Calcium oxalate monohydrate binding protein: A diagnostic biomarker for calcium oxalate kidney stone formers," *Urol. Res.* **32**, 357–361.
- Azevedo, N. (2002). "Estudos sobre pedras de rins através da técnica de Difração de Raios X de pó," Ph.D thesis, Departamento de Química, Universidade Federal do Espírito Santo, Vitória, Brazil (in Portuguese).
- Bellanato, J., Delatte, L. C., Hidalgo, A., and Santos, M. (1973). "Application of infrared spectroscopy to the study of renal stones," in *Urinary Calculi: Recent Advances in Aetiology, Stone Structure and Treatment: Proceedings of the International Symposium on Renal Stone Research*, edited by L. C. Delatte, A. Rapado, and A. Hodgkinson (S. Karger AG, Basel, Switzerland), pp. 237–246.
- Coe, F. L., Parks, J. H., and Asplin, J. R. (1992). "The pathogenesis and treatment of kidney stones," *N. Engl. J. Med.* **327**, 1141–1152.
- Elliot, J. S. (1973). "Structure and composition of urinary calculi," *J. Urol. (Baltimore)* **109**, 82–83.
- Ferreira, F. F., Granado, E., Carvalho, Jr., W., Kycia, S. W., Bruno, D., and Droppa Jr, R. (2006). "X-ray powder diffraction beamline at D10B of LNLS: Application to the Ba₂FeReO₆ double perovskite," *J. Synchrotron Radiat.* **13**, 46–53.
- FIZ and NIST (2006). "Inorganic Crystal Structure Database (ICSD)," version 2006–02. Fachinformationszentrum Karlsruhe (FIZ), Karlsruhe, Germany and the National Institute of Standards and Technology (NIST), Gaithersburg, Maryland.
- Gibson, R. I. (1974). "Descriptive human pathological mineralogy," *Am. Mineral.* **59**, 1177–1182.
- Giles, C., Yokaichiya, F., Kycia, S. W., Sampaio, L. C., Ardiles-Saravia, D. C., Franco, M. K. K., and Neuenschwander, R. T. (2003). "High-resolution X-ray diffraction beamline at the LNLS for the study of charge, orbital, and magnetic structures," *J. Synchrotron Radiat.* **10**, 430–434.
- Grases, F., Costa-Bauzá, A., and García-Ferragut, L. (1998). "Biopathological crystallization: A general view about mechanisms of renal stone formation," *Adv. Colloid Interface Sci.* **74**, 169–194.
- Hodgkinson, A. (1971). "A combined qualitative and quantitative procedure for the chemical analysis of urinary calculi," *J. Clin. Pathol.* **24**, 147–151.
- ICDD (2005). "Powder Diffraction File," *International Centre for Diffraction Data*, edited by W. F. McClune, Newtown Square, PA, 19073–3272.
- Kaloustian, J., El-Moselhy, T. F., and Portugal, H. (2003). "Determination of calcium oxalate (mono- and dihydrate) in mixtures with magnesium ammonium phosphate or uric acid: The use of simultaneous thermal analysis in urinary calculi," *Clin. Chim. Acta* **334**, 117–129.
- Kaloustian, J., Pauli, A. M., Pieroni, G., and Portugal, H. (2002). "Use of thermal analysis in determination of some urinary calculi of calcium oxalate," *J. Therm Anal. Calorim.* **70**, 959–973.
- Koide, T., Oka, T., Tanaka, M., and Sooda, T. (1986). "Urinary tract stone disease in modern Japan," *Eur. Urol.* **12**, 403–407.
- Kuplich, L. (2004). "Estudos sobre o CaC₂O₄·H₂O presente em pedras de rins," Ph.D thesis, Departamento de Química, Universidade Federal do Espírito Santo, Vitória, Brazil (in Portuguese).
- Larson, A. C. and Von Dreele, R. B. (2000). *General Structure Analysis System (GSAS)* (Report LAUR 86–748). (Los Alamos National Laboratory, Los Alamos, New Mexico).
- Lonsdale, K., Sutor, D. J., and Wooley, S. (1968). "Composition of urinary calculi by X-ray diffraction. Collected data from various localities. I. Norwich (England) and District," *Br. J. Urol.* **40**, 33–36.
- NIST (2000). Certificate of Analysis, Standard Reference Material 660a, Lanthanum Hexaboride Powder (National Institute of Standards and

- Technology, Gaithersburg, Maryland) (https://srms.nist.gov/view_detail.cfm?srm=660A).
- NIST (2005). Certificate of Analysis, Standard Reference Material 676, Alumina Internal Standard (National Institute of Standards and Technology, Gaithersburg, Maryland) (https://srms.nist.gov/view_cert.cfm?srm=676).
- Singh, S., Singh, V. R., and Dhawan, U. (1999). "X-ray diffractometric and spectroscopic analysis of renal calculi," *J. Mater. Sci. Lett.* **18**, 2001–2003.
- Söhnle, O. and Grases, F. (1995). "Calcium oxalate monohydrate renal calculi. Formation and development mechanism," *Adv. Colloid Interface Sci.* **59**, 1–17.
- Spector, M., Garden, N. M., and Rous, S. N. (1978). "Ultrastructure and pathogenesis of human urinary calculi," *Br. J. Urol.* **50**, 12–15.
- Takasaki, E. (1971). "An observation on the analysis of urinary calculi by infrared spectroscopy," *Calcif. Tissue Res.* **7**, 232–240.
- Toby, B. H. (2001). "EXPGUI, a graphical user interface for GSAS," *J. Appl. Crystallogr.* **34**, 210–213.
- Westbury, E. J., and Omenogor, P. (1970). "A quantitative approach to the analysis of renal calculi," *J. Med. Lab Technol.* **27**, 462–474.