

CYSTINE-APATITE RENAL CALCULI: EPMA, RAMAN & ESEM-CL STUDY. A. Iordanidis¹, J. Garcia-Guinea², V. Correcher³, ¹Department of Geotechnology and Environmental Engineering, Technological Educational Institute (TEI) of Western Macedonia, Kila, 50100 Kozani, Greece, aiordanidis@yahoo.co.uk, ²Museo Nacional Ciencias Naturales, CSIC, Abascal 2, 28006 Madrid. Spain. ³CIEMAT. Av. Complutense 22, Madrid 28040, Spain.

Cystine stones are produced by an inherited disorder of the transport of amino acid cystine that results in excess of cystine in the urine (cystinuria). Cystinuria is characterized by the elimination in the urine of increased amounts of L-cystine which can provoke clinical manifestations. Cystine is a rare renal stone (less than 2% of the patients forming urinary stones), an organosulphur amino-acid compound with a chemical formula $(\text{SCH}_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H})_2$. During the last few years, systematic examinations have been undertaken in certain districts of northern Greece in order to detect the incidence of cystinuria among local population. These studies have been focused on diagnosis and treatment of cystinuric patients with stone formation. This study focuses on special hydroxyapatite-collagen-cystine calculi formed in the kidneys of humans living in such areas of the northern Greece. A comprehensive analytical study took place, employing the following analytical techniques: Electron Probe Micro-Analysis (EPMA), Raman microspectroscopy and Environmental Scanning Electron Microscopy (ESEM) coupled to a Cathodoluminescence (CL) tube. A characteristic concentric texture is clearly shown under the Electron Microprobe and the ESEM, with thick cystine layers inter-bedded with thin calcium hydroxyapatite layers.

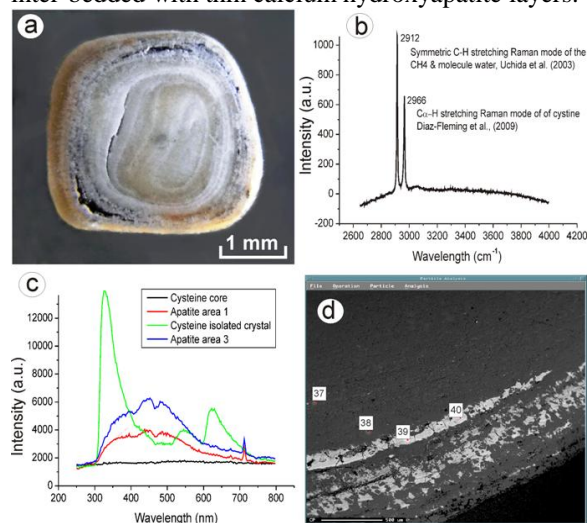


Figure 1. a) Macroscopic view of a cystine-apatite calculus, b) Raman spectrum of cystine crystals, c) CL spectra of cystine and apatite areas, d) ESEM image of cystine core and apatite layers (see Table 1 for chemical spot analyses).

The ESEM pictures exhibit larger concentration of hydroxyapatite and collagen in the external ring and

only cystine in the internal core with minor composed mixtures. The elevated concentrations of sulphur are clearly shown under electron microprobe, while calcium and phosphorous prevail within the apatite regions. Cathodoluminescence and Raman spectra were obtained from several areas of the stone [1,2]. The observed features might suggest that the human kidneys isolate the undesirable S-S sulphur bonds encapsulating the cystine with an external bond container. In conclusion, the application of powerful analytical techniques could substantially help the physicians to determine precisely the stone composition and recommend an appropriate prophylactic therapy for the patient and thus prevent or delay the cystine stone recurrence.

Table 1. EPMA spot analyses on the cystine calculus

Element	37	38	39	40
SiO ₂	0.025	0.024	-	0.027
Al ₂ O ₃	0.016	0.008	0.074	0.057
MnO	0.046	-	0.046	0.013
MgO	0.032	0.008	2.749	2.272
CaO	0.159	0.042	44.661	45.696
Na ₂ O	0.012	0.051	1.154	1.102
K ₂ O	0.008	0.015	0.068	0.048
TiO ₂	0.006	0.003	-	0.010
Cr ₂ O ₃	0.035	0.004	0.029	0.050
P ₂ O ₅	0.180	0.067	39.495	39.413
SO ₃	98.757	99.327	0.415	0.357
CuO	0.013	0.016	-	-
SrO	0.019	0.054	0.121	0.129
F	-	-	0.822	0.811
Cl	0.022	0.059	0.145	0.095
Total	99.330	99.678	89.779	90.080

References:

- [1] Diaz Fleming G. et al. (2009) *J. Raman Spectrosc.* 40, 632–638.
- [2] Uchida T. et al. (2003) *Can. Jour. Phys.*, 81 (1-2), 359-366.