



UNIVERSITY OF PATRAS

Department
Of Chemical
Engineering



Applied Physical Chemistry and Materials Technology

Presented by P.G.Koutsoukos

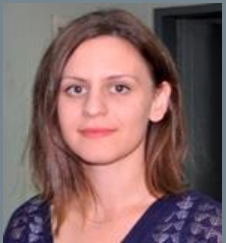
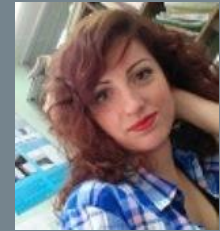


Professor George N. Angelopoulos
High temperature Processes of Materials
Technology of Materials



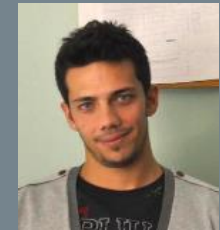
Dr. A. Christogerou

Rallou Chatzimichail



MSc. D. Koumpouri

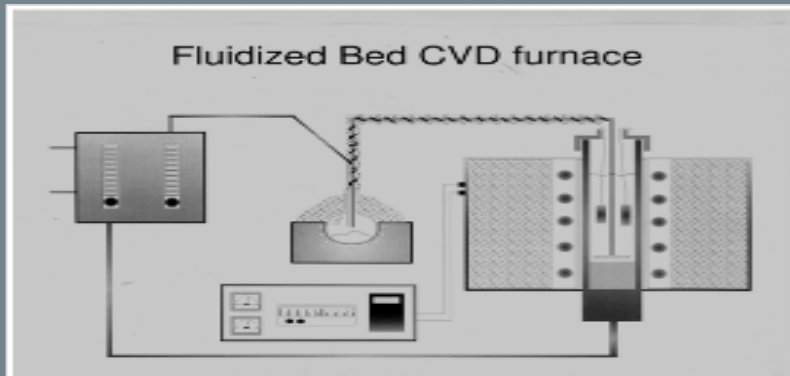
Konstantinos Pittas



Surface Modification processes (CVD, FBCVB)

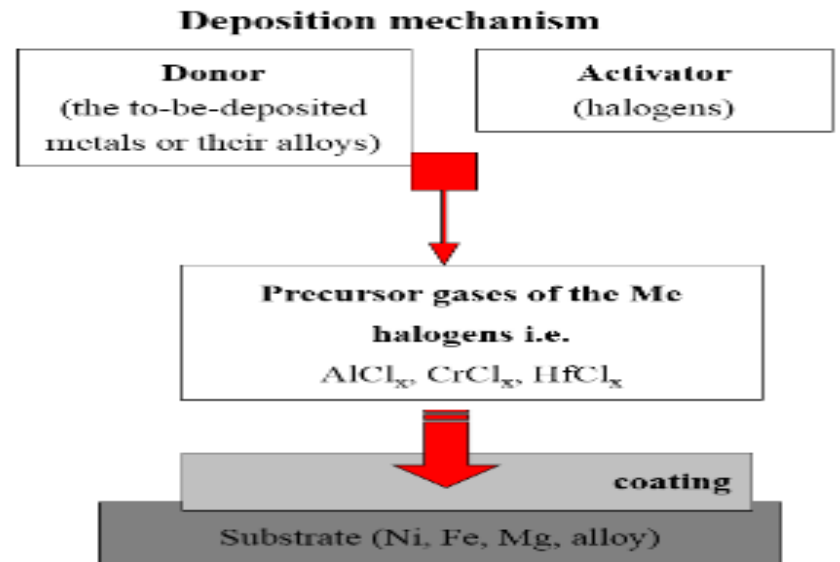
formation of cementing and diffusion coatings in order to improve wear, oxidation and corrosion resistance of metals

The process



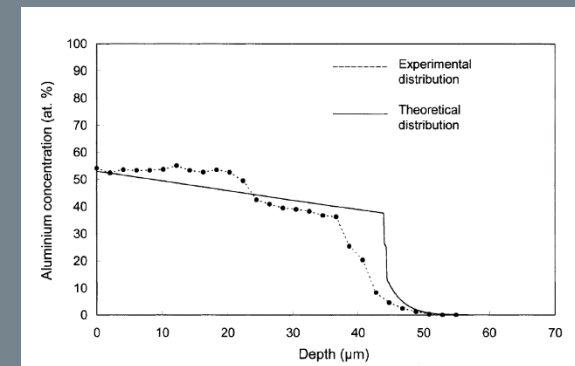
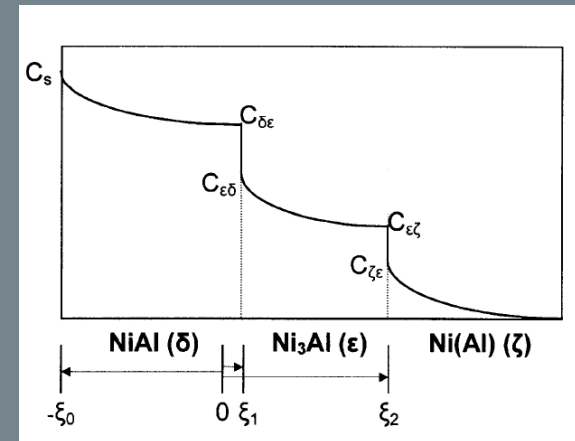
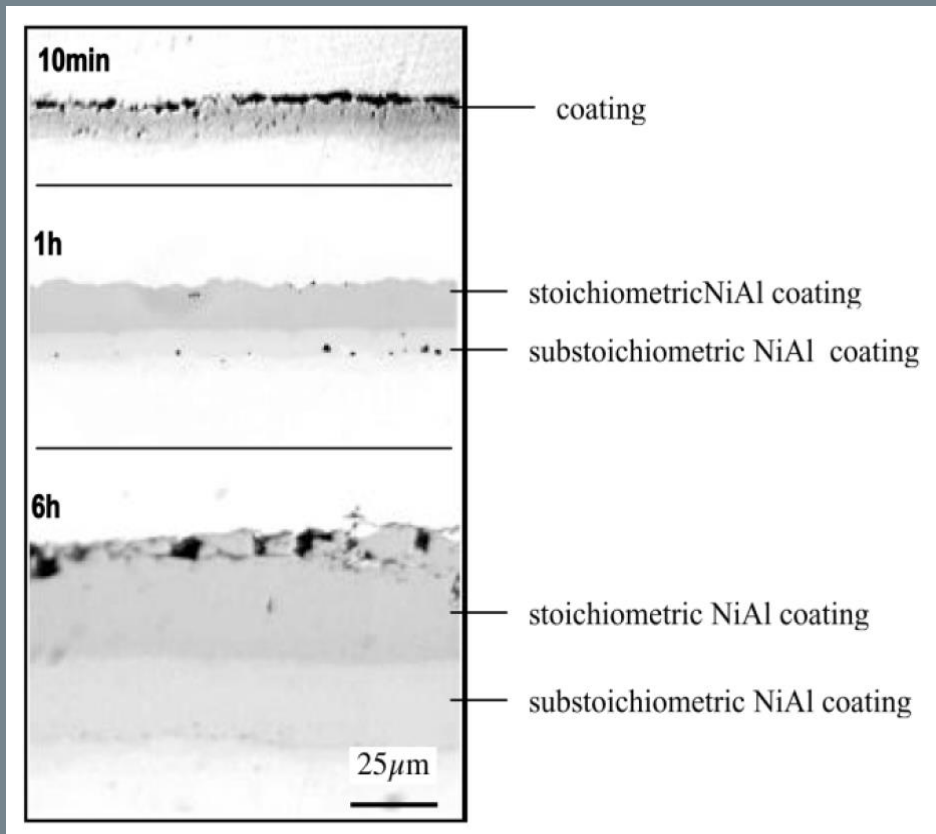
- **Carburisation**
- **Nitridation**
- **Nitrocarburisation**
- **Carbonitridation**
- **Protective corrosion and wear resistant surface coatings Al, TiC, Al-Cr, Al-Cr-RE on steel alloys, Fe, Ni, Mg and Mg alloys**

The principle



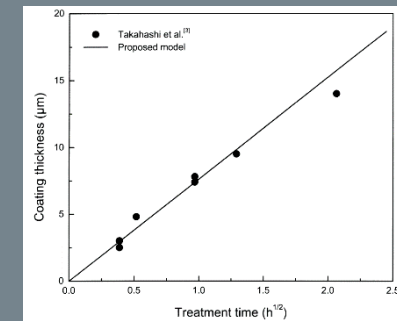
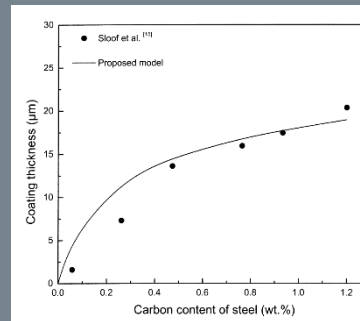
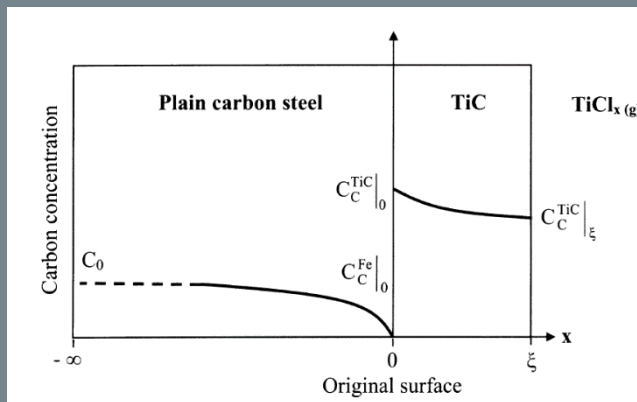
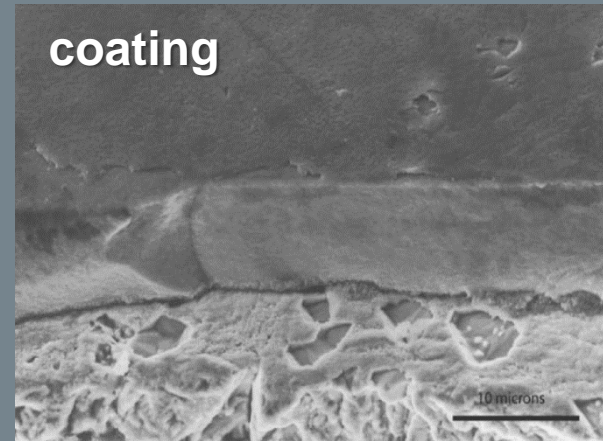
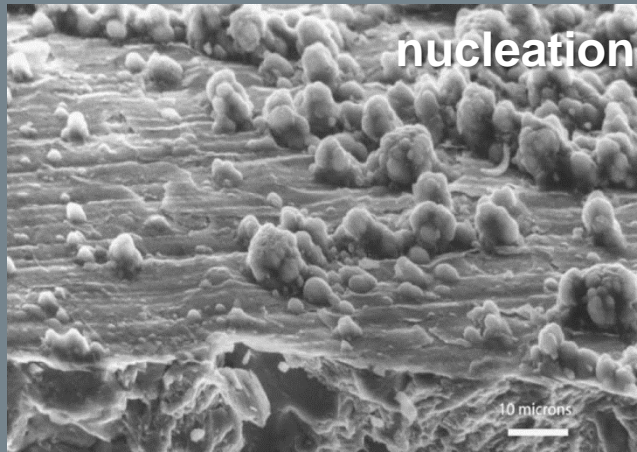
Surface Modification processes (CVD, FBCVB)

formation and modelling of diffusion coatings
Al- coating on steel



Surface Modification processes (CVD, FBCVB)

formation and modelling of cementing coatings
TiC coating on steels



FBCVD process has been discussed in a review, invited paper in *Materials Science and Engineering R: Reports*, a journal with high impact factor (13.9)

Selected publications

- [Vahlas, C., Caussat, B., Serp, P., Angelopoulos, G.N.: “Principles and applications of CVD powder technology”, *Materials Science and Engineering R: Reports* 53 \(1-2\), \(2006\), pp. 1-72.](#)
- [Christoglou, Ch., Voudouris, N., Angelopoulos, G.N., Pant, M., Dahl, W. “Deposition of aluminium on magnesium by a CVD process” *Surface and Coatings Technology* 184 \(2-3\), \(2004\), pp. 149-155.](#)



Research Group of Assoc. Prof. Symeon Bebelis



Main Research activities : Fuel cells, Catalysis and electrocatalysis

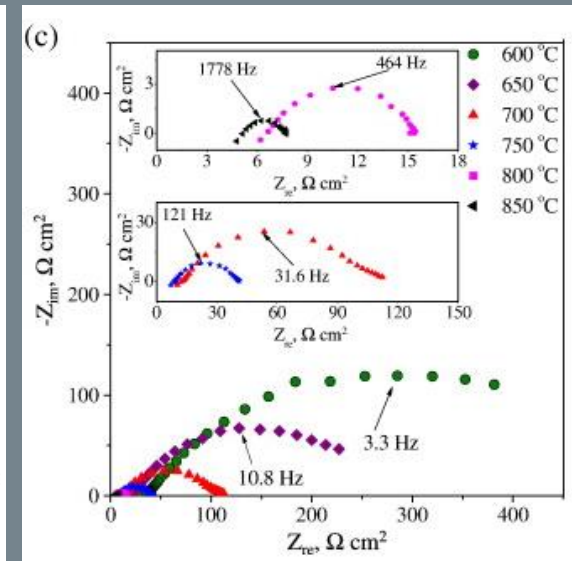
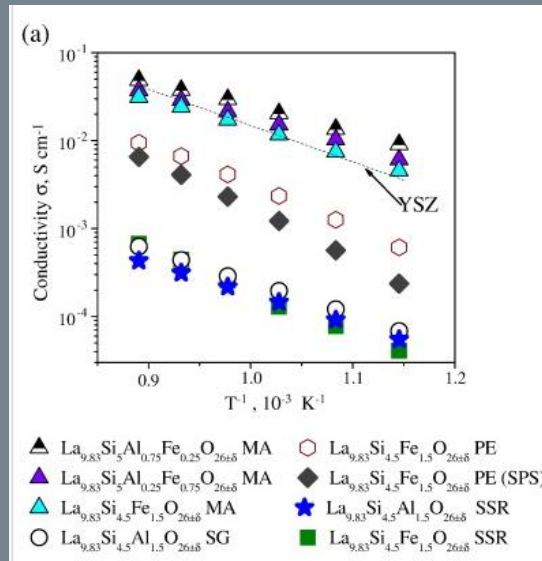
- Synthesis, electrical and electrochemical characterization of materials for solid oxide fuel cell (SOFC) applications

Doped apatite-type lanthanum silicates $La_{9.83}Si_{6-x}Al_xFe_yO_{26\pm\delta}$

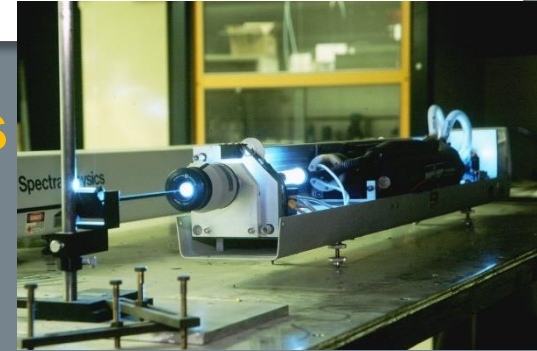
(a) Conductivity dependence on temperature for samples prepared via different methods

(Mechanochemical activation (MA), Solid state reaction (SSR), Sol-gel method (SG), Pechini method (PE))

(c) Nyquist plots for the best performing sample



Reference: "Synthesis and characterization of doped apatite-type lanthanum silicates for SOFC applications", H. Gasparyan et al, Solid State Ionics 192 (2011)158

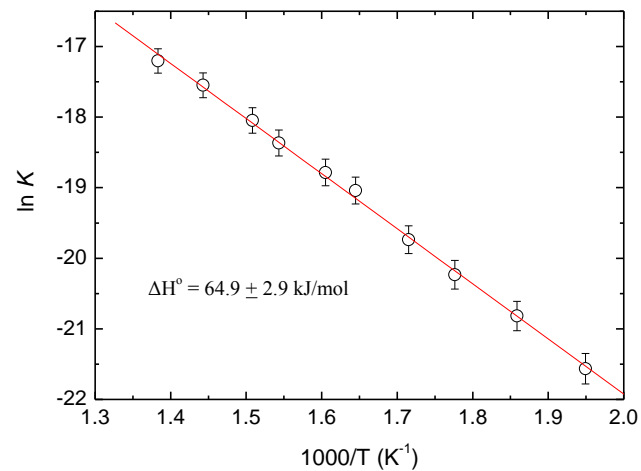
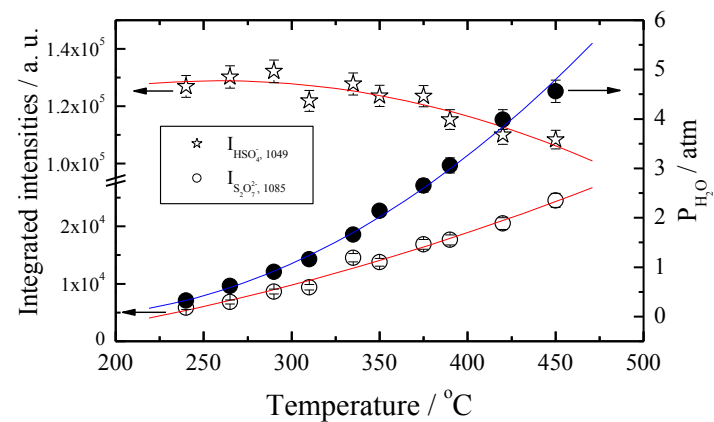
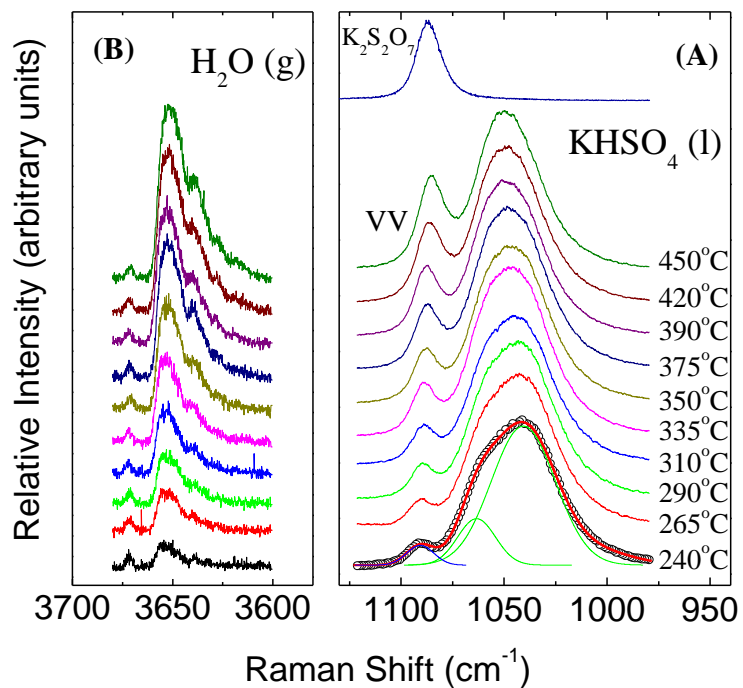


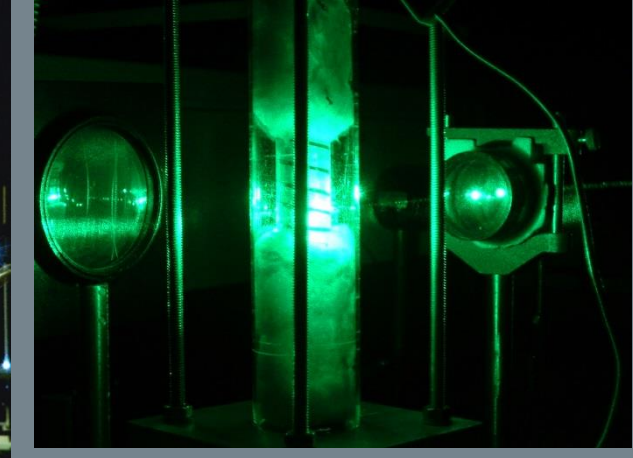
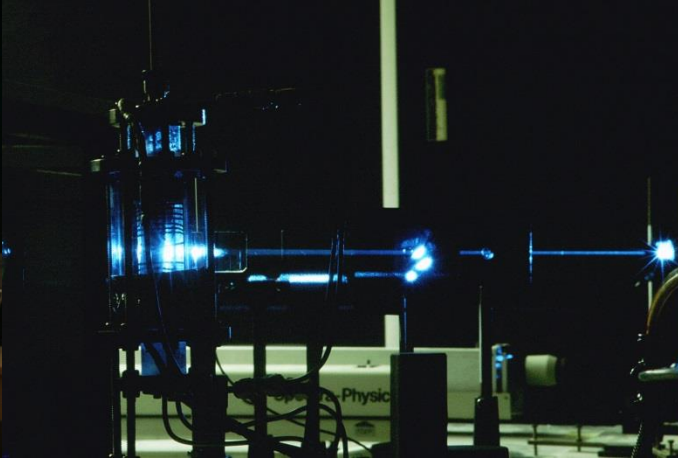
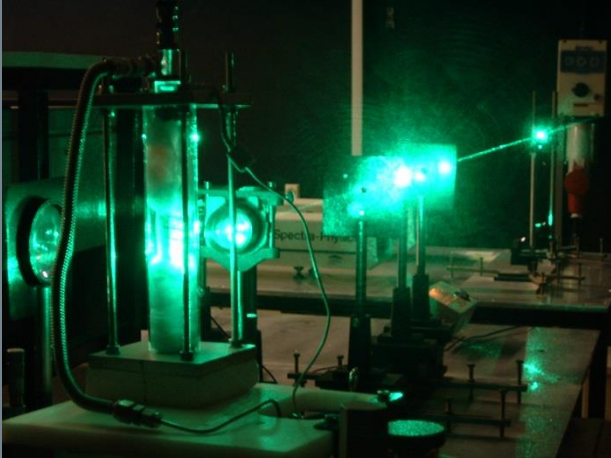
Raman Spectroscopy and Thermodynamics

THERMODYNAMIC ANALYSIS OF REACTION EQUILIBRIA IN MOLTEN SALTS AND IONIC LIQUIDS BY RAMAN SPECTROSCOPY

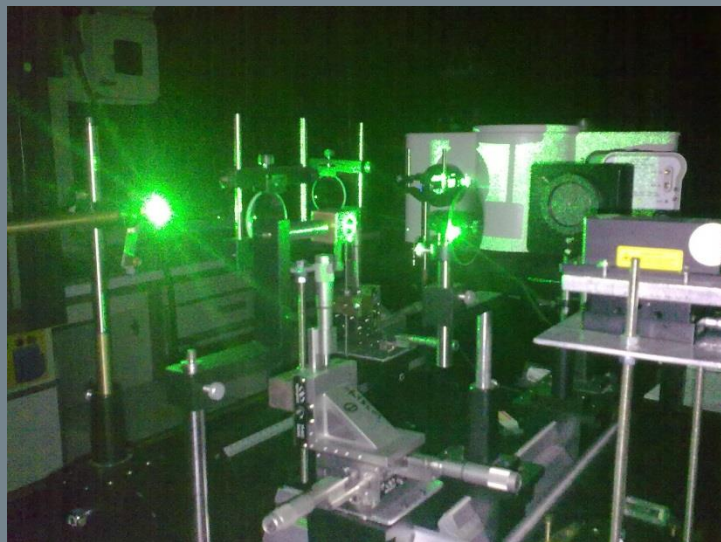
- Correlations of Raman spectral intensity data with the **stoichiometry**, the **equilibrium constant** and the **thermodynamics** of reactions in solution and in gaseous phase
- Gaseous reaction equilibria: correlation of Raman band intensities with stoichiometric coefficients (n), partial pressures, (p_i) equilibrium constants (K_p) and thermodynamics (ΔH , ΔS). Calculation of n , p_i , K_p , ΔH , ΔS
- Procedure for determining the stoichiometry of solutes in molten salt solvents
- Formalism for correlating relative Raman band intensities with stoichiometric coefficients, the equilibrium constant and the enthalpy of reaction equilibria in solution involving also a gaseous component, i . Determination of p_i and ΔH

The case of the dissociation (molten salt/gas) equilibrium:
 $2\text{HSO}_4^-(\text{l}) \leftrightarrow \text{S}_2\text{O}_7^{2-}(\text{l}) + \text{H}_2\text{O}(\text{g})$

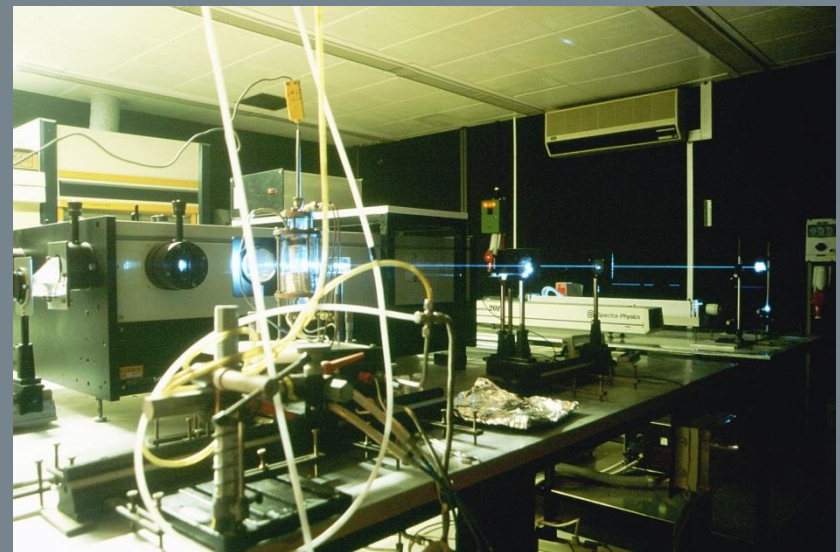




Sectional view of «open geometry» Raman set ups with multi-wavelength visible laser excitation

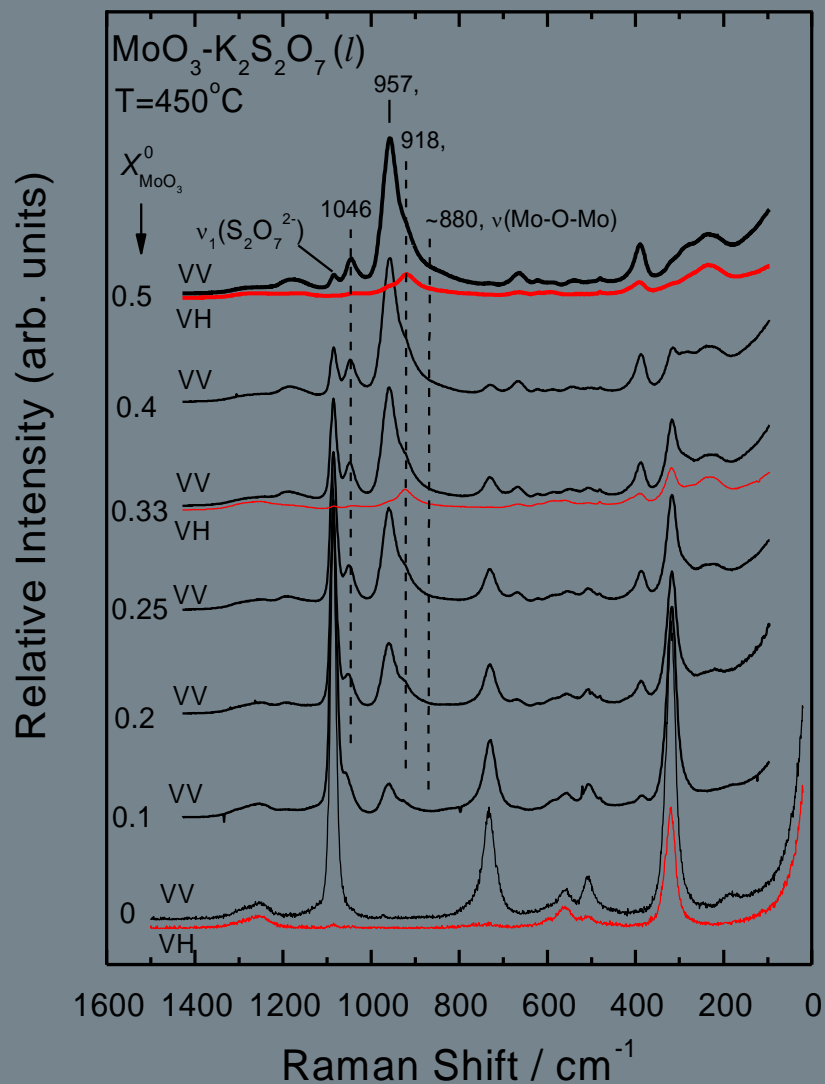


Single spectrometer, multichannel CCD detection

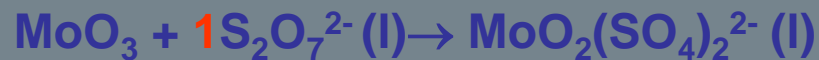
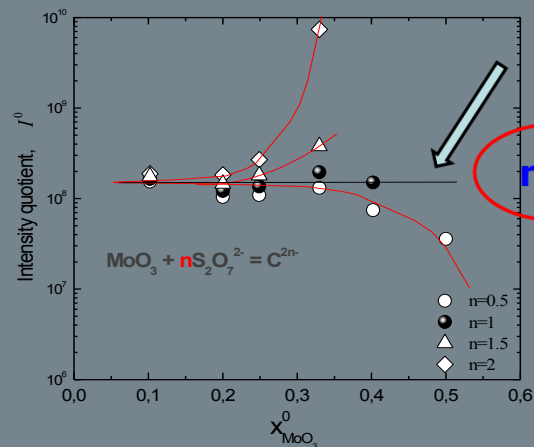


High resolution, double spectrometer, PMT detection

DISSOLUTION OF TRANSITION METAL OXIDES IN MOLTEN SALTS. STOICHIOMETRY, VIBRATIONAL PROPERTIES OF COORDINATION COMPL AND STRUCTURAL IMPLICATIONS.



- reactions/stoichiometry
- MO_x configuration
- structure



Handling of air-sensitive / hygroscopic materials



- Two inert atmosphere dry glove boxes
- All-glass vacuum lines

Publications of the reported research activity in peer reviewed journals: 9
Conference presentations of the reported research activity: 10

Selected representative publications of the reported research activity:

Thermal dissociation of molten KHSO_4 : Temperature dependence of Raman spectra and thermodynamics.

C. Knudsen, A. G. Kalampounias, R. Fehrmann and S. Boghosian

J. Phys. Chem. B, 2008, 112, 11996.

Thermodynamic analysis of reaction equilibria in ionic and molecular liquid systems by high-temperature Raman spectroscopy

A. G. Kalampounias and S. Boghosian

Applied Spectroscopy, 2009, 63, 1050.

Stoichiometry, vibrational modes and structure of niobium(V) oxosulfato complexes in the molten $\text{Nb}_2\text{O}_5 - \text{K}_2\text{S}_2\text{O}_7 - \text{K}_2\text{SO}_4$ system studied by Raman spectroscopy

A. L. Paulsen, F. Borup, R. W. Berg and S. Boghosian

J. Phys. Chem. A, 2010, 114, 7485.

Raman spectroscopic study of tungsten(VI) oxosulfato complexes in $\text{WO}_3 - \text{K}_2\text{S}_2\text{O}_7 - \text{K}_2\text{SO}_4$ molten mixtures: stoichiometry, vibrational properties and molecular structure

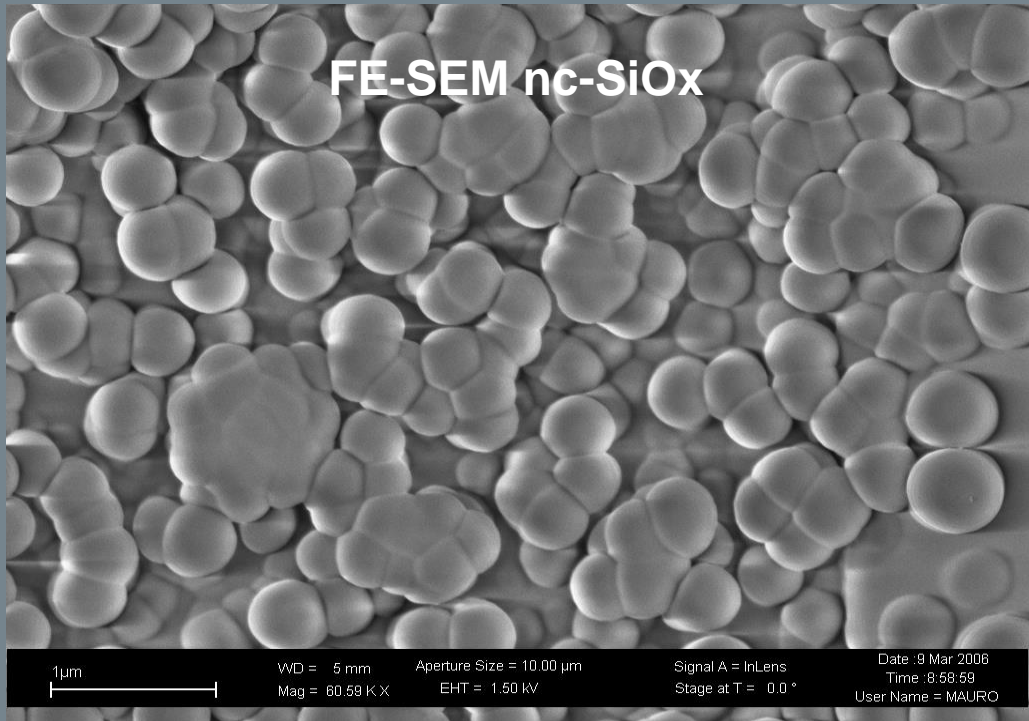
A. L. Paulsen, A. G. Kalampounias, R. W. Berg and S. Boghosian

J. Phys. Chem. A, 2011, 115, 4214.

Molybdenum (VI) oxosulfato complexes in $\text{MoO}_3 - \text{K}_2\text{S}_2\text{O}_7 - \text{K}_2\text{SO}_4$ molten mixtures: stoichiometry, vibrational properties and molecular structures

A. G. Kalampounias, G. Tsilomelekis, R. W. Berg and S. Boghosian

J. Phys. Chem. A, 2012, 116, 8861-8872 doi: 10.1021/jp306701k



High Power MO-PECVD of SiO_x coating

Plasma Technology Laboratory

Metal-Organic PECVD of inorganic oxides

PLASMA TECHNOLOGY GROUP

- Prof. D. Mataras: Plasma Enhanced Chemical Vapor Deposition of inorganic oxides
- Assist. Prof. E. Amanatides: Inorganic nanostructured materials, materials characterization



- 1 Professor, 1 Assistant Professor, 1 Lecturer, 2 PhD Student, 5 diploma thesis students



D. Mataras, Prof.



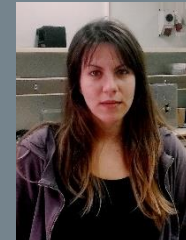
E. Amanatides
Assist. Prof



N. Spiliopoulos
Lect.(Physics Dept.)



E. Farsari, PhD
YSZ, hydrophobic
coatings



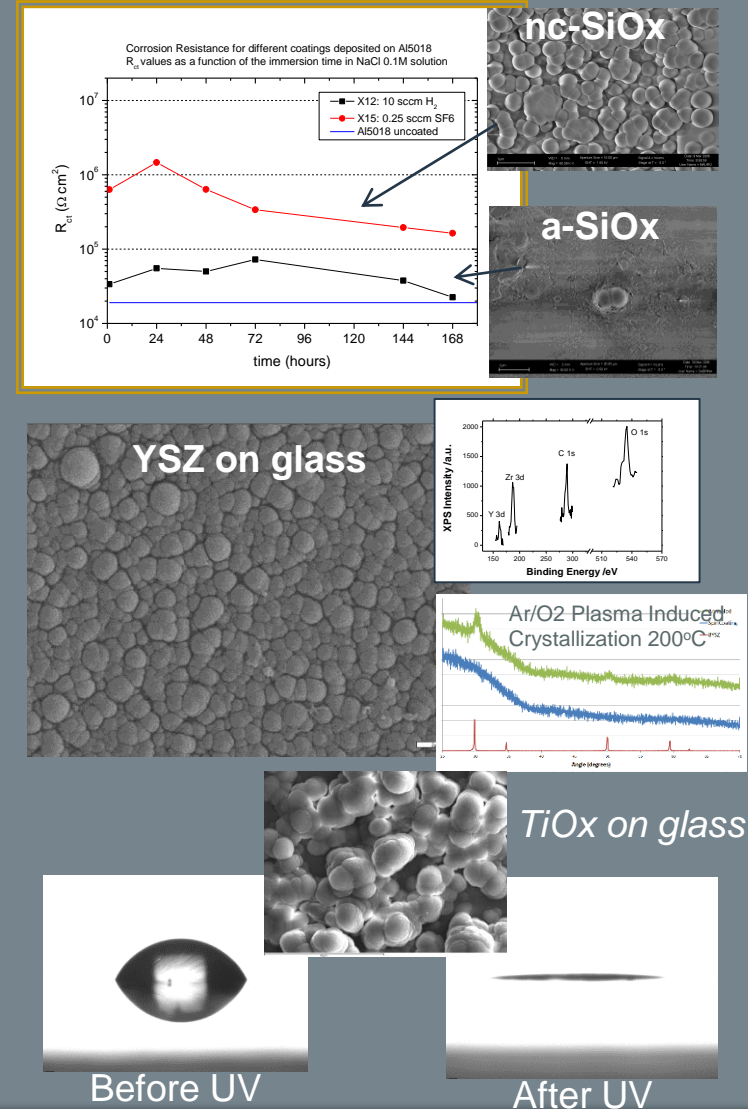
V. Vrakatselli, PhD
TiO_x, Superhydrophilic
coatings



General description of the Research Area

- Development of Metal-Organic Plasma Enhanced Chemical Vapor Deposition (MOPECVD) processes for inorganic oxides coatings (SiO_x, TiO_x, YSZ, DLC).

- MO-PECVD of SiOx coatings for corrosion protection of light metals (Magnesium, Aluminium)
- Sol-Gel and MO-PECVD of YSZ coatings for Solid Oxide Fuel Cells. Low temperature Plasma Induced Crystallization
- Superhydrophilic sol gel and plasma deposited TiOx coatings. UV and visible light activation and application in microfluidic devices

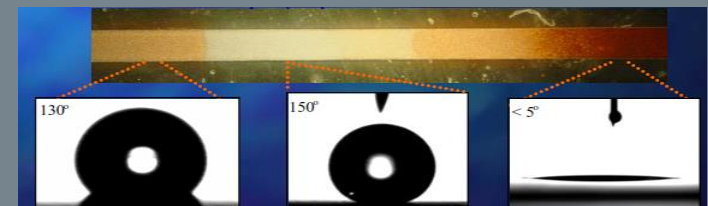
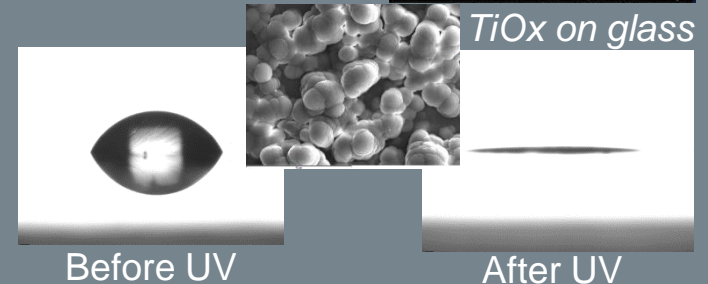
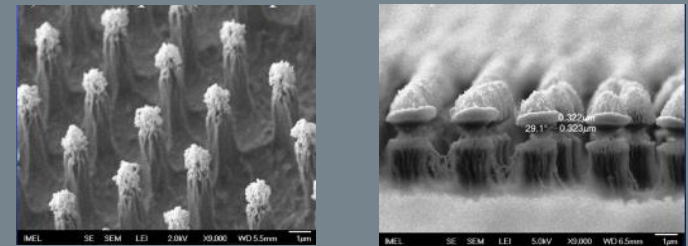


Research Activity A Description

Design and fabrication of super hydrophobic/hydrophilic surfaces and their application in “smart” microfluidic valves

- Step 1: Theoretical design of superhydrophobic surface morphologies (shape)
- Step 2: Fabrication of mechanically and thermodynamically stable superhydrophobic materials
- Step 3: Fabrication of stable superhydrophilic materials
- Step 4: Implementation of stable super hydrophilic – hydrophobic surfaces into smart microfluidic devices

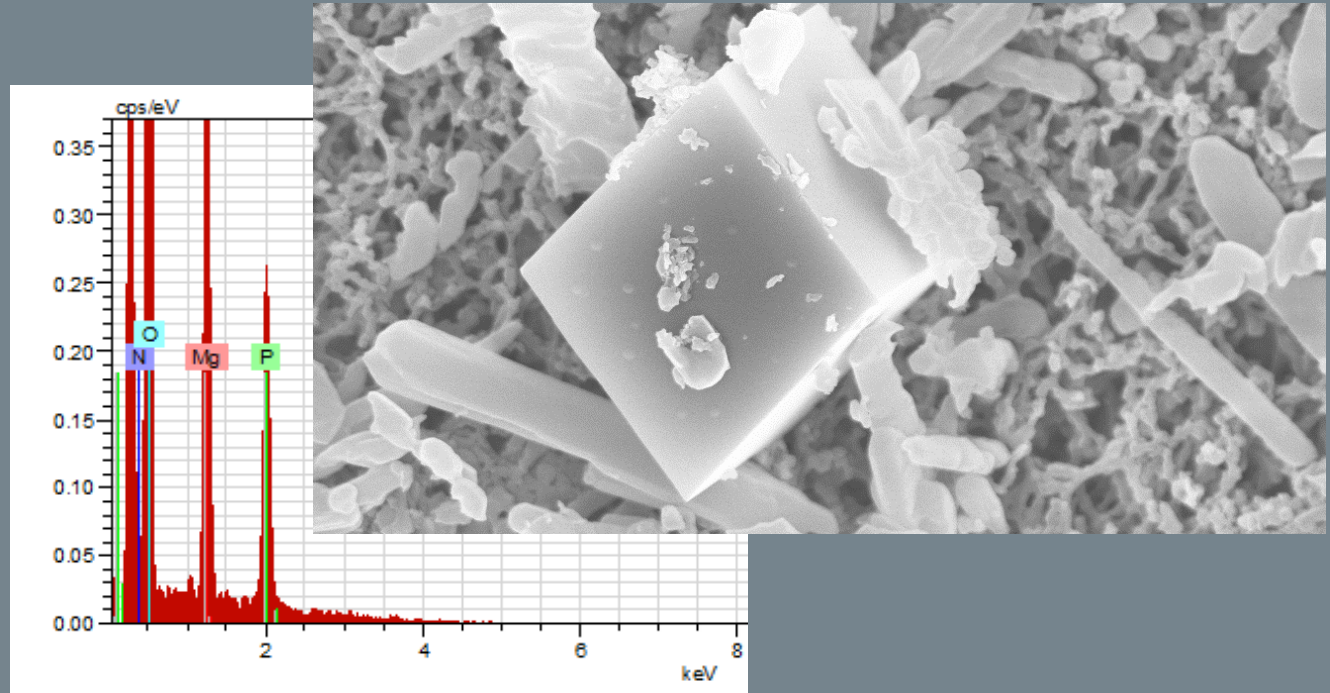
Superhydrophobic surfaces



THALIS “DESIREDROP” 2012-2015, UPAT, NTUA, Demokritos
Application: Microfluidic devices

- THALIS, DesireDrop: " Design and fabrication of Robust super hydrophobic/hydrophilic surfaces and their application in the realization of "smart" microfluidic valves ", 2012-2015, 280k€
- PEP Western Greece "Production of Smart Building Materials", 2008-2010 145k€
- PENED – "Development of nano-structured electrodes and electrolytes for prototype solid state fuel cells" – 2006-2010 41k€
- EU FP6 ""Development Of Innovative Nanocomposites Coating for Magnesium Castings Protection (Nanomag)", 320k€

1. "Comparative study of plasma deposited fluorocarbon coatings on different substrates", E. Farsari, M. Kostopoulou, E. Amanatides, D. Mataras and D.E. Rapakoulias, *J. Phys. D - Appl. Phys.*, 44 194007 (2011)
2. "Diagnostics and Mechanistic Studies in Plasma Treatment of Polyester Textiles", M. Kostopoulou, E. Amanatides, and D. Mataras, *J. Optoelectronic & Adv. Mater.* 10, 2043 (2008)
3. "Improved Surface Energy Analysis for Plasma Treated PET Films", Daphne Papakonstantinou, Eleftherios Amanatides, Dimitrios Mataras, Vasilis Ioannidis, Panagiotis Nikolopoulos, *Plasma Processes and Polymers*, Volume 4, Issue S1, Pages: S1057-S1062 (2007)
4. "Plasma Treated and a-C:H Coated PET Performance in Inhibiting Bacterial Adhesion", Maria G. Katsikogianni, Christos S. Syndrevelis, Eleftherios K. Amanatides, Dimitrios S. Mataras, Yannis F. Missirlis, *Plasma Processes and Polymers*, Volume 4, Issue S1, Pages: S1046-S1051 (2007)
5. "Plasma 2D modeling and diagnostics of DLC deposition on PET" E. Amanatides, P. Gkotsis, Ch.Syndrevelis and D. Mataras, *Diamond and Related Materials* 15, 904 (2006)
6. "Plasma deposited SiO_x coatings for the corrosion protection of aluminum and magnesium alloys", Ch. Voulgaris, E. Amanatides, D. Mataras and S. Grassini, E. Angelini, F. Rosalbino, *Surf. Coat. Technol.* 200, 6618 (2006)
7. RF Power Effect on TEOS/O₂ PECVD of SiO₂ Thin Films», Ch. Voulgaris, E. Amanatides, D. Mataras, *Surf. Coat. Technol.* 198, 351 (2005)



Research Group on Crystal Growth and Dissolution Processes

Interfacial phenomena: Adsorption from solution, stability of suspensions, electrified interfaces



Prof. P.G.Koutsoukos



Ioannis Mpountas

B.Sc.Chem., PhD candidate



E. Athanassopoulos

B.Sc.Chem., PhD candidate

Dr. St. Rokidi, Dipl. Chem. Eng., MSc. PhD

Senior undergrad Students-Diploma Thesis:

Ap. Voulgaridis

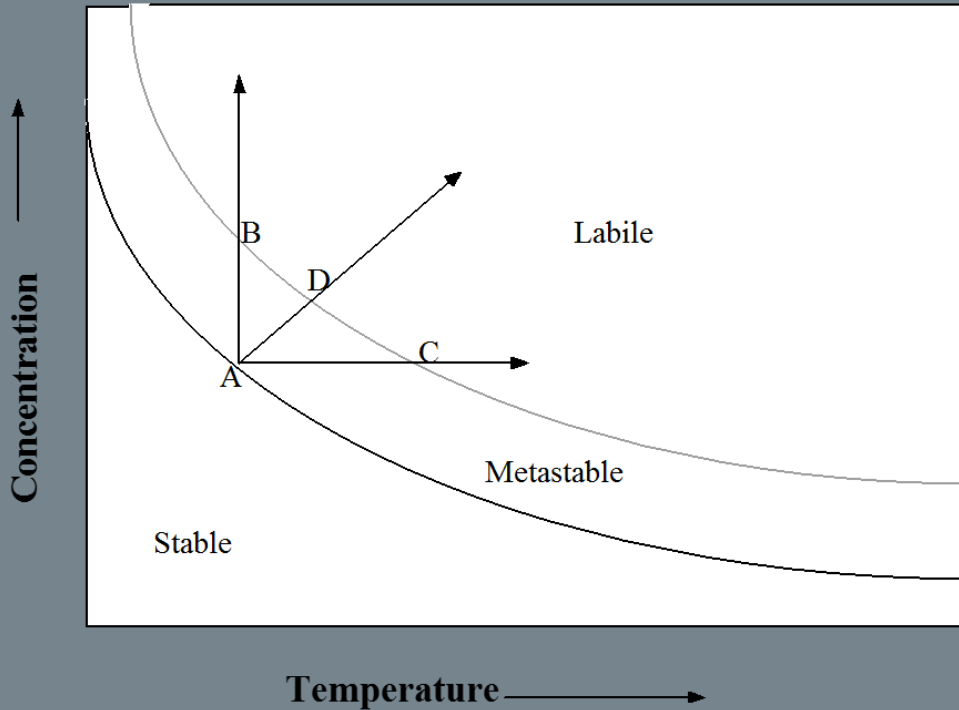
E.Kapetanaki

K.Pagrati

E.Mila



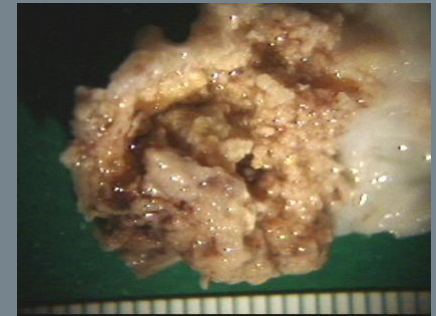
Crystal Growth from Solutions



Crystallization in continuous media takes place when supersaturation (driving force) present. Control of supersaturation critical for mechanistic information



Scale formation

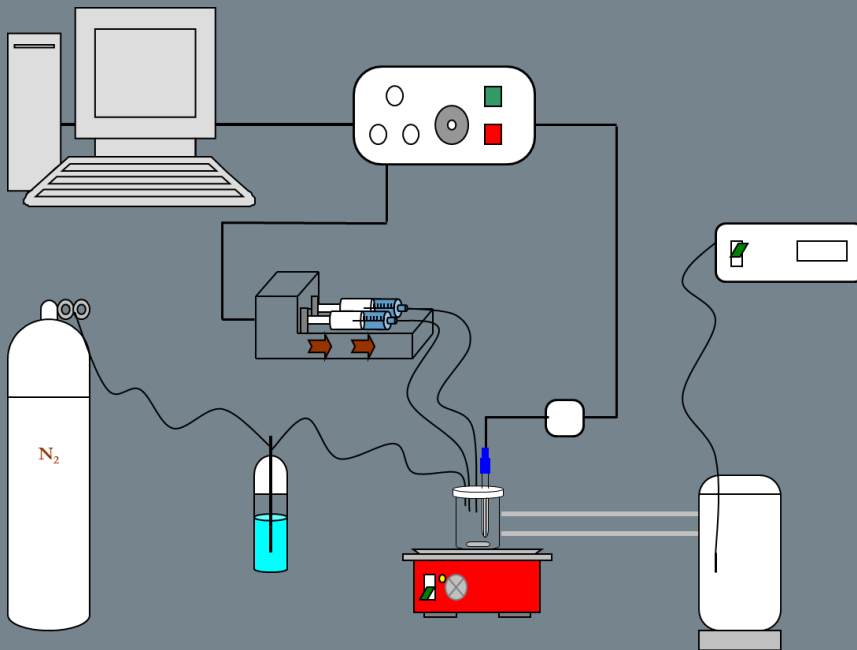


Pathological formation of minerals:
Calcification of heart valves

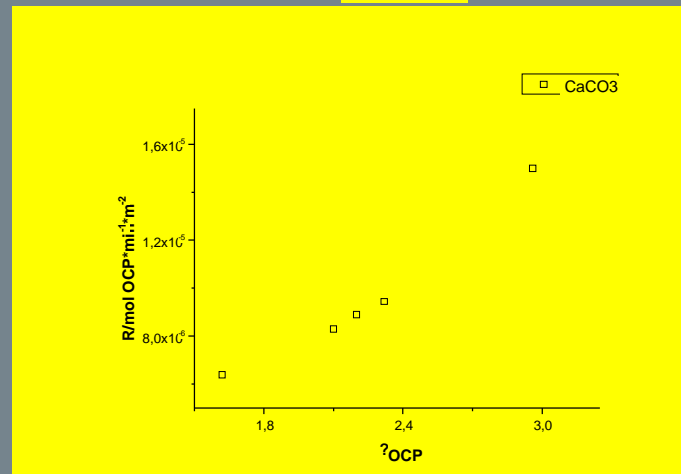
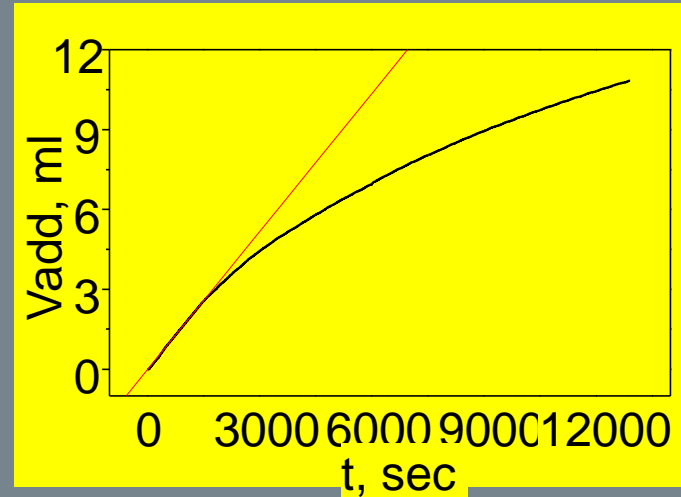


Conservation of monuments based on mechanistic information on crystal growth and dissolution

- Mechanistic investigations at constant supersaturation



High precision and reproducibility in measured rates, complete characterization of the solids crystallizing



- M.G. Lioliou, A. N. Kofina, C.A. Paraskeva, P. G. Klepetsanis, T. Østvold, | A.C. Payatakes, and P. G. Koutsoukos, Controlled Precipitation of Sparingly Soluble Phosphate Salts Using Enzymes. I. Controlled Development of Solution Supersaturation in Situ, *Crystal Growth and Design*, **8** (2008)1390-1398
- H.Ehrlich, K.D.Demadis, O.S.Pokrovsky, P.G.Koutsoukos, Modern Views on Desilicification: Biosilica and Abiotic Silica Dissolution in Natural and Artificial Environments, *Chem. Rev.*, **110** (8), pp 4656–4689, 2010, DOI: 10.1021/cr900334y
- I. D. Kovaios, C.A. Paraskeva , P.G. Koutsoukos, Adsorption of atrazine from aqueous electrolyte solutions on humic acid and silica, *Journal of Colloid and Interface Science* **356**, 277–285,2011.
- S.Rokidi and P.G.Koutsoukos, Crystal growth of calcium phosphates from aqueous solutions in the presence of strontium, *Chem.Eng. Science*, **77**, 157-164 , 2012
- Amjad Z., P.G.Koutsoukos, Mineral Scales and Deposits: An Overview, In *The Science and technology of Industrial Water Treatment*, Z.Amjad (Ed.) IWA Publ. & CRC Press, pp.1-30, 2010.