

Radio-environmental impacts and uranium radiochemistry of phosphogypsum disposed at a coastal area in Cyprus

Ioanna Liatsou and Ioannis Pashalidis

Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia,
e-mail: pspasch@ucy.ac.cy, Telephone Number: 22892785, Fax Number:
22895460

ABSTRACT

Phosphogypsum is the by-product of the phosphate fertilizer industry. Approximately 300 000 tons of phosphogypsum produced by a former phosphate fertilizer industry in Cyprus have been disposed at a coastal area of about 50 000 m². Long-term storage and maintenance of this material presents potential environmental concerns and needs to be characterised in order to assess chemical behaviour and migration of the toxic impurities in the near environment and evaluate the associated environmental impacts. The present study deals with the radio-environmental impacts (e.g. gamma radiation, radionuclide levels and radon emanation) related to the phosphogypsum disposal and the environmental radiochemistry of uranium in the phosphogypsum system. Uranium is one of the key radionuclides found in phosphogypsum and its chemistry is strongly affected by the physicochemical parameters existing and the composition of the hosting matrix.

Radiometric measurements have shown that the phosphogypsum contains increased amounts of uranium (21 – 320 Bq kg⁻¹) and radium (430 – 1050 Bq kg⁻¹) and emanates radon at levels that could be of radiological concern if the phosphogypsum would be used as building material (e.g. gypsum boards). On the other hand, experimental investigations along with thermodynamic calculations have shown that increased salinity affects the solubility of phosphogypsum, resulting in increased uranium levels in the corresponding solutions and different composition of stack fluids and leachates results in significantly different uranium speciation in the corresponding solutions. Furthermore, changes in the redox conditions (e.g. after the application of a vegetative cover) affect the redox speciation of uranium and subsequently the mobility of uranium in the system.

Keywords: phosphogypsum, seawater, environmental impact, vegetative cover, redox conditions, uranium.

1.0 Introduction

Phosphogypsum is a by-product of the phosphate fertilizer industry and is obtained by reacting phosphate rock with sulphuric acid, during the production of phosphoric acid. Worldwide, large amounts of phosphogypsum have been produced up to now and it is estimated that if historic trends continue, production will increase to several hundred million metric tonnes annually. Only a relative small portion of the phosphogypsum produced (14%) is reprocessed, a significant part is dumped into water bodies (28%) and the main part of the material is stockpiled [1].

Although phosphogypsum is composed mainly of calcium sulphate dihydrate (gypsum), it contains elevated levels of impurities, which originate primarily from the source phosphate rock used in the phosphate fertilizer production. The main impurities associated with phosphogypsum are: acidity, fluoride and sulphate anions, toxic trace elements (e.g. heavy metal ions) and natural radionuclides from the U-238 decay series such as uranium, radium and radon [1, 2].

Because of the relatively high amounts of impurities, there is concern that the material may pose a

negative impact on the environment. The main environmental concerns associated with phosphogypsum are: migration of environmentally sensitive chemical species into ground water supplies, radon exhalation, which may affect workers on the phosphogypsum disposal site or people living close to stacks and radon exhalation from soil into residential homes when agricultural land previously treated with phosphogypsum is converted to residential usage [1-3].

In order to understand the environmental impact of phosphogypsum, it is necessary to understand the geochemical processes that control the release of the impurities from the phosphogypsum bulk and their migration into the surrounding soil environments and water bodies. In this context, knowledge of the levels of natural radionuclides and their chemical behaviour in the phosphogypsum system is of fundamental importance. This paper presents and discusses the radiological characteristics of phosphogypsum disposed on a coastal area in Cyprus and the chemical behaviour of uranium in the system.

2.0 Materials and methods

The research reported here covers the phosphogypsum stack at the Vasiliko site, which is a coastal area in front of a former phosphate fertilizer industry in Cyprus (Figure 1). Although small in size, the phosphogypsum disposal site is of particular interest because it is adjacent to the sea, receiving large amounts of seawater. This saline water covers the area in winter and evaporates in summer leaving behind its salt content, which affects the composition and the stability of the phosphogypsum disposed on this area. For phosphogypsum and stack fluid sampling there have been drilled four monitoring/probing wells into the phosphogypsum body and samples were obtained each meter with a maximum well depth of 5 meters.

Radiological characterisation included gamma measurements carried out by high-resolution semiconductor detection systems (HPGe detectors, Canberra), alpha spectroscopy (Alpha Analyst Integrated Alpha Spectrometer, Canberra) and a radon monitoring system (Radon/Thoron monitor RTM1688-2, Sarad). Prior gamma analysis, all samples have been dried, homogenized and covered with epoxy glue to prevent the radon exhalation from the sample containers and the measurements have been performed after at least 30 days after sealing of the samples. Uranium analysis in solid and aqueous samples by alpha spectroscopy [4-6] and radium analysis by radon emanation measurements after sample dissolution [7, 8] has been carried out as described elsewhere. In addition the uranium series nuclides ^{238}U , ^{234}U and ^{230}Th were analysed to obtain information on uranium behaviour in the system. Phosphogypsum samples were extracted in aqua regia and the uranium series nuclides were analysed by alpha spectroscopy after separation of the radionuclides by ion exchange chromatography [4-6].

Solubility and leaching experiments have been performed by conducting powdered phosphogypsum samples (2.5 g) with de-ionized water (100 mL) in PE bottles under ambient conditions and continuous stirring. Compositional analysis of stack fluids and leachates was carried out by standard classical (wet-chemistry) and instrumental methods of analysis (ICP-OES and Ion-Chromatography HPLC, Shimadzu).

The redox potentials in the tailings dump solutions prior to vegetative cover have been determined using a calibrated platinum redox electrode. For the anoxic conditions (after application of the vegetative cover) the redox potential (E_H) was calculated based on the S(+VI)/S(-II) redox couple, because the redox measurements “under anoxic conditions” are strongly affected by the presence of oxygen, which enters the system during borehole drilling and sampling [9]. The S(+VI)/S(-II) redox couple was selected for the redox potential calculations because sulphur is the predominant

redox sensitive species in the system and other possible redox couples such as Fe(III)/Fe(II) are present in trace amounts [1] and difficult to analyze in the phosphogypsum matrix and solutions. Speciation calculations were performed using commercially available chemical speciation software MINTEQA2 (Allison Geoscience Consultants Inc.). Calculations were performed for saturated gypsum solutions and 0.03% CO₂ atmosphere.

3.0 Results and discussion

3.1 *Radioactive impurities and radio-environmental impacts of phosphogypsum*

Phosphate rock contains high levels of naturally-occurring radionuclides and hence phosphogypsum, which is derived from phosphate rock, is enriched in radioactivity relative to host geological and soil materials. The source of radioactivity comes mainly from the two parent nuclides, ²³⁸U and ²³²Th. In the case that phosphate rock originates from sedimentary rock deposits, the contribution of thorium-series to the radioactivity of the material is not significant, because the thorium content of sedimentary phosphate ores is usually low [1-3]. Table 1 summarizes the activities of key radionuclides in phosphogypsum, phosphate rock and fertilizer samples as well as in natural gypsum found in Cyprus.

As expected, the radionuclide content of phosphogypsum is much higher than the radionuclide content in natural gypsum found in Cyprus. In addition, radioactive equilibrium found in the parent material is disrupted during the wet phosphoric acid process because the radionuclides are portioned into two phases according to their solubility under the given process conditions (Figure 2). Uranium distributes primarily into the phosphoric acid, while most of the radium (Ra-226) portion into the phosphogypsum. The relatively high radionuclide content results in increased radiation doses close to the stack. The radiation dose above the stack reaches values up to 400 nSv h⁻¹, which is about six times higher than the average external radiation dose in Cyprus due to natural radiation sources [10] and exceeds the limits recommended by European Union for radiation exposure due to natural radiation sources [11]. Furthermore, radon exhalation rates measured and attributed to the radium content of phosphogypsum are significantly higher (almost two orders of magnitude) than corresponding rates obtained for local natural gypsum and soil samples [12, 13].

3.2 *Uranium radiochemistry*

3.2.1 *Stack fluids Compositions and Leaching Experiments*

Determination of the phosphogypsum solubility/leachability and the prevailing physico-chemical conditions in stack fluids and leachates is of fundamental importance to understand and model chemical behaviour and migration of toxic impurities from the stack to the terrestrial environment [9, 14, 15]. To determine phosphogypsum leachability and prevailing conditions in stack fluids and leachates, leaching experiments have been performed. The data obtained are summarized graphically in Figure 3 and show a remarkable increase in the solubility of phosphogypsum with increasing salinity indicating the significant effect of marine inputs (basically NaCl) on the phosphogypsum solubility/stability. The relative increase of the phosphogypsum solubility is about 20% and can be attributed to the salt/ionic strength effect on the activity coefficients of Ca²⁺ and SO₄²⁻. Increasing salinity results in lower values of the activity coefficients decrease and subsequently in higher molar concentrations of the ions forming the solid phase and increased phosphogypsum solubility. In addition, species calculation for hexavalent uranium, which is based on the solution composition, has indicated that the uranium phosphate complexes (e.g.

$\text{UO}_2(\text{H}_2\text{PO}_4)_n^{(2-n)+}$ predominate in the stack fluids whereas uranium fluoride complexes (e.g. $\text{UO}_2\text{F}_n^{(2-n)+}$) are the predominant species in the leachates. However, when uranium enters seawater, because of the increased pH and the seawater composition, the uranium carbonate complexes (e.g. $\text{UO}_2(\text{CO}_3)_n^{(2n-2)-}$) govern the speciation of uranium in seawater [14].

3.2.2 Redox Studies and Isotopic Measurements

The redox potentials of the open tailings dump vary between +500 mV and +600 mV [9], indicating that sulphate and uranium(VI) are the predominant species in solution for sulphur and uranium, respectively. The increased redox potentials found in the open tailings dump are attributed to the unrestricted oxygen diffusion and oxygen infiltration within the tailings dump and are in agreement with corresponding literature data [17].

On the other hand, after application of a soil/vegetative cover, the redox conditions are determined principally by runoff containing increased amounts of natural organic matter, bacterial activity and restricted oxygen diffusion within the tailings dump. Because of the restricted oxygen diffusion and the continuous supply of natural organic matter, the redox potential decreases dramatically to values of about -100 mV [9] resulting in more or less suboxic conditions below the vegetative cover. At such low redox potentials (from -75 mV to -150 mV) bacterial reduction of sulphate to sulphide begins [17, 18]. Natural organic matter acts as an energy source for the bacterially assisted sulphate reaction and the consumption of protons during sulphate reduction results in weak acidic to near neutral pH values in the corresponding systems. In the studied system the pH increase is about 1 pH unit, indicating that sulphate reduction was proceeding.

Reduction of sulphate to sulphide may dramatically affect the stability and leachability of phosphogypsum because of the different solubility between the CaSO_4 and CaS solid phases and partial deterioration of the gypsum matrix, which results in increased weathering and release of its contaminants. Sulphide may form very insoluble compounds with toxic metal ions found in phosphogypsum (e.g. CdS , PbS), which are expected to reduce the mobility of the respective metal ions in phosphogypsum matrix. Moreover, suboxic conditions will favour the reduction of U(VI) to U(IV) resulting in the formation of $\text{U}(\text{OH})_4$. $\text{U}(\text{OH})_4$, which is expected to be the predominant uranium species under the given conditions, is characterized by its very low solubility and mobility [9].

In order to study the mobility of uranium under oxic and suboxic conditions the concentration of uranium has been determined in similar phosphogypsum samples obtained prior and after the application of the vegetative cover. In contrast to the oxic samples (PGypsum), which were characterized by a white colour, the phosphogypsum samples after application of the vegetative cover were dark brown indicating the presence of natural organic matter (NOM). The relative content of natural organic matter in the NOM contaminated samples was about 3%. For comparison, the uranium concentration was also determined in the phosphate rock (PRock) used as raw material in the fertilizer production. According to the analytical data, the uranium concentration in the PR (73 mg kg^{-1}) is much higher than in the PGypsum samples because during the phosphoric acid production process the uranium remains basically in the liquid phase (phosphoric acid). However, there is significant difference in the uranium concentration between the two different PGypsum samples. Specifically, the PGypsum NOM (12 mg kg^{-1}) contains higher uranium than the PGypsum sample (5 mg kg^{-1}), which is most probably related to the NOM content of the former. The presence of NOM is expected to result in higher uranium concentration in the

PGypsum NOM sample due to the retardation of the radionuclide in the material by complexation or reduction of U(VI) to U(IV), which is less mobile.

Furthermore, the isotopic ratios $^{230}\text{Th}/^{238, 234}\text{U}$ in PR are close to unity (Figure 4) indicating that the radioactive equilibrium between ^{230}Th and $^{238, 234}\text{U}$ does exist in the raw material. However, this is not the case in the phosphogypsum samples because during the production process this equilibrium is disturbed due to the fact that thorium becomes enriched in the solid phase (e.g. phosphogypsum) compared to uranium, which is rather stabilized in the liquid phase (e.g. phosphoric acid) [1, 2]. Nevertheless, even between the two different types of phosphogypsum samples (e.g. PGypsum and PGypsum NOM) there is significant difference in the $^{230}\text{Th}/^{238, 234}\text{U}$ ratios. The $^{230}\text{Th}/^{238, 234}\text{U}$ ratio is almost twice as high in PGypsum compared to PGypsum NOM, indicating uranium accumulation in the presence of NOM. This uranium accumulation could be attributed whether to the reduction of U(VI) present in PGypsum to U(IV) in the presence of NOM, supported most probably by bacterial activity [18], or to the binding of U(VI) by NOM. Previous experimental and calculated data indicate rather the reduction of U(VI) in a phosphogypsum disposal site after application of a vegetative cover and contamination of the material with NOM [9, 17].

4.0 Conclusions

Phosphogypsum disposed onto a coastal area in Cyprus contains increased amounts of (radio)toxic impurities that require the area to become controlled and restricted for agricultural and residential use. The stability as well as the leachability of phosphogypsum is affected by increased salt (NaCl) amounts associated with seawater inputs. Hence, dissolution/leaching processes are expected to be faster close to the sea, which in the long-term point of view presents the final receptor of the gradually dissolved phosphogypsum and its impurities. The uranium chemistry and migration under oxic conditions is governed by the formation of U(VI) phosphate and fluoride complexes in stack fluids and leachates, respectively. On the other hand, under suboxic conditions (after the application of the vegetative cover) the hydrolysis of U(IV) determines the uranium chemistry in the phosphogypsum system. In addition, the uranium concentration in NOM contaminated phosphogypsum (PGypsum NOM) is significantly higher than in corresponding non-contaminated phosphogypsum, because of higher uranium retardation attributed to both, the binding of U(VI) by NOM and significantly lower mobility of U(IV) under suboxic conditions. Although the vegetative cover and the reduced conditions affect the chemistry decreasing the mobility of toxic metal ions, the phosphogypsum dissolution and dispersion of its contaminants into the surrounding environment is expected to be more effective in the case of the Vasiliko tailings dump because the disposal site is adjacent to the sea and exposed to waves receiving large amounts of seawater.

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References

1. Rutherford, P.M., Dudas, M.J., Samek, R.A.: Environmental impacts of phosphogypsum. *Sci. Total. Environ.* 149, 1-38 (1994)
2. Burnett, W.C., Elzerman, A.W.: Nuclide migration and the environmental radiochemistry of Florida phosphogypsum. *J. Environ. Radioact.* 54, 27-51 (2001)
3. Laiche, T.P., Scott, L.M.: A radiological evaluation of phosphogypsum. *Health. Phys.* 60, 691-693 (1991)
4. Kiliari, T., Pashalidis, I.: Simplified alpha-spectroscopic analysis of uranium in natural waters after its separation by cation-exchange. *Rad. Measurement.* 45, 966-968 (2010)
5. Kiliari, T., Pashalidis, I.: Selective separation of actinyl(V,VI) cations from aqueous solutions by Chelex-100. *Radiochim. Acta* 100, 439-444 (2012)
6. Efstathiou, M., Pashalidis, I.: Simplified determination of uranium in contaminated sea sand samples by alpha spectroscopy after acidic desorption and radiolysis. *J. Radioanal. Nucl. Chem.* 304, 41-45 (2015)
7. Liatsou, I., Pashalidis, I.: Determination of radium by radon emanation after EDTA-mediated sample dissolution. *J. Radioanal. Nucl. Chem.* 306, 445-449 (2015)
8. Liatsou, I., Pashalidis, I.: Radium concentration in uranium-bearing rocks and minerals by radon emanation after acidic sample dissolution. *J. Radioanal. Nucl. Chem.* (2016). DOI: 10.1007/s10967-016-4737-1
9. Papanicolaou, F., Antoniou, S., Pashalidis, I.: Redox chemistry of sulphate and uranium in a phosphogypsum tailings dump. *J. Environ. Radioact.* 101, 601-605 (2010)
10. Fokianos, K., Sarrou, I., Pashalidis, I.: A Two-sample model for the comparison of radiation doses. *Chemometr. Intell. Lab. Syst.* 79, 1-9 (2005)
11. Radiation Protection 112: 'Radiological Protection Principles concerning the Natural Radioactivity of Building Materials' European Commission Report, Brussels (1999)
12. Sarrou, I., Pashalidis, I.: Radon levels in Cyprus. *J. Environ. Radioact.* 68, 269-77 (2003)
13. Lysandrou, M., Charalambides, A., Pashalidis, I.: Radon emanation from phosphogypsum and related mineral samples in Cyprus. *Radiat. Meas.* 42, 1583-1585 (2007)
14. Lysandrou, M., Pashalidis, I.: Uranium chemistry in stack solutions and leachates of phosphogypsum disposed at a coastal area in Cyprus. *J. Environ. Radioact.* 99, 359-366 (2008)
15. Papanicolaou, F., Antoniou S., Pashalidis, I.: Experimental and theoretical studies on physico-chemical parameters affecting the solubility of phosphogypsum. *J. Environ. Radioact.* 100, 854-857 (2009)
16. Konstantinou, M., Pashalidis, I.: Speciation and spectrophotometric determination of uranium in seawater. *Medit. Mar. Sci.* 5, 55-60 (2004)
17. Carbonell-Barrachina, A., DeLaune, R.D., Jugsujinda, A.: Phosphogypsum chemistry under highly anoxic conditions. *Waste Manage.* 22, 657-665 (2002)
18. Luo, J., Weber, F.-A., Cirpka, O.A., Wu, W.-M., Nyman, J.L., Carley, J., Jardine, P.M., Criddle, C.S., Kitanidis, P.K.: Modeling in-situ uranium(VI) bioreduction by sulfate-reducing bacteria. *J. Contam. Hydrol.* 92, 129-148 (2007)

Tables

Table 1. Radioactivities of key radionuclides in phosphogypsum, phosphate rock and fertilizer samples as well as in natural gypsum found in Cyprus.

Sample	Radionuclide / (Bq kg ⁻¹)		
	U-238	Ra-226	Th-232
Phosphogypsum average (max-min) value	85 (330-21)	723 (1053-428)	37 (62-4)
Phosphate rock	942	991	22
Fertilizer	24	35	3
Gypsum (natural)	6	1	1

Figure Captions

- Fig. 1.** Schematic illustration showing the phosphogypsum disposal site at Vasiliko, Cyprus.
- Fig. 2.** Specific radioactivity (Bq kg^{-1}) of radionuclides of the U-238 series in phosphate rock and phosphogypsum samples.
- Fig. 3.** $[\text{SO}_4^{2-}]$ as a function of the $[\text{Cl}^-]$ in the stack fluids obtained from the phosphogypsum disposal site at Vasiliko, Cyprus.
- Fig. 4.** $^{230}\text{Th}/^{238,234}\text{U}$ ratio values determined in phosphate rock (PRock) and in phosphogypsum samples under oxic conditions (PGypsum) and under suboxic conditions and in the presence of NOM (PGypsum NOM).

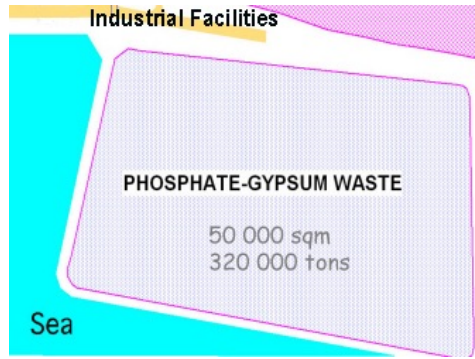


Figure 1

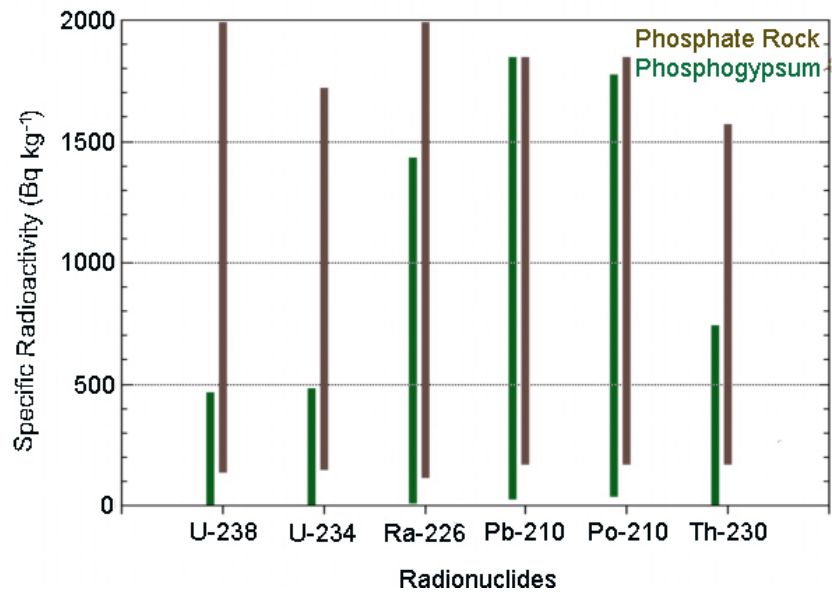


Figure 2

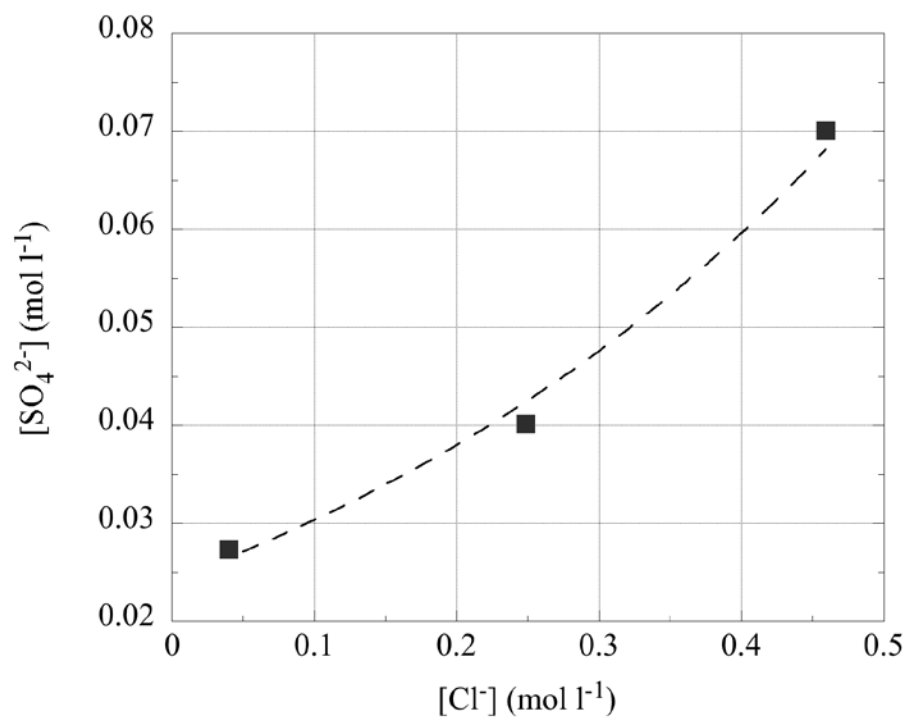


Figure 3

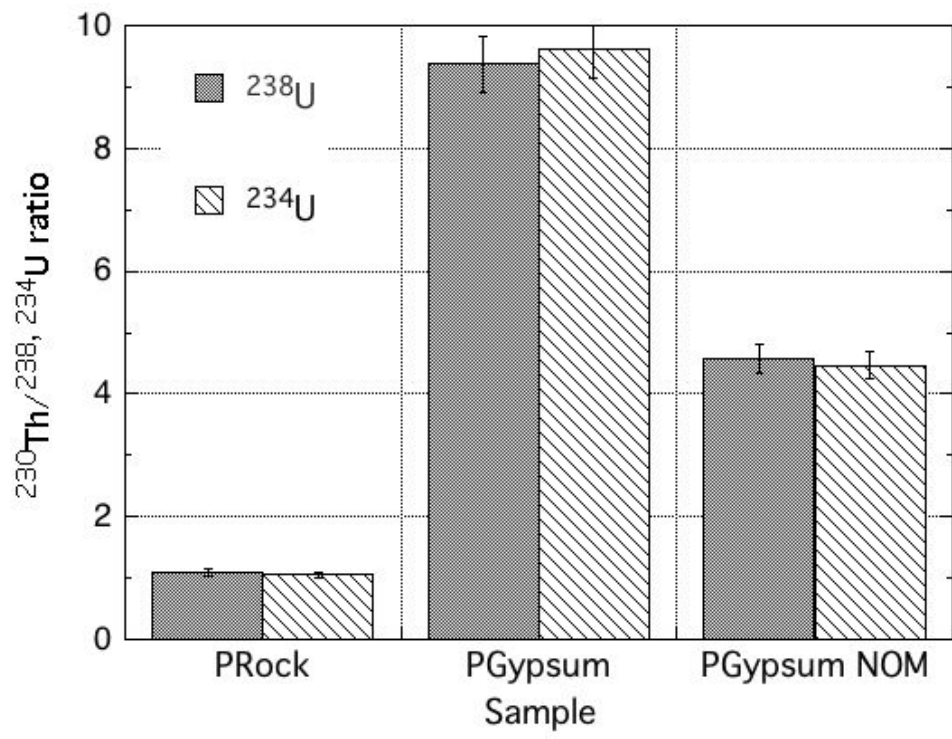


Figure 4