# The problem

The classic approach to deep sea investigation consists of using seismic or electromagnetic techniques, or by retrieving core samples from deep sea drilling programs. Seismic and electro-magnetic techniques have limitations to reliable characterize and quantify geochemical deep sea deposits while drilling expeditions are expensive. In order to efficiently explore the ocean floor for Methane Hydrates and Rare Earth deposits, the further development of affordable advanced sensors is needed.

Deep sea sediments as a resource of Methane Hydrates and Rare Earth Elements

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The solution

We propose the construction of neutron sensor based on fast neutron activation with associated alpha particle technique. In this technique the 14 MeV neutron beam is produced in Deuterium-Tritium nuclear reaction together with 3.5 MeV alpha particles. 14 MeV neutrons are very penetrative enabling usage of method underwater. At the same time technique enables elemental chemical analysis of profiles up to 30-100 cm in one measurement only.

Advanced deep sea sediments exploration of MH and REE helps fight climate changes

• MH deposits found in deep sea sediments are important storage of carbon. Destabilisation of MH can have tremendous implications for the global carbon cycle.

• Today it is known that MH deposits could dissociate under changes of 1-2°C and/or by changing of pressure.

• Their instability can be induced by climate changes and be their accelerator.

• Climatic changes related to the massive release of MH before 55 Ma have had huge consequences for global life on Earth [2].

• It is important to monitor stability of MH deposits in order to avoid their massive uncontrolled and rapid release.

• On the other hand, MH deposits may be utilized in a near future as a new and environmentally sound energy resource, which can contribute to the reduction of net CO_2 emissions from fossil fuels given that the release of the gas bound in hydrates can be induced by the injection of CO_2. In this way even more stable hydrate material is produced and stability of the geological formation remains intact, yet another greenhouse gas is sequestered.

• REE are crucial for high-tech products such are green-energy technologies. Neodymium and Samarium are used for production of currently the strongest permanent magnets and lanthanum is a main constitute of the rechargeable batteries for electric cars.
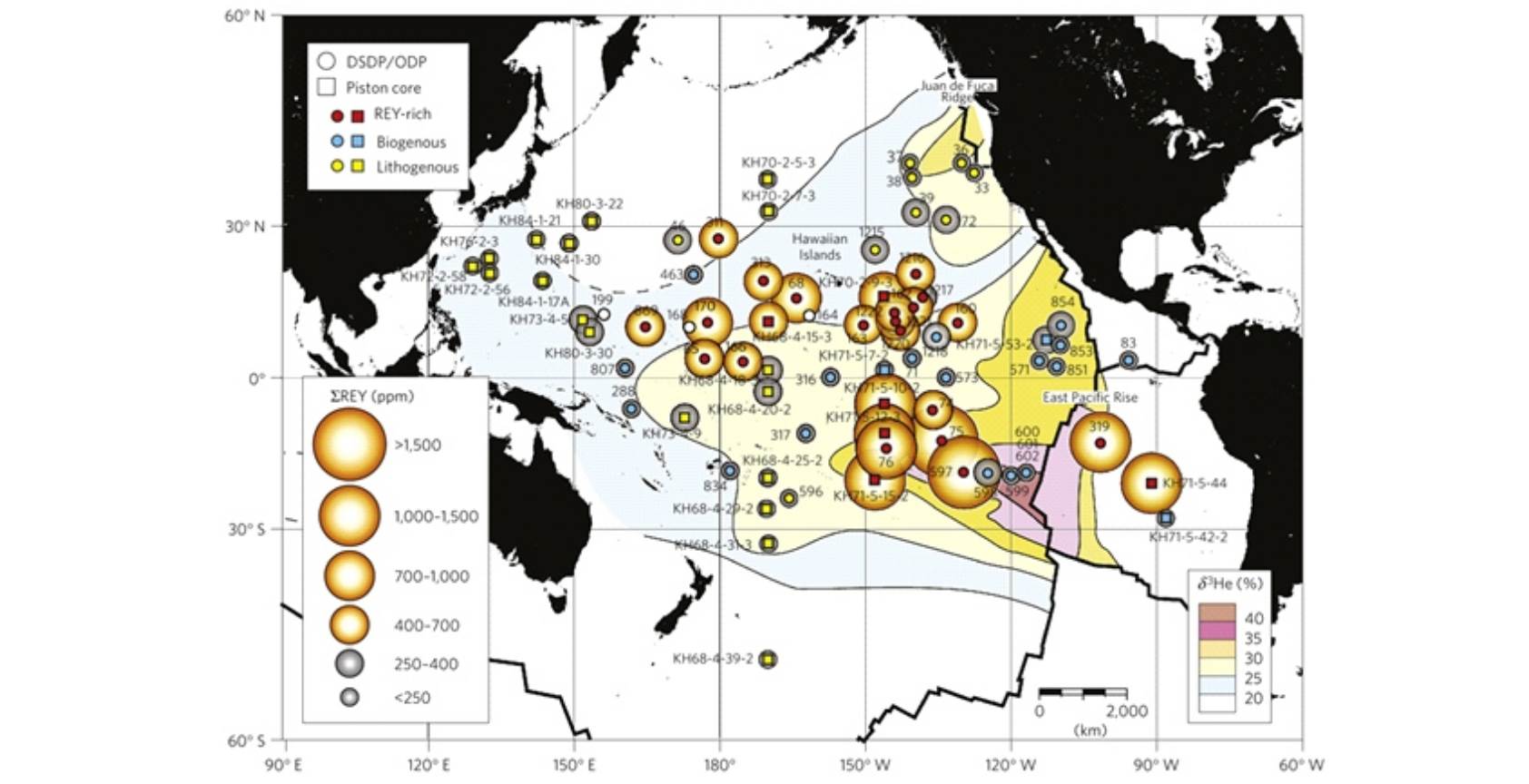
Distribution of average total REY contents for surface seabed sediments (< 2 m depths) in Pacific Ocean [3].


MH global distribution [4].

References

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Abstract

The exploring of seafloor is becoming crucial for littoral nations economies as the valuable minerals and energy resources become more expensive and less available. Methane Hydrate (MH) and Rare Earth Elements (REE) can be found in large quantities on the seafloor and near the seafloor layer at the sea depths from 400 to 1000 m, thus on continental shelves and in deep sea sediments. In this presentation we demonstrate how 14 MeV neutrons can be used for non-destructive *in-situ* chemical characterization of the MH and REE deposits in deep sea sediments. Neutron sensor can be attached to the remotely operated vehicle (ROV) as shown in Figure bellow.
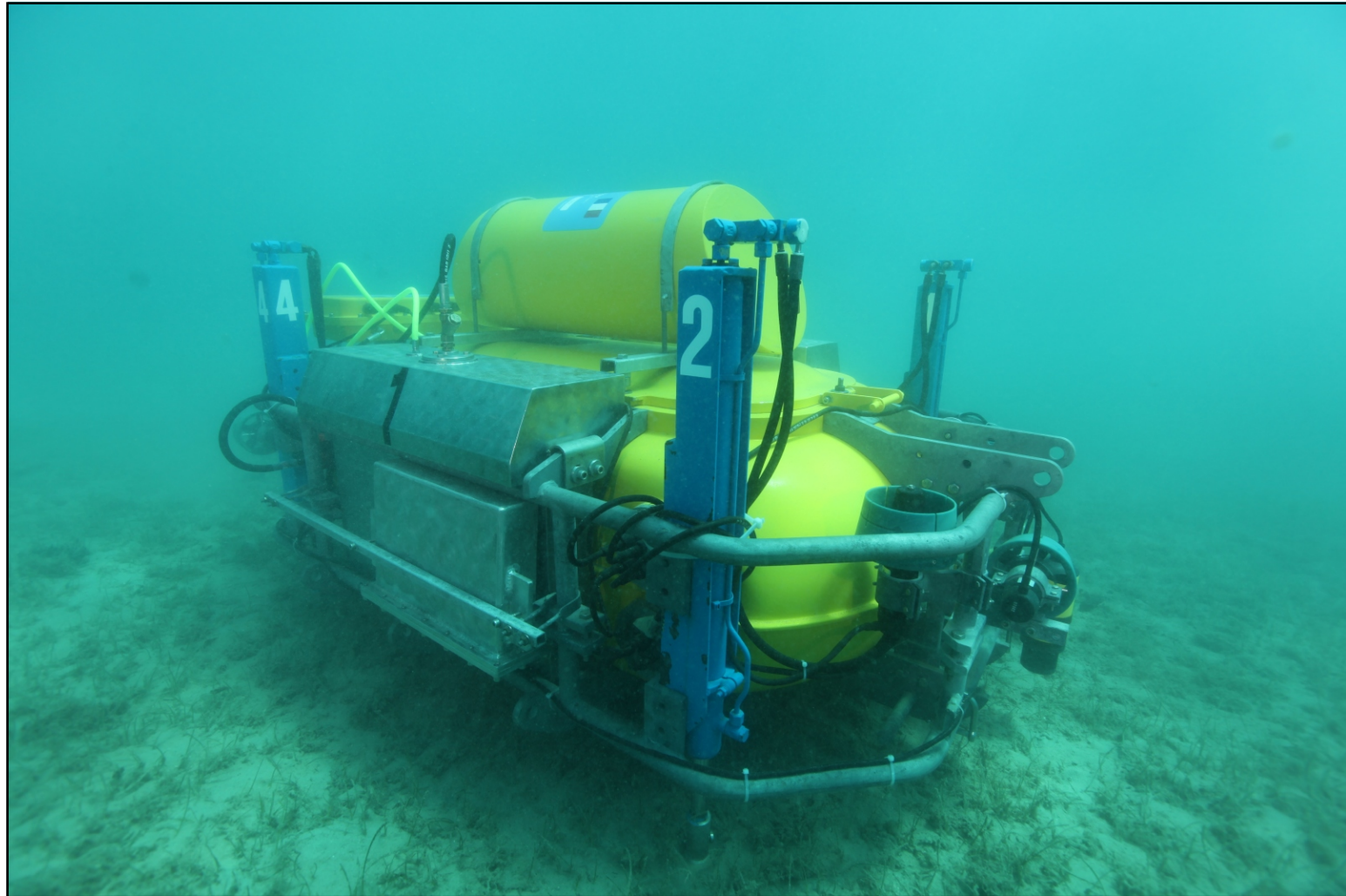
UNCOSS ROV carrying neutron sensor during the field test, Punat, island of Krk, Croatia, 06. May 2012. ROV was designed for depths up to 30 m. We have proved for the first time that neutron sensor can be used for underwater chemical analysis of objects and their content, as well as for the chemical characterization of the seafloor in the background. The aim of the UNCOSS project was to detect objects containing threat materials such as explosives and chemical warfare agents dumped at the seabed after World War I and II [1]. The ROV carrying the neutron sensor can be adjusted for the purpose of deep sea geoprospecting.

Gadolinium MC simulated Spectrum
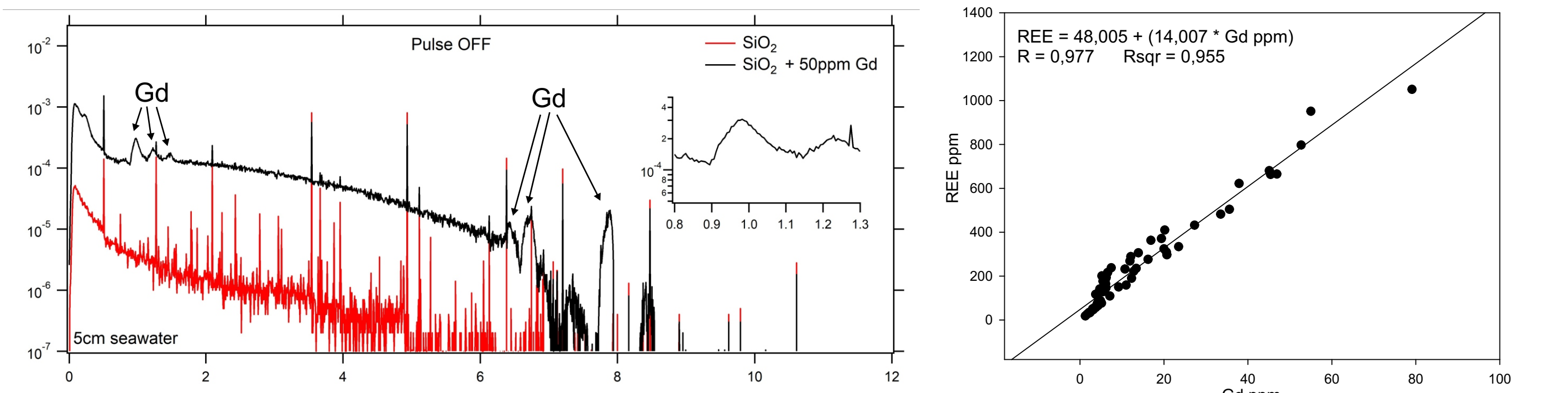
Energy distribution of prompt gamma-rays emerging from the seabed simulated by Monte Carlo model as pure SiO_2 containing 50 ppm of Gd. The neutron source was modeled as monodirectional point source operated in the pulsed mode, contained within a volume of seawater and emitting 10^7 neutrons towards the seabed. Neutron source was 5 cm distant from the seabed. The pulse width was set to 10 μs and the pulse frequency to 100 μs. The spectrum shows only what is counted when the pulse is "OFF".

Correlation between Gd and total REE content in deep sea sediments (< 0,25 cm depths) in Pacific Ocean. Data were taken from supplementary material of Kato et al. [3]. According to these data Gd concentration of 68±2 ppm indicates REE rich deposits, i.e. deposits exceeding 1000 ppm of total REE.
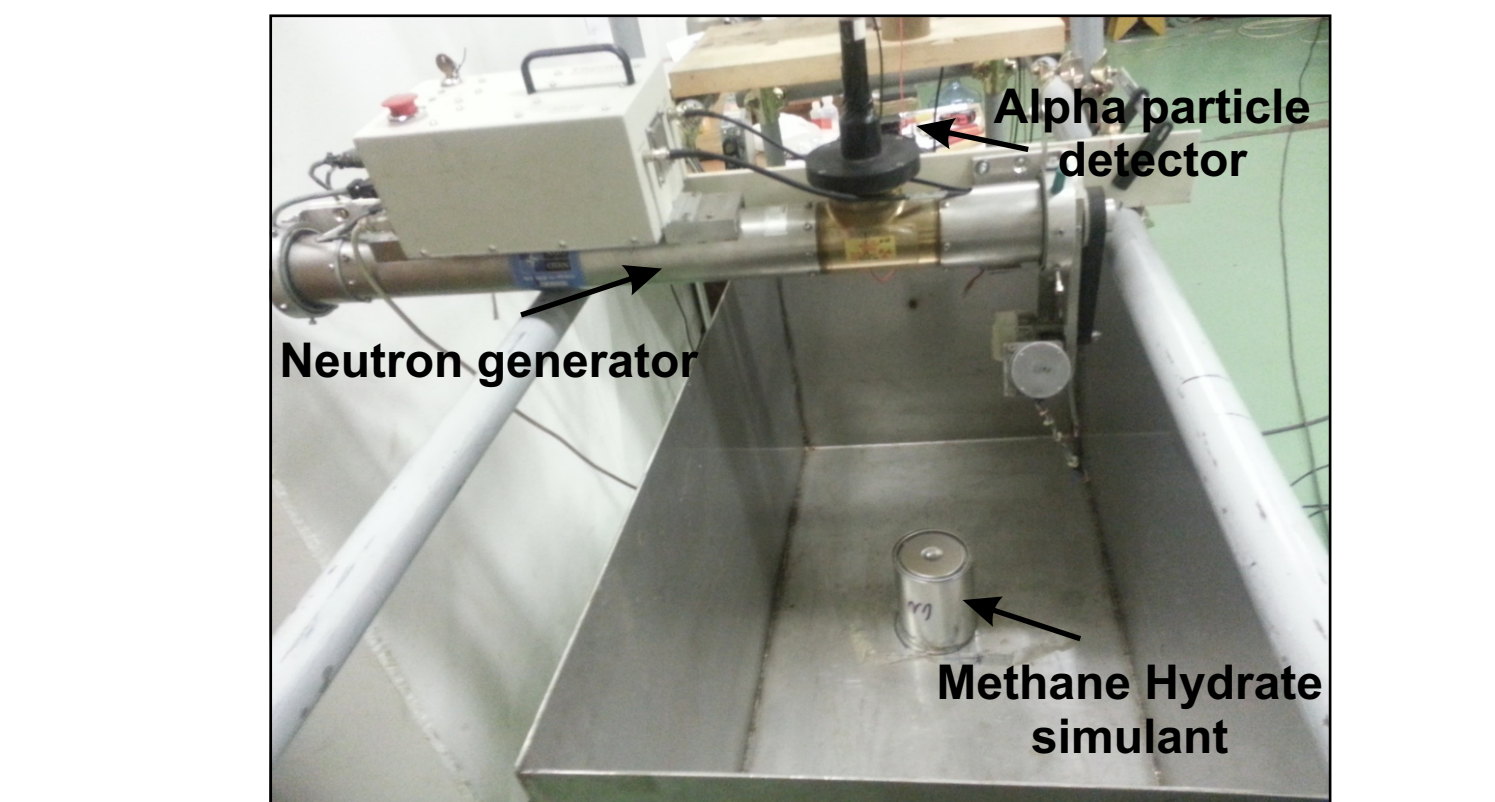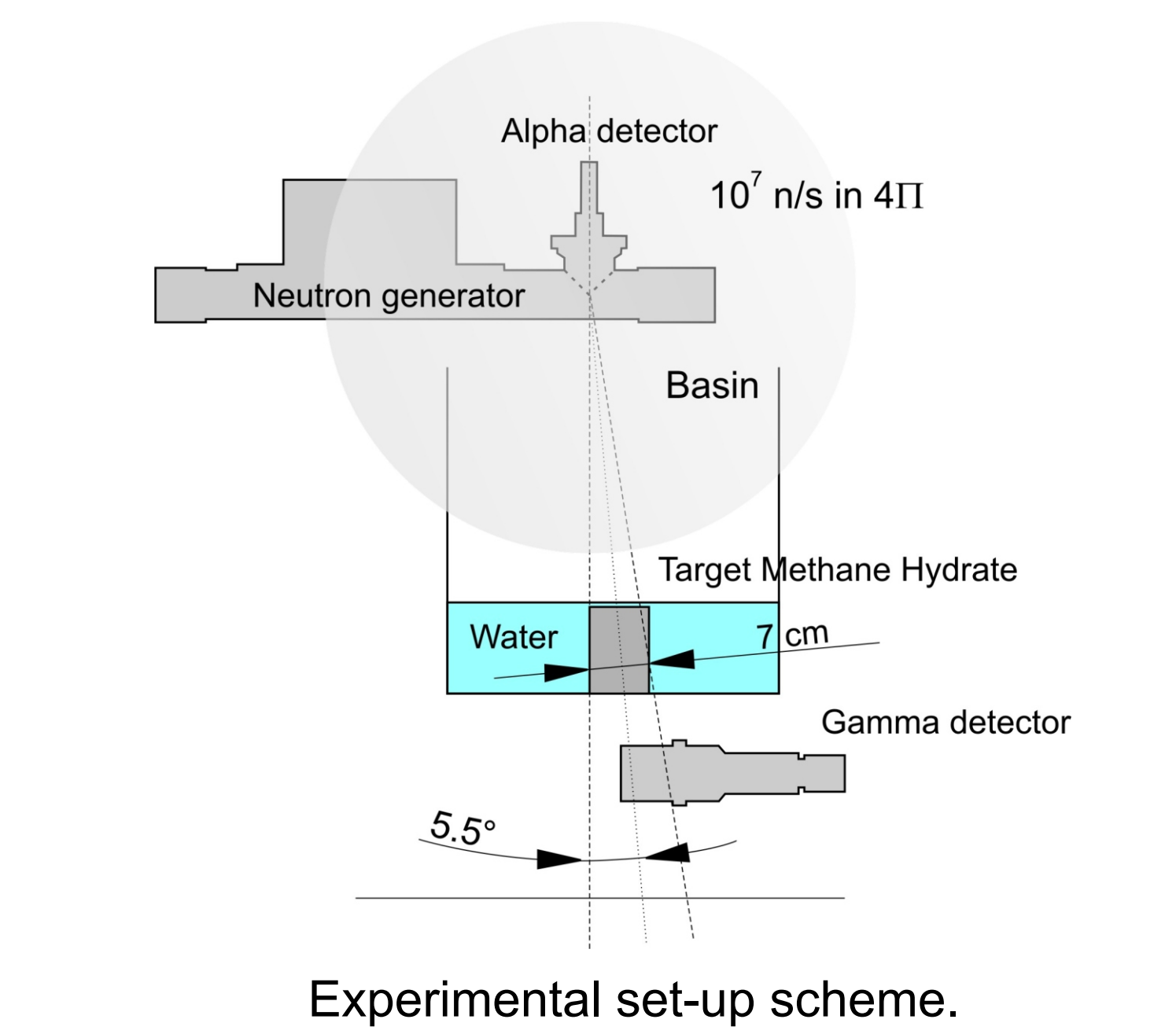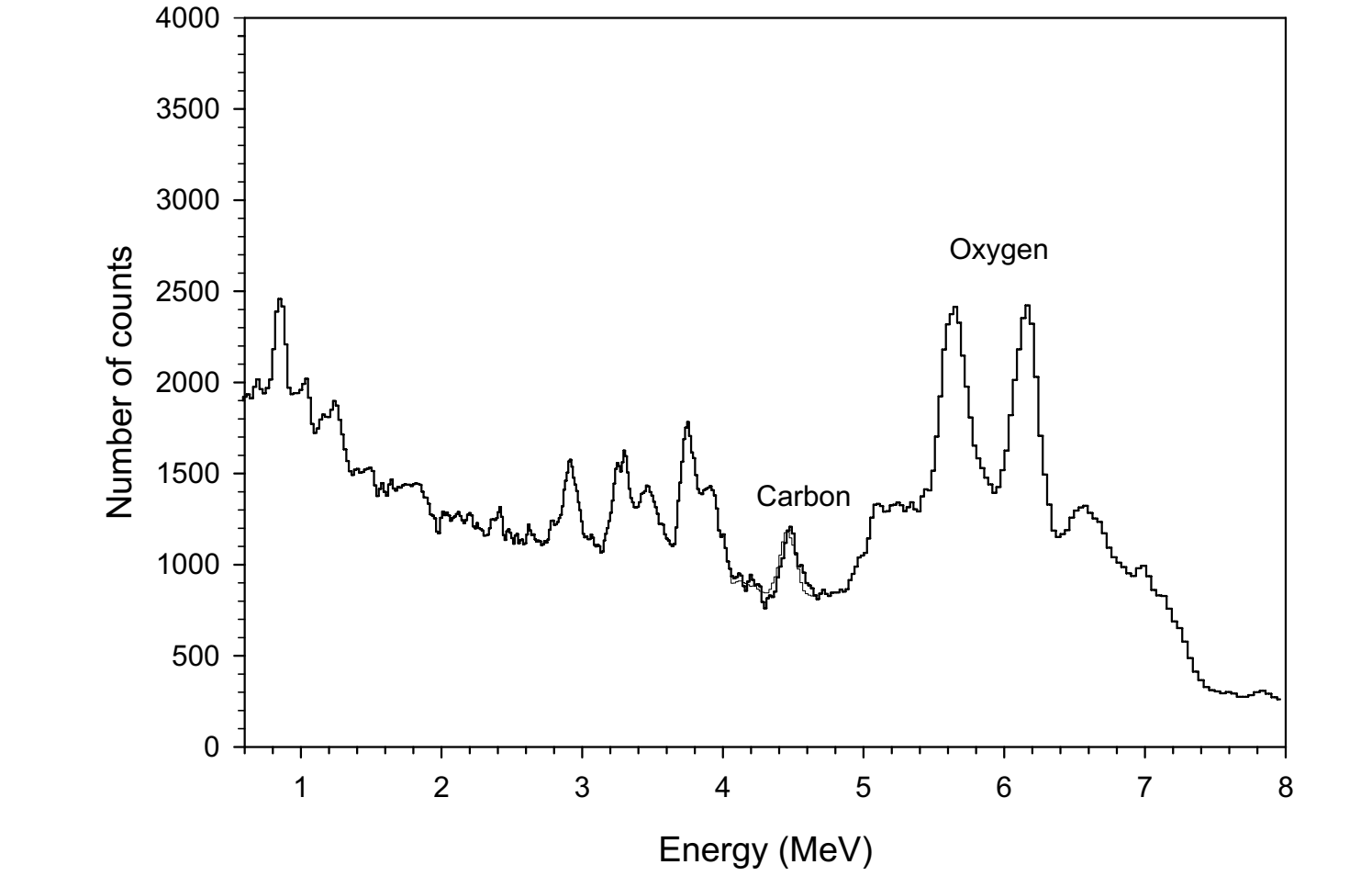
Conclusion

• The experimental set-up used in this study requires 2.5 hours to detect MH in sediment of 40% porosity.

• The measurement time may be reduced by increasing number of detectors, e.g. by using four 3"x3" $LaBr_3$:Ce gamma detectors the measurement time could be reduced by factor of 4.

• Gadolinium has the highest cross section for thermal neutrons in periodic table of the elements (49000 barns). The second highest is samarium (5922 barns). Since concentration of Gd shows the strong linear correlation to the total REE concentration in deep sea sediments, it is possible to deduce the total REE content by measuring Gd concentration only.

• According to the Monte Carlo modelling, 50 ppm of Gd can be detected easily in sea sediment. Concentration of 68±2 ppm determines rich REE deposits.

Experimental set-up

Experimental set-up scheme.

Laboratory experimental set-up.

MH Spectrum

The gamma ray spectrum of calcium carbonate sea sediment (porosity 40%) saturated with MH simulant measured in basin filled with water. MH simulant was made from sugar sucrose $C_{12}H_{22}O_{11}$ and water. Sucrose mass fraction was 25%. For 500 g of simulant, 125 g of sugar needs to be dissolved in 375 g of water. The chemical formula of MH simulant obtained in this way is $C_4H_{46}O_{23}$. The solution volume was 470 ml and the density was 1.06 g/ml, which was a bit higher than the density of the methane hydrate (0.9 g/ml).

About the first author

Dr. Jasmina Obhođaš is a Head of Laboratory for Nuclear Analytical methods at Experimental Physics Department of Ruđer Bošković Institute. Her background is in geosciences and she has specialized in physics. Her expertise encompasses development of x-ray fluorescence and neutron activation techniques for various applications and data analysis.

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