Nurturing connections across geochemistry

Having devoted her career to studying geological processes that change the Earth's surface, **Dr Liliana Lefticariu**, talks about her latest work researching the stable isotopes of elements that play key roles in the biogeochemical processes, and what relevance this has for education and training

Can you explain how the Isotope Ratio Mass Spectrometry technique works?

Isotope-ratio mass spectrometry (IRMS) is a powerful analytical technique that can accurately measure the relative abundance of isotopes of a chemical element, such as $^{18}O/^{16}O$ and $^{34}S/^{32}S$, in a given sample. An isotope is a variant of a particular chemical element that differs from other isotopes of the same element by the number of neutrons in its nucleus. The main chemical properties of an element are not affected by the number of neutrons in the nucleus; however, the mass differences of isotopes influence their behaviour in physical, chemical and biological processes, such that the compound with the lighter isotope reacts faster. Thus, natural processes could fractionate the isotopes of a chemical element, leading to the occurrence of various products with distinct isotopic compositions.

Why are isotopes so vital to the study of science?

Knowledge of the isotope behaviour during physical, chemical, and biological changes is a key to deciphering natural processes. Isotope ratios can provide exclusive insights into the sources and movement of materials through the geosphere and biosphere and have been applied over the last 70 years to problems ranging from climate variability through geological time to deep-crustal processes, ecosystem dynamics and to the diet of ancient humans. A short list of topics and disciplinary areas that often employ stable isotopic analysis includes: paleoclimatology, paleoecology, hydrology, petrology, pollution and toxicology, forensic science, animal migration, nutrient cycling, physiology and food web studies. Stable isotope analyses are also extremely precise and accurate and require very small amounts of sample.

How will the Isotope Ratio Mass Spectrometry benefit radiation chemistry at large?

A recent application of the IRMS techniques has been to unravel the biogeochemical processes associated with the decay of long-lived, naturally occurring radionuclides in natural systems. Analyses of groundwater in the vicinity of uraninite–pyrite mineralisation are frequently associated with plumes of partially to fully oxidised sulfur species inferred to result from radiolysis of water coupled to oxidative weathering of sulfide minerals. The presence of abundant oxidised nitrogen species in deep fracture water from the Witwatersrand Basin, South Africa was also associated with radiolytic oxidation of reduced nitrogen species in the deep crust. Laboratory anoxic experiments have shown that isotopically distinct oxidising products are being produced during irradiation. Mounting evidence suggests that the decay of long-lived, naturally occurring radionuclides can be an important source of energy and nutrients for microorganisms in subsurface settings, from shallow aquifers and marine sediments to deep terrestrial subsurface.

Will there be an attempt to continue with the IRMS after your grant runs out next year?

Absolutely! The interest in isotope-ratio measurements is increasing rapidly, fuelled by precise automated measurement of mixtures of stable isotopes in natural samples and by a growing appreciation of the simplicity, versatility and robustness of this method with different applications in the Earth and environmental sciences. The instrument is being fully utilised and producing important data for Southern Illinois University Carbondale (SIUC) investigators. Researchers from entities and institutions outside of the SIUC, such as The University of Illinois at Urbana/Champaign and the Illinois State Geological Survey have started using our facility. Funding to support continued operation of the instrument will mainly come from the SIU Office of the Vice Chancellor for Research and from the analytical fees charged to IRMS users and grants and contracts in which IRMS is a substantial component of the project.

Where do you see this type of technology developing in the future?

Another aim of our laboratory is to develop a new range of analytical capabilities that are critical to our diverse projects and provide efficient and automated sample analysis in a timely fashion and low cost. In particular, investigators using stable isotope in their research are looking at the development and applications of compound-specific stable isotope analysis (CSIA) with GC-C-IRMS (gas chromatography coupled to a combustion furnace and isotope ratio mass spectrometer) in the fields of ecology and environmental sciences. CSIA analysis measures C, H and N isotope ratios in individual compounds within a complex mixture, which can provide critical information that cannot be obtained from the analysis of bulk sample. Known applications of CSIA include ecology and environmental sciences, organic geochemistry, forensic science, archaeology, microbiology and soil science. We also expect to see the development of online methods for in-situ sampling within solid materials for stable isotope analysis using laser ablation in conjunction with IRMS for micro-sampling.

Shaping the future of **isotope research**

Southern Illinois University Carbondale is at the forefront of stable isotope science. Its innovative analytical tools are now being used to investigate some of the world's most pressing environmental questions

EXPLORING HIGHLY-RELEVANT scientific topics with the use of stable isotope analysis is a rapidly developing area of research. With the acquisition of a new state-of-the-art isotope ratio mass spectrometer (IRMS), the Southern Illinois University Carbondale (SIUC) Department of Geology is breaking new ground in science and education. Funded by both the US National Science Foundation and SIUC, the IRMS and four inlet systems have been installed at the University's Mass Spectrometer Facility to support detailed studies into the isotopes of light elements. Dr Liliana Lefticariu, an Assistant Professor in the Department, is the Principal Investigator in charge of this project and explains that the new IRMS instrumentation is having a significant impact upon the research now being conducted at SIUC, with wide-ranging applications across diverse disciplines, from paleoclimatology right through to ecosystem dynamics.

AN IMPRESSIVE INFLUENCE ON RESEARCH TOPICS

Entitled the 'Acquisition of an Isotope Ratio Mass Spectrometer for Geochemical Biological and Petrologic Research, Education and Training at Southern Illinois University', this project has been in place since 2009 and is due for completion mid-2013. The IRMS venture has immensely improved the capabilities for research undertaken at SIUC. "Having this instrument on the SIUC campus has had an amazing effect on the breadth of studies being conducted at the University," notes Lefticariu. In particular, she has been pleased to see the way the new IRMS has facilitated interdisciplinary research and fostered collaboration among different departments and research centres in a variety of projects. The IRMS has also made possible the integration of stable isotope research and IRMS techniques into many of the undergraduate and graduate courses. This means that many of the graduate students can access highly specialised training whilst they are conducting thesis-related or independent research.

A primary focus of the Mass Spectrometry Facility has been the development and optimisation of a number of analytical techniques used for measuring stable isotope ratios. These measurements can be made across a numerous materials, including plant and animal tissues, carbonates, teeth and bones, soils, aqueous and organic liquids, coal, sediments and gases. There are a number of potential applications which help to highlight the versatility of the IRMS: It can be used to analyse animal hair or tissue for carbon and nitrogen isotopes, which means researchers can improve their understanding of animal metabolism and relationships with the environment. The same approach can be applied to plant tissues. Furthermore, bird feathers, natural waters and fish bones can be assessed for oxygen, carbon and hydrogen isotopes to help decode the migration routes of bird or fish species. "We are also supporting the analysis of calcite samples collected from hydrothermal veins and fossils for carbon and oxygen isotopes to refine the geologic or climate history of a particular area," Lefticariu points out.

DIVERSE APPLICATIONS

Exploring paleoclimate and environmental questions through analysis of stable isotopes is a rapidly developing area of investigation, so researchers interested in climate science and their students have taken advantage of the new IRMS to generate up-to-date records of changing climates. To illustrate such collaborations, Dr Matthew D Therrell, from the Department of Geography and Environmental Resources, is working with Lefticariu to identify the temporal relationships between oxygen isotope trends in tree ring α-cellulose and various climate parameters, such as precipitation and temperature. Dr Scott Ishman, a colleague of Lefticariu in the Department of Geology, and his associates are researching the use of calcareous skeletal remains of foraminifera as proxies for paleo-oceanographic and paleo-environmental conditions. "Our $\delta^{18}O$

measurements of planktonic and benthic foraminifera have indicated that the Larsen B ice shelf has been thinning throughout the Holocene," explains Ishman. "This implies that the recent prolonged period of warming in the Antarctic Peninsula region, in combination with the long-term thinning, has led to collapse of the ice shelf." Clearly, the stable isotope findings are having an important impact in understanding major changes in the ice shelves.

The IRMS is also of value for improving knowledge about fish ecology and environmental dynamics. For example, Dr Greg Whitledge, an Associate Professor in the Center for Fisheries, Aquaculture and Aquatic Sciences at SIUC, is benefiting from using stable oxygen, hydrogen and carbon isotope analysis of fish bones and otoliths to help identify the natal environment of fishes in North American river systems. Whitledge describes how being able to analyse the stable isotope and elemental composition across the otoliths can help identify environments that an individual fish has used during its lifetime: "Early life stages of fishes are difficult to track in large river systems, as a result stable isotope analysis of otolith and bone samples is providing new information about natal environments of invasive species, commercially and recreationally important fishes and species of conservation concern". Other isotope analysis research endeavours within this discipline include the use of stable isotopes to help improve knowledge about the effects of anthropogenic disturbances and habitat changes on the ecology of wildlife species, which is being undertaken by Drs Eric Hellgren and Clayton Nielsen at the Cooperative Wildlife Research Laboratory. In SIUC's Department of Plant Biology Dr Dale Vitt is using carbon and nitrogen isotope analyses of plant materials to study nutrient cycles in peat bogs at sites around the world, including in Siberia and western Canada.

> The new IRMS instrumentation is having a significant impact upon the research now being conducted at the SIUC, with wide-ranging applications across diverse disciplines, from paleoclimatology right through to ecosystem dynamics

THE WIDER BENEFITS FOR ISOTOPE ANALYSIS

Recently, the IRMS techniques have been employed to decipher the complex biogeochemical processes associated with radiolysis of water during the decay of long-lived, naturally occurring radionuclides in subsurface settings. There is mounting evidence that microorganisms found deep underground can derive all their energy from the decay of radioactive rocks rather than from sunlight. The finding suggests life might exist in similarly extreme conditions both on Earth and in outer space: "Stable isotopes could provide critical knowledge about the water–rock–microbe interactions taking place within terrestrial and, potentially, extra-terrestrial environments where radiolysis is occurring as a result of radionuclide decay or ionising irradiation," observes Lefticariu.

Sulphur, hydrogen, and nitrogen isotopes are now being used to fingerprint and quantify radiolytic processes both in laboratory experiments and in the field at sites all over the world. For instance, the presence of hydrogen and oxidised sulphur species, compounds used by bacteria for nourishment and identified in fracture water collected in deep mines from the Witwatersrand Basin in South Africa, was connected with the radiolytic oxidation of reduced sulphur species found in the deep crust.

The IRMS Laboratory researchers are proud of the influence they have had over diverse investigations so far and are excited about what the future will hold for both the work that will be completed at the SIUC and for the global application of the IRMS techniques.

INTELLIGENCE

ACQUISITION OF AN ISOTOPE RATIO MASS SPECTROMETER FOR GEOCHEMICAL BIOLOGICAL AND PETROLOGIC RESEARCH, EDUCATION AND TRAINING AT SOUTHERN ILLINOIS UNIVERSITY

OBJECTIVES

To acquire an IRMS system and three sample preparation peripherals for research, education and training. The instrument will support multiple disciplines (geology, zoology, wildlife science, fisheries, chemistry, biochemistry, plant biology, anthropology, coal research, engineering and microbiology).

KEY COLLABORATORS

Dr Matthew D Therrell

Dr Scott Ishman

Dr Greg Whitledge

Dr Eric Hellgren

Dr Dale Vitt

Dr Clayton Nielson

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DR LILIANA LEFTICARIU is an Assistant Professor in the Department of Geology at Southern Illinois University Carbondale. She attained a BSc from the University of Bucharest in 1989, followed by an MSc and PhD from Northern Illinois University in 2001 and 2004 respectively. Her research is primarily devoted to solving diverse theoretical and practical problems with application in the geological and environmental sciences. Her speciality is low-temperature geochemistry with an emphasis on the stable isotopes of elements that play key roles in biogeochemical processes.

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