

NATIONAL FACILITY FOR STABLE ISOTOPE GEOCHEMISTRY AT IIT, KHARAGPUR

Introduction

About 59 years back Prof. Meghnad Saha, while discussing the need of determining the chronology of Indian rocks and minerals lamented “some of the fundamental apparatus for routine operation e.g. mass spectrograph for isotope ratios, are still unavailable in this country. It is hoped that with future co-operative efforts greater strides in the path of progress will be made in this field of fundamental work” (Trans. Nat. Inst. Sci. India, 2, 273, 1947, Source: Mass Spectroscopy, S. Karmahapatra, 1995, West Bengal State Book Board). The situation perhaps did not change much until the beginning of 21st century when Department of Science & Technology, New Delhi, under its Impact Research in High Priority Areas (IRHPA) programme, decided to create several national isotope facilities in earth sciences across the country which can cater to the need of scientists engaged in studying both radiogenic and stable isotope concentrations in varied kind of geological materials. The latest addition in this effort is the establishment of the National Facility of Stable Isotope Geochemistry at the Department of Geology and Geophysics, IIT, Kharagpur. Although use of stable isotopes in various branches of earth sciences has continuously increased over the last decade, lack of such a facility within India seriously hampered quality isotope research in the country. Even now earth scientists are forced to generate these data through international collaboration and a huge gap exists in the stable isotope data base of Indian rocks, minerals and fossils. It is expected that the facility at IIT, Kharagpur should be able to bridge this gap and particularly help students and researchers from earth science departments of various universities in generating necessary stable isotope data for their research programmes. A close look at the Indian research papers on stable isotope application over the last two decades will reveal that most of these were published in the field of low temperature sediment/water isotope chemistry of modern or Quaternary systems. Relatively less publications were made in the field of isotope systematics in metamorphic rocks and virtually no publications were made in igneous petrology, crust-mantle interaction or related fields. This is a sorry state of affairs considering the fact that a large chunk of our knowledge on crustal evolution comes from application of stable isotope tracers in hard rocks. Likewise very little work has been carried out on stable isotope application of Phanerozoic sedimentary systems of India.

The Kharagpur Facility

While a single national facility may not be sufficient in this regard at least an attempt will be made to increase the versatility of the IIT, Kharagpur facility over the next few years. As a beginning, users working on the following thrust areas will be encouraged to use the facility.

- a) Phanerozoic sediment/climate record of global importance
- b) High resolution Palaeoclimatic and Palaeoecological studies from Late Quaternary continental sediments with special emphasis on past precipitation records on lands
- c) Palaeoclimatic studies from the sedimentary records of NE Himalaya since data from this region are sparse

However, other than the above mentioned thrust areas, users having bright innovative geological ideas of any kind (Archaeo to Quaternary time scale) will also be encouraged to use the facility.

The IIT facility is equipped with a Thermo made Delta^{Plus} XP continuous flow mass spectrometer (CFIRMS, installed towards the end of 2005) along with several peripheral equipments like Gas bench, Elemental analyser and TC-EA, capable of analysing different types of geological materials including water, carbonate, sulphide/sulphate, organic matter, graphite, clay etc. The Delta^{Plus} XP is an ultra-sensitive CFIRMS with extended ion optics, dynamic signal range (up to 50V) and high ohmic resistors variable under computer control (thereby facilitating analysis of both natural abundance and isotopically enriched samples). Fitted with 5 Faraday collectors it has a mass range of 1-70 Daltons at 3 kV, carbon (C), nitrogen (N), oxygen (O) and sulfur (S) resolution of $m/\Delta m = 95$ (10 % valley) and H/D $m/\Delta m = 10$ (10 % valley). Absolute sensitivity is ~1500 molecules CO_2 per mass 44 ion at the collector even with high He load. The Ion source linearity ~0.02 %/nA ion current (m/z 44). Sample consumption is ~0.15 nmol/s CO_2 for 10 nA signal at m/z 44 (10^{-2} mol/As) and H_3^+ factor is less than 10 ppm/nA with stability better than 0.03 ppm/nA/h. The gas bench (coupled with Combi-Pal autosampler) provides rapid analysis of large number of water and carbonate samples. Likewise the Flash Elemental analyser (EA) provides rapid analysis of carbon isotopes in organic matter, graphite and sulphur isotopes in sulfide/sulfate. The high temperature pyrolysis TC-EA peripheral can analyse sub-microlitic water.

samples or hydrogen isotopes in clay/mica. Using gas chromatographic (GC) techniques these peripherals completely avoid the complications of glass vacuum off-line experiments yet provide rapid and precise on-line measurements of variety of geological materials.

Gas Extraction

For carbonate analysis ~100-300mg of powdered sample is reacted at 72°C with ~98% phosphoric acid in sealed reaction vessels flushed with helium gas. Headspace sampling of evolved carbon dioxide is performed with the Gas-Bench and isotopic ratios measured. For $\delta^{13}\text{C}$ analysis of sedimentary organic matter powdered rock sample is decarbonated using 0.5N HCl, repeatedly washed and dried. Using an autosampler about 50 mg of treated sample, wrapped in a tin capsule, is dropped into a quartz tube reactor, pre-filled with chromium oxide, reduced copper and silvered cobaltous, over-night conditioned at ~1050°C. Sample is combusted in a stream of He flow and oxidized by a constant flow of high purity O_2 . The evolved CO_2 is purified through a moisture trap and separated from other gases by a molecular sieve GC column and is introduced via a Finnigan ConFlo III interface to the mass spectrometer for its $\delta^{13}\text{C}$ analysis. Likewise, for $\delta^{34}\text{S}$ analysis of sulfides/sulfates powdered pure mineral phase is oxidized to SO_2 and analysed. For $\delta^{34}\text{S}$, however, the quartz tube reactor is replaced by tungsten oxide and copper catalysts. For δD analysis of mica or clay about 1 mg separated sample, wrapped in a silver foil capsule, is dropped into the high temperature conversion elemental analyzer (TC-EA) glassy carbon graphite-silver wool containing ceramic reactor using an autosampler. Sample reacts with graphite in the TC-EA furnace at 1450°C in a helium stream generating H_2 gas. The evolved gas passes through a 5Å molecular sieve GC column and is introduced into the IRMS via ConFlo III for δD composition.

Calibration and Standardisation

Over the last few months it has been possible to generate reproducible isotopic values in the IIT facility and also test the absolute delta values of a variety of geological materials and standards that can be analyzed using these peripherals. Materials analysed include Benzoic acid, Acetaldehyde, Merck Carbonate supplied by the Thermo as well as IAEA (International Atomic Energy Agency) C-3 cellulose, NBS-19 and carrara marble carbonate, NBS-30 Biotite, IAEA water standards, NBS sulfur standard Sphalerite analysed using Gas Bench, Flash EA and TC-EA peripherals. Figure 1 shows the external reproducibility and absolute delta values for both carbon and oxygen isotopes of internal

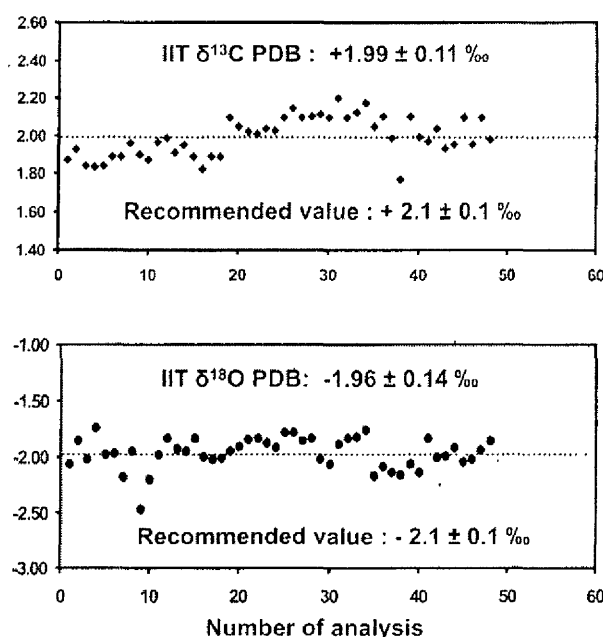


Fig.1.

standard z-carrara marble over the last 4 months. Figure 2 shows the calibration of international standard GISP (Greenland Ice Sheet Precipitation) by both VSMOW (Vienna Standard Mean Ocean Water) and SLAP (Standard Light Antarctic Precipitation) standards obtained from IAEA, Vienna. Excellent reproducibility and agreement have been obtained in both cases.

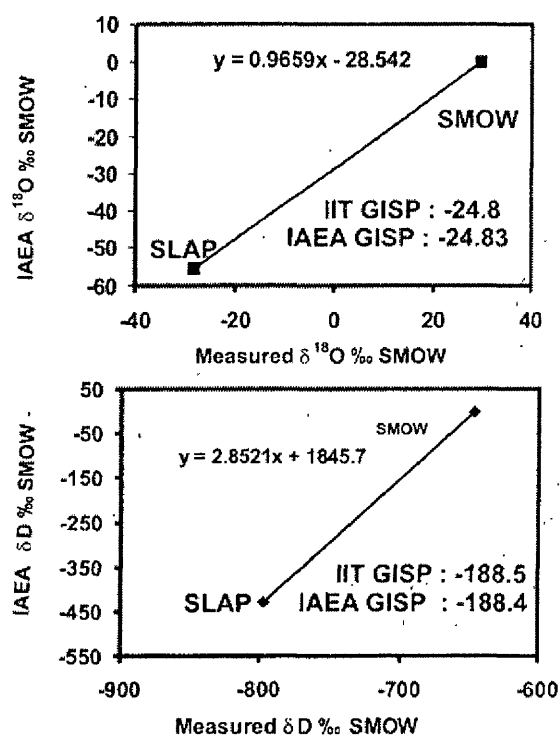


Fig.2.

Table 1

Standard#	Z-CARRARA; PRL	BDH, Univ. College, London (UCL)	C3-Cellulose IAEA	NARM water PRL	NBS-23 Sphalerite IAEA	NBS-30 Biotite	Arsenic-rich water sample
IIT $\delta^{18}\text{O}$ value	-1.96 ± 0.11 (n=48) [@]	-2.01 ± 0.16 (n=10)		-4.54 ± 0.04 (n=8)	-	-	-4.68 ± 0.03 (n=3)
Recom. $\delta^{18}\text{O}$ value	-2.1 ± 0.1	-1.97 ± 0.1		-4.51 ± 0.06	-	-	-4.75^s
IIT $\delta^{13}\text{C}$ value	$+1.99 \pm 0.1$	$+1.93 \pm 0.08$	-24.46 ± 0.18 (n=17)		-	-	-
Recom. $\delta^{13}\text{C}$ value	$+2.11 \pm 0.1$	$+1.95 \pm 0.05$	-24.91 ± 0.15		-	-	-
IIT δD value				-35.21 ± 1.57 (n=6)	-	-65.42 ± 0.93 (n=5)	-32.64 ± 0.9 (n=3)
Recom. δD value				-35.78	-	-65.00	-31.6^s
IIT $\delta^{34}\text{S}$ value					17.09 ± 0.02 (n=3)	-	-
Recom. $\delta^{34}\text{S}$ value					17.1	-	-

Carbonate/Organic carbon, Water/Biotite and Sulphide values are with respect to VPDB, SMOW and VCDT respectively. @ - Number of samples analysed; \$ - Measured in NERC Isotope Facility, Nottingham, UK

Present Capability

Inter-laboratory calibration experiments also showed excellent agreement between absolute delta values of standards and natural samples measured at IIT and other laboratories in India and abroad (Table-1). However, initially the facility will be able to analyse only the following categories of geological samples and isotope ratios those are easier to analyze:

- Carbon and oxygen ($\delta^{13}\text{C}$ - $\delta^{18}\text{O}$) isotope ratios in carbonates
- Carbon and nitrogen ($\delta^{13}\text{C}$ - $\delta^{15}\text{N}$) isotope ratios in organic matter/graphite etc.

Although it has been possible to measure precise and reproducible $\delta^{34}\text{S}$ values in the present set up, it has been decided that the routine measurement of Sulphur isotope ratio should be attempted later as the facility is in its development stage. This is because SO_2 being a rather sticky gas, has a long residence time in the ion source and can potentially affect the measurements of the other isotope ratios which are more in demand. Also the users intending to analyse $\delta^{18}\text{O}$ - ΔD in water should send their samples to the upcoming Isotope facility of Physical Research Laboratory, Ahmedabad exclusively devoted for water analysis. It is planned that in about two years time the IIT facility will also acquire a laser ablation silicate analysis

peripheral that can cater to the needs of scientists working on various hard rock related problems.

User Enquiries

Intended users should write to IIT, Kharagpur informing about the analytical requirements. Analysis will be carried out against fixed nominal charges and the rates can be obtained from the same. Users will also be required to fill up a pro-forma indicating number of analyses, nature of samples and isotope ratios to be measured. A brief write up explaining the scientific merit of the use of stable isotope data in their research programme should also be included. Applications will be reviewed by members of the expert committee constituted by the DST and associated with the national facility before accepting the samples. In due course the facility will also conduct short courses/workshops on application of stable isotope geochemistry in geology. All queries about the facility should be directed to: In-charge, National Stable Isotope Facility, Department of Geology & Geophysics, Indian Institute of Technology, Kharagpur - 721 302, West Bengal.

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