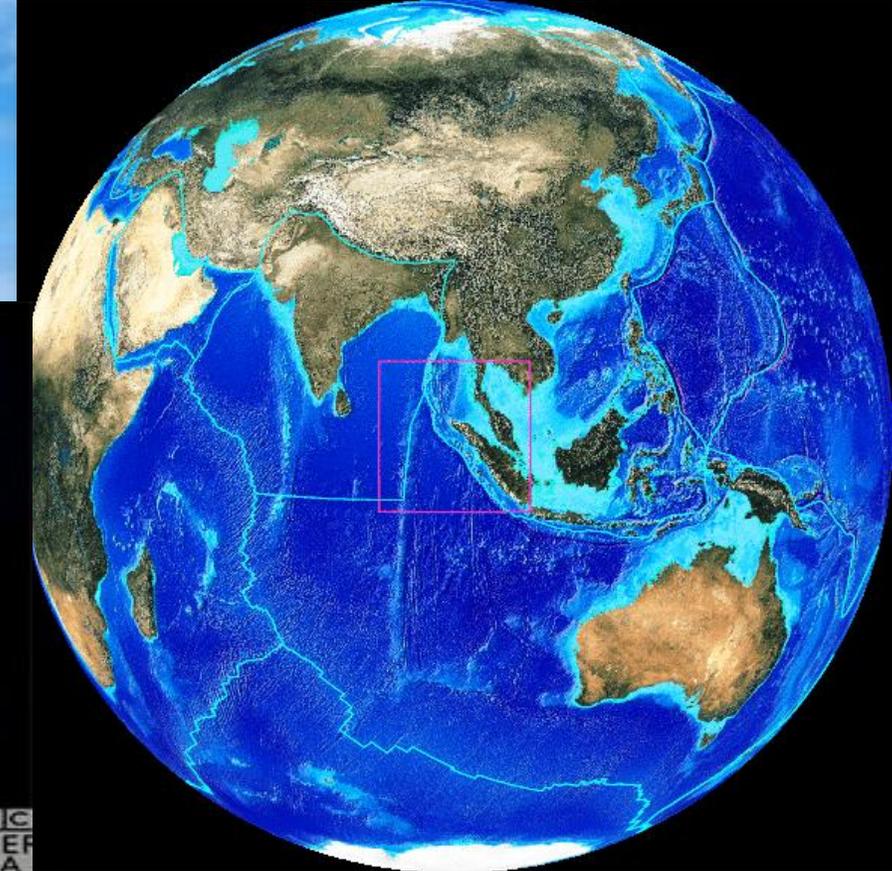


Deep-Sea Mineral Deposits as a Source of Critical Metals for High-and Green-Technology Applications: A Sustainable Approach or an Invitation to Another Catastrophe?



V. Balaram
CSIR - National Geophysical Research Institute,
Hyderabad – 500 007, India

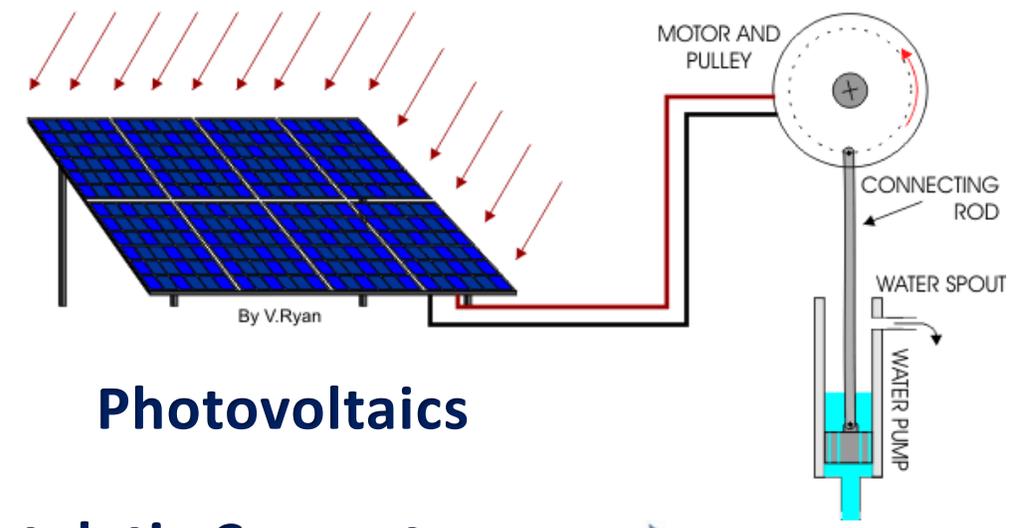
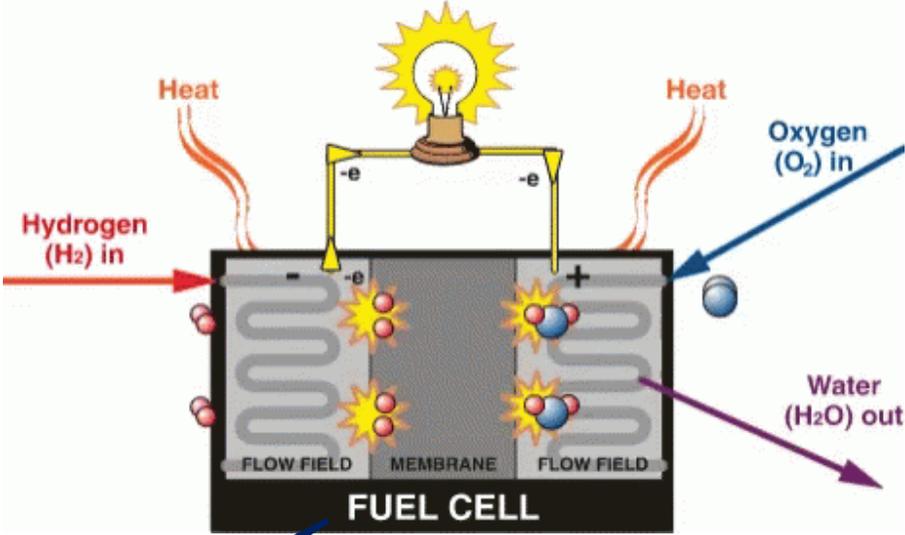
Email: balaram1951@yahoo.com



Outline

- Net-Zero by 2050, what are the metals needed?
- Mineral potential of deep-sea
- Types of minerals available
- Deep-Sea mining technologies
- Analytical techniques for *in-situ* studies during exploration & mining
- Environmental issues
- What we must do?
- Conclusions





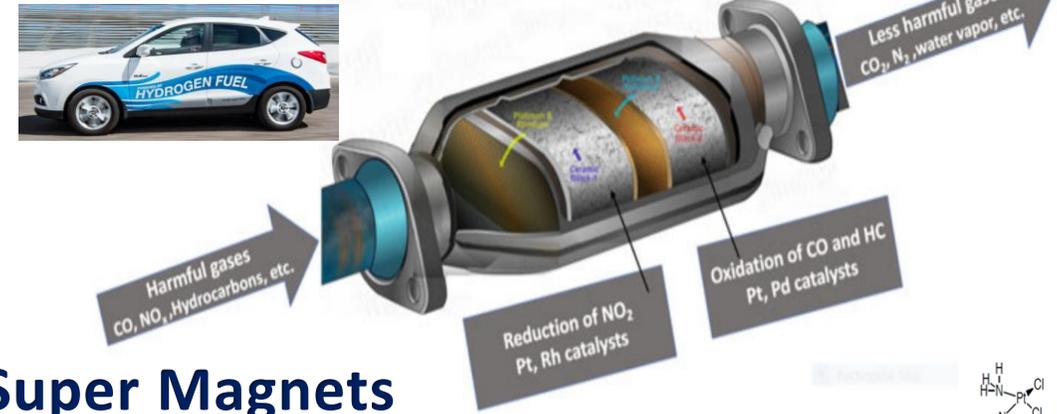
Pt

Co, Li, Ni, Cu, V & In

Lightweight structural alloys



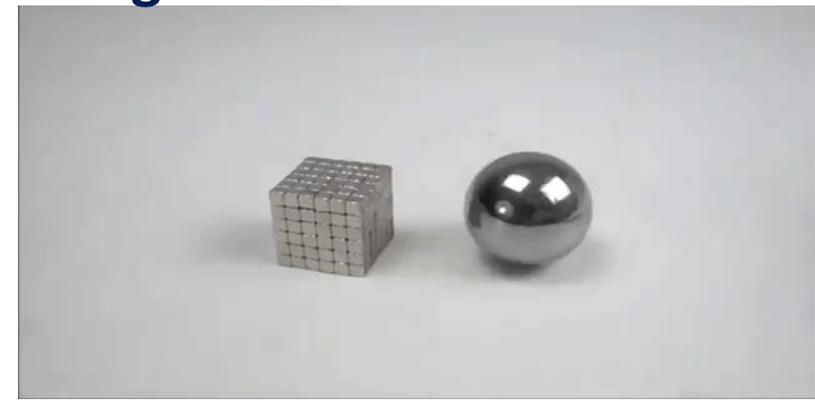
Autocatalytic Converter



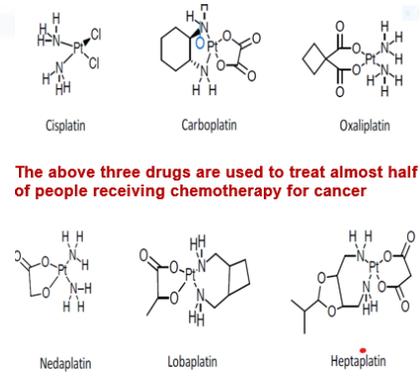
Super Magnets

Nd

NdFeB Magnet
are the most powerful magnets



Cancer Drugs



The above three drugs are used to treat almost half of people receiving chemotherapy for cancer

Structures of FDA and Non-FDA approved platinum drugs used in cancer treatment
Nkem Azu et al 2017



Industrial Applications of REE & Other Critical Metals



Pr
Sm
Tb
Nd
Gd
Dy

Hybrid Vehicles & Magnets

- Computer Hard Drives
- Disk Drive Motors
- Anti-Lock Brakes
- Automotive parts
- Frictionless Bearings
- Magnetic Refrigeration
- Microwave Power Tubes
- Microphones & Speakers
- Communication Systems
- MRI



Y
Eu
Tb

Phosphors

- Display phosphors - CRT, LPD, LCD, LED
- Fluorescent lighting
- Medical imaging
- Lasers
- Fiber Optics



Y
La
Ce

Rechargeable Batteries

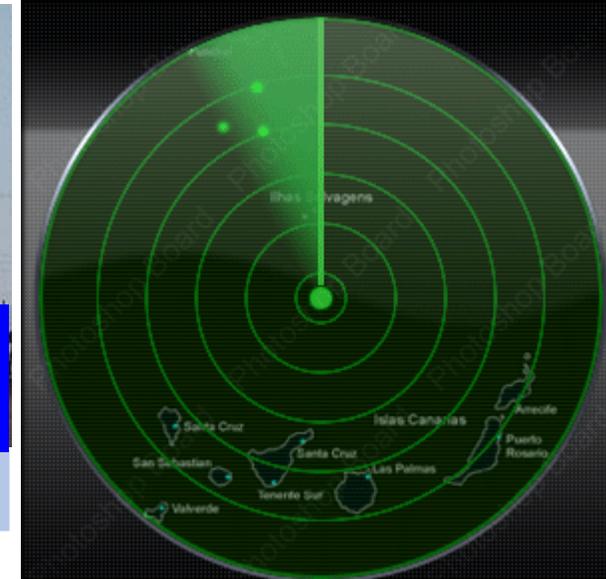
- NiMH Batteries
- Batteries for EVs
- Fuel Cells
- Super Alloys



Pt
Pd

Catalysts

- Petroleum Refining
- Autocatalytic converter
- Fuel Additives
- Chemical Processing



Defence radars



Y
Ce
Eu
Yb



Paints



Electronics

Ni
Ga
Ta



Pr
Nd
Dy

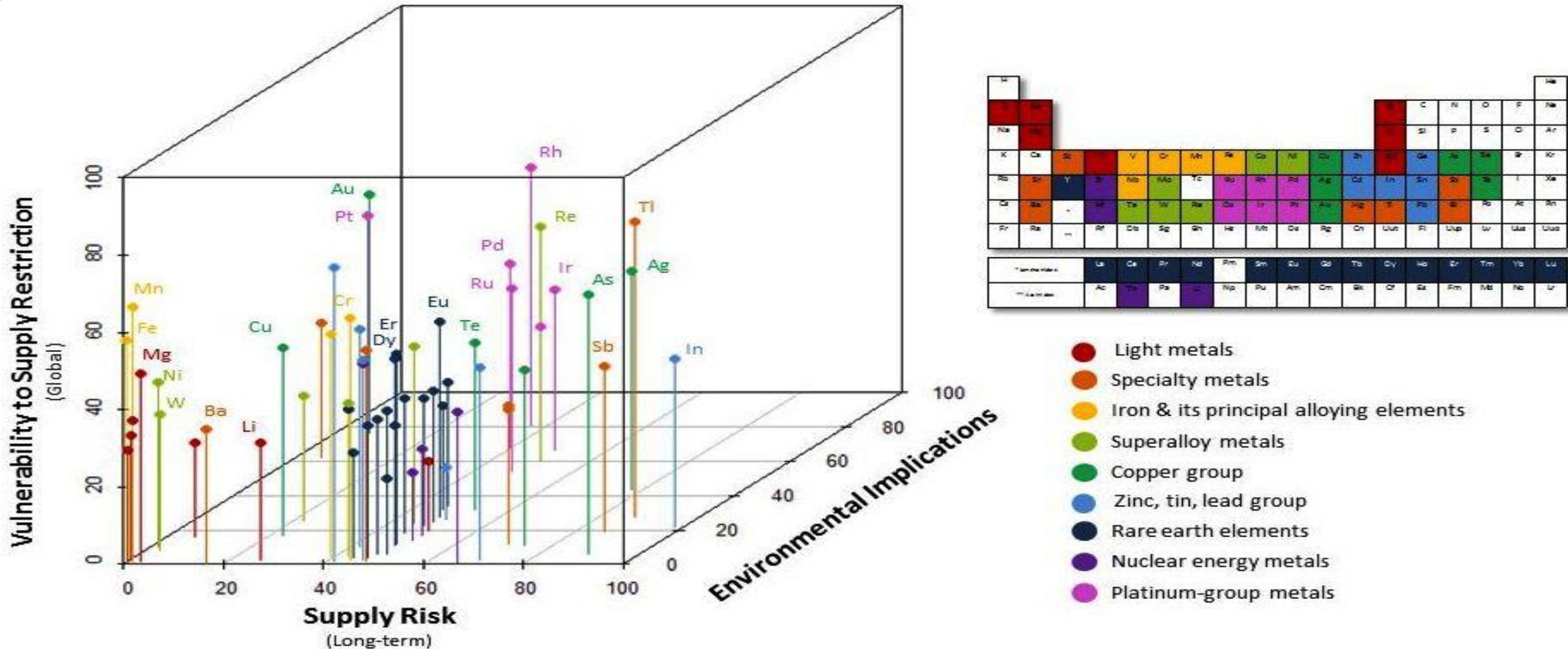
Permanent magnets are used in such demanding applications as electric motors for hybrid cars, wind turbines, and magnetic storage.

in "Sources and sustainable technologies for efficient rare earth elements (REE) extraction" (eds. J. K. Stille, J. M. Sinharoy and Piet N. L. Leppik), IWA Publishing London, 2019 (in press). For some metals like Li, Co, Te, REE which are needed for meeting the target of net-zero by 2050, currently the demand is much more than the supply resulting in driving up prices. For this reason, the mining industry is actively looking towards new frontiers in mining such as deep-sea mining and space mining.



Fluorescent lighting

Metals Used in High-Tech Applications Face Supply Risk



In this three-dimensional graphic, researchers illustrate the "criticality" of all 62 metals based on their scores in three areas: **supply risk**, environmental implications, and **vulnerability to supply restrictions**. Metals with the higher levels of risk appear in the upper back right corner of the box. Graede, 2015

The Earth's Surface is 71% Water Covered

(Dry land: 29%; Pacific Ocean area is greater than the entire Earth's land area)

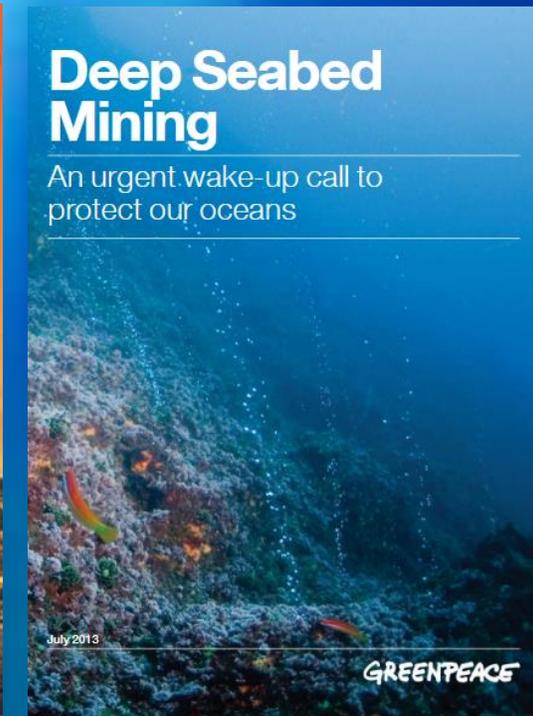
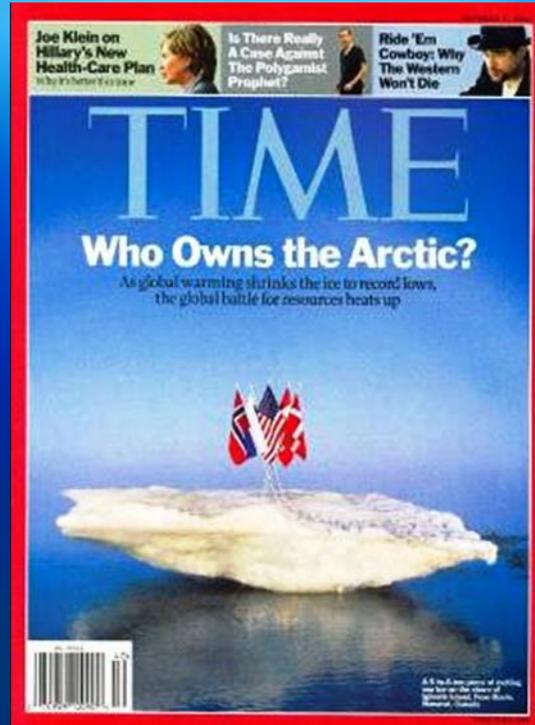
Unfortunately land-based mineral deposits are producing lower grades at higher production costs, and new discoveries are becoming harder to locate.



So, mining of marine minerals would gain momentum in future in order to meet the growing demands of the metals such as REE, Cu, Ni, Al, Mn, Zn, Li and Co, coupled with rising demand for these metals to produce high-tech applications such as smartphones and green technologies such as wind turbines, solar panels and electric storage batteries. .

Ocean Mining

- Ore deposits in the ocean
- Minerals from seawater
- Minerals in ocean sediments
- Hydrothermal deposits
- Manganese-rich nodules
- Ferromanganese Crust
- Oil, gas & gas hydrates
- Mining issues in international waters
- Environmental issues



Who Owns Deep-Ocean Mineral Deposits?

United Nations Convention on the Law of the Sea (UNCLOS; 1982). To adequately represent the interests of developing nations in portioning out mining rights (Common Heratage of Mankind)

Ocean Basins

Are mostly covered by

- **Abyssal Plains**
- **Mid-Oceanic Ridges**

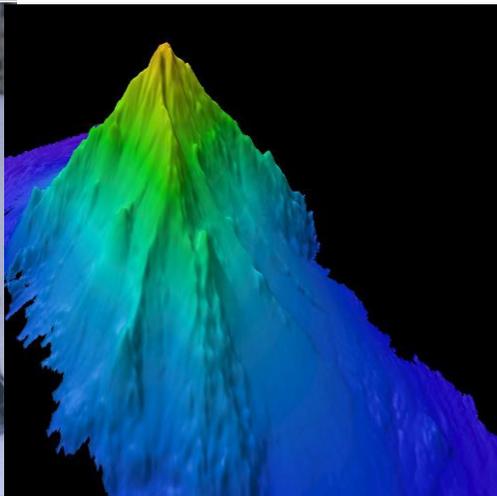


Both these areas are covered by Potential Deposits of

- **Manganese Nodules**
- **Cobalt-rich Crusts**
- **Hydrothermal Sulfides**
- **Marine Mud**
- **Phosphorites**
- **Gas hydrates, crude oil, etc.**

Deep-Sea Mineral Resources

Fields of manganese (polymetallic) nodules on the abyssal plains contain significant quantities of Mn, Fe, Cu, Co & Ni



1

2

3



Cobalt-rich crusts (CRCs) on the flanks of seamounts

Seafloor massive (polymetallic) sulfides around hydrothermal vents



Marine mud

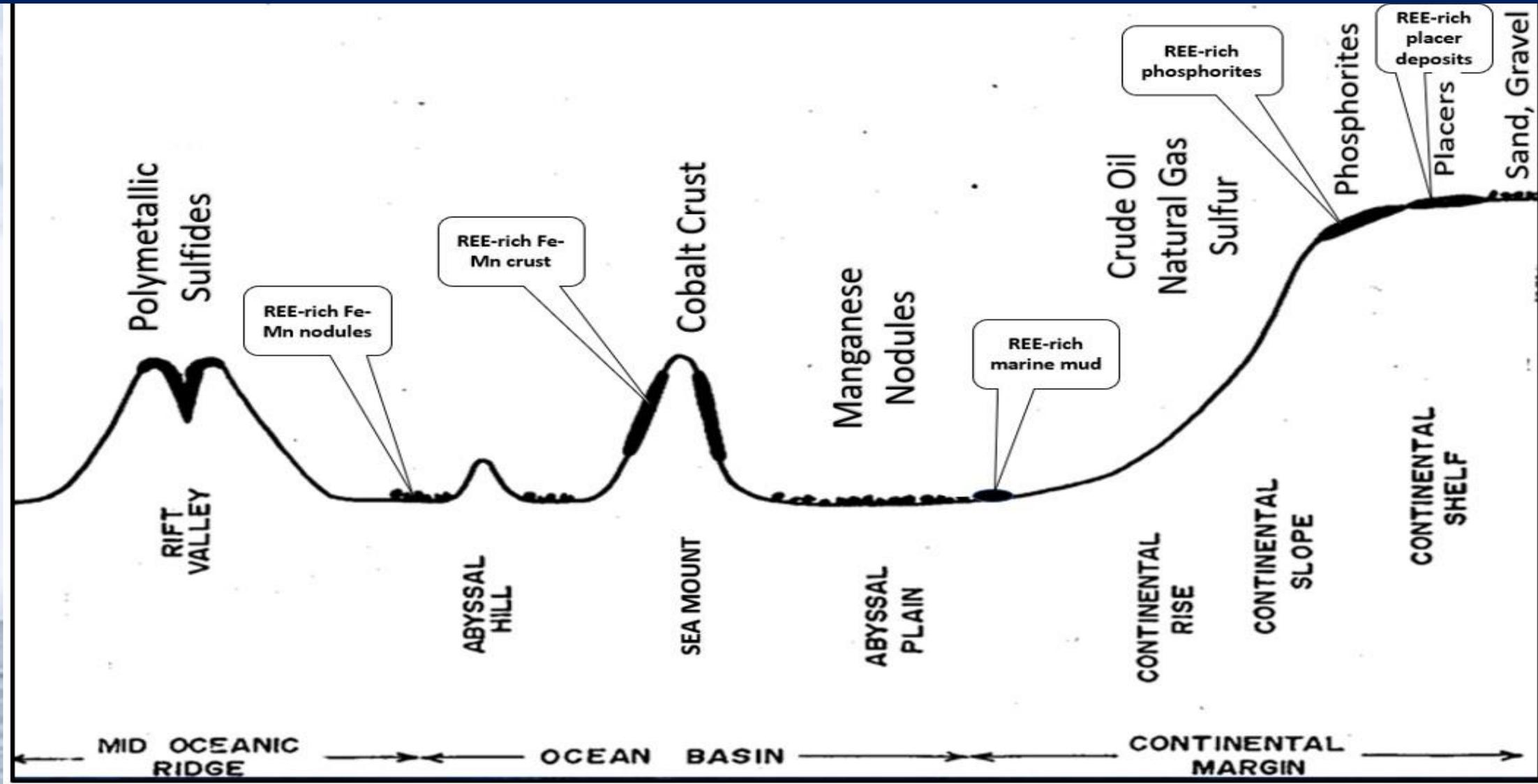
4

5

Phosphorites are often deposited within estuarine environments

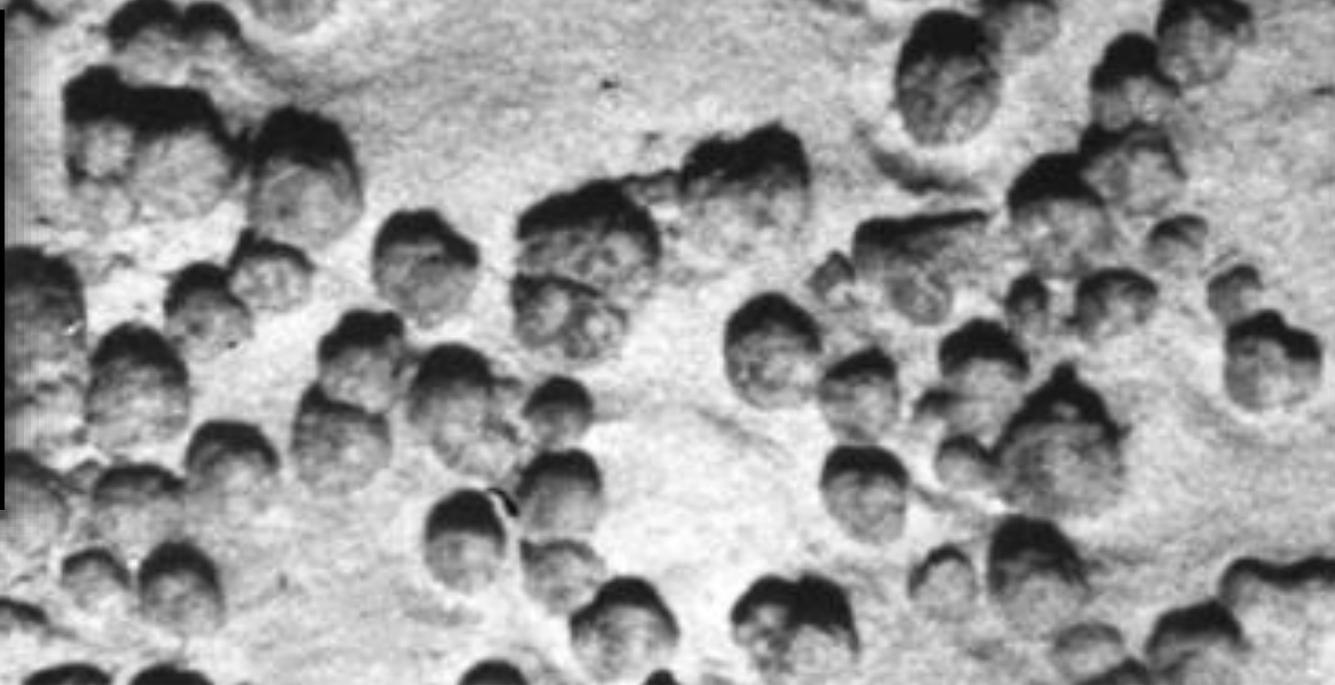
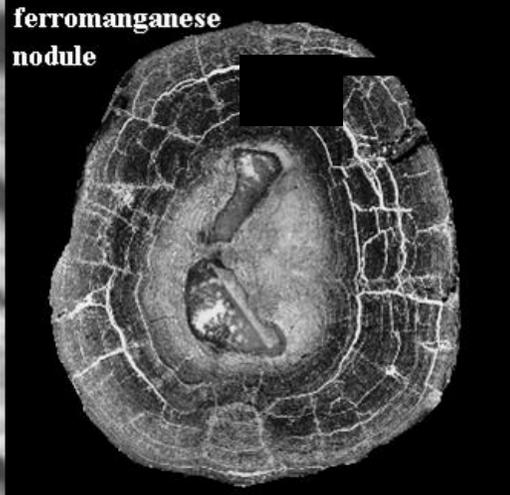


Distribution of Mineral Resources with respect to Tectonic-Geomorphic Settings



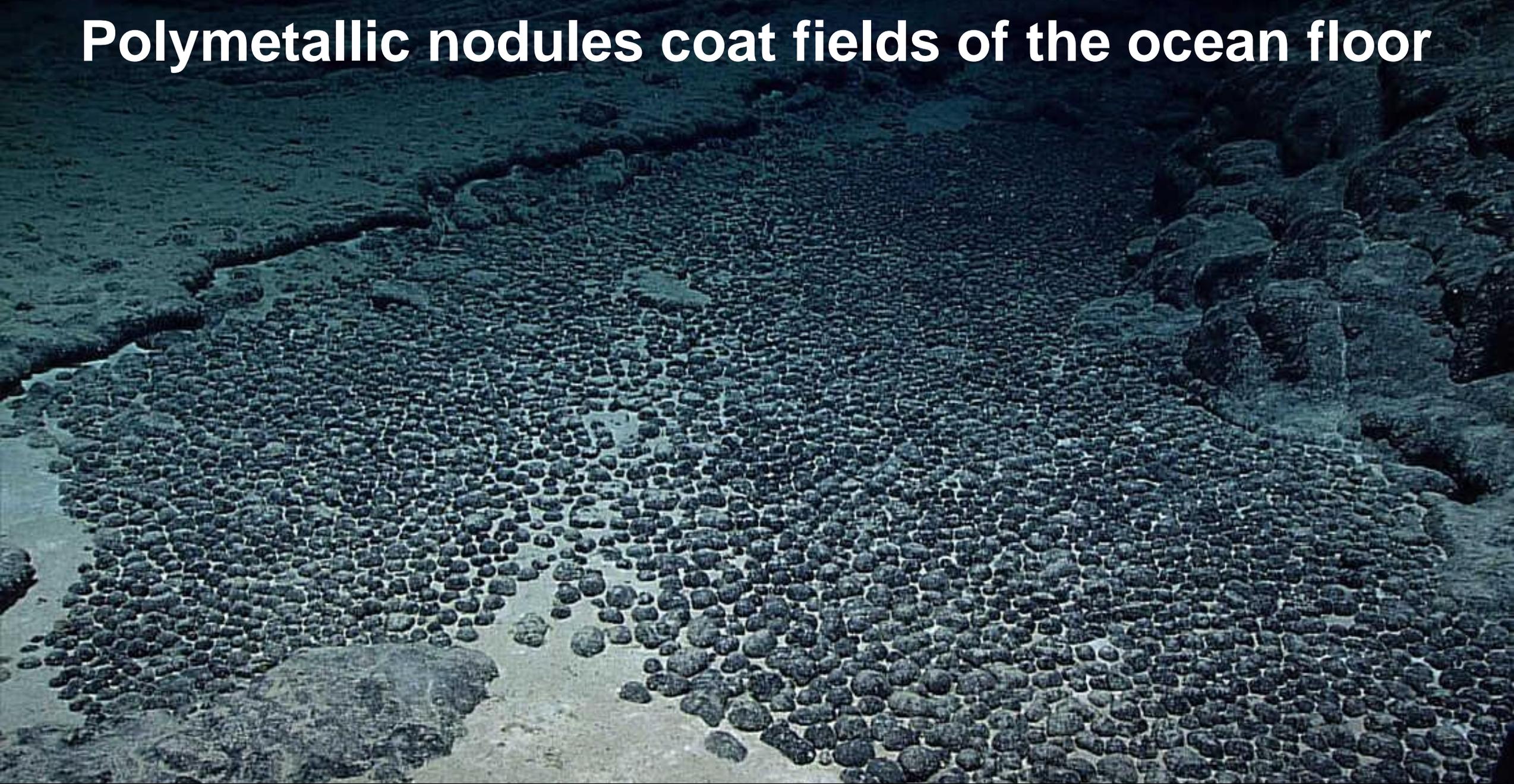
Sediment defined : unconsolidated organic and inorganic particles that accumulate on the ocean floor originate from various sources - weathering and erosion of the continents, volcanic eruptions, biological activity, chemical processes within the oceanic crust and seawater, impacts of extra-terrestrial objects, etc.

Manganese Nodules



- ❖ Polymetallic nodules were first discovered during the 1872-6 expedition of HMS Challenger, accumulate only in areas of low sedimentation rate .
- ❖ Manganese nodules are usually golf-ball to baseball size and grow very slowly like ferromanganese crusts (growth rates $\sim 1-3$ mm/million years).
- ❖ They acquire their metals from sea water and also from the pore-waters of the sediment on which they sit.

Polymetallic nodules coat fields of the ocean floor



Polymetallic nodules are mainly composed of phyllosulfates such as vernadite, birnessite, buserite, and todorokite. They are enriched in Cu, Ni, Co, Zn, Mo, REE, and other metals

Polymetallic Nodules – Depth & Accretion Rates

- Form on the sediment-covered abyssal plains (4,500 – 6,000 m water depths). Accretion rates can vary from about 1-10 mm/Ma. Form by precipitation from cold ambient bottom water and from sediment pore fluids. They are small balls, dark-brown colored and lightly flattened, 5 to 10 centimeters in diameter, which lay on the seabed at 4,000 to 6,000 meters deep and contain various metals including Ni, Cu, Co and Mn.
- The grade and abundance of nodules determine the amount of metals contained in a given area in the general range 1.1-1.6% Ni, 0.9-1.2% Cu, 0.2-0.3% Co and 25-30% Mn with ranges between 5.0-15 kg per square meter

Nath, Balam, Sudhakar and Plugger (1992) *Marine Chem.*, 38:185-208.

Nath, Roelandts, Plugger, and Balam (1994) *Marine Geology*, 120, 385-400



Growth rates are more in Pacific Ocean (up to 29 mm/Ma) due to extensive tectonic plate movement and submarine volcanic activity



**Polymetallic
nodules
support life in
the deep sea
ecosystem by
providing a
critical
habitat for an
array of
unique and
largely
understudied
species**

Stratmann et al 2021, Scientific Reports

Development of Polymetallic Nodule CRM 2388 from Indian Ocean

**NATIONAL METALLURGICAL LABORATORY
JAMSHEDPUR**

Certificate of Analyses

Standard Sample of Ocean Bed— Polymetallic Nodules No. 2388

The nodules were received from National Institute of Oceanography, Goa. These were crushed and powdered in the National Metallurgical Laboratory. The final sample was tested for homogeneity before analysis. Each sample was analysed simultaneously for moisture and other certified constituents. The following analytical results were then calculated on *dry basis*.

ANALYSES

Analysis by*	SiO ₂	Fe	Mn	Ni	Co	Cu
1.	16.37	14.45	21.80	0.70	0.15	0.46
2.	15.44	-	20.92	0.66	0.13	0.47
3.	16.16	14.70	20.98	0.75	0.16	-
4.	16.45	-	21.24	0.70	0.13	0.47
5.	15.79	15.90	21.43	0.64	0.12	0.51
6.	16.79	15.09	22.42	0.72	0.15	0.48
7.	15.77	14.28	20.36	0.70	0.15	0.49
8.	-	14.89	-	0.71	0.13	-
9.	15.78	15.16	20.59	-	0.13	0.50
10.	-	15.01	21.78	0.77	-	0.53
Average	16.07	14.94	21.28	0.71	0.14	0.49

***List of organisations participated in Analysis :**

1. National Metallurgical Laboratory, Jamshedpur
2. Hindustan Zinc Limited, Udaipur
3. Regional Research Laboratory, Bhubaneswar
4. Geological Survey of India, Calcutta
5. Geological Survey of India, Calcutta
6. Bhabha Atomic Research Centre, Bombay
7. Hindustan Copper Limited, Khetri
8. Hindustan Copper Limited, Ghatsila
9. Indian Bureau of Mines, Nagpur
10. National Geophysical Research Institute, Hyderabad

Sd/- L. P. Pandey
Head, Analytical Chemistry &
Standard Samples Division
National Metallurgical Laboratory
Jamshedpur-7



Sd/- V. A. Altekar
Director,
National Metallurgical Laboratory,
Jamshedpur-7



Balaram, Anjaiah & Reddy(1995) Analyst ,120,1401-1406.
Balaram (1999) Marine Geosour & Geotechnol, 17: 17-26.



ISSN 0005-2654

PAPER
Huanan Ying, Chengshu Shen, Xiaohu Cai et al.
Non-invasive and prospective diagnosis of coronary heart disease
with urine using surface-enhanced Raman spectroscopy

MARINE GEORESOURCES & GEOTECHNOLOGY

Volume 39, 2021

John Wiltshire
Editor-in-ChiefIncluded in this print edition:
Number 12

Determination of Precious Metal Concentrations in a Polymetallic Nodule Reference Sample from the Indian Ocean by ICP-MS

V. BALARAM

National Geophysical Research Institute
Hyderabad, India

A polymetallic nodule reference sample (No. 2388) collected from the Indian Ocean, and seven other samples, two from the United States Geological Survey, USA (Nod-A-1 and Nod-P-1), three from Russia (OOPE 601, OOPE 602, and OOPE 603), and two from China (GSPN-2 and GSPN-3), collected from different locations, are available for calibration purposes and as control samples in the analytical programs for polymetallic nodules and associated sediments to ensure accurate measurements. They are not certified for precious metal concentrations, however, and the data available are very scanty. An attempt has been made to provide working values for platinum, palladium, gold, and silver and indicative values for osmium, iridium, and ruthenium in these eight ferromanganese nodule reference samples, using inductively coupled plasma mass spectrometry (ICP-MS). To assess the accuracy of the method, certified reference materials, WPR-1, WMS-1, WMG-1, and WGB-1 Canadian Certified Materials Project (CCRMP, Canada) were analyzed, and the data obtained were compared with the certified values. The estimate of analytical reproducibility was found to be better than $\pm 15\%$ RSD for most elements with comparable accuracy. The data presented for this set of manganese nodule reference samples may be useful in geochemical studies of manganese nodules and associated sediments.

Keywords polymetallic nodule reference sample No. 2388, ICP-MS, precious metals, internal standard, molecular ion interferences, detection limits

The precious metals include silver (Ag), gold (Au), and the platinum group elements (PGE), platinum (Pt), palladium (Pd), rhodium (Rh), iridium (Ir), ruthenium (Ru), and osmium (Os). The precious metals are found together in the Periodic Table and are also found together in nature, with Pt and Pd predominating in all known deposits (Kallmann, 1984). These elements are generally present at exceedingly low concentrations (ng/g levels) on the surface of the earth, in both continents and oceans. Much of what is known about their geochemistry is derived from detailed studies in ore formation and mineral exploration. Their siderophilic and chalcophilic character and diverse redox chemistries give this group of elements considerable potential for blending into magmatic, metamorphic, and aqueous processes. For example, the geochemical behavior of Au in marine sediments

Accepted 17 November 1998.

The author is grateful to Dr. H. K. Gupta, Director, NGRI, for his kind permission to publish this article. Thanks are due to Dr. S. M. Naqvi, who constantly supported this work. Dr. S. H. Jaffri is thanked for helpful suggestions on the manuscript.

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Comparative Study on the Trace and Rare Earth Element Analysis of an Indian Polymetallic Nodule Reference Sample by Inductively Coupled Plasma Atomic Emission Spectrometry and Inductively Coupled Plasma Mass Spectrometry*

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M. R. P. Reddy

Centre for Materials for Electronic Technology, Hyderabad-500 762, India

The results of the semi-quantitative and quantitative characterization of an Indian polymetallic nodule reference sample (No. 2388) using ICP-AES and ICP-MS methods are presented. Acid dissolution using HF, HNO₃, HClO₄ and H₂O₂ in a PTFE beaker was adopted for sample dissolution. The calibration was performed with synthetic reference solutions that contained the reagents used for sample dissolution. The data thus obtained were corrected using the data obtained on United States Geological Survey (USGS) polymetallic nodule reference samples (NOD-A-1 and NOD-P-1) to minimize matrix and other effects. Over 30 trace elements were determined using both techniques. The accuracy of the determination was assessed by comparing the values obtained with the certified values for three RIAP reference samples. Indicative values were obtained on sample No. 2388 for about 60 elements by semi-quantitative analysis using ICP-MS.

Keywords: Inductively coupled plasma mass spectrometry; inductively coupled plasma atomic emission spectrometry; polymetallic nodule reference sample; trace element; rare earth element

Introduction

Data on rare earth elements (REEs) and trace elements in manganese nodules contribute to the understanding of the chemical and mineralogical compositions and the processes that control their genesis.¹ REE concentrations, in particular in manganese nodules and the associated phases, have helped in constraining models for REE cycling in the ocean environment.² These studies require sensitive, precise, accurate and rapid determinations of several trace elements in a large number of samples. The analytical procedures adopted in most instrumental methods require the use of appropriate reference samples which help to minimize the analytical uncertainties such as matrix effects and inter-element interferences. Two well certified manganese nodule reference samples (NOD-A-1 and NOD-P-1) have been available from the United States Geological Survey (USGS) since 1980.³ Three more manganese nodule reference samples (OOPE 601, OOPE 602 and OOPE 603) have been made available more recently by the Research Institute of Applied Physics

(RIAP) jointly with the Institute of Oceanology of the USSR Academy of Sciences.⁴ These three samples also have reasonably good major, minor, trace and REE data.⁵ Recently Roelands⁶ supplemented the trace element data by providing some new REE data on all these five reference samples.

In India, an ocean bed polymetallic nodule reference sample (No. 2388) from the Indian Ocean was prepared by the National Metallurgical Laboratory, Jamshedpur, jointly with the National Institute of Oceanography, Goa, in 1981. Subsequently, a collaborative investigation of the sample was carried out by ten National Research Laboratories including NGRI, details of which were given by Pandey.⁷ 'Certified values' are assigned for only six of the major and minor elements, namely Si, Fe, Mn, Ni, Co and Cu (Table 1), most crucial from the exploration point of view, and data are not available on several other geochemically significant trace elements such as REEs, U and Th.

In this work, we attempted to provide working values on several geochemically significant trace elements in this reference sample by using two of the most popular multi-element analytical techniques, inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). Indicative values were obtained for several other trace elements using semi-quantitative analysis by ICP-MS.

Experimental

Reagents, Calibration Standards and Internal Standard for ICP-MS

Electronic and analytical-reagent grade acids and high-purity doubly distilled water were used throughout. Three sets of

Table 1 Certified data on sample No. 2388 for some major and minor elements*

Component	Concentration (% m/m)*	s_x (%)
SiO ₂	16.07	2.80
Fe	14.94	3.28
Mn	21.28	3.05
Ni	0.71	5.63
Co	0.14	7.14
Cu	0.49	4.08

* Average of 8 or 9 determinations.



Rare earth element geochemistry of ferromanganese deposits from the Indian Ocean

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^cE401, Sea-Use Programme, London School of Economics, Houghton Street, London WC2A 2AE, UK

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115 Citations

ABSTRACT

Nagender Nath, B., Balaram, V., Sudhakar, M. and Plüger, W.L., 1992. Rare earth element geochemistry of ferromanganese deposits from the Indian Ocean. *Mar. Chem.*, 38: 185–208.

Fourteen manganese nodules and three ferromanganese crusts from the Indian Ocean were analysed for major and minor elements and the 14 naturally occurring rare earth elements (REE). The REE were analysed by inductively coupled plasma–mass spectroscopy (ICP–MS). The samples were selected systematically from the Western Indian Ocean and the Central Indian Basin, to represent a seamount top, slope, an abyssal hill, siliceous sediment affected by terrigenous influx, a highly productive siliceous environment, red clay and carbonate sedimentary domains.

Although REE zonation is observed in one oriented nodule, with relative enrichment in the top, evidence of top–bottom fractionation appears to have been obliterated as a result of the nodules being turned over. Correlations between Ca, P, Fe and REE in nodules suggest that the REE primarily reside in the iron oxyhydroxide and phosphatic phases. An authigenic origin is attributed to these elements. The nodules and crusts from the Western Indian Ocean and the shallower depths of the Central Indian Basin are δ -MnO₂ rich, and are characterized by high concentrations of REE and higher positive cerium anomalies. These two areas are in the realm of cold Antarctic Bottom Water (AABW), which may enhance the oxidative scavenging of Ce by particles and its subsequent incorporation into manganese nodules. All the nodules and crusts show Gd–Tb anomalies. A diagenetic nodule with a palagonitic, smectite-rich nucleus exhibits an unusual heavy REE (HREE) enrichment with no significant Ce anomaly.

INTRODUCTION

Numerous studies of the chemical and mineralogical compositions of ferromanganese nodules have documented large variations both regionally and

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Marine Geology 120 (1994) 385–400

MARINE GEOLOGY

INTERNATIONAL JOURNAL OF MARINE
GEOLOGY, GEOCHEMISTRY AND GEOPHYSICS

Cerium anomaly variations in ferromanganese nodules and crusts from the Indian Ocean

B. Nagender Nath^a, I. Roelandts^b, M. Sudhakar^a, W.L. Plüger^c, V. Balaram^d

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^d Geochemistry Division, National Geophysical Research Institute, Uppal Road, Hyderabad 500007, India

(Received 7 September 1993; revision accepted 2 May 1994)

Abstract

Fifty analyses of rare earth elements as well as mineralogical studies have been carried out on a suite of manganese nodules and crusts from the Central Indian Basin and the Western Indian Ocean. The aim was to identify the processes controlling the REE patterns of the phases hosting the REE in the manganese nodules, with an emphasis on an understanding of the Ce anomaly. This has involved separating the encrusting layers and nuclei physically as well as Fe–Mn oxides from the aluminosilicate phase chemically (using a 2 M HCl leach) prior to analysis.

The presence of nodule nuclei seems to have little influence (mostly <5% to a maximum of 30%) on the overall magnitude of the Ce anomalies in these nodules. The ratios of concentrations of elements in the acid leachates and the corresponding bulk values yield flat REE patterns indicating that the aluminosilicate phase contributes very little to the Ce anomalies. Interelement relations indicate that the Ce anomalies are largely controlled by the amorphous mineral phase FeOOH.xH₂O. The relationship of Fe, Ce anomaly and δ -MnO₂ further suggests that Ce is chemisorbed onto iron oxyhydroxides which are epitaxially intergrown with δ -MnO₂.

The regional distribution of the Ce anomaly values appears to depend on many of the factors responsible for the uptake of other minor metals in nodules and crusts.

1. Introduction

The factors controlling the distribution of the rare earth elements (REE) in the marine environment is becoming increasingly well known. The preferential deposition of Ce from seawater in the tetravalent state leads to Ce anomalies in the marine environment, negative Ce anomalies in seawater (Goldberg, 1961) and positive anomalies in many manganese nodules (e.g. Piper, 1974a). Positive Ce anomalies in manganese nodules have been widely reported from all the oceans (e.g. Addy, 1979; Elderfield et al., 1981; Tlig, 1982;

Nath et al., 1992), as well as some negative anomalies. Although the negative anomalies were initially thought to be the result of hydrothermal activity (Elderfield and Greaves, 1981), they have now been reported in nodules far removed from the known hydrothermal sites (Calvert et al., 1987; Glasby et al., 1987; Kundendorf et al., 1987; Piper, 1988).

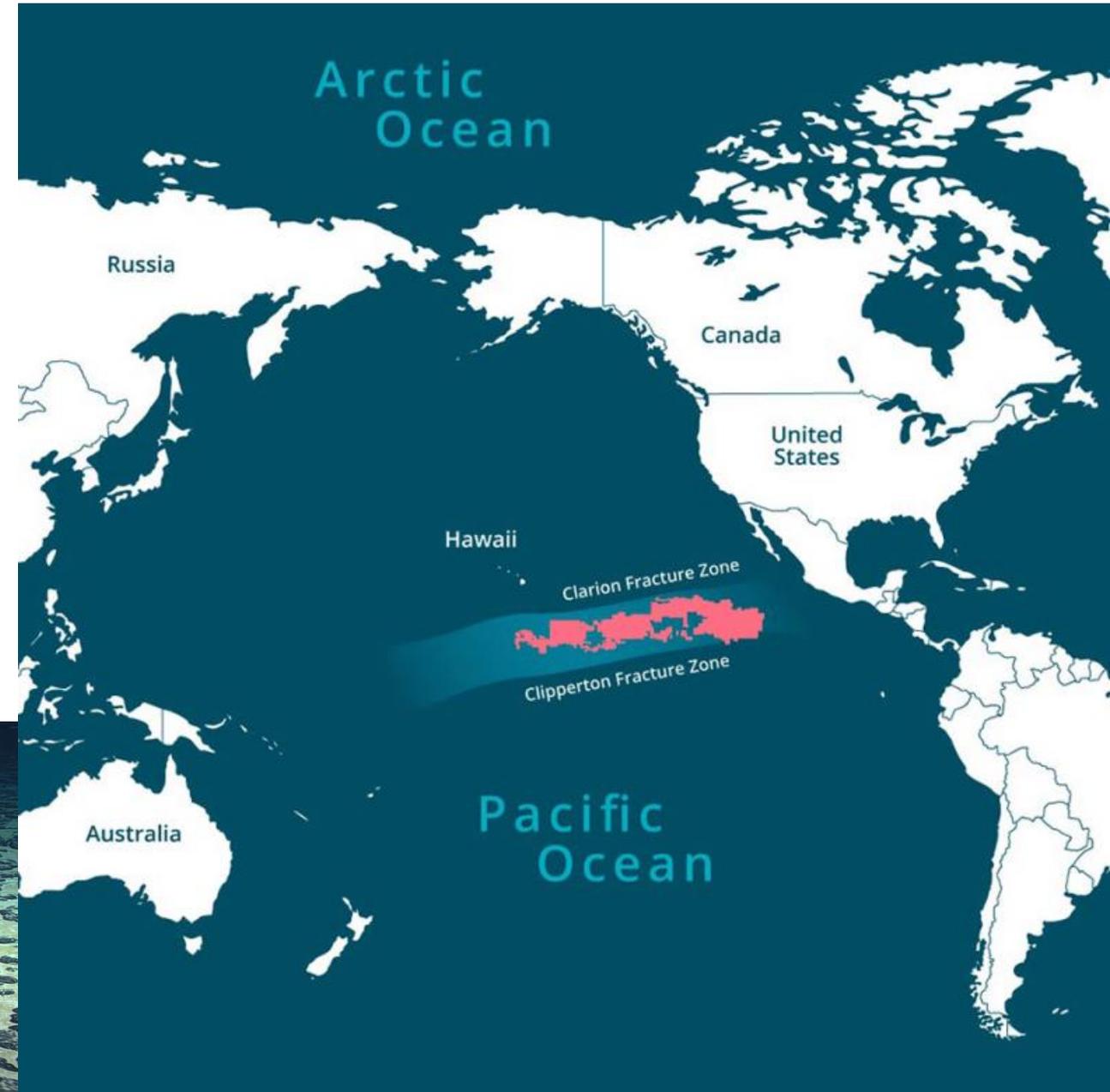
In this paper we wish to concentrate on the following problems related to the Indian Ocean ferromanganese deposits:

(1) What are the controlling factors of Ce anomaly variations in manganese nodules, (2)

The CCZ hosts trillions of mineral-rich nodules

- ❑ Although the nodules appear in various places around the deep ocean, the primary target of potential mining is the Pacific's Clarion-Clipperton Zone (CCZ), a 4.5 million square kilometers stretch of seafloor between Hawaii and Mexico that extends 4,000–5,500 meters deep.
- ❑ The two studied regions of APEI-6 have a variable morphology, typical of the CCZ, with hills, plains and occasional seamounts.
- ❑ By 2020, 16 international companies have contracts to explore the CCZ for nodules, and two companies have permits to do so in the Indian Ocean and the West Pacific Ocean.
- ❑ CCZ one of the most intensely studied regions of the deep ocean

Jones et al. 2021



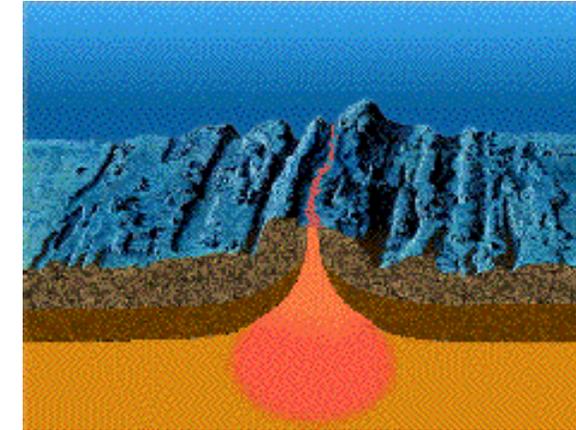
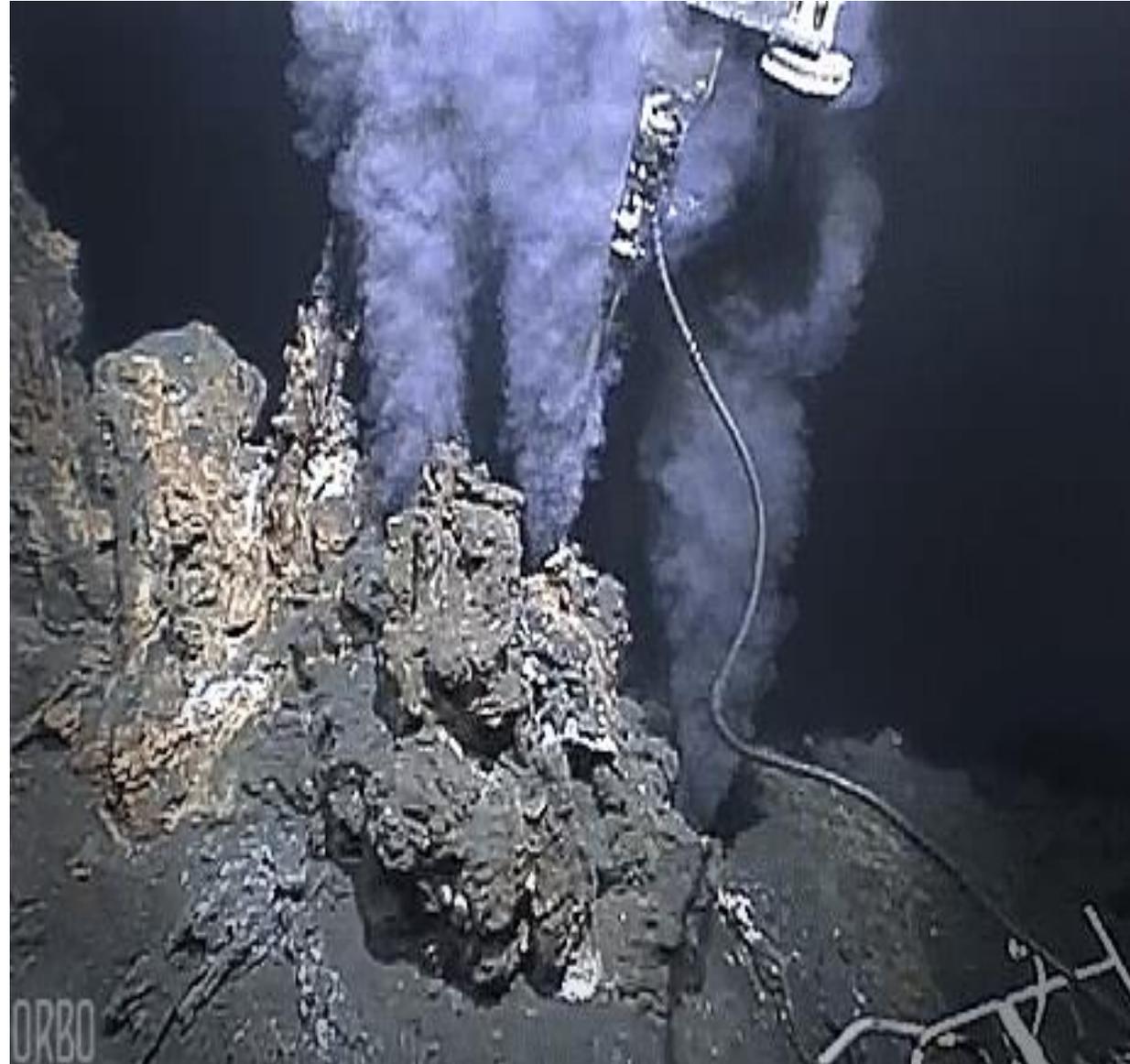
Polymetallic Sulphides

- Seafloor massive sulfide ore deposits form at hydrothermal vents when seawater penetrates the ocean's crust, chemically modified through, heat, interaction with crustal rocks, and, sometimes by input of magmatic fluids. A wide variety of minerals form through hydrothermal activity, but seafloor massive sulfides are formed from reduced sulfur and may be enriched in Cu, Zn, Fe, Au and Ag.

- Thus, the modern ocean floor is an exceptional **Natural Laboratory** for studying processes and environments responsible for the formation of ancient massive Zn, Cu, Fe, Ag, and Au sulfide ores that are now being mined on land.

- Hydrothermal vents were first discovered in 1977 while exploring an oceanic spreading ridge near the Galapagos Islands. These vents spaced along the spreading ridges every 3 to 20 kilometers.

- As of 2009 there were approximately 500 known active submarine hydrothermal vent fields, with about half visually observed at the seafloor and the other half suspected from water column indicators and/or seafloor deposits.



A close-up showing a mid-ocean ridge topography with magma rising from a chamber below, forming new oceanic plate which spreads away from ridge -

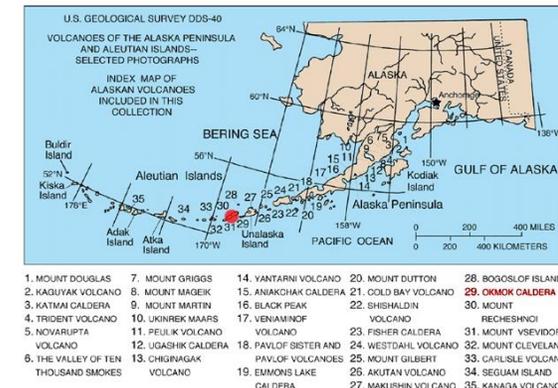
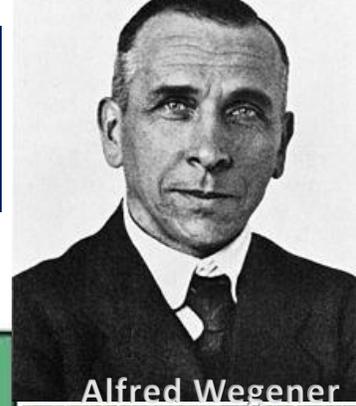


Plate Tectonic Boundaries

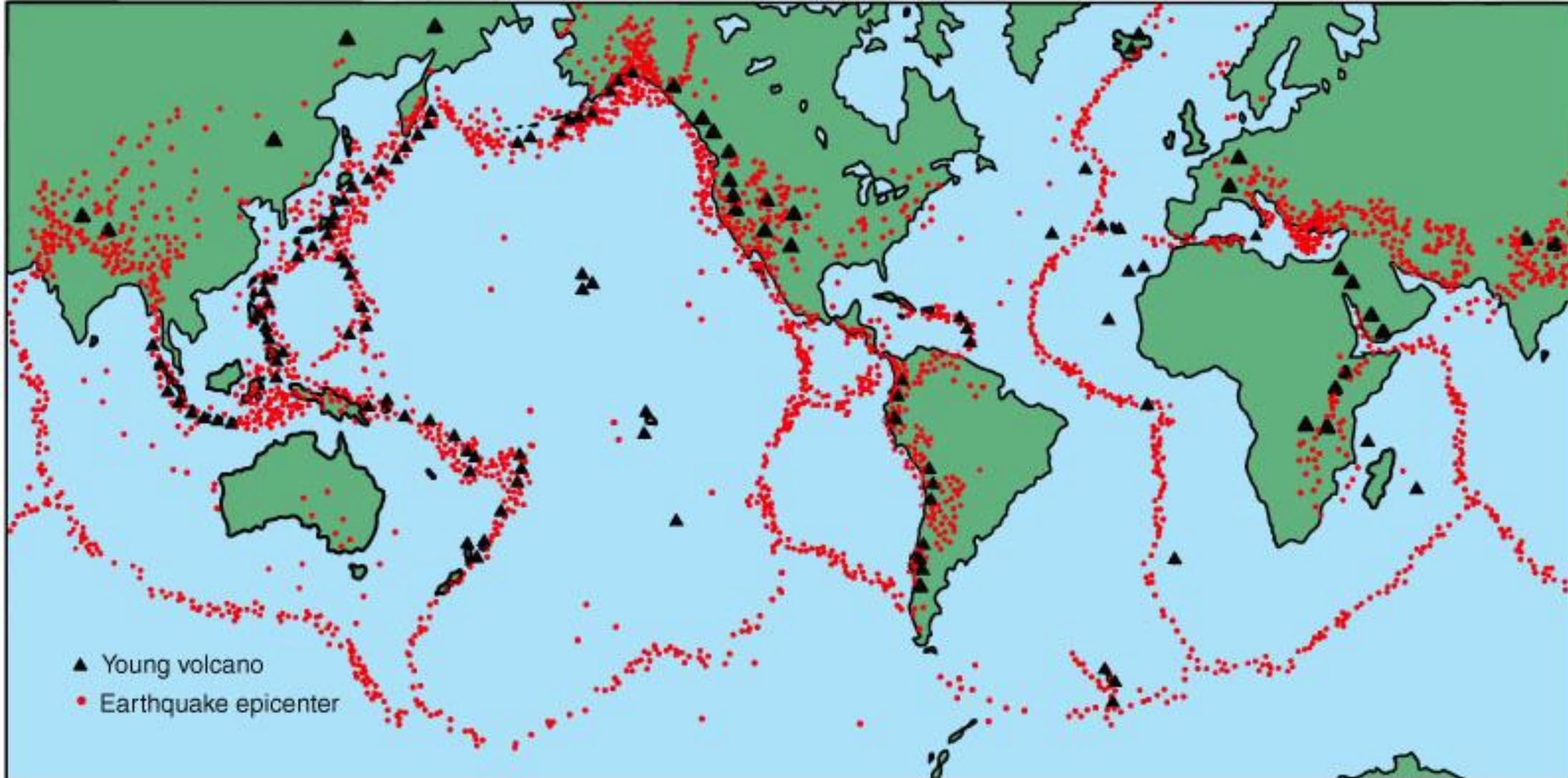
The heat from radioactive processes within the planet's interior along with the pressure causes the plates to move, sometimes toward and sometimes away from each other.



Alfred Wegener

One of the top 10 Scientific Discoveries

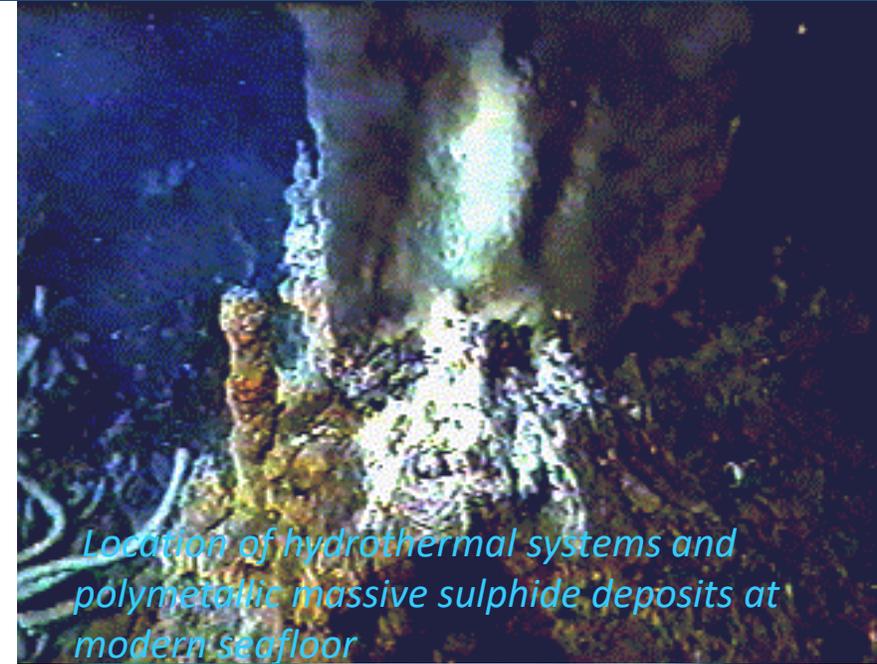
Earthquakes occur along fault lines, cracks in Earth's crust where tectonic plates meet. They occur where plates are subducting, spreading, slipping, or colliding. As the plates grind together, they get stuck and pressure builds up. Finally, the pressure between the plates is so great that they break loose. **Plate tectonics also plays a major role in creating ore deposits. There is a relationship between magmatic and metamorphic activities and the formation of ore deposits.** These type of activities commonly occur along plate boundaries



Taiwan, 2011

Polymetallic Sulphide Deposits – Depth & Size

- Polymetallic massive sulphide deposits are found at water depths up to 3,700 m in a variety of tectonic settings at the modern seafloor including mid-ocean ridges, back-arc rifts, and seamounts
- Polymetallic seafloor sulphide deposits can reach a considerable size (**up to 100 million tonnes**) and often carry high concentrations of Cu (chalcopyrite), Zn (sphalerite), and Pb (galena) in addition to Au and Ag.
- The minerals are dissolved in fluids at temperatures as high as 380°C flowing at 1-5 m/sec, pressure of 350 bar
- Black smokers - chimneys formed from deposits of iron sulfide (bathyal zone - between 200 and 2,000 m below the surface)
White Smokers- Fore arc / Back arc environment (white smokers are chimneys formed from deposits of Ba, Ca, and Si, which are white).



Location of hydrothermal systems and polymetallic massive sulphide deposits at modern seafloor



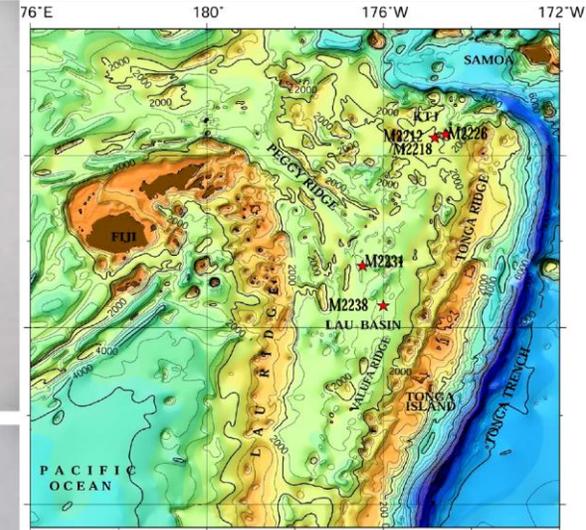
Geochemical Characteristics of Hydrothermal Deposits at Kings Triple Junction, northern Lau back-arc Basin, SW Pacific

- The back-arc and marginal basins in south-west Pacific Ocean are well known for sea floor hydrothermal activity and associated massive sulfide deposits.
- A study was undertaken to understand the mineralogical and geochemical characteristics of three types of samples (*pedestal slab, peripheral chimney and Fe-Mn precipitate*) collected from northern part of Lau basin, SW Pacific.
- The pedestal slab displays significant enrichment of chalcopyrite, pyrite, and barite with minor presence of sphalerite, wurtzite and manganosite showing high concentration of Cu (av.11.73%) and Fe (av.9.74%) followed by Zn (av.3.56%) and Mn (av.0.01%).
- The chemical composition of the chimney sample has major contribution from Zn (23-34%), followed by Fe (1.2-4.3%, Cu (1.0-1.5%) and Mn (0.03-0.06%), with higher concentrations of **Au (1.6 – 5.7 µg/g)** and **Ag 12.2 – 35.4 µg/g)**

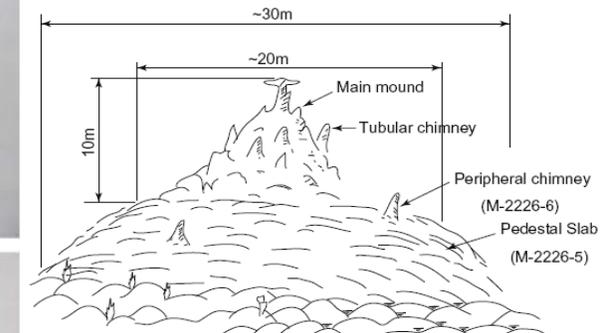
Paropakari, Balaram and others (2010) J. Asian Earth Sci., 38: 121-130.



Hydrothermal sulfides



Hydrothermal Mound (10-20 m height)



Signatures of rare-earth elements in banded corals of
Kalpeni atoll—Lakshadweep archipelago in response to
monsoonal variationsS A S Naqvi¹ & B Nagender Nath²Chemical Oceanography Division¹, Geological Oceanography Division², National Institute of Oceanography,
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Concentrations of rare-earth elements (REE) have been determined in seasonal bands of *Porites* species collected from the Lakshadweep lagoon. Total REE (Σ REE) are very low (< 3 ppm) in these corals. Seasonal variations in REE appear to have occurred with Σ REE and the light rare-earths (LREE) enriched in the high density (representing monsoon season) bands. In contrast, the heavy rare-earths (HREE) are enriched in the low density bands. LREE enrichment in the high density bands is attributed to their higher availability during the rainy season due to the increased weathering of the continental sources. Elemental ratios and SEM photographs reveal the increased incorporation of terrigenous material into the growth bands during the monsoon season.

The growth bands of scleractinian corals were found to record the variations in environmental conditions in which they grow^{1–7}. Trace metal concentrations in skeletal aragonite of corals have been suggested to reflect the concentrations in surface seawater (ref. 8 and references therein). Since the corals consist of dark and light bands of different densities and an adjacent pair of low and high density bands represent one year's growth⁹, studies on trace metal variations in the growth bands shall yield valuable information on the changing chemistry of surface ocean waters. Studies on corals around India and in the Indian Ocean assume further significance since they tend to record the intensity of the monsoons. Monsoons govern the sea-surface temperature and thus the annual density banding of the corals¹⁰.

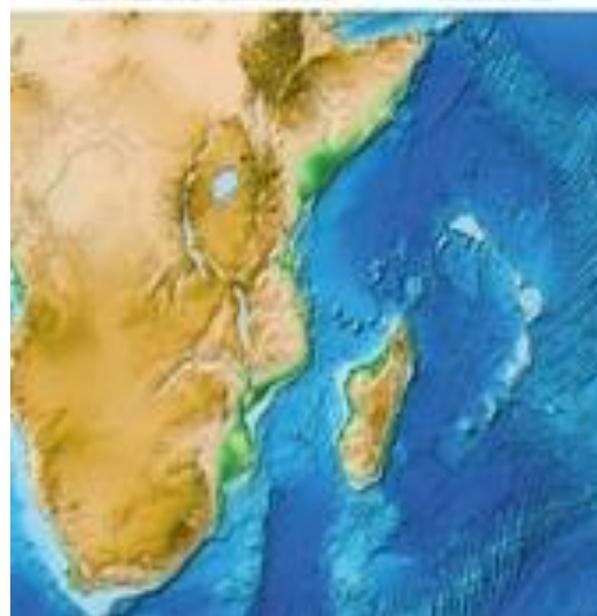
REE in sedimentary phases are increasingly being used as indicators of several geological and oceanographic processes, the paleo-redox conditions, depositional environment, and also to assess the crustal sources (ref. 11 and references therein). While myriad data are available on REE in marine sediments especially carbonates and non-carbonates¹², very few data are reported in corals^{13–16} and data from the Indian Ocean region are especially scarce. In addition, earlier studies were carried out on bulk coral samples. No attempt has been made so far, to study the variation in REE in seasonal bands. The present study aims to understand the incorporation

of REE in corals in monsoon and non-monsoon seasons. Deciphering the location of REE in various phases of corals has also been attempted to explore the possibility of utilising this data for paleoclimatic inferences. Diagenetic processes may alter the REE composition of sedimentary phases^{17,18} but may not be affecting the corals since these are of very recent origin. This paper reports the rare-earth elements (REE) variation in a coral *Porites* sp. collected from the Kalpeni Island, Lakshadweep region.

Materials and Methods

Samples of hard coral *Porites* sp. were collected from the lagoons of the Kalpeni atoll (lat. 10°05'N, long. 73°39'E) at a depth of 1.5 m. Slices of coral were taken along the growth axis using a dental drill, and X-radiography was carried out using the industrial X-ray films. Sixteen subsamples were separated representing the seasonal bands (high density and low density). The age of the growth bands was determined by assuming the sample collection time as the first year (1985 in this case)¹⁹.

The analyses were carried out using inductively coupled plasma mass spectrometer (ICP-MS). Powdered sample (0.1 g), of each seasonal band, was treated with 10 ml of acid mixture (7 ml, 48% HF and 3 ml conc. HNO₃) in a teflon beaker and digested through repeated heating on a sand bath. Subsequently Indium (1 ppm) solution was added as a

Western Indian Ocean
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Marine ScienceEDITOR-IN-CHIEF
M.F. ZHOU

Formation of hydrothermal deposits at Kings Triple Junction, northern Lau back-arc basin, SW Pacific: The geochemical perspectives

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ABSTRACT

An inactive hydrothermal field was discovered near Kings Triple Junction (KTJ) in northern Lau back-arc basin during 19th cruise of R/V Akademik Mstislav Keldysh in 1990. The field consisted of a large elongated basal platform 'the pedestal' with several 'small chimneys on its periphery and one 'main mound' superposed over it. The surrounding region is carpeted with lava pillows having ferromanganese 'precipitate' as infillings. The adjoining second field consisted of small chimney like growths termed as 'Christmas Tree' field. The basal pedestal, the peripheral chimneys and small 'Christmas Tree' like growths (samples collected by MIR submersibles) though parts of the same hydrothermal field, differ significantly in their mineralogy and elemental composition indicating different history of formation. The pedestal slab consisting of chalcopyrite and pyrite as major minerals and rich in Cu is likely to have formed at higher temperatures than sphalerite dominated peripheral chimney. Extremely low concentration of high field strength elements (e.g. Zr, Hf, Nb and Ta) and enrichment of light REE in these sulfides indicate prominent influence of aqueous arc-magma, rich in subduction components. The oxide growths in the 'Christmas Tree' field have two distinct layers, Fe rich orange-red basal part which seems to have formed at very low temperature as precipitates from diffused hydrothermal flows from the seafloor whereas Mn rich black surface coating is formed from hydrothermal fluids emanated from the seafloor during another episode of hydrothermal activity. Perhaps this is for the first time such unique hydrothermal oxide growths are being reported in association with hydrothermal system. Here, we discuss the possible processes responsible for the formation of these different hydrothermal deposits based on their mineralogy and geochemistry.

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1. Introduction

The back-arc and marginal basins in south-west Pacific Ocean (e.g. Okinawa Trough, Mariana Trough, Manus basin, Lau basin, North Fiji basin, Woodlark basin), are well known for sea floor hydrothermal activity and associated massive sulfide deposits (Hawkins and Helu, 1986; Gamo et al., 1993; Lisitsyn et al., 1997; Herzig and Hamington, 2000; Glasby and Notsu, 2003). During the 19th cruise of R/V Akademik Mstislav Keldysh in May, 1990 hydrothermal fields of Lau basin have been explored thoroughly with MIR submersibles. Massive sulfide and associated andesitic lava (Falloon et al., 1992) were collected from two locations, one from an extinct field (Lau-North) while another was active (Lau-Center) (Lisitsyn et al., 1992). Here we deal with the samples collected from the northern part of the Lau basin. As this region is characterized by the presence of an inactive field, the hydrother-

mal fluid characteristics could not be determined. Based on ship-board analyses, Lisitsyn et al. (1992) preliminarily described the geochemical characters of these deposits and inferred that hydrothermal activity here might have ceased in the recent past. Nevertheless as these data are very limited, we undertook detailed mineralogical and geochemical investigations on three types of samples collected from this field to understand the formation of these hydrothermal deposits.

2. Geophysical setting and description of the hydrothermal field

The Lau basin, a trapezoidal-shaped back-arc basin, separating the Lau ridge from Tonga volcanic island-arc, is located near the Pacific and Indo-Australian convergent plate boundary. In the northeastern part of this basin, three well defined spreading axes meet at a ridge-ridge-ridge type triple junction (Hawkins, 1995) known as Kings Triple Junction (KTJ) or Mangatolu Triple Junction (MTJ) (15°30'S, 174°35'W, Fig. 1). Geological Long Range Inclined Asdic (GLORIA) side-scan sonar surveys showed that the KTJ consist

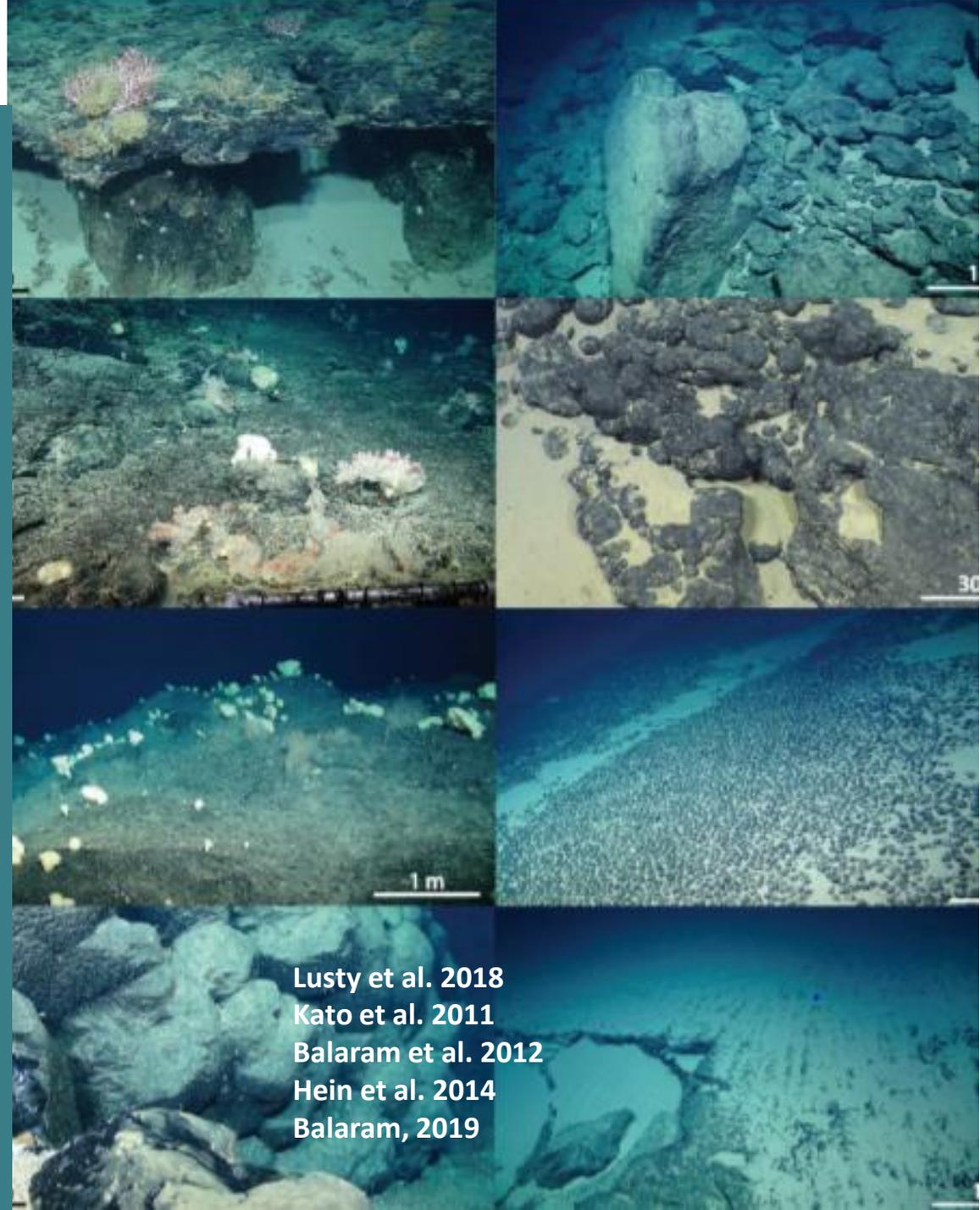
Cobalt-rich Crusts

- High concentrations of technologically critical elements (such as Co, REE, Nb, Pt, W, Bi, Ni, Mn, Te & Ti) occur throughout the global ocean basins where they are incorporated into thick Fe-Mn crusts.

- Recent estimates of the potential global tonnage of these metal rich crusts suggest about **200 billion tonnes** exists on the seafloor.

International interest is growing with China and Japan applying for mining licenses from the International Seabed Authority.

- Hence the need to address concerns about the sustainability of these crusts as a resource and their potential environmental impacts if exploited.



Lusty et al. 2018

Kato et al. 2011

Balaram et al. 2012

Hein et al. 2014

Balaram, 2019

Exploration for Cobalt-rich Seamount Ferromanganese Crusts in the Indian Ocean (2008-13)



NIO, Goa

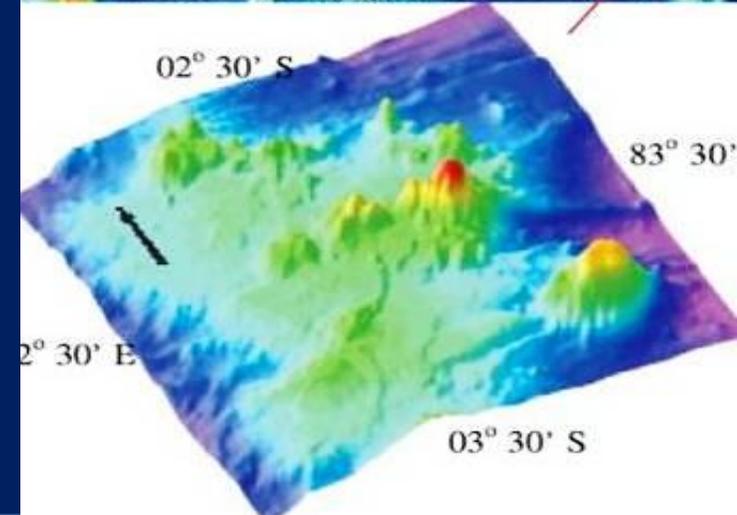
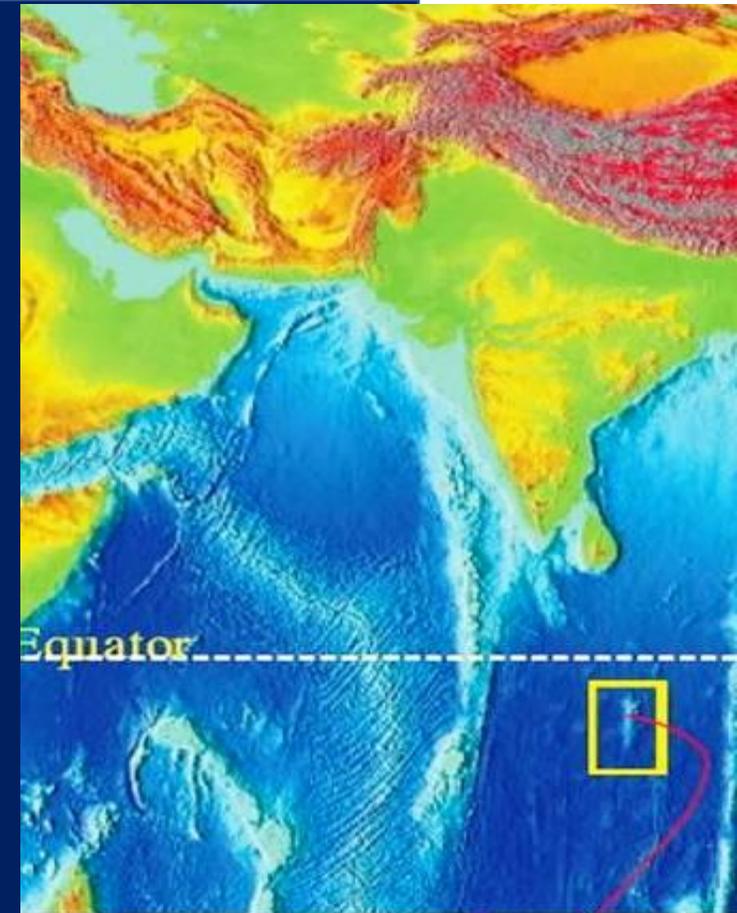


NGRI, Hyderabad



NCPOR, Goa

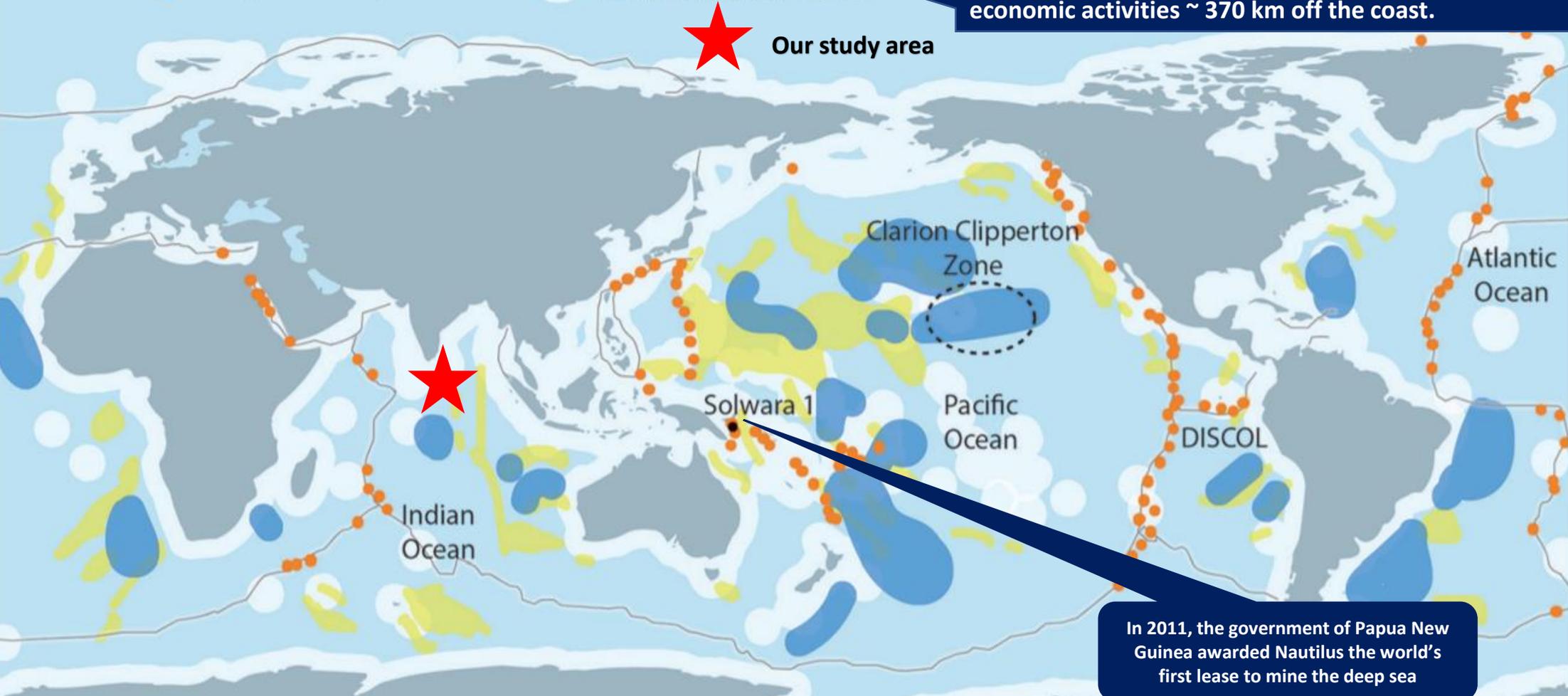
MoES Funded Project



A world map showing the locations of the three main marine mineral deposits

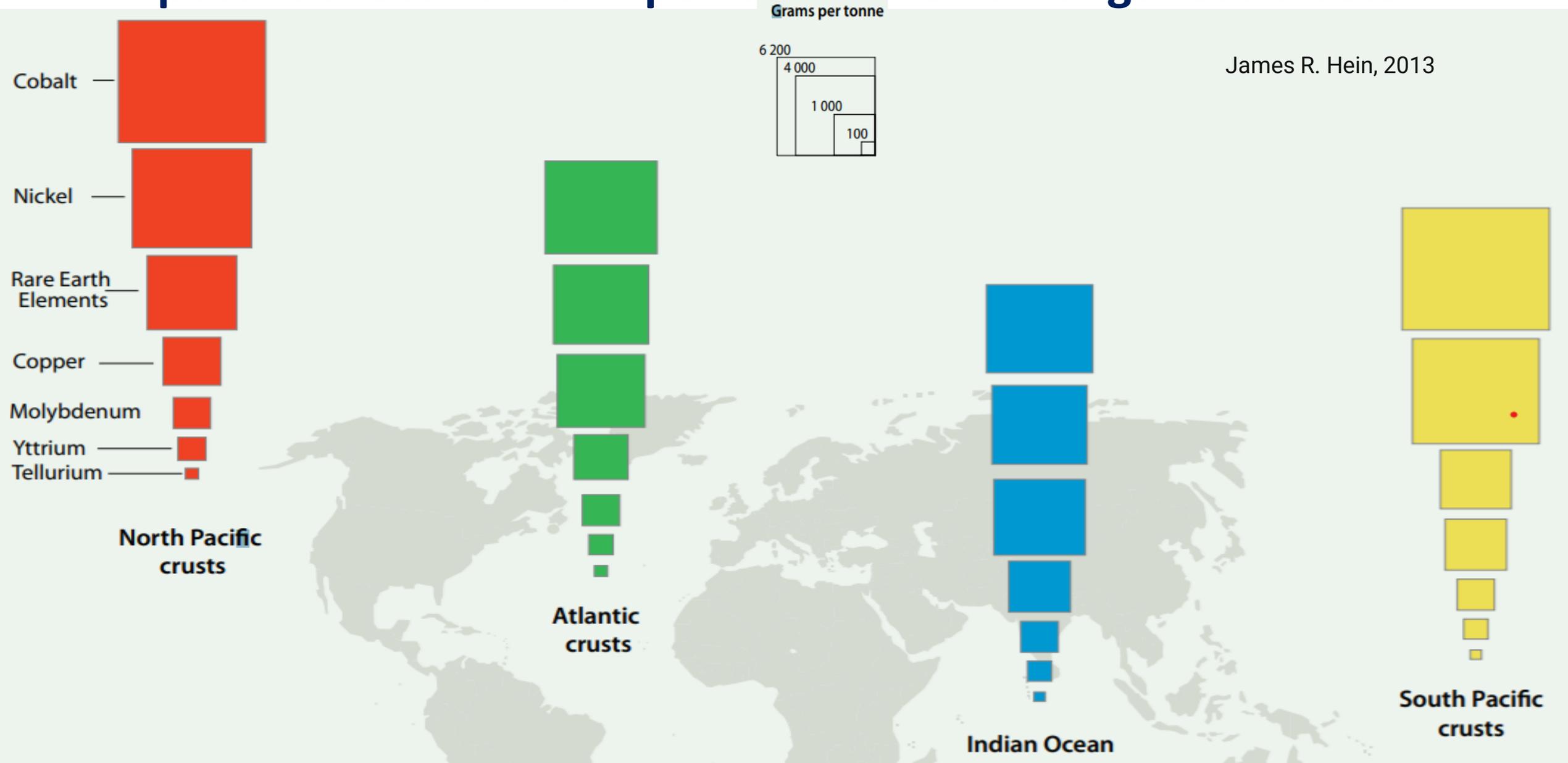
- Polymetallic nodules
- Polymetallic sulphides / vents
- Cobalt-rich crusts
- Exclusive economic zones

An area of coastal water and seabed within a certain distance of a country's coastline, to which the country claims exclusive rights for fishing, drilling, and other economic activities ~ 370 km off the coast.



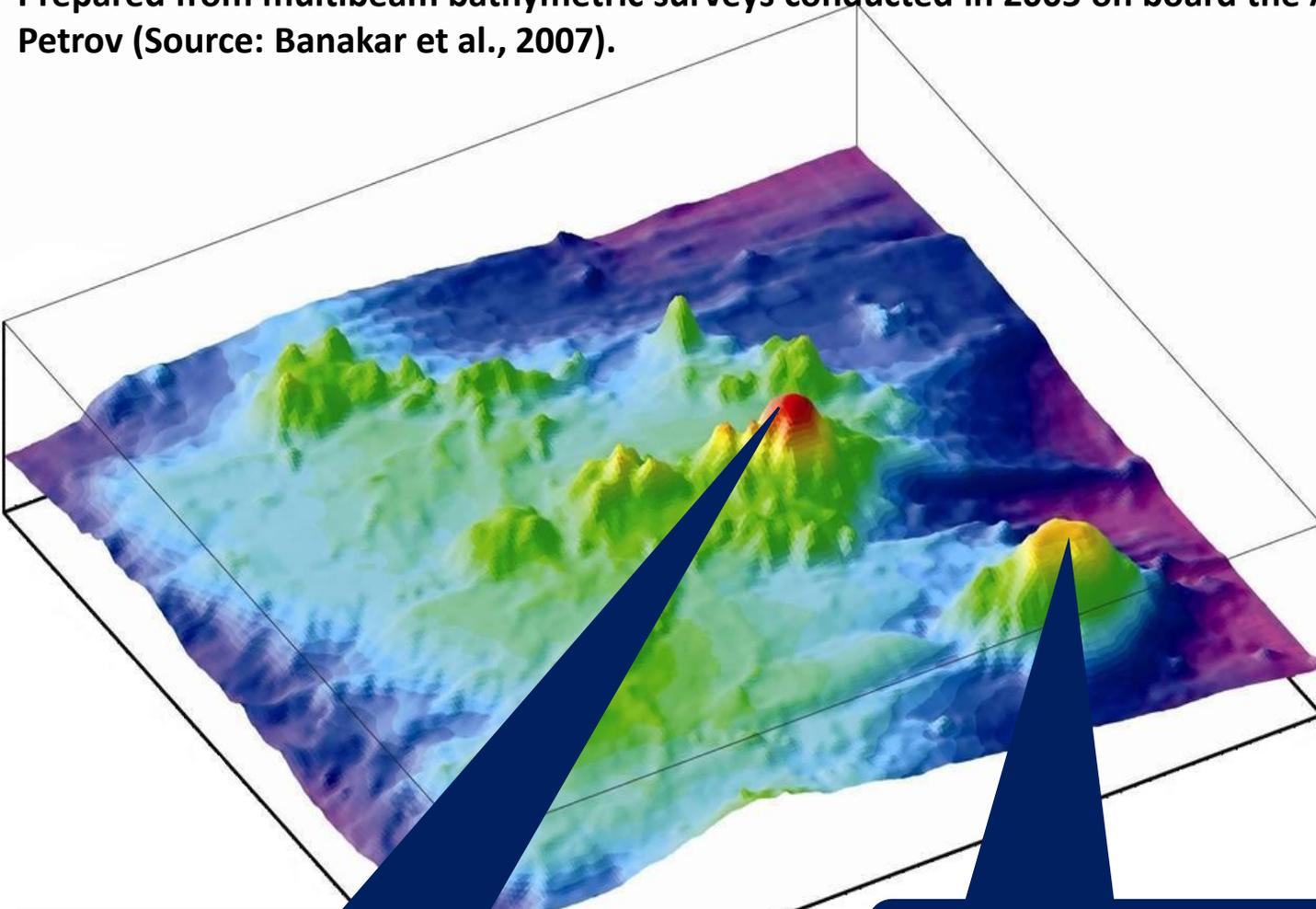
In 2011, the government of Papua New Guinea awarded Nautilus the world's first lease to mine the deep sea

Comparison of the concentration of Co, Ni, REE, and other metals of potential economic importance in ferromanganese crusts



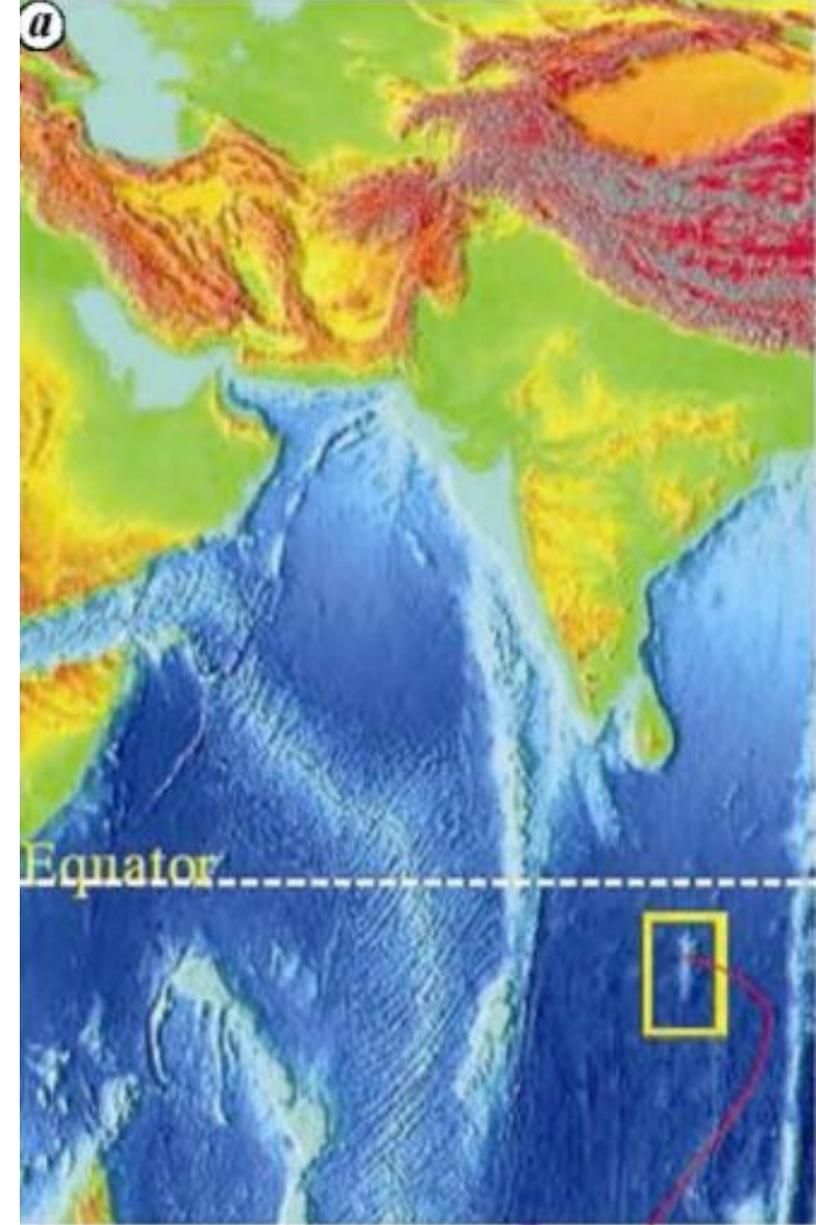
3D Map of the Northern Part of the Afanasiy-Nikitin Seamount Region

Prepared from multibeam bathymetric surveys conducted in 2005 on board the A B. Boris Petrov (Source: Banakar et al., 2007).



Fe-Mn crust samples were collected from the top of a mount at 1.7 km water depth

Afanisi Nikitin sea mount is ideal for the growth of cobalt crusts because of shallower nature --



This seamount region is punctuated with clusters of smaller volcanic seamounts rising up to 1.7 km water depth. This area is under detailed study for cobalt-rich ferromanganese crusts.

Sample Collection at ANS by NGRI Scientists along with NIO & NCPOR Scientists



Boris Petrov-Russian Vessel



NGRI Geochemistry Colleagues



**Sample collection by Dredging
at ~ 4 km depth**



Oceanic Basalt sample



Fe-Mn crust sample



Layer of Fe-Mn crust over Basalt

Sea Water Sample Collection at ANS by NGRI Scientists



Collection of sediments from sea floor by sedimentary corer



CTD (Conductivity, Temperature, Depth) operation - collection of sediment core and water samples

Major and Minor Element Data of Crust Samples

Analyte (%)	CC-1-DR-12	ABP37-DRG-10Q(D)	AA-8	CCE-ADR-25
SiO ₂	8.65	14.27	4.2	6.99
Al ₂ O ₃	2.37	4.52	0.71	1.94
Fe ₂ O ₃	27.99	16.27	17.76	23.89
MnO	27.2	18.85	33.37	21.86
MgO	2.65	6.15	5.11	4.76
CaO	4.06	10.3	9.93	2.16
Na ₂ O	2.1	1.62	1.03	2.45
K ₂ O	0.55	0.95	0.42	0.4
TiO ₂	1.47	1.33	1.31	1.07
P ₂ O ₅	1.04	5.26	4	0.64
Co (µg/g)	6420.19	3362.68	6579.5	6459.90
LOI	36.791	28.102	35.56	27.088



Extreme enrichment of a few elements such as **Co (up to ~ 0.9%)** and **Ce (~ 1700 µg/g)** in the crusts have been attributed a surface oxidation process: CoII CoIII and Ce III Ce IV

Koschinsky et al (2005); Murry and Dillard, 1979; Goldberg,1963; Takahashi et al.2000

Trace Element Data of Crust Samples

(Extreme enrichment of some metals)

	CC-1-DR-12	CC-2-ADR-20	ABP37/10Q(D)	AA-8	ABP37/10D	CC2-ADR-24	CCE-ADR-25
Sc	13.591	9.843	9.882	8.201	10.61	9.649	10.888
V	1217.433	948.831	865.183	917.544	1706.248	738.66	599.555
Cr	22.08	30.333	31.712	29.179	40.142	29.929	44.577
Co	6420.187	4997.063	3362.678	6579.528	4941.454	4622.25	6459.898
Ni	3980.889	4501.792	3902.911	4383.843	4734.853	2977.222	3436.858
Cu	1259.629	1029.67	1248.394	623.481	1569.248	497.2	881.79
Zn	731.156	627.524	605.352	545.534	687.381	493.75	492.12
Ga	13.92	13.027	13.789	12.735	15.826	10.511	12.341
Rb	9.248	5.836	12.988	4.491	10.381	5.847	8.851
Sr	1869.698	1622.87	1332.772	1693.091	1727.703	1265.272	1352.261
Y	196.703	129.725	245.056	227.445	251.407	137.426	136.937
Zr	668.72	567.488	400.504	344.648	475.298	456.907	513.513
Nb	213.225	36.244	87.964	27.706	32.757	27.902	91.611
Cs	0.245	0.314	0.405	0.284	0.385	0.326	0.431
Ba	1894.914	1653.259	2028.939	1869.636	2385.596	1094.509	1362.703
La	324.674	236.933	199.58	253.337	227.44	228.957	215.848
Ce	1447.114	1251.908	1003.194	1667.555	1419.487	1262.783	1413.853
Pr	54.853	39.858	26.585	36.115	32.019	39.208	32.811
Nd	234.496	170.626	115.219	152.485	138.358	167.104	139.293
Sm	48.962	36.509	22.426	29.893	27.651	35.817	29.201
Eu	11.203	8.405	5.581	7.082	6.904	8.073	6.822
Gd	58.695	44.626	32.236	42.486	39.407	43.824	38.914
Tb	9.319	6.989	4.791	6.094	5.852	6.843	5.695
Dy	48.739	36.488	26.76	33.114	31.838	35.829	30.411
Ho	11.949	9.016	7.43	8.91	8.656	8.626	7.831
Er	23.477	17.702	15.246	18.19	17.714	16.992	15.73
Tm	4.42	3.354	2.77	3.412	3.289	3.164	2.992
Yb	28.121	21.755	17.012	21.567	20.559	20.109	19.101
Lu	4.418	3.422	2.722	3.408	3.333	3.148	3.066
Hf	13.256	10.626	7.782	5.472	8.828	8.54	11.073
Ta	3.069	1.295	1.389	1.329	1.268	1.293	1.579
Pb	1490.863	1443.991	1007.7	1567.149	1434.062	1291.963	1334.824
Th	36.818	26.222	13.026	21.888	19.615	36.711	35.373
U	10.929	9.052	5.915	8.779	8.004	7.18	7.517



Balaram et al (2012)
Current Science, 103
(11) 1334-1338

HR-ICP-MS Work on Co-Crust Samples

	La		Ce		Pr		Nd		Sm		Eu		Gd	
	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS
NOD P1	133.3	126.1	352.5	131.5	30.1	32.3	140.1	141.5	31.7	34.8	8.1	8.3	32.7	33.5
GSMS-2	79.8	76.1	93.1	35.9	18.3	18.8	82.4	83.2	19.2	20.2	4.9	5.4	19.9	20.0
GSPN-2	206.7	198.8	652.4	648.5	47.2	46.6	200.4	200.1	46.7	48.3	11.6	11.0	50.2	48.8
GSPN-3	100.1	101.2	249.8	95.3	25.9	27.2	120.8	119.7	29.3	30.5	7.2	7.4	30.2	28.6
AA8	264.9	253.3	1661.6	1667.6	35.6	36.1	150.5	152.5	30.8	29.9	7.2	7.1	37.0	42.5
ABP-37/10D	228.6	227.4	1389.8	1419.5	30.8	32.0	137.6	138.4	27.5	27.7	6.8	6.9	35.8	39.4
CC2/ADR/20	244.1	236.9	1235.1	1251.9	38.0	39.9	172.7	170.6	37.8	36.5	8.6	8.4	42.6	44.6
ABP/3710Q	208.5	199.6	993.3	1003.2	26.0	26.6	115.8	115.2	20.2	22.4	5.7	5.6	29.5	32.2
CC1/DR/12	339.5	324.7	1423.2	1447.1	53.1	54.9	231.2	234.5	48.9	49.0	11.6	11.2	57.2	58.7
CC2/ADR25	225.4	215.8	1387.1	413.9	31.3	32.8	141.6	139.3	27.9	29.2	6.9	6.8	31.9	38.9
2388	290.8		1066.5		60.8		261.7		61.3		14.3		61.2	
	Tb		Dy		Ho		Er		Tm		Yb		Lu	
	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS	HR-ICPMS	ICPMS
NOD P1	5.8	5.8	28.5	29.4	6.6	6.7	12.7	12.6	1.9	2.3	14.5	14.8	2.2	2.2
GSMS-2	3.7	3.7	21.0	20.0	4.8	4.9	10.1	9.4	1.5	1.7	10.6	10.8	1.6	1.7
GSPN-2	8.8	8.5	43.8	43.2	10.1	9.9	19.1	18.7	3.2	3.4	22.2	21.9	3.4	3.3
GSPN-3	5.2	5.2	23.7	26.6	5.9	6.0	11.7	11.3	1.9	2.1	13.1	13.4	2.0	2.0
AA8	6.0	6.1	31.8	33.1	9.0	8.9	18.4	18.2	3.1	3.4	21.6	21.6	3.4	3.4
ABP-37/10D	5.7	5.9	33.8	31.8	8.7	8.7	16.9	17.7	3.0	3.3	20.3	20.6	3.3	3.3
CC2/ADR/20	7.0	7.0	38.2	36.5	9.1	9.0	17.5	17.7	3.1	3.4	21.6	21.8	3.4	3.4
ABP/3710Q	4.8	4.8	27.9	26.8	7.5	7.4	15.1	15.2	2.6	2.8	17.2	17.0	2.8	2.7
CC1/DR/12	9.3	9.3	49.7	48.7	12.0	11.9	25.2	23.5	4.0	4.4	28.0	28.1	4.4	4.4
CC2/ADR25	5.6	5.7	27.8	30.4	7.8	7.8	15.8	15.7	2.7	3.0	18.8	19.1	3.0	3.1
2388	10.5		47.8		11.4		19.8		3.5		23.6		3.5	

❖ ^{157}PrO directly overlaps on ^{157}Gd in a Quadrupole ICP-MS

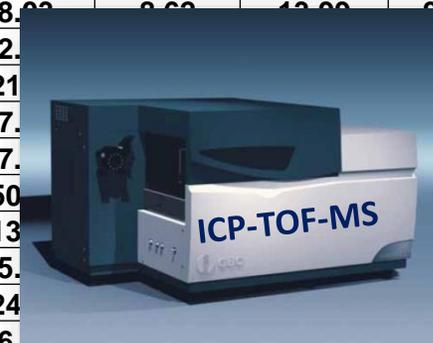
(Balaram, 2021)

❖ In HR-ICP-MS these two peaks are clearly resolved



More Trace Elements in Co Crust

	Analyte	Li	Be	B	S	As	Se	Mo	Cd	Cd	Sn	Sb	Te	W	Tl	Bi	
	Mass	7	9	11	32	75	82	98	114	112	120	121	130	184	205	209	
	Std	76.1	5.6	120	3350	310	3.9	390	7.5	7.5	3	33.8	30.9	87	120	10.2	
	NOD-A-1	76.83	5.83	119.07	3341.99	315.69	3.51	400.26	7.81	7.66	2.99	34.17	28.86	85.71	121.08	10.38	
Crust	AA-8	7.56	4.52	154.81	3312.78	301.78	2.61	684.36	3.24	4.43	2.80	29.72	54.60	64.43	159.85	51.87	
	ABP 37-DRG 10D	16.50	5.05	133.77	3453.23	350.65	4.67	816.11	3.88	5.02	3.38	42.01	78.38	43.72	62.99	38.46	
	CC-1 DR-12	6.10	5.57	92.00	2868.53	341.20	5.42	508.05	2.90	4.72	17.33	69.76	38.42	98.45	178.01	26.23	
	CC2-ADR-20	10.48	6.24	89.45	3139.61	288.76	4.66	277.74	3.45	5.30	2.43	24.65	39.68	35.24	144.27	32.24	
	CCE-ADR-25	11.64	4.87	146.67	3457.65	271.52	4.02	315.20	3.13	5.01	3.16	46.70	44.26	100.97	115.33	28.81	
	ABP-37 DRG 10Q	22.41	4.52	139.97	3481.07	343.84	2.36	507.34	3.60	4.85	2.95	47.60	19.95	79.84	49.13	31.65	
Basalt	CC2 ADR 24	57.99	2.77	107.61	3269.14	382.99	1.62	119.29	0.68	2.08	8.02	8.62	12.02	20.61	4.16	1.36	
	CC2-ADR-24	11.77	4.78	522.99	3635.32	284.93	3.63	270.09	3.05	4.64	2.11	2.11	2.19	142.66	39.10		
	ABP-37 DRG 1A	87.49	0.96	90.17	3541.87	327.16	0.86	54.50	0.43	1.12	21.00	21.00	8.43	1.07	0.48		
	ABP-37 DRG 4	30.81	1.14	87.90	3380.24	334.84	3.55	45.26	0.32	1.05	7.00	7.00	8.17	1.17	0.22		
	ABP-37 DRG 4A	69.52	1.23	92.33	3370.86	311.25	3.55	84.51	0.48	1.03	7.00	7.00	5.71	2.01	0.47		
	ABP-37 DRG 4B	19.63	1.90	84.67	3255.38	338.33	3.41	346.76	0.46	0.09	50.00	50.00	37.04	16.64	2.35		
	ABP-37 DRG-7	21.57	0.93	85.65	3239.08	371.58	3.15	77.37	0.50	1.18	13.00	13.00	3.27	1.68	0.86		
	ABP 37DRG 10A	26.64	3.79	85.93	3020.02	331.50	0.72	34.43	0.36	2.31	5.00	5.00	7.58	0.20	0.10		
	ABP37 DRG-10B	21.06	5.72	83.13	2787.03	191.26	1.62	38.74	-0.10	2.16	24.00	24.00	7.87	0.43	0.09		
	ABP-37 DRG-10C	16.11	0.82	81.30	2934.88	423.58	3.28	159.03	1.10	2.02	6.00	6.00	2.06	5.34	2.83		
	ABP-37 DRG-10C SOFT	15.67	1.31	81.29	2961.03	401.57	0.86	348.36	1.08	2.32	8.78	8.78	38.75	586.69	235.09	9.87	3.90
	ABP-37 DRG-14A	54.10	3.09	77.35	2927.50	362.45	0.60	41.34	0.26	1.90	6.00	6.00	54	0.55	0.17		
	ABP-DRG-14E	34.71	3.85	86.61	3072.93	380.84	3.41	1224.20	1.44	3.16	6.00	6.00	19	22.67	9.54		
	ABP 37DRG 14B	48.82	2.74	82.39	3059.10	252.18	1.11	49.47	0.25	1.81	8.00	8.00	00	0.85	0.40		
	ABP 37DRG 14C	63.60	2.86	79.86	3077.63	356.14	2.26	51.77	0.52	2.11	5.00	5.00	26	0.85	0.64		
	ABP-37 DRG 14D	53.98	2.95	124.34	3013.76	79.88	0.85	63.26	0.37	1.72	6.00	6.00	27	1.98	1.24		
Reference Standards	MAG-1	92.68	3.70	77.61	3126.07	346.25	4.95	38.66	0.34	1.10	6.00	6.00	67	1.05	0.61		
	NOD-P-1	151.00	2.60	100.14	3251.66	117.20	3.65	348.40	25.03	21.61	3.00	3.00	49	205.30	5.22		
	GSPN-3	223.58	1.98	269.95	3181.94	77.29	6.34	436.51	22.69	20.23	2.32	2.32	120.84	182.45	5.58		
	GSPN-2	87.33	4.23	299.98	3329.92	210.05	6.19	247.88	9.61	10.27	2.30	2.30	74.91	175.93	17.57		
	GSMS-2	61.31	2.01	75.40	3182.78	329.31	7.10	180.01	0.43	1.30	5.55	10.26	3.38	244.43	1.73	1.22	



Deep-Ocean Mineral Deposits as a Source of Critical Meta/s

Concentrations ($\mu\text{g/g}$) of REE in ferromanganese crust (cobalt crust) samples collected from the Afanasy Nikitin Seamount (ANS) in the Eastern Equatorial Indian Ocean.

Elements	CC2-ADR24 Ferro manganese crust	CC2-ADR25 Ferro manganese crust	CC1-DR-12 Ferro manganese crust
La	217 ± 3	189 ± 3	236 ± 5
Ce	1163 ± 34	1186 ± 35	1041 ± 31
Nd	232 ± 8	122 ± 5	185 ± 6
Sm	35.4 ± 0.7	27.0 ± 0.5	39.0 ± 0.8
Eu	8.5 ± 0.3	6.4 ± 0.2	9.2 ± 0.2
Tb	6.8 ± 0.8	4.7 ± 0.6	6.5 ± 0.7
Yb	17.3 ± 1.5	15.5 ± 1.3	19 ± 2
Lu	2.4 ± 0.2	2.1 ± 0.2	2.5 ± 0.2
Sc	8.8 ± 0.4	9.0 ± 0.4	11.0 ± 0.5

Note: The samples were determined by NAA facility by the author at the Institute of Energetic and Nuclear Research, Sao Paulo, Brazil.

Counting Laboratory Nuclear Reactor, Sao Paulo, Brazil Prof. Maria



REE geochemistry of seawater from Afanasy-Nikitin Seamount in North Central Indian Ocean by high resolution inductively coupled plasma mass spectrometry

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REE (Rare Earth Elements) and yttrium in sea water samples, from the Afanasy-Nikitin Seamount (ANS) located around 3° South latitude and 83° East longitude in the north central Indian Ocean were precisely determined by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) method. A modified procedure has been designed for determination of REE and yttrium wherein the water samples were subjected to a pre-concentration step using bis-2-ethylhexyl phosphoric acid (HDEHP) complexing agent. Sea water reference materials such as NASS-5 and SLEW-3 were used for calibration as well as to check the accuracy of the procedure adopted. Samples were analyzed for REE and yttrium by HR-ICP-MS. Precisions achieved for various rare earths and yttrium is better than 8% RSD with comparable accuracies. Limit of detection (3σ) were generally in the range of 0.02-1.2 pg/ml range for all these elements. This method facilitates rapid and interference-free determination of REE and yttrium from relatively small volume of sea water (10 ml). Recoveries for different REE and Y were better than 5%, and accuracy and precision of the determinations are within 8% RSD. The Ce-negative anomalies with smooth normalized-REE patterns obtained for both certified reference materials and samples further substantiate that the procedure adopted and the data generated are extremely accurate. A slight enrichment of heavy REE were observed in the central Indian Ocean waters which might be attributed to the river flows containing more dissolved trace elements including REE. A sharp negative Ce-anomaly in the normalized REE distribution patterns indicates that the source of REE in particular Ce in marine sediments is seawater. Results of the variation in REE concentrations with depth indicated that the physico-chemical conditions of bottom ocean water follow a very complex mechanism.

Key Words: Sea water, rare earth elements, Afanasy-Nikitin Seamount, Indian Ocean, HR-ICP-MS, HDEHP, Ce-anomaly

Introduction

Several types of seafloor sediments harbor high concentrations of rare earth elements^{1,2}. Oceanic ridges are the primary sites of volcanic activity where new oceanic crust is generated. During the last few decades, there has been quantum leap of knowledge on the concentrations and distributions for trace elements in the oceans. REE gained particular attention because of their unique physical and chemical properties and a remarkable coherent behavior. The concentrations of REE in rocks and marine sediments are in microgram per gram order and those in seawater samples are still low level, i.e., picogram per milliliter (pg/ml) or less^{3,4}. Recently more attention has been paid on the sea water geochemistry of REE⁵, because they serve as; i) a useful probe in understanding scavenging processes of particulate matter, ii) natural analogs of actinides and transuranics such as Ac, Th, Pu, Am, Cm and Cf in the marine environment and iii) tracers of water masses and ocean circulation⁶. In addition, the REE water chemistry is also extremely important in understanding the interaction between the ferromanganese crust on the seamount and oceanic water. Although lot of REE data are available on the waters of Atlantic and Pacific oceans, not much data are available on the waters of Indian Ocean. In particular, very scanty information is

available on the Ocean waters of ANS in north central Indian Ocean. Geochemical studies on the Afanasy-Nikitin Seamount (ANS) located around 3° South latitude and 83° East longitude in the north central Indian Ocean (Fig. 1) are being carried out to understand evolution of the structure, apart from locating hydrothermal vent sites^{7,8,9,2}. The chemistry of REE makes them particularly useful in studies of marine geochemistry and chemical characterization of water masses at ANS. At present, all three forms of inductively coupled plasma mass spectrometry namely ICP quadrupole mass spectrometry (ICP-MS), ICP high resolution mass spectrometry (HR-ICP-MS) and ICP time of flight mass spectrometry (ICP-TOF-MS) provide powerful, alternatives for the determination of REE in a variety of geological materials including sea water¹⁰. Nevertheless, its application to the determination of REE at ultra-trace concentration level in seawater is limited because of very high total dissolved solids in sea water that can cause both spectral and matrix interference effects. Consequently, separation from matrix elements and pre-concentration of REE are prior requirements for the precise analysis of trace elements in seawater by these techniques. The purpose of this paper is to design a reliable and rapid analytical procedure for the separation, pre-concentration and precise determination



Yttrium and rare earth element contents in seamount cobalt crusts in the Indian Ocean

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Cobalt-rich Fe-Mn crusts occur on almost all seamounts and plateaus of the world oceans. Fe-Mn crusts are formed through layer-by-layer accretion of colloidal precipitates from cold ambient seawater onto exposed seamount rock substrates. This study reports high concentrations of rare earth elements (REE) and yttrium ranging from 1,727 to 2,511 µg/g in the crust samples collected from the Afanasy Nikitin Seamount (ANS) in the Eastern Equatorial Indian Ocean. The concentrations of REE in the ANS Fe-Mn crusts are much higher than those of the mid-Pacific seamount and nodules (1,180-1,434 µg/g). Ce-enrichment up to 0.17% has been recorded in the present study as against ~0.1% content in global seamount Fe-Mn crusts. This enrichment is attributed to oxidative removal of Ce from seawater to the marine Fe-Mn crust. The negative Ce-anomalies obtained for seawater samples from the ANS region coupled with strong positive Ce-anomalies in Fe-Mn crusts clearly indicate that the source of Ce in ANS Fe-Mn crusts is seawater. This investigation warrants further detailed exploration studies in order to make an estimate of these highly useful elements in the cobalt enriched Fe-Mn crusts of Indian Ocean.

Keywords: Cobalt crust, rare earth elements, seamount, yttrium.

The future of India's and the world's enthusiastically envisaged green technologies depends on the availability of several trace and ultra-trace metals, including rare earth elements (REEs) in adequate quantity. REEs are critical constituents to many of the world's most advanced technologies such as defence metallurgy, consumer electronics, medical applications, etc. More than 97% of the world's REE ore production is from mines in China, which have restricted their exports recently for reasons unknown. Other countries with notable production are Brazil, India, Kyrgyzstan and Malaysia. Mainly, monazite from beach placers is mined in India as the principal ore mineral for REE, although xenotime holds out some

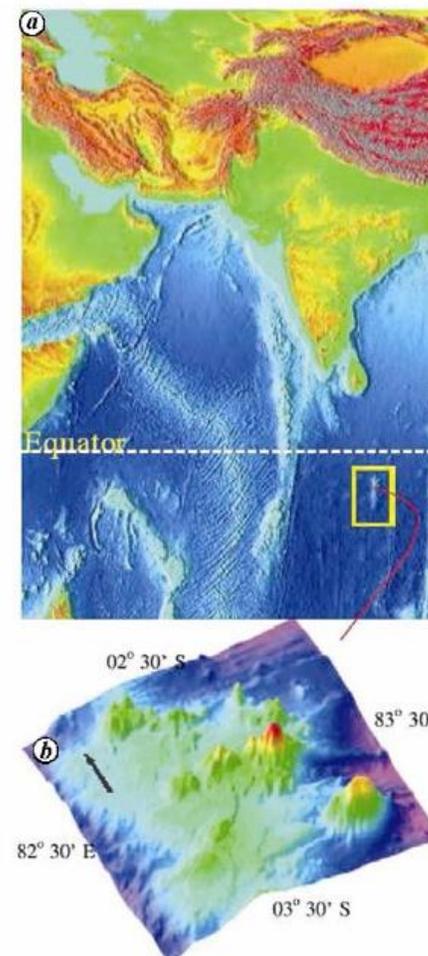


Figure 1. a, Location of the Afanasy Nikitin Seamount (ANS) enclosed by a box in the Eastern Equatorial Indian Ocean. b, 3D colour-coded multibeam swath bathymetric map of the northern part of the seamount (100 x 100 km). Pink colour indicates deepest (> 4,500 m) region and red colour indicates shallowest (< 1,700 m) region. North shown by arrow in lower panel (Source: Banakar *et al.*⁸).

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Platinum Group Element (PGE) Data (in ng/g) of Manganese Crust Samples from Central Indian Ocean

Ru

Rh

Pd

Ir

Pt

Au

Sample	Ru		Rh		Pd		Ir		Pt		Au	
	USGS	NGRI	USGS	NGRI	USGS	NGRI	USGS	NGRI	USGS	NGRI	USGS	NGRI
ANS-1	17+1	11+2	40+4	35+3	13+1	13+1	11+1	7+2	636+30	580+20	18+2	21+2
ANS-2	1+1	6+1	13+1	6+1	5+1	13+1	6+1	2+1	149+8	65+5	7+1	16+1
ANS-3	1+1	8+2	13+2	17+2	6+2	13+2	6+1	2+1	166+10	88+6	11+1	277+1
ANS-4	30+3	25+2	33+3	30+3	10+1	13+2	10+1	7+2	610+25	523+19	10+1	9+1
ANS-5	20+3	18+3	38+4	35+3	8+2	11+1	9+1	7+2	568+22	512+20	13+1	9+1
ANS-6	12+2	8+1	31+3	28+3	11+1	13+2	8+1	5+1	673+30	623+25	14+2	26+2
ANS-7	12+1	10+2	7+2	6+2	4+2	15+2	4+1	2+1	101+10	80+8	19+2	13+1
ANS-8	15+3	12+2	9+2	8+2	11+1	11+1	5+1	3+1	110+9	89+7	29+3	16+2
ANS-9	12+2	8+1	6+1	6+2	6+1	12+2	3+2	2+1	102+8	79+6	15+2	7+1
ANS-10	31+4	20+2	23+3	21+3	20+2	11+1	10+1	6+2	286+21	229+20	18+2	10+1
ANS-11	15+1	5+1	10+1	5+1	8+1	9+1	5+1	1+1	111+10	36+3	13+1	3+1
ANS-12	12+2	10+2	13+2	13+2	7+1	11+2	5+2	4+1	148+11	150+11	11+1	8+1
ANS-13	17+1	14+2	25+2	21+2	13+2	11+1	10+1	6+2	292+20	223+20	22+2	22+2

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Determination of the platinum – group elements (PGE) and gold (Au) in manganese nodule reference samples by nickel sulfide fire-assay and Te coprecipitation with ICP-MS

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Platinum group elements (PGE) and Au data in polymetallic oceanic ferromanganese nodules reference samples and crust samples obtained by inductively coupled plasma mass spectrometry (ICP-MS), after separation and pre-concentration by nickel sulfide fire-assay and Te coprecipitation, are presented. By optimizing several critical parameters such as flux composition, matrix matching calibration, etc., best experimental conditions were established to develop a method suitable for routine analysis of manganese nodule samples for PGE and Au. Calibrations were performed using international PGE reference materials, WMO-1 and WMO-1. This improved procedure offers extremely low detection limits in the range of 0.04 to 0.016 ng/g. The results obtained in this study for the reference materials compare well with previously published data wherever available. New PGE data are also provided on some international manganese nodule reference materials. The analytical methodology described here can be used for the routine analysis of manganese nodules and crust samples in marine geochemical studies.

Key words: Platinum group elements (PGE), gold, manganese nodule reference samples, manganese crust, NiS fire-assay, ICP-MS

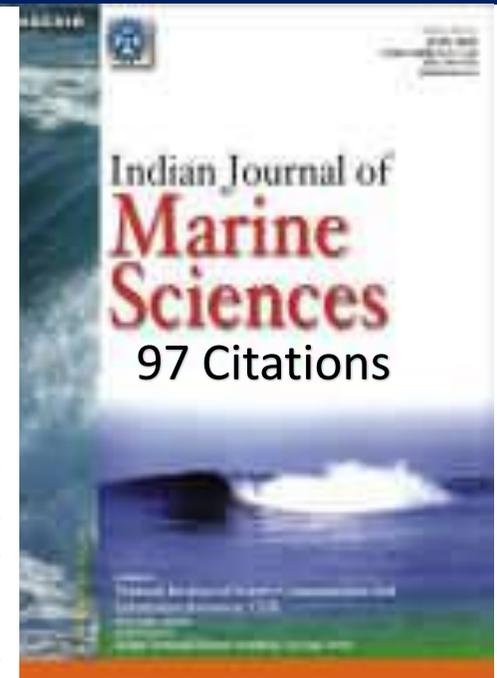
[IPC code: Int. Cl. (2006) G01 N 31.07]

Introduction

Platinum group elements (PGE: Ru, Rh, Pd, Os, Ir and Pt) along with gold (Au) are gaining importance in understanding processes such as paleo-climate, weathering, diagenesis and enrichment, particularly in marine geochemical studies. Compared to the chemistry of the remaining PGE, platinum (Pt) changes its valency under changing redox conditions and this property has been extensively used for understanding the enrichment processes during sedimentation. The distribution of platinum in the ferromanganese crusts in particular, has gained considerable attention after high Pt concentrations (up to 1.5 µg/g), were reported for Central Pacific seamount ferromanganese crusts¹. Hence, for a comprehensive understanding of the genesis and economic potential of ferromanganese crust deposits

and associated sediments, high precision PGE and Au data are required in addition to major, minor and trace-element compositions.

Despite striking advancements in analytical methods, PGE remain the most poorly studied group of elements, mainly due to analytical difficulties in generating accurate data for these elements, especially in complex matrices such as iron/manganese oxyhydroxides/oxides, and the low concentrations in other oceanic sediments. Determination of precious metals in geological samples is generally a two-step process. The first step involves preparation of a representative sample and then separation / pre-concentration of PGE and Au from the rock/ore matrix. For example, the low abundance of PGE in marine sediments requires use of a separation and pre-concentration method such as Pt/NiS fire-assay. The second step involves measurement of their



NiS Fire - Assay



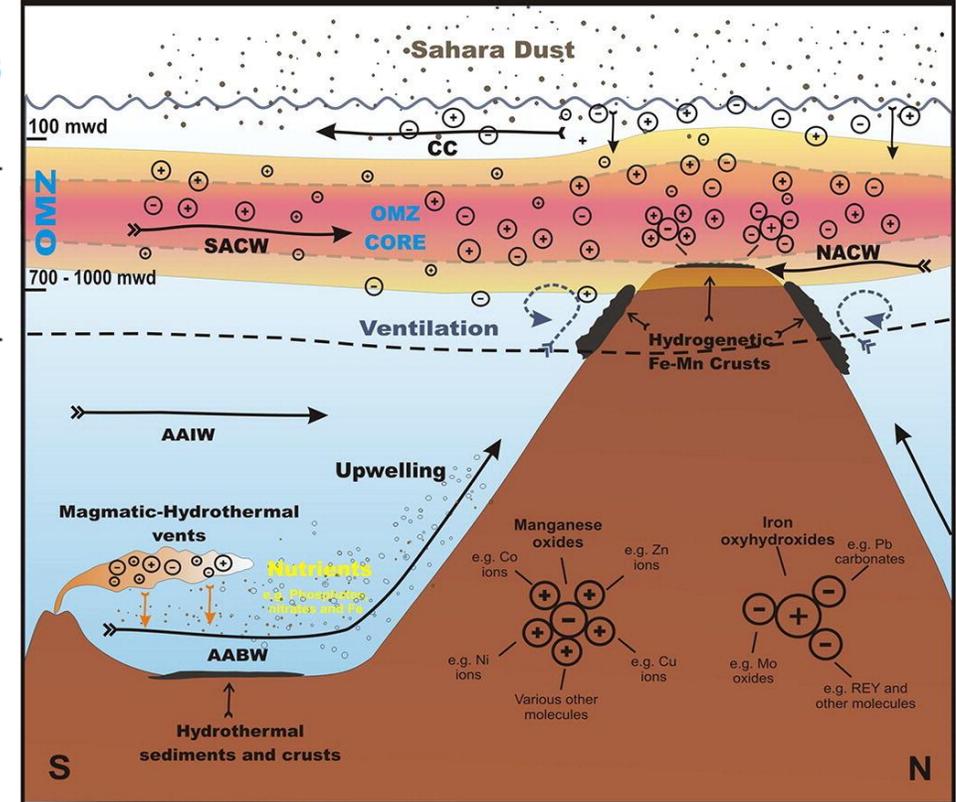
NGRI : NiS fire-assay (1100°C) – Te coprecipitation – ICP-MS
USGS, Menlo Park, California : NiS fire-assay (1200°C) – ICP-MS

Balaram et al (2006) Indian J. Marine Sciences, 35 (1) 7-16

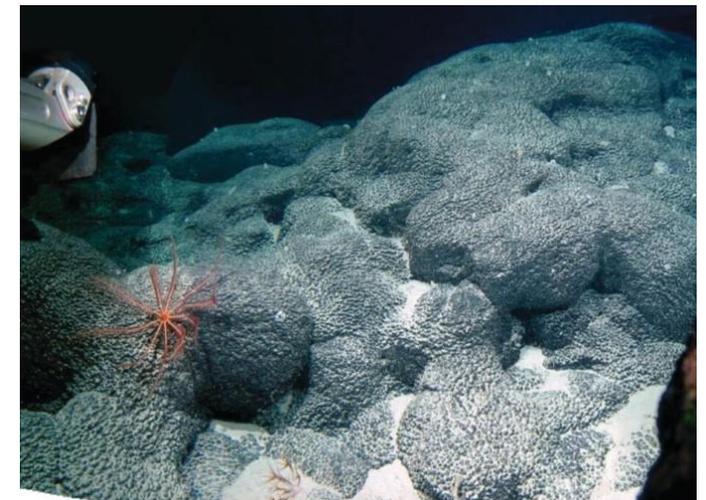
Balaram et al (2005) Proc. 10th International Platinum Symposium, University of Oulu, Finland, pp 33-36

Table 4.3 Overview of Σ REE range ($\mu\text{g/g}$) in marine sediments from different oceans (modified after Balaram, 2019).

Ocean	Σ REE/ Σ REY Range ($\mu\text{g/g}$)	Matrix	Reference
Afanasy Niktin Seamount (ANS) in the Eastern Equatorial Indian Ocean.	1727–2511	Cobalt crust	Balaram <i>et al.</i> (2012)
Mid-Pacific seamount	2085	Cobalt-rich crust	Cui <i>et al.</i> (2009)
Indian Ocean	928–1570	Ferromanganese crust	Nath <i>et al.</i> (1992)
Scotia Sea	3400	Ferromanganese crust	Gonzalez <i>et al.</i> (2010)
Eastern South Pacific	1000–2230	Deep sea mud	Kato <i>et al.</i> (2011)
North Pacific (east & west of Hawaiian Islands)	400–1000	Deep sea mud	Kato <i>et al.</i> (2011)
Mid Pacific Ocean	1178–1434	Fe-Mn nodules	Bu <i>et al.</i> (2003)
Pacific Ocean	1326	Deep nodules	Piper (1974)
Pacific Ocean	1398	Shallow nodules	Piper (1974)
Pacific Ocean	22 000	Ocean-floor sediments	Milinovic <i>et al.</i> (2021)



Canary Island Seamount Province (northeastern tropical Atlantic); Marino *et al.* 2017



Marine Mud Deposits

Japan's Discovery of a Giant REE Deposit

Kato et al. (2011) discovered mud covering an extensive area (2000 seafloor sediments sampled at depth intervals of around one meter, at 78 sites that cover a large part of the Pacific Ocean. on the deep (4000m) in the Pacific Ocean that contains:

1. High concentrations of REE (Σ REE 400-2230) with Σ HREE 70-430,
2. The quantity of resource is enormous, and exploration is easy
3. Radioactive elements are largely absent
4. REE can be easily extracted using H_2SO_4
5. After, hydrothermal sulfide, manganese nodule and manganese crust deposits, marine mud represents the 4th major seabed mineral resource
6. Uptake of REY by mineral phases such as hydrothermal iron-oxyhydroxides and phillipsite seems to be responsible for their high concentration.

Kato et al. (2011) Nature Geoscience, 4, 535-539

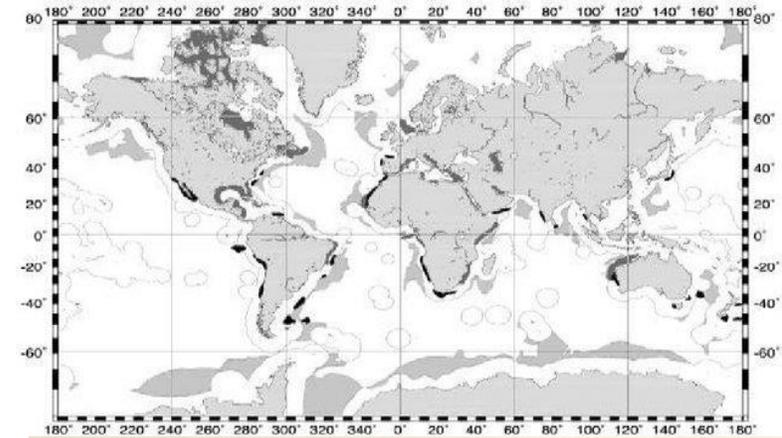


Deep-sea mud containing over 5,000ppm total REY content was discovered in the western North Pacific Ocean near Minamitorishima Island, Japan, in 2013. The resource amount was estimated to be 1.2Mt of REE oxide for the most promising area (105km²×0–10mbsf), which accounts for 62, 47, 32, and 56 years of annual global demand for Y, Eu, Tb, and Dy, respectively.

Takaya et al. Scientific Reports, 2018

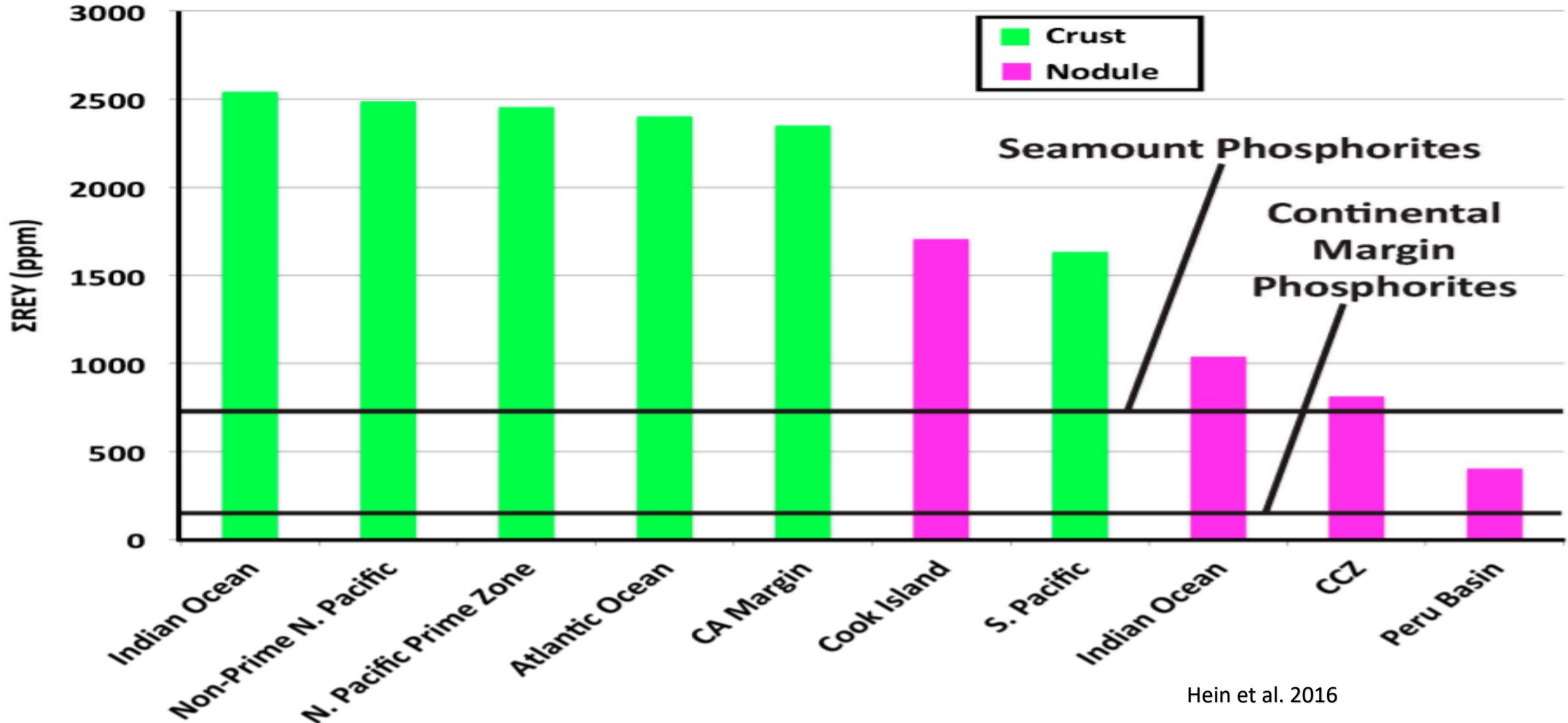
Phosphorite Deposits

- ❑ Phosphorites are P-rich sedimentary rocks, usually composed of carbonate hydroxyl fluorapatite $\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3\text{F}$ which occurs as nodules and crusts originally formed in oceanic environments
- ❑ Phosphorites occur in the global ocean in three general environments, **continental margins** (shelf, slope, banks, and plateaus), **seamounts**, especially the old (Cretaceous) seamounts in the NW Pacific, and **lagoon/insular deposits**.
- ❑ **Phosphorus is absorbed by plants and animals and released back to seawater. In the warmer surface waters, phosphate precipitates out of solution and then sinks to the seafloor forming deposits of phosphorite.**
- ❑ Phosphorite is a non-detrital sedimentary rock that **contains high amounts of phosphate minerals**. Considering other ocean sediments, phosphorite deposits have a higher potential as a resource for REE than most conventional REE deposits. (**ΣREE up to 2000 $\mu\text{g/g}$**).
- ❑ These are mined in **Brazil, Canada, Finland, Russia, South Africa**. Phosphate rock is mined mostly by surface methods using draglines and bucket wheel excavators for large deposits and power shovels or earthmovers for smaller deposits Hein et al. 2016; Balaram, 2022



Laminated Phosphatic Rock

Seamount phosphorites contain higher concentrations of REE than continental margin phosphorites



Uranium (U) concentration and its genetic significance in the phosphorites of the Paleoproterozoic Bijawar Group of the Lalitpur district, Uttar Pradesh, India

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Abstract The paper presents the uranium (U) concentration and distribution pattern in the Paleoproterozoic phosphorites of Lalitpur district of Uttar Pradesh. The study of thin sections, SEM and XRD reveal that apatite is the essential phosphate mineral while quartz and feldspars are the dominant gangue in the phosphorites of the investigated area. The colophane is observed to be mostly oolitic in form and microspherulitic in texture. The major element geochemistry indicated that the phosphorite samples are rich in P_2O_5 , CaO, SiO_2 and Fe_2O_3 whereas depletion of MgO, MnO, K_2O and Al_2O_3 was observed. The CaO/ P_2O_5 ratio ranges from 1.13 to 1.46 which is slightly lower than that of cations and anions substituted francolite (1.621) and close to that of carbonate-fluorapatite (1.318). The trace element geochemistry indicates that the phosphorites of Lalitpur have the significant range of U concentration (1.67 to 129.67 $\mu\text{g/g}$) which is more than that of Th (0.69 to 0.09 $\mu\text{g/g}$) among the analysed trace elements in the phosphorite samples of the area. The positive correlation of U with P_2O_5 , CaO and U/ P_2O_5 indicates a close association of U with phosphate minerals like colophane (apatite), whereas negative correlation of U with SiO_2 and Fe_2O_3 may be due to mutual replacement.

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The antipathetic relationship of U with Ni may be an indication of high oxidizing conditions, whereas sympathetic relationship of U with K_2O points towards higher alkaline condition basin of deposition during phosphatization. The variation of U and its relationship with significant trace elements in most of the phosphorite samples lead us to believe that the deposition of these phosphorites may have taken place in highly alkaline medium during fairly to weakly reducing environmental conditions of geobasin.

Keywords Uranium concentration · Phosphorites · Paleoproterozoic · Bijawar Group · Lalitpur · India

Introduction

Phosphorites are widely used as a raw material for the production of phosphatic fertilizers. Major and trace elements are important for the elucidation of general relationship behaviour of elements in sedimentary rocks and for the rational agrochemical utilization of phosphorites. Some elements in phosphorites are micro-fertilizers, whereas others, for instance, uranium (U), etc., are ecologically hazardous (Graschenko et al. 1981; Zanin and Zamirailov 2004). Phosphatic rocks distributed among Proterozoic, Tertiary and Quaternary Formations are known to be secondary potential sources of U in the world. Early Proterozoic phosphorites of Aravalli, Bijawar and Cuddapah are reported to be rich in elements like U, V, Mo and Ni and form large tonnage of low-grade uranium deposits (Rao et al. 2004). The Proterozoic rocks of the Bijawar Group of Sonrai, bordering the southern fringe of the Bundelkhand massif, constitute a metallogenic province in the southern part of Uttar Pradesh. Geological investigations by different organizations (DGM, UNDP, GSI and AMD) resulted in establishing a polymetallic

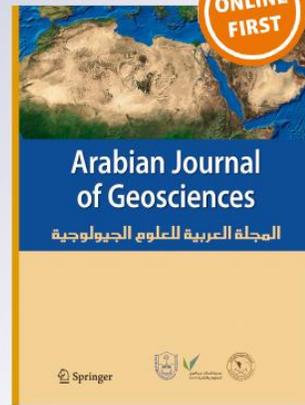
Uranium (U) concentration and its genetic significance in the phosphorites of the Paleoproterozoic Bijawar Group of the Lalitpur district, Uttar Pradesh, India

Shamim A. Dar, K. F. Khan, Saif A. Khan, Akhtar R. Mir, H. Wani & V. Balaram

Arabian Journal of Geosciences

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DOI 10.1007/s12517-013-0903-8



Springer

2.5 to 1.6 Ga
In marine environment

The chemical analysis data of 23 sedimentary phosphorite deposits contained ΣREE up to 18,000 $\mu\text{g/g}$ and ΣHREE up to 7000 $\mu\text{g/g}$, suggesting phosphorite deposits are highly potential resources for REE than most conventional REE deposits.

Dar et al. (2013); Emsbo et al. (2015) & Balaram (2022)

Spectroscopy Techniques in Deep-Sea Research



LIBS
Raman Spectrometer
Near IR Spectrometer
Laser Induced Fluorescence Spectrometer, etc.

- The classic approach to investigate metals in deep sea sediments is to obtain samples by drilling that is followed by laborious laboratory analysis. This is very expensive, time consuming and not appropriate for exploring vast areas.
- Several different spectroscopic techniques have been used to enhance the capabilities of robotic technologies, some of which include near infrared spectroscopy, Raman spectroscopy and LIBS.
- The use of Raman spectroscopy technologies during exploration studies provides chemical properties of a given sample, such as its phase and polymorphism, crystallinity, and molecular interactions
- LIBS devices have already demonstrated their ability to measure a wide range of chemical elements present within seawater and underwater mineral deposits. LIF sensors have also successfully detected and measured the concentrations of dissolved oil hydrocarbons present underwater Cuffari, 2020

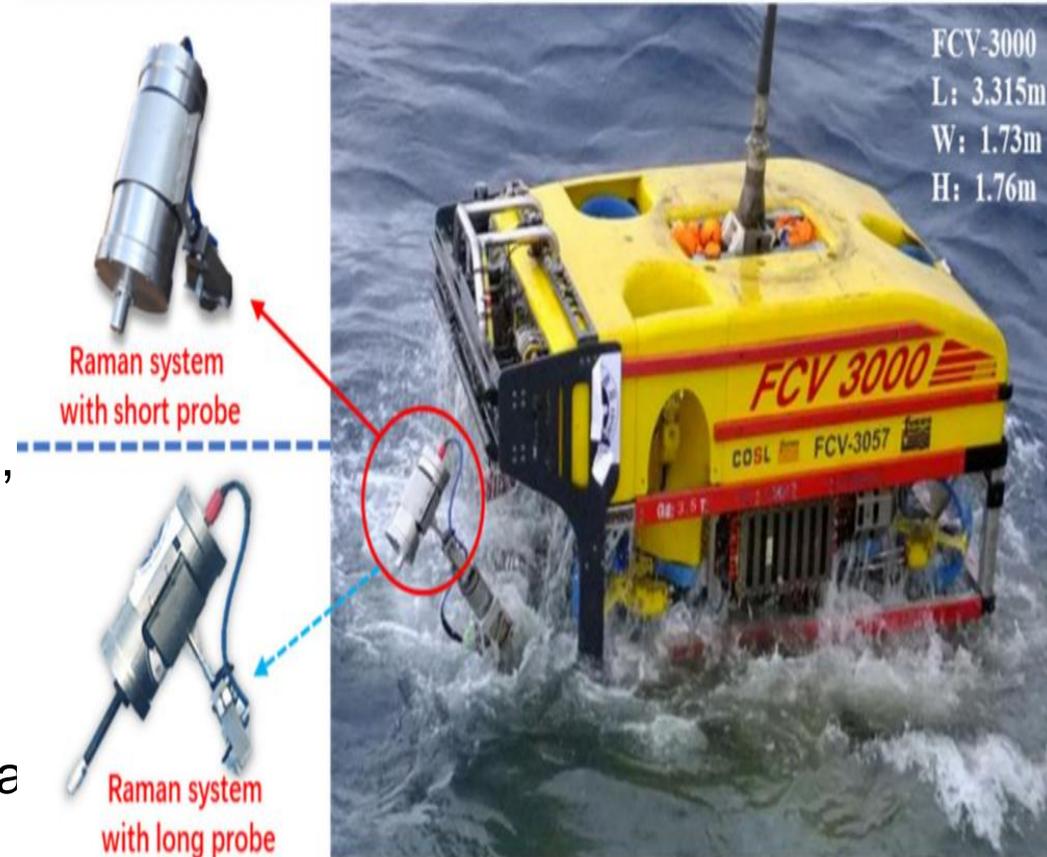
Deep-Sea Survey by Raman Spectroscopy

- Raman spectroscopy is becoming a popular underwater investigation method, especially in deep-sea research through the use of a titanium pressure vessel as housing.

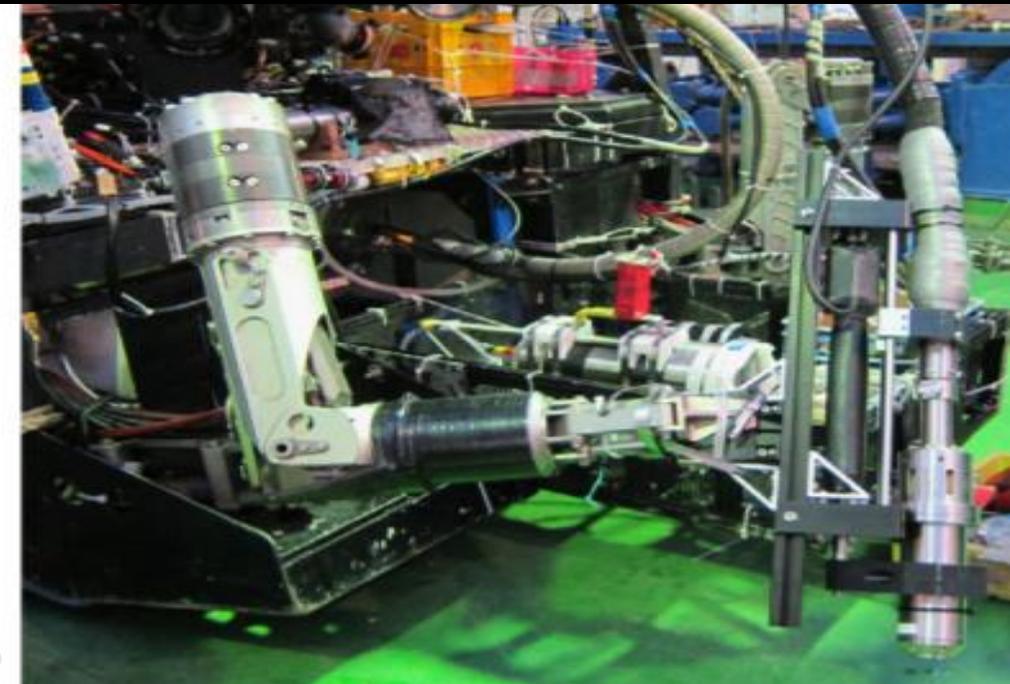
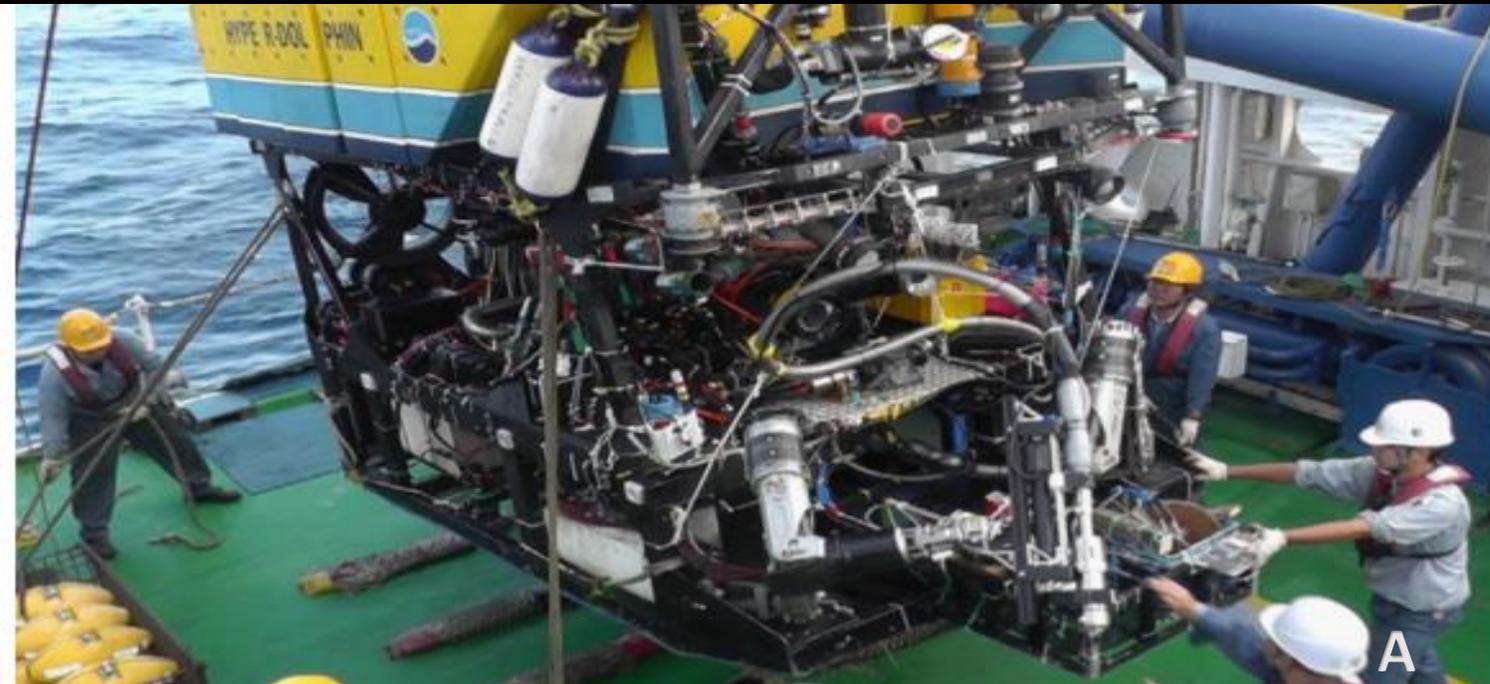
- The first sea trial was carried out with the aid of a 3000 m grade remotely operated vehicle (ROV) “FCV3000” in October 2018

- Over 20,000 spectra were captured from the targets interested, including methane hydrate, clamshell in the area of cold seep, and bacterial mats around a hydrothermal vent, with a maximum depth of 1038 m.

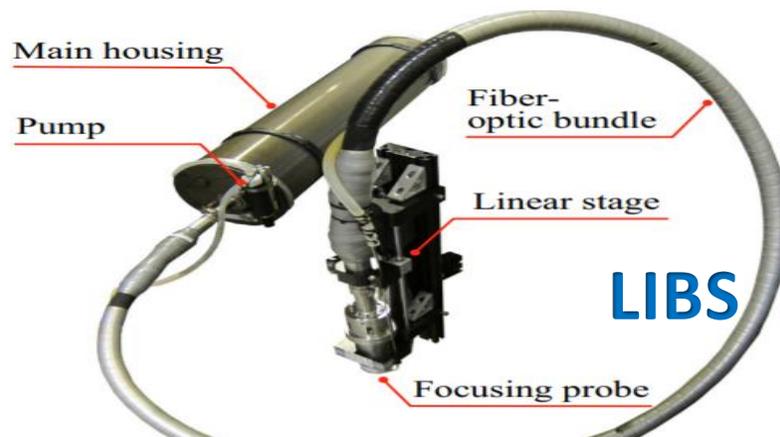
- A Raman peak at 2592 cm^{-1} was found in the methane hydrate spectra, which revealed the presence of H_2S in the seeping gas. In addition, sulfur was also found in the bacteria mats, confirming the involvement of micro-organisms in the sulfur cycle in the hydrothermal field. It is expected that the system can be developed as a universal deep-sea survey and detection equipment in the near future. [Liu et al, 2021](#)



In-Situ Multi-Element Analysis by LIBS in Deep-Sea Environment



(A) ChemiCam mounted on the ROV Hyper-Dolphin 3000 about to be deployed in the Okinawa trough, and (B) a close-up of the linearly actuated focusing probe held by the ROV's manipulator



Composition of sediment and rock samples obtained from the seafloor in the NW Pacific. Elements with concentrations >1% are shown in bold.

Sample	Depth m	Zn %wt	Cu %	Pb %	Fe %	Mn %	Co %	Ni %	Mg %	Al %	Ca %	Ti %	Ag ppm	Sb ppm	As ppm
Jade chimney	1340	19.80	4.39	12.20	10.20	0.08	<0.01	-	0.02	0.01	0.02	<0.01	182	215	628
Hatoma chimney	1485	12.00	5.25	10.30	3.50	0.46	<0.01	-	0.05	0.51	0.06	-	486	5940	7550
Yoron chimney	569	0.64	0.10	0.76	2.52	<0.01	<0.01	-	<0.01	0.04	0.11	-	532	3330	8550
Manganese crust	1390	0.10	0.06	0.21	9.50	16.20	0.57	0.46	1.03	0.98	6.32	0.34	<100	<100	217
Basalt	1418	0.02	0.02	0.02	8.66	0.20	<0.01	0.02	4.99	6.79	9.96	1.45	-	-	<100
Limestone	1147	<0.01	0.01	<0.01	0.38	0.47	<0.01	0.03	0.09	0.25	25.20	0.04	-	-	<100

Nuclear Techniques for REE Exploration in Deep-Sea

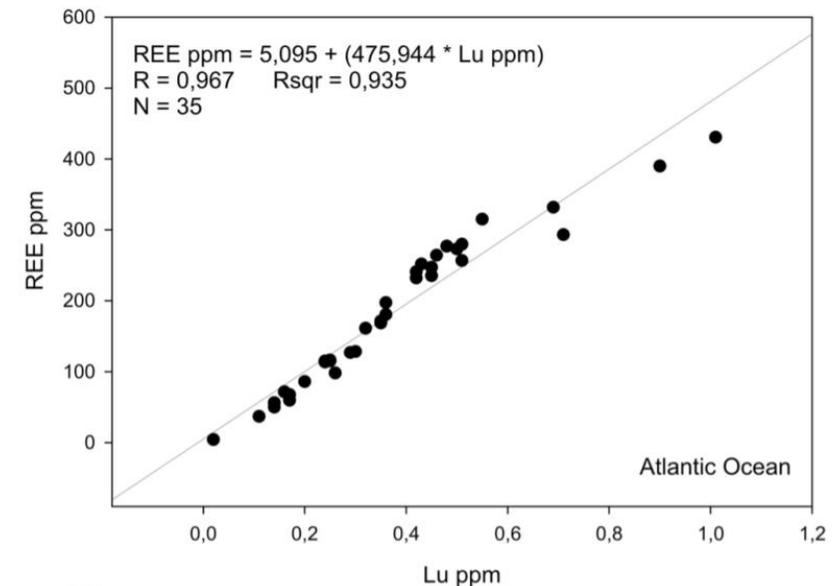
Two nuclear techniques for exploring REE in surface deep sea sediments:

1. Passive measurement of ^{176}Lu radioactivity, appropriate if long-term *in-situ* measurements are possible, and
2. The use of the neutron sensor attached to a remotely operated vehicle for rapid *in-situ* measurement of Gd by thermal neutron-capture. Since concentrations of Lu and Gd show strong linear correlation to the total REE concentrations in deep sea sediments, it is possible to deduce the total REE content by measuring Lu or Gd concentrations only.

Obhořař et al. 2018



UNCOSS ROV carrying neutron sensor during the Feld Test



Chapter 4

Sources and applications of rare earth elements

V. Balaram

4.1 INTRODUCTION

The International Union of Pure and Applied Chemistry (IUPAC) has defined the rare earth elements (REE) [REE: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), yttrium (Y) and scandium (Sc)] as a group of 17 chemically similar metallic elements that comprise the 15 lanthanide elements (La-Lu), Y and Sc. Due to the similar geochemical behavior of Y and Sc to the lanthanides in most environments in the earth's crust, they are very often grouped with the lanthanides and referred to as REE (Taylor & McLennan, 1985). The lower atomic weight elements La to Sm, with atomic numbers 57 to 62, are referred to as the light REE (LREE); while Eu to Lu, with atomic numbers 63 to 71, are known as the heavy REE (HREE) (Walters *et al.*, 2010). Despite their low atomic weights, Y and Sc are included with the HREE subgroup because of their co-occurrence, ionic radius and closer behavioral properties to the HREE than to the LREE (Table 4.1).

Another related consequence is the so-called 'lanthanide contraction' in which the ionic radius progressively decreases from La^{3+} (1.06 Å) to Lu^{3+} (0.85 Å) with the increase of atomic number. In lanthanide atoms, the configuration of the valence electrons of the outermost shell is the same for all the species while the

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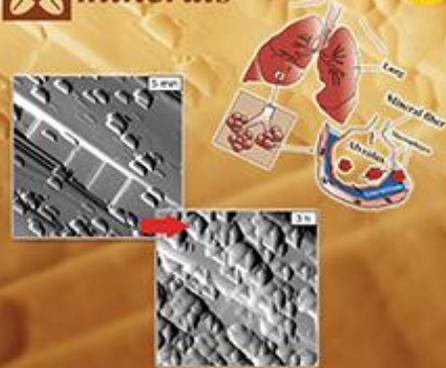
Environmental Technologies to Treat Rare Earth Element Pollution

Principles and Engineering

Editors: Arindam Sinharoy and Piet N.L. Lens



IMPACT FACTOR 1.835



Real-Time Observation of Fibrous Zeolites Reactivity with Simulated Lung Fluids

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minerals



Review

Indicator Minerals, Pathfinder Elements, and Portable Analytical Instruments in Mineral Exploration Studies

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Abstract: Until recently, the classic approach to mineral exploration studies was to bring the field samples/drill cores collected during field studies to the laboratory, followed by laborious analysis procedures to generate the analytical data. This is very expensive, time-consuming, and difficult for exploring vast areas. However, rapid technological advances in field-portable analytical instruments, such as portable visible and near-infrared spectrophotometers, gamma-ray spectrometer, pXRF, pXRD, pLIBS, and μ Raman spectrometer, have changed this scenario completely and increased their on-site applications in mineral exploration studies. LED fluorimeter is a potential portable tool in the hydrogeochemical prospecting studies of uranium. These instruments are currently providing direct, rapid, on-site, real-time, non-destructive, cost-effective identification, and determination of target elements, indicator minerals and pathfinder elements in rock, ore, soil, sediment, and water samples. These portable analytical instruments are currently helping to obtain accurate chemical and mineralogical information directly in the field with minimal or no sample preparation and providing decision-making support during fieldwork, as well as during drilling operations in several successful mineral exploration programs. In this article, the developments in these portable devices, and their contributions in the platinum group elements (PGE), rare earth elements (REE), gold, base metals, and lithium exploration studies both on land and on the ocean bed, have been summarized with examples.

Keywords: portable instruments; indicator minerals; pathfinder elements; core scanners; pXRF; pXRD; pNIR-SWIR spectrometer; μ Raman spectrometer; LIBS; mineral exploration; on-site analysis



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Mining the Deep Sea



- ❖ A new legal code issued by the ISA that regulates seabed mining in international waters is being adopted by 167 countries. This code will regulate the exploitation of minerals such as Mn, Co, Au, Cu, Fe, , REE & Pt, for commercial purposes.
- ❖ Until now, companies and states have only been able to survey and explore the territories they lease, but this new provision paves the way for future forms of commercial extraction.
- ❖ Many anti-deep sea mining organizations and communities are pushing for a moratorium on deep sea mining until 2030. They argue that the available scientific knowledge is not enough to go forward.

Deep Sea Mining Machine



The Patania II prototype on the floor of the Pacific Ocean

- The 25-ton robotic mining machine was developed by a Belgian company, to collect manganese nodules.
- The goal is to extract valuable metals such as Co and Ni, which are important for low-carbon technologies including electric cars.
- **(Korea and China seek the most contracts)**
- In April 2021, Belgian company Global Sea Mineral Resources (GSR) tested its 27-ton mining robot, Patania II, in the CCZ, which at one point became stranded at a depth of thousands of metres as it attempted to collect polymetallic nodules
- **1st May, 2021, Deep-sea mining tests resume after robot rescued from Pacific Ocean floor**

Mining of Deep-Sea Nodules



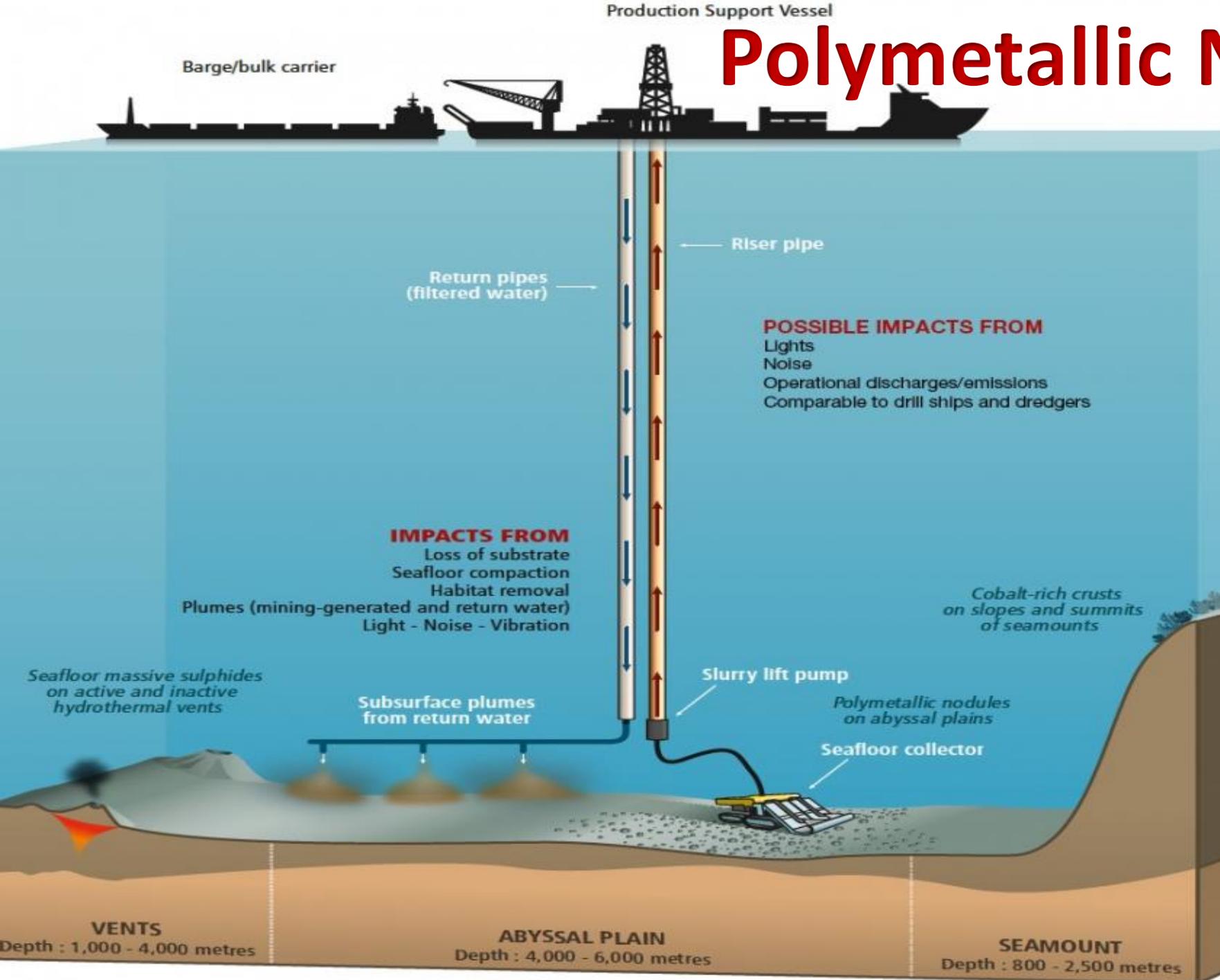
UN Ocean Economics and Technology Branch developed the following criterion for selecting a manganese nodule mine-site (UNOET, 1987):

- Cut off grade = 1.8% Cu+Ni
 - Cut off abundance = 5 kg / sq. m.
 - Topography = acceptable
 - Duration (D) = 20 years
 - Annual recovery (Ar) = 3 million dry tones
- A “mine site” is defined as an ocean bottom area where under specific geological, technical and economic conditions,

- A few private companies have collected nodules on exploratory missions in CCZ. They are pressuring the ISA to approve commercial operations.
- A typical area of 75,000 sq km with an estimated nodule resource of >200 mt., is expected to yield about 54 million tons of metals (Mn+Ni+Cu+Co)



Polymetallic Nodule Mining



○ All proposed seabed minerals mining operations are based on a similar concept of using a seabed resource collector, a lifting system and support vessels involved in offshore processing and transporting ore.

○ Remotely operated vehicles, which would extract deposits from the seabed using mechanical or pressurized water drills



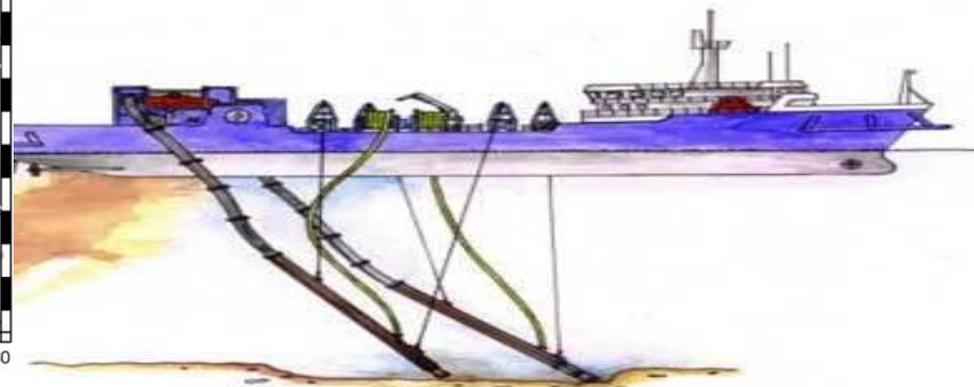
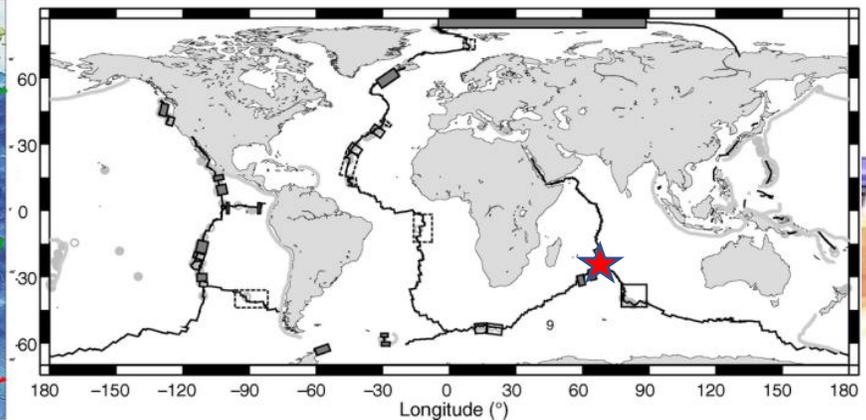
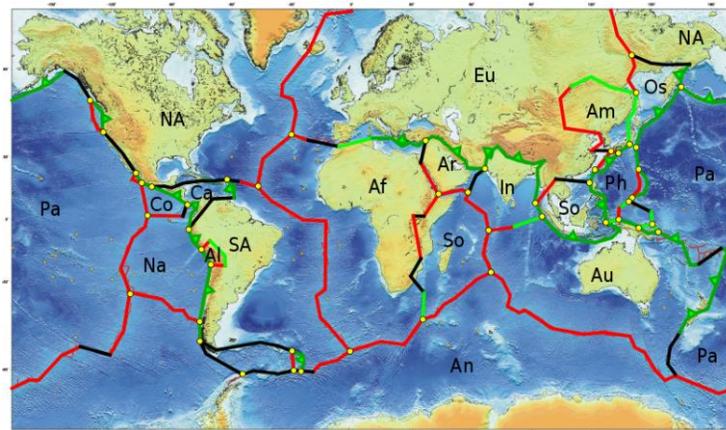
SARMIENTO DE GAMBOA is a Research/Survey Vessel that was built in 2007 and is sailing under the flag of Spain

Video of Mining of Polymetallic Nodules



Crust Mining

- Crust mining is technologically much more difficult than Fe-Mn nodule mining. Nodule mining concepts developed by mining consortia in the last decades consist of a **hydraulic dredge** and a **slurry lift system**.
- In contrast, Fe-Mn crusts are weakly to strongly attached to substrate rock. For successful crust mining, it is essential to recover Fe-Mn crusts without collecting substrate rock, which would significantly dilute the ore grade.
- Five possible Fe-Mn crust mining operations include **i) fragmentation, ii) crushing, iii) lifting, iv) pick-up, and v) separation**. The proposed method of Fe-Mn crust recovery consists of a bottom-crawling vehicle attached to a surface mining vessel by means of a hydraulic pipe lift system and an electrical umbilical.
- According to some studies, Rodriguez Triple Junction (international waters) in the Southern Indian Ocean is likely to become a mining target in the near future.



Example of Chain-bag Dredge with Crust Haul,
KK84 = Cruise, NW Hawaiian Islands.



Freshly cut crusts.jpg
006C4EBF!!Macintosh 160 GB HD BC848C5A:

Papua New Guinea's first offshore project Deep Sea Mining of Submarine Hydrothermal Deposits - Solwara 1



- Controversial deep sea mining project approved in Papua New Guinea, first of its kind. The Papua New Guinea government has granted a 20-year license for Cu, Au & Ag mining around a mile (1.6 kilometers) below the ocean's surface (0.1 square kilometer of seafloor) jump-starting **the world's first commercial deep sea mining venture**. The operation in PNG targeted hydrothermal vents.
- In 2007, a submersible with a large drill descended 1,600 meters into the sea off the coast of Papua New Guinea (PNG), landing near a network of hydrothermal vents that host an array of rare and unique sea life. The machine operators, working for Canadian mining company Nautilus Minerals, Inc., Canadian Company began drilling into the seabed, searching for Cu, Au, Zn and Ag. In the years that followed, the company drilled again and again.
- By 2019, Nautilus, the first company to ever receive a deep-sea mining license, had gone bankrupt before extracting any minerals, and the PNG government, which had invested in the project, was left with millions of dollars in debt.

The Project was Stopped

The first deep-sea mining project (The Solwara 1) at the international level was **approved but failed** before the extraction phase. Therefore, we the Alliance of Solwara Warriors call on the Government to revoke the Project and **put a total ban on further seabed mining projects** in our customary waters.



The maritime communities from the Bismarck and Solomon Seas have been resisting Nautilus Minerals experimental projects since 2008. The company stopped its activities in 2018

- The local residents (About 20 local communities) of New Ireland province in PNG were worried because the mining is experimental, there are no examples anywhere in the world, and Papua New Guinea has no regulatory framework.
- They knew that there is an active undersea volcano at that site, could it cause a tsunami?
- It also affected their unique shark calling culture which is their identity. They are a major source of food for their people. When Nautilus started its exploration activities the sharks left their waters

Environmental Impact of Deep-Sea Mining

- Exploration contracts for deep-sea resources have been awarded to companies from countries including China, the UK, Belgium, Germany, France and Japan for three different mineral resources: seafloor massive sulfides (SMS), ferromanganese crusts and polymetallic nodules.
- Mining the seabed carries significant environmental concerns. Millions of animals tiny, small and big live in deep ocean, ecosystem and to the connectivity to the rest of the planet. Environmental scientists feel that the planet is under threat and even our oceans. Our deep oceans are not deeply explored and poorly understood. If we move forward before we have the appropriate information to manage these impacts, we could be losing species, habitats and many of the functions and services that life on this planet relies on
- Hence, marine experts are calling for a moratorium on deep-sea mining until its ecological consequences can be better understood [Miller et al. 2018](#)



Coral Reefs are Dying Around the World



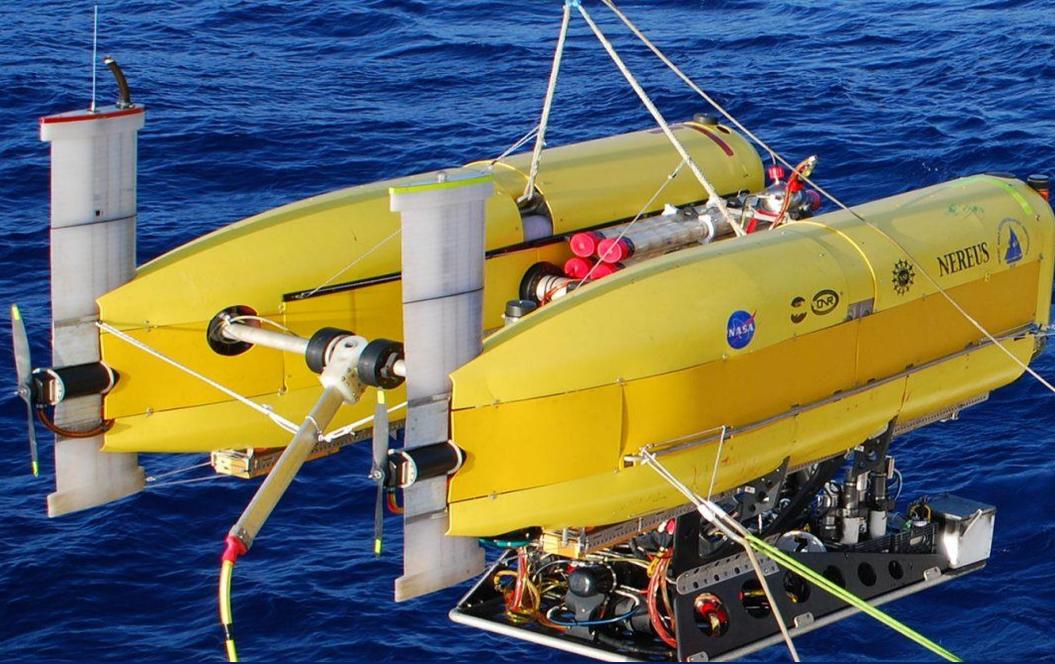
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BBC

- Corals are mined because they are a source of limestone and other construction materials. In some places they are also used as bricks, while in others they are used to lay roads
- Due coral mining, metal mining, pollution (organic and non-organic), overfishing, blast fishing, the digging of canals and access into islands and bays.
- Rising sea surface temperatures and acidic waters could eliminate nearly all existing coral reef habitats by 2100.

Balaram et al. 2022

Environmental Impact Studies by Different Groups Across the World



The hybrid remotely-operated vehicle was used by scientists of Lehigh University, Pennsylvania, US, to collect seafloor samples, in addition to remotely operated vehicle, at Piccard hydrothermal vents at mid-cayman rise. The discovery of hydrothermal vents—where volcanoes at the seafloor produce hot fluid exceeding 350° C fundamentally changed our understanding about Earth and life in the 1970s. Yet, life at and underneath the seafloor is still very much a mystery today.

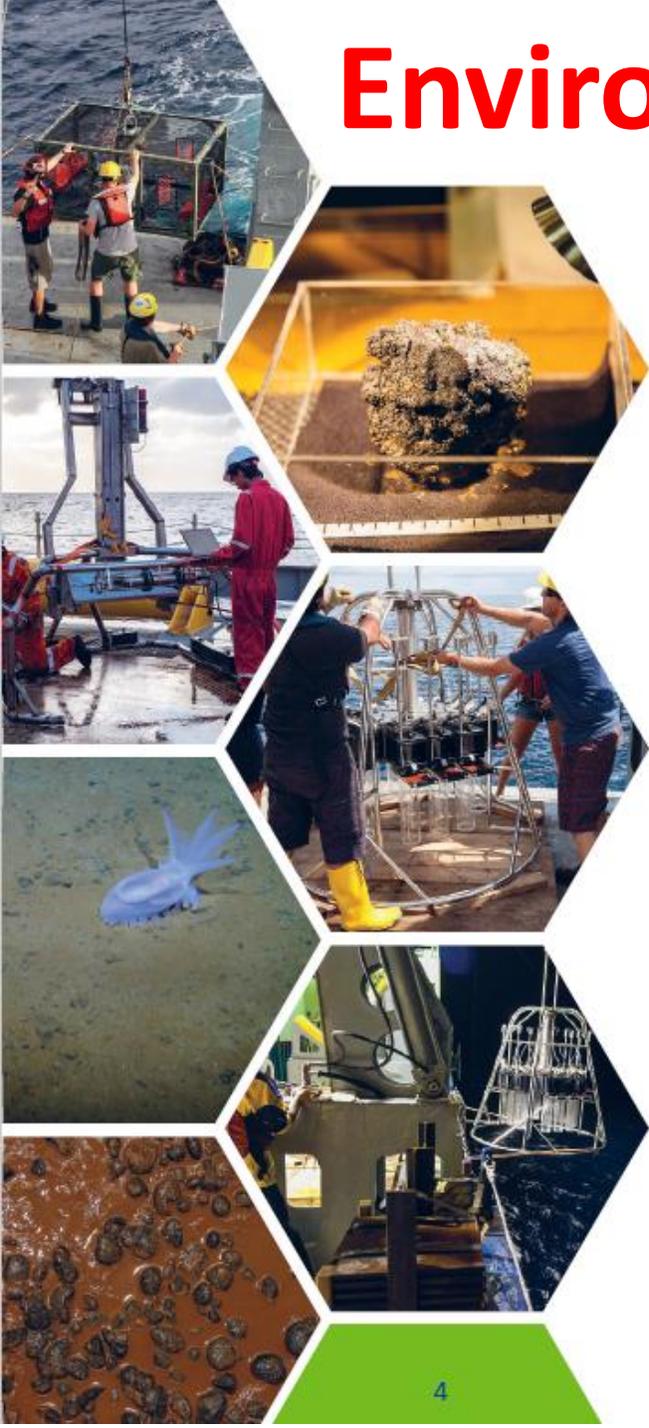
**Abiotic redox reactions in hydrothermal mixing zones:
Decreased energy availability for the
subsurface biosphere**

PNAS, 2021

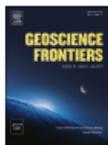
Jill M. McDermott^{a,1,2}, Sean P. Sylva^a, Shuhei Ono^b, Christopher R. German^c, and Jeffrey S. Seewald^a

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Environmental Impact of Sea-Bed Mining



- James Cook University in Australia and the University of the South Pacific, with a main campus in Fiji, reviewed 250 scientific articles. It analyzed current mining interests in the Pacific Ocean and various mining processes, and assesses the potential impacts on local ecosystems, biodiversity, fisheries, and social and economic dimensions.
- It also highlighted many gaps in knowledge about deep-sea habitats and species, and how very little is known or understood about the risks of deep-sea mining.
- The environmental impacts of nodule mining are manifold. Polymetallic nodules, which take millions of years to form, provide a critical habitat for an array of unique and largely understudied species, including deep-sea corals, sponges, sea urchins, starfish, jellyfish, squid, octopus, shrimp, and sea cucumbers. Deep-sea habitats and species are slow-growing, so a full recovery after mining could take thousands, if not millions, of years — if a recovery is possible at all. Mining of polymetallic nodules is predicted to lead to a significant loss of biodiversity in the marine environment
- The sediment plumes and waste discharge from mining could upset phytoplankton blooms at the sea's surface, and introduce toxic metals into marine food chains. This mining waste could also travel through the ocean and damage nearby seamounts and coral reef systems, which many fish and marine mammal species depend upon for shelter and food, and put entire fisheries at risk.
- The potential impacts of light pollution, which could disrupt a multitude of species attuned to living in the dark, and noise pollution that could change the swimming and schooling behavior of tuna, and cause dolphins and whales to strand.
- On the other hand, the ISA is under a lot of pressure to get the regulations finalized that would allow the mining to start.



Focus Paper

Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact



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ABSTRACT

Rare earth elements (REE) include the lanthanide series elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) plus Sc and Y. Currently these metals have become very critical to several modern technologies ranging from cell phones and televisions to LED light bulbs and wind turbines. This article summarizes the occurrence of these metals in the Earth's crust, their mineralogy, different types of deposits both on land and oceans from the standpoint of the new data with more examples from the Indian subcontinent. In addition to their utility to understand the formation of the major Earth reservoirs, multi-faceted updates on the applications of REE in agriculture and medicine including new emerging ones are presented. Environmental hazards including human health issues due to REE mining and large-scale dumping of e-waste containing significant concentrations of REE are summarized. New strategies for the future supply of REE including recent developments in the extraction of REE from coal fired ash and recycling from e-waste are presented. Recent developments in individual REE separation technologies in both metallurgical and recycling operations have been highlighted. An outline of the analytical methods for their precise and accurate determinations required in all these studies, such as, X-ray fluorescence spectrometry (XRF), laser induced breakdown spectroscopy (LIBS), instrumental neutron activation analysis (INAA), inductively coupled plasma optical emission spectrometry (ICP-OES), glow discharge mass spectrometry (GD-MS), inductively coupled plasma mass spectrometry (including ICP-MS, ICP-TOF-MS, HR-ICP-MS with laser ablation as well as solution nebulization) and other instrumental techniques, in different types of materials are presented.

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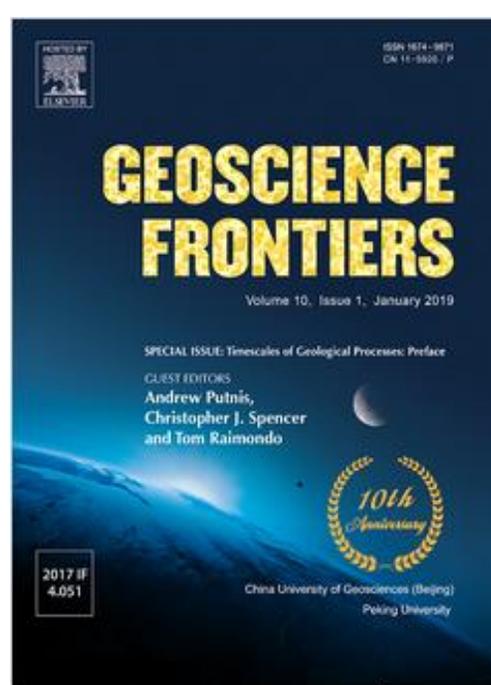
1. Introduction

Rare-earth elements (hereinafter referred to as REE) are a group of seventeen chemical elements in the periodic table, in particular the fifteen lanthanides as well as yttrium and scandium as defined by the International Union of Pure and Applied Chemistry (IUPAC). Scandium and yttrium are considered REE since they tend to occur in the same ore deposits as the lanthanides and exhibit similar chemical properties. All REE occur in nature but not in pure metal form, although Promethium, the rarest, only occurs in trace quantities in natural materials as it has no long-lived or stable isotopes (Castor and Hendrik, 2006). In lanthanide atoms, the configuration of the valence electrons of the outermost shell is the same for all the species while the 4f orbitals are progressively filled with increasing

atomic number. Screening of the 4f orbitals leads to the extremely similar physical and chemical properties of the elements. Another related consequence is the so-called "lanthanide contraction" in which the ionic radius progressively decreases from La³⁺ (1.06 Å) to Lu³⁺ (0.85 Å). REE are the elements that have become extremely important to our world of technology owing to their unique magnetic, phosphorescent, and catalytic properties. These elements are critical to technologies ranging from cell phones and televisions to LED light bulbs and wind turbines. The estimated average concentration of the REE in the Earth's crust which ranges from around 130 µg/g to 240 µg/g which is actually significantly higher than other commonly exploited elements, and much higher than their respective chondritic abundances (Zepf, 2013). Table 1 presents the average abundances of REE (in µg/g) in Earth's crust in comparison with chondritic abundances. This review aims to provide an updated understanding of the global scenario of REE, starting from their applications in high technology products, occurrence, different types of economic deposits both on land and oceans, their

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Recent advances in MC-ICP-MS applications in Earth and environmental sciences: Challenges and solutions

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marine

ABSTRACT

The development of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) in 1992 opened up new opportunities for geochemical, mineral exploration, and environmental studies. Recent developments in MC-ICP-MS and its hyphenation to techniques such as laser ablation including femto-second laser sampling, advances in detection system and several other developments made MC-ICP-MS, one of the most versatile analytical techniques for the determination of isotopic compositions in several types of earth and environmental materials. Different studies in recent times indicated that MC-ICP-MS can routinely produce isotopic data that is similar in precision to those obtainable by secondary ion mass spectrometry (SIMS), sensitive high resolution ion microprobe (SHRIMP), and thermal ionization mass spectrometry (TIMS), with striking advantages such as relatively higher throughputs, ease of analysis as the source operates at atmospheric pressure, and possibility of sample introduction by other means such as laser ablation and chromatographic techniques. Recent studies demonstrate the decisive benefits of MC-ICP-MS analysis (both solution and laser ablation modes) not only isotopic ratio determinations, but also absolute element concentration determinations of several elements in the periodic table in different types of geological and environmental materials in terms of versatility, accuracy, precision and for improved spatial resolution. Laser ablation split stream (LASS) technique with ability to do dating, and capability to obtain isotopic and elemental information simultaneously in rocks and minerals on a single sampling event, when coupled to a second ICP-MS system (typically a quadrupole ICP-MS or a high resolution-ICP-MS) demonstrated its potential to become an important analytical tool in solving important problems, especially in geochemistry. The performance characteristics of MC-ICP-MS are compared with those of other similar analytical techniques such as TIMS, SHRIMP, and SIMS with recent examples. This review contains detailed descriptions of the development of MC-ICP-MS instrumentation, analytical procedures, reference materials, and focused applications in the area of geochemistry, mineral exploration, and environmental areas.

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1. Introduction

Geochemistry is a rapidly expanding and has become a dominant subject in solving the mysteries of the Earth such as evolution of life, formations of the Earth's crust, oceans and a variety of mineral deposits, and even the current climate change crisis. Many of the discoveries made in geochemistry including the discoveries of new mineral deposits over the last half-century, were driven by spectacular inventions and developments in the area of analytical instrumentation (Balam, 2021a; V. 2021b, 2021c). For exam-

ple, studies using secondary ion mass spectrometry (SIMS), Raman Spectrometry, scanning electron microscopy (SEM), transmission X-ray microscopy and other analytical techniques were instrumental in the landmark discoveries of the Earth's known rock record of 4.4 Ga in the detrital zircons from Jack Hills, metasedimentary belt, W. Australia, and the emerging of biogenic origin (life on Earth) by 4.1 Ga (Bell et al., 2015). The invention of quadrupole inductively coupled plasma mass spectrometry (ICP-MS) by Prof. Sam Houk in 1980 at the Department of Chemistry, Iowa State University, US, in association with Prof. Alan Gray, Department of Chemistry, University of Surrey, Guildford, UK (Houk et al., 1980) provided an invaluable analytical tool to the geoscientists. ICP-MS simplified the geochemical analysis with its multi-element and multi-

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India's deep ocean mission to study



<https://byjus.com/current-affairs/deep-ocean-mission-india/>

DEEP OCEAN MISSION

- Deep Sea Mining through 'Underwater Vehicles' and 'Underwater Robotics'
- Asserting exclusive rights to explore polymetallic nodules from seabed **over 75,000 sq km of areas in international water**
- Estimated polymetallic nodules resource potential: **380 million tonnes (MT)**

THESE POLYMETALLIC NODULES CONTAIN

Manganese	92.6 MT
Nickel	4.7
Copper	4.3
Cobalt	1

(*figures are rounded off)

- Development of ocean climate change advisory services
- Technology for sustainable utilisation of marine bio-resources

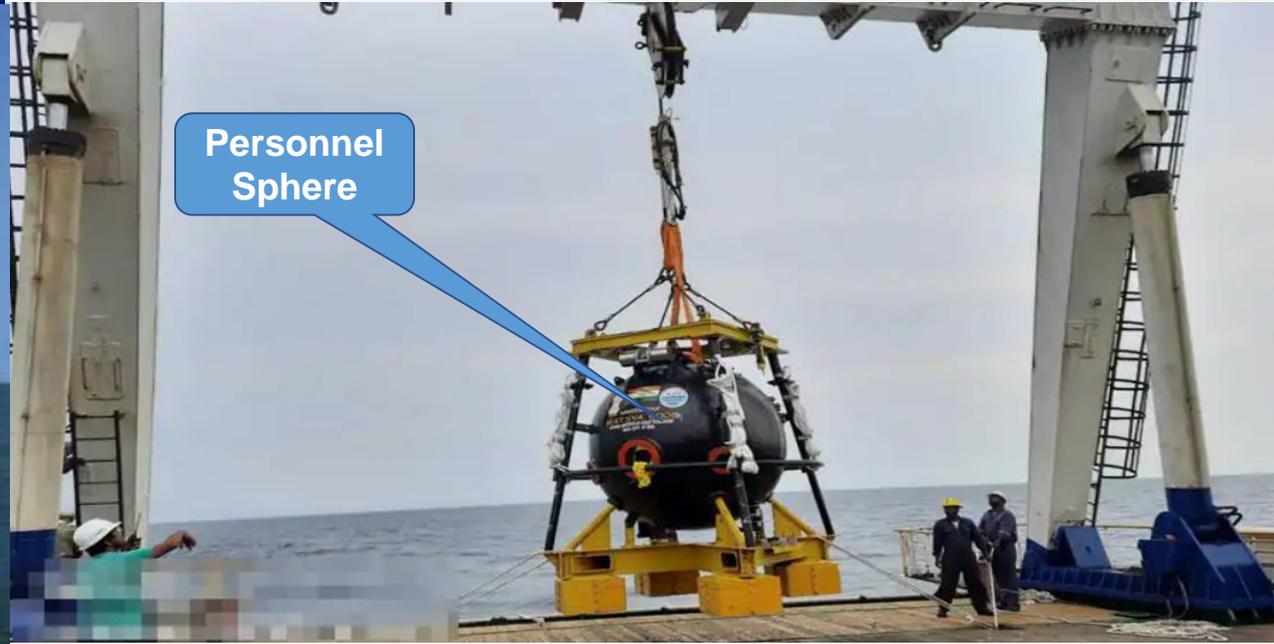
- Deep ocean survey and exploration
- Energy from the ocean and offshore-based desalination
- Krill fishery from southern ocean

The major objectives of the Deep Ocean Mission are as follows:

- ❑ Development of technologies for deep sea mining, underwater vehicles and underwater robotics;
- ❑ Development of ocean climate change advisory services;
- ❑ Technological innovations for exploration and conservation of deep sea biodiversity;
- ❑ Deep ocean survey and exploration, etc.

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Indian Samudrayaan Project for Deep Ocean Exploration, NIOT, Chennai



- ❖ NIOT, Chennai, had developed a '**Personnel Sphere**' built of mild steel and tested it as an unmanned trial, using the Ocean Research Vessel Sagar Nidhi, in Bay of Bengal. This trial was a precursor and the sphere was lowered upto a depth of 600 metres, off Chennai coast. The next one wherein a sphere of 2.1m diameter will be built in which three humans can sit and be sent off to a depth of 6,000 meters.
- ❖ According to Dr. Ramadass (Director, NIOT, Chennai), the manned-submersible will be ready for qualification trials by December 2024, the Union minister wished the nation could set a record by sending a man to deep ocean and deep space simultaneously. ISRO is planning for Gaganyaan, a manned space mission, in early 2023. The final MATSYA 6000 will be capable of carrying three crew members with an endurance of 12 hours and an additional 96 hours in case of emergency. It will be maneuvered at the deep sea floor autonomously using a battery-powered propulsion system at 6,000 meters depth.
- ❖ As India is a pioneer investor and continuing contract for deep sea mineral exploration under United Nations ISA, this vehicle helps India harvest the resources and assist in development of Integrated Mining System.

Should We Mine on the Ocean Floor?

Almost 70 % of our planet is an ocean and of that, 90 % is the deep sea. It houses countless species ranging from tiny zooplankton to the heaviest whales. This combination supports in maintaining the ecological cycle of our planet. Many feel that deep-sea mining may cause potentially irreversible damage to aquatic life.

GREENPEACE

Protect the Oceans- The seas provide half of our oxygen, food for a billion people, and a home for some of the most spectacular wildlife on Earth. But the impacts of climate change, pollution and destructive industries mean they're in more danger than ever. We urgently need to turn things around.

British scientists recently found that an underwater mountain near the Canary Islands holds some of the richest deposits of rare minerals anywhere on Earth.

<https://www.bbc.com/news/av/science-environment-39572104/should-we-mine-on-the-ocean-floor>

David Attenborough, called for a moratorium on all deep-sea mining plans



What can be done?

- ❑ A better understanding of the deep sea is necessary to guide mitigation strategies and proper enforcement of regulations in order to limit the environmental impacts of mining activities.
- ❑ **Baseline studies:** Comprehensive baseline studies are needed to understand what species live in the deep sea, how they live, and how they could be affected by mining activities.
- ❑ **Environmental impact assessments:** High-quality environmental assessments are needed to assess the full range, extent and duration of environmental damage from deep-sea mining operations.
- ❑ These assessments are also needed to ensure that the loss of biodiversity as a result of mining operations is properly accounted for in mining regulations set by authorities, well before any decision to mine is approved.



EXPEDITION 335



SUPERFAST SPREADING RATE CRUST 4

INTEGRATED OCEAN DRILLING PROGRAM

APRIL 13 - JUNE 3, 2011

EXPEDITION 340



LESSER ANTILLES

INTEGRATED OCEAN DRILLING PROGRAM

MARCH 3 - APRIL 17, 2012

My collaborators



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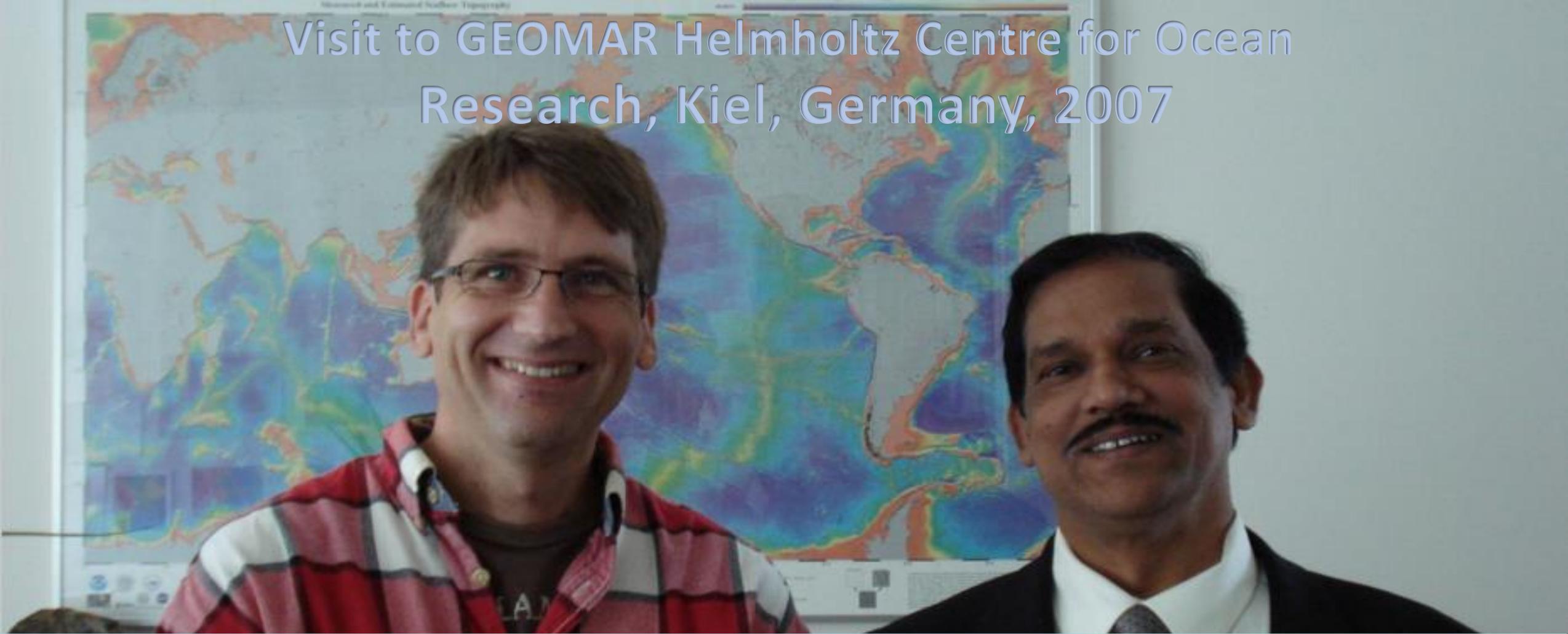
34th IGC, Brisbane, Australia, 2012



Dr. James R. Hein, USGS

Menlo Park, California,

Visit to GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany, 2007





Conclusions & Future

- Deep-sea minerals with respect to global economy suggest that seafloor massive (polymetallic) sulfides around hydrothermal vents, cobalt-rich crusts on the flanks of seamounts or fields of manganese (polymetallic) nodules on the abyssal plains will be increasingly important in meeting the deficit of metals such as Co, REE, Mn, Ni, Cu, Co, and others.
 - In addition to mineral deposits, there is interest in extracting methane from gas hydrates on continental slopes and rises.
 - Crust mining is technically much more difficult than manganese-nodule mining. Recovery of nodules is easier because they sit on a soft-sediment substrate, whereas crusts are weakly to strongly attached to substrate rock.
 - *In-situ* analytical techniques are more appropriate and useful for the successful exploration, mining of deep-sea minerals, and to understand the ecosystem.
 - Many of the regions identified for future seabed mining are already recognized as vulnerable marine ecosystems. Several studies suggest that mining on the ocean floor could do irreversible damage to marine ecosystems.
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Wish You All a Glorious Future