

#### Studies on the development of accretionary prisms and arc magmatism [Keywords: Geology, Tectonics, Geochemistry, Geochronology, Paleo-environment] Professor: Ryo Anma

Faculty of Science and Technology





Analogue modelling of accretionary complex (above)

Shape and intensity of flow structures defined by alignment of orthoclase megacrysts inside the Yakushima pluton, SW Japan (left)

> Flow fabrics defined by anisotropy of magnetic susceptibility obtained from the Cocos plate oceanic crust and lateral migration of magmas in the spreading ridge (left)



Rain-water sampling in West Asian countries and the rain-water composition

#### Content:

My main interest is in the processes of continental crust formation at subduction zones, especially those formed in ridge-subduction environment. My interests extend to the development of accretionay prisms and distribution of seismogenic faults, accretion processes of oceanic crust at spreading ridges and mechanisms of magma intrusion. Fieldwork based on structural geological methods is my main approach to understand these processes, but I also take paleomagnetic, geochronological, geochemical approaches. My focal area for this study is in Southwest Japan and Chile-ridge subduction zone. Utilizing IODP drilling ships and research vessels and submersibles run by JAMSTEC, I studied structures and development of accretionary prism in the Nankai trough, sedimentation nearby seismogenic zones in the Chile margin, oceanic crust accretion processes off Panama. More recently, I run an archaeological project on development of urban mine in the early Mesopotamian cities and its relation to the environmental changes surrounding the cities.

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## **Basic Laws in Elementary Particle Physics**

#### Professor Ken-ichi Izawa

Faculty of Science and Technology



Content: As shown in the left pannel, particle contents of matter and its interactions are well known at present almost in every respect. Such accumulated knowledge of particle interactions culminates in the so-called standard model of elementary particles. The model itself seems sufficient to describe nature observed so far.

However, the origin of the particle content is unclear in the standard model of elementary particles. The model has been built on quantum theory and relativity, whose restriction on the model building is not so strong as to pin down the standard model. Moreover, the quantum theory seems generic enough to describe observed data of physical phenomena, while theory of relativity is not inevitable from a theoretical point of view.

Our research on basic laws in elementary particle physics aims to reveal fundamental structures that select the standard model among other possibilities. The candidate structure is a new physical symmetry called supersymmetry, yet to be observed in nature. In particular, maximal supersymmetry may be sufficiently restrictive to fix the corresponding theory uniquely. A substructure of supersymmetry might lead to relativity under mild assumptions in the quantum theory.

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## **Environmental Analytical Chemistry** Prof. Dr. Shoji IMAI

**Faculty of** Science and Technology Tokushima Universit



Laboratory.

# 5

## Catalytic Asymmetric Synthesis of Planar-Chiral Transition-Metal Complexes

Faculty of Science and Technology



Synthesis of  $\pi$ -Arene-Cr Complexes and Application



### Professor Masamichi OGASAWARA

#### Content:

The two faces of an unsymmetrically substituted cyclopentadienyl anion are enantiotopic each other. The  $\eta$ 5-coordination of a metal cation to the Cp anion discriminates the two faces, and the obtained metallocene becames chiral. This type of chirality is called "planar-chiral". Planar-chiral metallocenes are important chiral scaffords in asymmetric synthesis, however, their effective preparations in scalemic forms are limited. We have demonstrated that the olefin metathesis can be applicable to the transformation of various metallocenes, and chiral metathesis of planar-chiral metallocenes.

Analogous planar-chirality can be seen in unsymmetrical  $\pi$ -arene-Cr complexes as well, and we have also succeeded to achieve the catalytic asymmetric synthesis of various planar-chiral  $\pi$ -arene-Cr by the asymmetric ring-closing metathesis. The phosphinoderivatives from the planar-chiral compounds have been clarified to be excellent chiral ligans in the Rh-catalysis.

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## NMR study of Ion Dynamics in Electrode Materials for Ion Rechargeable Battery

Faculty of Science and Technology



### Professor Koichi Nakamura

Content:

Energy device materials such as ion rechargeable battery and fuel cell are key materials for sustainable energy resource. Conventional electrical measurement technique is inadequate to study electrochemical reaction microscopically. In special, microscopic insights for ion intercalation/de-intercalation are required to develop electrode materials for the advanced rechargeable battery.

NMR is a powerful tool to study local ion dynamics and electronic state in electrode materials because of probing nucleus directly. Spin-lattice relaxation, Spin-spin relaxation, and FT spectrum give an important information to the development of materials for ion rechargeable batteries.

We aim to understand diffusion mechanism and ionic conducting behavior in various ion conductors/electrode materials with NMR technique.

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Faculty of Science and Technology Search for cosmic dark matter particles Professor Ken-Ichi Fushimi





Content:

We search for the particle candidates of cosmic dark matter by means of an inorganic crystal scintillator. The well-known atoms (Upper Picture) accounts for only 5% of the components of the Universe. The other part of the Universe consists of unknown dark matter (23%) and unknown dark energy(72%). Many candidates of the dark matter are proposed by various theories which describes beyondstandard theory.

Our project to search for dark matter named PICO-LON aims to find particle candidates for cosmic dark matter by means of a large volume and highly radiopure NaI(TI) crystal. NaI(TI) is highly sensitive to various candidates of dark matter particles.

The dark matter experiments are needed to be performed under extremely low background environment: the expected event rate is less than a few events per day. Our laboratory has developed a highly radiopure Nal(TI) detector whose impurity was lowest in the world (Lower Picture).

We are developing a larger (total mass of 1 ton) and purer Nal(TI) scintillator to construct the dark matter search detector PICO-LON (<u>Pure Inorganic Crystal Observatory for LOwbackground Neutralino</u>).

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## Molecular Developmental and Evolutional Biology Professor Kazuhiro, Makabe



Proposal for the evolution of Huntingtin (Hd) expression in the Metazoa.

A. Early embryonic expression of Hd has been observed in fruit flies, sea urchins, ascidians, and zebrafish.

B. The adult expression pattern of Hd.

C. Expression of Hd found in both ectoderm and mesendodermal tissues in vertebrates.

D. Polymorphisms in the polyQ repeat lengths are seen in primates and swine, but not in other vertebrates. Danio and Fugu HD contain only 4 Qs, and in Drosophila the CAG repeat is not present, indicating that the polyQ expansion of HD is a tetrapod, possibly mammal, specific character.

Collaboration with Professor R. Raff at Indiana University, USA.

#### Content:

Huntington's disease is a progressive neurodegenerative disorder in humans, which is characterized by onset of dementia, muscular ataxia, and death. Huntington's disease is caused by the expansion of the polyglutamine (polyQ) tract in the N-terminus of the HD protein (Huntingtin). The evolutionary origins of the vertebrate Hd gené are not well understood. We have cloned and characterized the expression of the Hd gene in two invertebrate deuterostomes, and have examined the expression patterns in a phylogenetic context. Echinoderms are basal deuterostomes and ascidians are basal chordates: both are useful for understanding the origins of and evolutionary trends in genes important in vertebrates. Expression of Hd RNA is detected at all stages of development in both the echinoderm and ascidian studied. In the echinoderm, Hd is expressed in coelomic mesodermal tissue derivatives, but not in the central nervous system. In the ascidian, expression is located in both mesoderm and nervous tissue. We suggest that the primitive deuterostome expression pattern is not neural. Thus, neural expression of the Hd gene in deuterostomes may be a novel feature of the chordate lineage, and the original role(s) of HD in deuterostomes may have been non-neural.

Keywords: marine and freshwater invertebrates,

gene expression E-mail: kwmakabe@tokushima-u.ac.jp Phone: +81-88-656-7269 Fax : +81-88-656-7269 Web : http://pub2.db.tokushima-u.ac.jp/

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## Novel Properties in Strongly Correlated Electron System Professor Ko-ichi Magishi

Faculty of Science and Technology Tokushima University



#### Content:

The materials show a variety of physical properties, and the intermetallic compound including rare earth elements is known to show specific quantum phenomena such as a heavy-fermion state or anisotropic superconductivity caused by strong repulsive force between 4f electrons, called a strongly correlated electron system (Fig.1). It is expected to discover novel properties of physical phenomena by understanding the details of microscopic electronic states.

For example, the various properties of the caged compound are caused by the interaction between the 4f electrons of the rare earth elements in the cage, and show specific quantum states such as a heavy-fermion state or multi-pole ordering state. It is important to clarify the microscopic electronic states using the nuclear magnetic resonance (NMR) method. The NMR spectrum reflects the microscopic electronic states (Fig.2), and we can obtain the information for each site. We make use of this characteristic and investigate the microscopic origin of the novel quantum states.

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Technology Tokushima University

## Study on the Sr-mediated New Synthetic Methods Professor Ph, D Norikazu Miyoshi



- 1) N. Miyoshi, K. Kamiura, H. Oka, A. Kita, R. Kuwata, D. Ikehara, M. Wada, *Bull. Chem. Soc. Jpn.*, **77**, 341 (2004).
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- 5) N. Miyoshi, T. Matsuo, M. Mori, A. Matsui, M. Kikuchi, M. Wada, M. Hayashi, *Chem. Lett.*, **2009**, 996.
- 6) N. Miyoshi, M. Asaoka, Y. Miyazaki, T. Tajima, M. Kikuchi, M. Wada, *Chem. Lett.*, **2012**, 35.

Organometallic compounds are some of the most versatile reagents in organic synthesis and among them organometallic compounds of alkaline-earth are elements. However, few studies on the preparation and reactivity of organostrontium compounds were found in the literature<sup>1</sup> outside our study. We have been synthetic reactions using investigating strontium compounds and have reported that the alkylation of aldehydes or imines with alkyl iodides<sup>1,2</sup> and dialkylation of esters with alkyl iodides<sup>3</sup> proceeded smoothly using metallic strontium to afford the corresponding adducts in good yields. Moreover, various esters reacted with metallic strontium and alkyl iodides to give dialkylated products, followed by adding acid chlorides or acid anhydrides to afford the corresponding bulky tert-alcohol esters in good yields.<sup>6</sup> Furthermore, aliphatic carboxylic acids reacted with methyl iodide to give the corresponding methyl ketones in moderate to good yields, and benzoic acid proceeded to obtain the unexpectedly p-alkylated adducts in good yields.

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## Development of Oxide-based Solid Acid Catalysts and X-ray Spectroscopy

Tokushima University



2. Analysis of X-ray Emission from Pyroelectric Crystal, and Application of Pyroelectricity for Chemical Reactions



#### Professor Takashi Yamamoto

Content:

Zirconium oxide-based solid acids have been attracted much attention because of their strong acidic property which n-butane isomerization promotes even at ambient temperatures, highly thermal stability, and ease of preparation and handling. We have been investigating generation mechanism of the strong acidity and the active sites using typical reactions and spectroscopic techniques. Catalyses of new solid acid-base catalysts, and their chemical and physical properties was also examined.

X-ray absorption spectroscopy has been widely utilized as a powerful tool to investigate the chemical states and electronic structure of target elements in many research fields. We have characterized various kinds of catalyst and environmental samples using SR- and/or laboratory-type XAFS. Features of the pre-edge peaks were investigated from a view point of the selection rule, coordination number, number of d-electron and symmetry of the coordination sphere.

X-ray emission behavior from a pyroelectric single crystal, pyroelectricity-induced chemical reactions have been also investigated.

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## Research for tectonics with special focus on exhumation mechanism of high-P/T metamorphic rocks Associate professor: Mutsuki Aoya

Faculty of Science and Technology Tokushima University



#### Content:

Metamorphic rocks generate through solid-state chemical reactions under high-pressure (P) and high-temperature (T) conditions at depths of the earth. Tokushima is located on a high-P/T metamorphic belt, the Sambagawa belt, which contain rocks that formed at depths of several 10s km in a subduction zone (such as eclogite and blueschist: Fig.1&2). The exhumation mechanism of such metamorphic rocks is still unclear and is a main research interest of our laboratory.

We usually carry out field studies for metamorphic rocks mainly focusing on deformational structures and also take rock samples. We make thin-sections of the samples to study mineral assemblages and their microstructures under polarizing microscope. Thus far, for example, we recognized a chronologically close association of ridge subduction with exhumation of the Sambagawa metamorphic rocks, and an evidence for trapping and bringing-up of hanging-wall mantle material by subducted metamorphic rocks (Fig.3a,b).

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## Applications and technical developments of solid-state NMR Associate Professor Munehiro Inukai

Technology Tokushima University



Content:

Solid-state nuclear magnetic resonance (NMR) has been a powerful spectroscopy which provides atomiclevel structures and dynamics of solid materials.

[1] We have developed new solid- state NMR methods for mass-limited samples and functional thin films. A work in progress is the development of in-situ device highresolution NMR. The target devices include lithium ion batteries, fuel cells, and organic photovoltaics. We will address structures and dynamics of devices in working.

The inherent disadvantage of NMR is weak [2] sensitivity compared with those of other spectroscopies. We have developed the new method of dynamic nuclear polarization to overcome the weak sensitivity.

[3] The design of fast proton conducting solids is of interest to materials chemistry from the viewpoint of fuel technology. Based on state-art of NMR cell characterizations, we elucidated proton transport developed super proton mechanism. conductina coordination polymers, and performed first demonstration of coordination polymer fuel cell.

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#### Synthesis of Deoxysacchrides in Water

Faculty of Science and Technology

### Associate Professor Masaharu UENO



#### Content:

From the view point of "Green Sustainable Chemistry", now I research the development of the synthetic method of functionality material without organic solvents. Deoxysaccharides are one of the constitution unit of a natural product and pharmaceutical products, which has a big influence on the expression of our living body function. To synthesis of deoxysacchrides many protection/deprotection steps are required in organic solvents, because of its have hydrophilicity.

To overcome these problems, I developing the synthetic method of the deoxy sugars in water, including pentose (five monosaccharides) and hexose (six monosaccharides) from a common unit. Also I am trying to synthesis of natural bioactive compounds only in water. In the future, for the no use of any organic solvents even in the extraction or purification steps, I am planning to apply this method to the flow chemistry by using the immobilized catalyst in the column.

Keywords: Green Chemistry, Organic Synthesis

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Faculty of Science and Microscopic Study of Magnetism in Transition Metal Oxides Associate Professor Yu Kawasaki



#### Content:

Transition metal oxides with perovskite structure and their derivatives have been intensively studied in terms of technological application as well as fundamental physics, because of their rich variety of electromagnetic properties, such as high- $T_c$  superconductivity in copper oxides and colossal magnetoresistance in manganese oxides. However, the mechanisms of these physical phenomena are not yet well understood.

To clarify these issues, we study magnetic properties of transition metal oxides by NMR and  $\mu$ SR from a microscopic point of view. For example, we investigate the A-site randomness effect in Ba-based manganites. In this work, we investigate the magnetically ordered states of the A-site ordered RBaMn<sub>2</sub>O<sub>6</sub> (R: rare earth atoms), which are free from A-site randomness due to the layer-type ordering of R and Ba atoms at the A-site of the structure (Figs.1 and 2).

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Faculty of Science and Technology

## Study on weathering processes of rocks and landslides Associate Professor Ken-ichi NISHIYAMA



Landslide caused by the 2016 Kumamoto earthquake



Weathering profile of Neogene mudstone in Kumano Group Weathering influences the processes and rates of landform development such as mass movement. The study of these processes and rates of rock weathering is, therefore, important for engineering geology.

Geological and geomorphological principle and techniques necessary to locate potential landslide sites. To predict of potential landslide sites, we needs to understand of formative processes of weathering profiles and their physical and mechanical properties.

Changes in the rock structure and color of rocks due to weathering seem to be affected by changes of iron minerals. According to measurements of rock properties, changes in color to reddish and increasing pore volume play major roles in the weathering processes of rocks.

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## Structural basis for the molecular mechanisms of catalytic reaction and substrate recognition by nucleic acid enzymes. Associate professor Akira Hirata



Content:

Our research goal is to reveal the molecular of catalytic mechanisms reaction and substrate nucleic recognition of acid enzymes regarding transcription and post-transcription events. X-rav crystallography is a powerful tool to determine the structures of proteins and nucleic acids (DNA and RNA). Based on the structural information, we perform biochemical studies of the enzymes. These results obtained often provide a novel insight into the substrate specificity of enzymes.

Our favorite model microorganism is Archaea, which is one of three domains of life. There is strikingly similarity of structure and function of enzymes related to transcription and RNA maturation between archaea and eukaryote because the two domains are evolutionally divided from a common ancestor. So far, we have determined the X-ray structures of archaeal enzymes, two RNA polymerases (Fig. 1A and 1B), three RNAsplicing endonucleases (Fig 1C, 1D and 1E) and tRNA methyltransferase Trm11 (Fig. 1F).





## Elucidation of the origin of strata

#### Associate Professor Yu Saitoh

#### What can be read from the stratum

#### Past information

Sedimentary environment, climate, sea level, and crustal movement



Sandstone deposited in lower shoreface environment.



#### Current information

Sediment movement processes at difficult-to-observe situations (deep sea processes, storm coast, river mouth during floods, etc.)



Grain-size change in a sand laver from a river mouth suggesting fluctuation of flow velocity

**Disaster** information Flood/tsunami occurrence

Alternation of sand and mud

deposited on continental slope.

frequency, and thir reach range, debris flow occurrence risk



Sandy sediments formed in coastal wetlands by the tsunami caused by the 2011 earthquake

#### Content:

We are conducting research aimed at elucidating the origin, formative processes and depositional environment of sedimentary rocks that make up the stratum. By elucidating the origin of sedimentary rocks, 1) information on the past global environment and crustal movements, 2) information on the current sediment movement process on the seafloor, and 3) information leading to the evaluation of natural disasters, can be extracted from the strata.

Among the various methods used in our laboratory to elucidate the origin of sedimentary rocks, the most basic one is on-site geological description and sampling. The sedimentary processes and environments, which were existed behind the formation of strata can be understood from the particle size and sedimentary structure of the stratum. Depending on the purpose, we will extract highly accurate and high-resolution information by additionally performing particle size analysis, mineral analysis with a polarizing microscope, chemical analysis, and heavy element stable isotope analysis.

Specific research themes include 1) elucidation of the diversity of turbidites in the Paleogene accretionary complex, 2) study of the substrata of the Tokushima Plain, 3) extraction of water information from sediments, and 4)elucidation of the relationship between isotope ratios of river mud and watershed geology.

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# Search for functional materials from natural products, and their high functionalization

Faculty of Science and Technology



#### Associate Professor Mitsuhiro Nakamura

#### Content:

Chemical compounds produced by a living organism have various activities. These activities are useful for our life, like a medicine and a food additive.

In our research group, we have studied the biosynthesis of Cypridina luciferin. The luminescence of the ostracod *Cypridina hilgendorfii* (presently *Vargula hilgendorfii*) is produced by a luciferin-luciferase reaction in the presence of molecular oxygen. Cypridina luciferin is an imidazopyrazinone compound and is catalyzed by Cypridina luciferase to produce oxyluciferin,  $CO_2$ , and blue light ( $\lambda$ max = 460 nm). It has been reported that two imidazopyrazinone-type luciferins, Cypridina luciferin and coelenterazine, are biosynthesized from L-amino acids in living animals. During our studies on the biosynthesis of Cypridina luciferin, we found Cypridina luciferyl sulfate, which was more stable than Cypridina luciferin and might be a storage form of Cypridina luciferin.

Keywords: functional materials, bioorganic chemistry

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Science and Technology Tokushima University High-pressure research of strongly-correlated electron system Associate Professor Akihiko Hisada

intensity (arb. units) 1 mm  $\leftrightarrow$ 80 90 10 20 30 40 50 60 70 20 (° ) Fig.1 Crystal growth Fig.2 X-ray diffraction pattern SrCa13Cu24O41 Tc (single crystal) 20  $\Box T_{C}^{xx}$  $\blacktriangle$   $T_{C}^{1}$ FL 15 r (K) 10 SC Bulk SC 0 0 2 6 P (GPa) Fig.3 High-Pressure Fig.4 *P-T* phase diagram for ladder cuprates [1] apparatus

[1] A. Hisada et al., J. Phys. Soc. Jpn. 83, 073703 (2014)

#### Content:

We study strongly-correlated electron system, focusing on the substitution effects and the effects of high pressure. The application of an external pressure causes lattice shrinkage and induces interesting phenomena, such as superconductivity, magnetism and so on. The substitution also induces structural change, which is called as chemical pressure. The doping effects and the effects of structural change can be discriminated by comparing these pressures.

Recently, we performed electrical resistivity and alternating current susceptibility measurements for the two-leg–ladder cuprates. The bulk superconductivity and temperature quadratic behavior of the normal state resistivity were observed above 3.7 GPa. They suggest that a strong interladder interaction induces the bulk superconductivity. Our results also suggested the filamentary superconducting state on the crossover phenomenon. [1]

#### Keywords:

strongly-correlated electron system, superconductivity, high pressure, NMR E-mail: a-hisada@tokushima-u.ac.jp Tel. +81-88-656-7231



## Inorganic analytical chemistry of trace elements in natural samples

Faculty of Science and Technology



### Research associate Yuhei, Yamamoto

#### Content:

Natural samples are mixture of various elements, and the elemental composition is one the important controlling factor of chemical character of natural samples. Because heavy metals are often toxic elements even at a low concentration, understanding of behavior of heavy metals is important. To determine concentration of heavy metals in natural samples, chemical analyses is conducted using ICP-MS.

There are very small particles with a size from  $\mu$ m to nm order in natural water and air, which are called "colloid" and "aerosol". Heavy metals can adsorb onto these particles. Focusing on trace elements and small particles, natural sample (river water, groundwater, sea water, rain, snow, rime, air, and rock), various analyses have been conducted. In addition, development of analytical method for trace elements in natural sample is also research target.

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