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Rare Earth, Major and Trace Elements in the Kunimiyama  
Ferromanganese Deposit in the Northern Chichibu Belt,  
Central Shikoku, Japan

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**Abstract:** Rare earth, major and trace element geochemistry is reported for the Kunimiyama stratiform ferromanganese deposit in the Northern Chichibu Belt, central Shikoku, Japan. The deposit immediately overlies greenstones of mid-ocean ridge basalt (MORB) origin and underlies red chert. The ferromanganese ores exhibit remarkable enrichments in Fe, Mn, P, V, Co, Ni, Zn, Y and rare earth elements (excepting Ce) relative to continental crustal abundance. These enriched elements/Fe ratios and Post-Archean Average Australian Shale-normalized REE patterns of the ferromanganese ores are generally analogous to those of modern hydrothermal ferromanganese plume fall-out precipitates deposited on MOR flanks. However in more detail, Mn and Ti enrichments in the ferromanganese ores are more striking than the modern counterpart, suggesting a significant contribution of hydrogenetic component in the Kunimiyama ores. Our results are consistent with the interpretation that the Kunimiyama ores were uraniferous deposits that primarily formed by hydrothermal plume fall-out precipitation in the Panthalassa Ocean during the Early Permian and then accreted onto the proto-Japanese island arc during the Middle Jurassic. The presence of strong negative Ce anomaly in the Kunimiyama ores may indicate that the Early Permian Panthalassa seawater had a more striking negative Ce anomaly due to a more oxidizing oceanic condition than today.

**Keywords:** geochemistry, ferromanganese deposit, hydrothermal, accretionary complex, mid-ocean ridge (MOR), Permian

## Geochemical Features and Tectonic Setting of Greenstones from Kunimiyama, Northern Chichibu Belt, Central Shikoku, Japan

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**Abstract:** We report whole-rock chemical data for the greenstones from the Kunimiyama area in the Northern Chichibu Belt and their implications on the tectonic setting of these rocks. The Kunimiyama greenstones are associated with stratiform ferromanganese deposits or bedded cherts in the northern part of the study area, but are closely associated with a thick limestone block or bedded cherts in the southern part. The constituent minerals of greenstones are albitized plagioclase, clinopyroxene, chlorite, calcite, epidote, pumpellyite, prehnite, quartz, celadonite, sericite and opaque minerals such as iron oxyhydroxide and hematite. These mineral assemblages, epidote + pumpellyite + chlorite and chlorite + pumpellyite + prehnite, suggest that the metamorphic grade of greenstones from the Kunimiyama area is prehnite-pumpellyite facies. The whole-rock chemical compositions of greenstones associated with ferromanganese deposits are generally similar to those of normal mid-ocean ridge basalt (N-MORB). In contrast, the chemical compositions of the greenstones associated with the limestone block are comparable to those of ocean island alkaline basalt. Greenstones associated with bedded cherts are of enriched MORB and ocean island basalt, as well as N-MORB origins, suggesting they probably formed as a result of plume-related MOR volcanism in the Panthalassa Ocean in Early Permian and by tectonic mixing of ocean island basalts with oceanic ridge crustal fragments during accretion/subduction processes. These geological and geochemical lines of evidence suggest that the Kunimiyama greenstones are allochthonous blocks of accreted oceanic crust and seamounts. The ferromanganese deposits are frequently accompanied by reddish greenstones. Compared to common greenish greenstones, the reddish greenstones are characterized by high MnO and rare earth element contents and distinct negative Ce anomalies, implying a slight contribution of hydrothermal component forming the ferromanganese deposits.

**Keywords:** greenstone, geochemistry, mid-ocean ridge basalt (MORB), ocean island basalt (OIB), accretionary complex, Northern Chichibu Belt

Radiolarian Age of Chert-hosted Bedded Manganese Deposits  
from the Gen-otani Mine in the Tamba District,  
Northern Kyoto City, Japan

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**Abstract:** Numerous bedded manganese deposits sporadically distributed throughout the Tamba district, southwestern Japan are intercalated within chert sequence. It is well known that radiolarian remains are commonly included in both bedded manganese deposits and host cherts. The Gen-otani mine, one of these deposits, is located at Otani, Keihoku-Shimonaka, northern Kyoto City. Chemical composition and age of the chert sequence at the mine were examined. Mainly according to SiO<sub>2</sub> and MnO contents together with lithology, the chert sequence is divided into three sections; lower massive chert, middle bedded manganese deposit and upper bedded chert sections. Radiolarian faunas consisting of middle Jurassic species such as *Eucyrtidiellum unumaense*, *Dictyomitrella(?) kamoensis*, *Parvicingula dhimenaensis*, *Sethocapsa aitai*, *Sethocapsa kodrai*, *Transsum brevicostatum*, *Tricolocapsa plicarum*, *Unuma echinatus* and others were extracted from both the middle manganese section and overlying bedded chert of the upper section. This examination reveals that the bedded manganese deposit at the Gen-otani mine formed until Bajocian to early Bathonian (middle Middle Jurassic) in age.

**Keywords:** bedded manganese deposit, chert, radiolaria, Middle Jurassic, Gen-otani mine, Tamba district, Kyoto City

Chemical Profiles across a Jurassic Stratiform Manganese Deposit  
at Katsuyama in the Mino Terrane of Central Japan:  
Implications for Depositional Environment, Diagenetic  
Metal Redistribution and Paleoceanography

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**Abstract:** Inorganic chemical compositions are determined for a series of rocks crossing an Early Jurassic stratiform manganese ore deposit in a chert-dominant sequence at Katsuyama, in the Mino Terrane of central Japan. The lithology in the vicinity of the manganese ore bed is classified into lower bedded chert, black shale, massive chert, manganese ore and upper bedded chert, in ascending order. The rocks surrounding the manganese deposit are anomalously high in certain elements: Pb (max. 29 ppm), Ni (1140) and Co (336) in the lower bedded chert, Mo (438), As (149), Tl (29) and U (12) in the black shales, V (210) and Cr (87) in the massive chert, and MnO and W (24) in the manganese ore. The aluminum-normalized profiles reveal a distinct zonation of redox-sensitive elements: Pb-Zn, Ni-Co-Cu(-Zn) and U-Cr in the lower bedded chert, Mo-As-Tl in the black shale, V(-Cr) in the massive chert, and Mn-Fe-Ba-W in the manganese ore, in ascending order. The lower and upper bedded cherts and manganese ore generally exhibit flat rare earth element patterns with positive Ce anomalies, whereas the uppermost part of the lower bedded chert, the black shale and massive chert have flat patterns with weak or non-existent negative Ce anomalies and weak positive Eu anomalies.

The strong enrichment in Ni, Co, W, Tl and As detected in the Katsuyama section is not recognized in other sediments, including those of anoxic deposition origin, but is identified in modern ferromanganese nodules, suggesting that metal enrichment in the Katsuyama section is essentially due to the formation of ferromanganese nodules rather than to deposition in an anoxic environment. The observed elemental zonation is well explained by equilibrium calculations, reflecting early diagenetic formation and associated gradual reduction with depth. The concentration profiles in combination with litho- and biostratigraphical features suggest that formation of these bedded manganese deposits was triggered by an influx of warm, saline and oxic water into a stagnant deep ocean floor basin in Panthalassa at the end of the middle Early Jurassic. Paleoceanographic environmental controls thus appear to be important factors in the formation and preservation of this type of stratiform manganese deposit.

**Keywords:** stratiform manganese deposit, accretionary complex, chert, compositional zonation, diagenesis, Toarcian event, oxic deep water

Chemistry and Sulfur Isotopes in a Chert-dominant Sequence around  
the Stratiform Manganese Deposit of the Noda-Tamagawa Mine,  
Northern Kitakami Terrane, Northeast Japan:  
Implication for Paleooceanographic Environmental Setting

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**Abstract:** Chemistry and sulfur isotopes are analyzed for a series of rocks in the chert-dominant sequence around the stratiform manganese ore deposit of the Noda-Tamagawa mine in the northern Kitakami Terrane, northeast Japan. The sequence is lithologically classified into six units in ascending order: lower bedded chert, lower black shale, massive chert, manganese ore, upper black shale, and upper bedded chert. The rocks around the manganese ore deposit exhibit anomalous enrichment in Ni (max. 337 ppm), Zn (102) and U (30) in the upper part of lower bedded chert, Mo (122), Tl (79) and Pb (33) in the lower black shale, MnO, Cu (786) and Co (62) in the manganese ore, and As (247) and Sb (17) in the upper black shale. The aluminum-normalized profiles reveal zonal enrichment of redox-sensitive elements around the manganese bed: Zn-Ni-Fe-Mo-U(-Co), Tl-Pb(-Mo), Mn-Fe-Cu-V-Cr-Co(-Zn) and As-Sb in ascending order. The uppermost part of the lower bedded chert and black shale exhibit negative Ce/Ce\* values, whereas the massive chert, manganese ore and lower part of the upper bedded chert display positive values.

The isotopic  $\delta^{34}\text{S}$  values are  $0\pm 6$  ‰ in the lower part of the lower bedded chert,  $-19$  to  $-42$  ‰ in the upper part of the lower bedded chert,  $-36$  to  $-42$  ‰ in the lower black shale,  $-28$  to  $-35$  ‰ in the massive chert, manganese ore and upper black shale, and  $-23\pm 5$  ‰ in the upper bedded chert. Thus, there is a marked negative shift in  $\delta^{34}\text{S}$  values in the lower bedded chert, and an upward-increasing trend in  $\delta^{34}\text{S}$  through the manganese ore horizon.

The present data provide evidence for a change in the paleooceanographic environment resulting from inflow of oxic deepwater into the stagnant anoxic ocean floor below the manganese ore horizon. This event is likely to have triggered the precipitation of manganese oxyhydroxides. The redistribution of redox-sensitive elements through the formation of metalliferous black shale and manganese carbonate ore may have occurred in association with bacterial decomposition of organic matter during early diagenesis of initial manganese oxyhydroxides.

**Keywords:** sulfur isotope, stratiform manganese deposit, accretionary complex, chert, compositional zonation, oxic deep water, Noda-Tamagawa

Short Communication

Radiolarian Age of Red Chert from the Kunimiyama Ferromanganese Deposit  
in the Northern Chichibu Belt, Central Shikoku, Japan

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**Abstract:** The radiolarian age of red chert from the Kunimiyama area of the Northern Chichibu Belt was determined in order to constrain the depositional age of the Kunimiyama deposit that is among the largest ferromanganese deposits in Japan. *Pseudoalbaillella* cf. *scalprata* Holdsworth and Jones, *Pseudoalbaillella* cf. *longicornis* Ishiga and Imoto and *Pseudoalbaillella* sp. belonging to the *Ps. lomentaria* Zone are found in the red chert, indicating an age of middle Early Permian (middle Wolfcampian). The red chert occurs immediately above the ferromanganese deposit, and the boundary between them is gradual. Based on their mode of occurrence and geochemical features, it is most likely that radiolarian chert and ferromanganese precipitate accumulated simultaneously to produce red chert during the waning stage of submarine hydrothermal activity that was responsible for the Kunimiyama deposit. Consequently, the age of Kunimiyama stratiform ferromanganese deposit is constrained as middle Early Permian (middle Wolfcampian).

**Keywords:** Kunimiyama deposit, red chert, hydrothermal, ferromanganese sediment, Chichibu Belt, radiolarian age, Early Permian

## Temperature and pH Dependence of Some Metals Leaching from Fly Ash of Municipal Solid Waste

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**Abstract:** Municipal solid waste combustion leads to concentration of various metals in the solid residue (fly ash) remaining after combustion. These metals pose serious environmental hazard and require proper handling and monitoring in order to control their harmful effects. Leachability of some metals from fly ash was examined in fly ash and Milli-Q water mixture (liquid-to-solid ratio, 100) under various temperature and pH conditions in the laboratory. The leaching experiments conducted for 24 hours showed that pH was generally more important than temperature in controlling the amount of metals leached out of the fly ash. However, at a given pH, rise in temperature led to different degree of (usually one to two fold) enhanced or reduced leaching of metals. Owing to amphoteric nature of oxides of Al, Cr, Pb and Zn, these metals often yielded typical pattern of increase and decrease in their concentrations with change in pH. The extent of leaching of Cr and Pb in our experiments suggests that decrease of pH to acidic range in the case of Pb and to neutral to acidic range for Cr over a long period of storage of fly ash at solid waste dumping site may facilitate leaching of these metals from fly ash, leading to contamination of groundwater to the level that exceeds beyond the level permitted by the environmental laws.

**Keywords:** Municipal solid waste, fly ash, leaching, metals, organic matter

## Petrographic Characteristics and Alteration Geochemistry of Granite-hosted Tungsten Mineralization at Degana, NW India

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**Abstract:** Vein type tungsten mineralization at Degana is genetically and spatially associated with the Degana Granite. The deposit is characterized by pervasive wall rock alteration around the mineralized quartz veins. Laterally three different alteration zones, greisen, silicification and potassic zones, are marked based on the field features, mineral assemblages and geochemical characteristics. In the present paper, systematic mineralogical and chemical variation in these alteration zones is reported. Thick mono-mineralic (zinnwaldite) selvages around the veins characterize the deposit. Plagioclase and alkali feldspar are low in the greisen zones while K-feldspar shows more increase than plagioclase in the potassic zone. Quartz is uniformly high in all the alteration zones, but it shows an anomalous value in the silicification zone.  $Al_2O_3$  concentration shows initial depletion in greisen zone with gradual increase away from the contact. MgO and FeO are higher in greisen zone than silicification and potassic zones. The potassic zone is characterized by the depletion of  $Na_2O$  and higher value of  $K_2O$ .

The common presence of topaz and fluorite as both primary and secondary minerals and fluorine-bearing micas suggest fluorine partitioning in substantial amount between granitic melt and coexisting aqueous fluid phase and higher HF activity during the evolution of hydrothermal fluid. The mutual relationship of the fluorine minerals (topaz and fluorite) in the different alteration zones suggests an increase in the  $Ca^{2+}$  activity and decrease of  $H^+$  activity during the fluid evolution from greisenization towards alkali-metasomatized granite and the fluid is assumed to change from low to high activity ratio of  $Ca^{2+}/H^+$ .

**Keywords:** tungsten mineralization, greisen, silicification, potassic alteration, zinnwaldite, Degana, Balda-Tosham tungsten belt, India

## Mo-related Adakitic Granitoids from Non-island-arc Setting: Jecheon Pluton of South Korea

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**Abstract:** The Jecheon granitoids, having an elongated shape of NE-SW 27 km and NW-SE 13 km (190 km<sup>2</sup>), are composed mostly of magnetite-series hornblende-biotite granodiorite and biotite granite, which intrude into the Neoproterozoic metamorphic and Paleozoic sedimentary rocks of the Ogcheon Belt. The granitoids have Triassic-Jurassic age of  $202.7 \pm 1.9$  Ma with very high <sup>87</sup>Sr/<sup>86</sup>Sr initial ratio of 0.7140. The granodiorite has 63–69 % SiO<sub>2</sub>, 15.1–17.3 % Al<sub>2</sub>O<sub>3</sub>, <1.6 % MgO, 6–15 ppm Y and Sr/Y ratios of 24–76, and is depleted in HREE. Biotite granite together, the Jecheon pluton has adakitic characteristics, which are unique in a continental tectonic setting. The granitoids may have been generated by partial melting of an older adakitic granitoid of I-type basement, or by separation of early crystallized garnet and hornblende from an anatectic melt.

**Keywords:** South Korea, Jecheon, Triassic-Jurassic, granitoid, magnetite-series, high-Sr/Y ratio

## Kübler Index and K-Ar Ages of Illite in the Yinshan Polymetallic Deposit, Jiangxi Province, South China: Analyses and Implications

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**Abstract:** The Yinshan polymetallic deposit is a hydrothermal vein-type deposit closely related to Late Jurassic felsic-intermediate volcanic-subvolcanic activity in Jiangxi Province, South China. Illite is a major alteration mineral observed in the deposit. Our study shows that the Kübler index of the illite has a close relation to ore-forming fluids of different stages of hydrothermal alteration and mineralization. The early Pb-Zn-Ag mineralization dated at 130–136 Ma is characterized by relatively low water/rock ratios and diffusive fluid movement within phyllite, whereas the later Cu-Au-S mineralization at 122–125 Ma was accompanied by higher water/rock ratios and localized fluid flow through fractures and channels. Illite formed in the early Pb-Zn-Ag mineralization stage contains swelling layers while the illite formed in the later Cu-Au-S mineralization stage has no swelling layers but was associated with intensive chloritization. The last stage of mineralization (at 104 Ma) was minor and did not produce significant amounts of illite.

**Keywords:** illite, Kübler index, ore-forming fluids, Yinshan polymetallic deposit, China

*Review*

Types of Pyrophyllite Deposits in Foldbelts

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**Abstract:** Pyrophyllite deposits can be divided into five types on the basis of geology and genesis. The first two types are associated with hydrothermally altered rocks in felsic and intermediate volcanogenic suites. They are characterized by their metasomatites and their subsequent mineralogic transformations under varying volcanic conditions. The third type includes deposits and occurrences of metamorphic-metasomatic genesis, which is caused by transformations of terrigenous-sedimentary interbeds in felsic volcanics under greenschist facies conditions. The fourth type is associated with low and mid-temperature stages of hydrothermal vein formation at the limits of volcanogenic and metamorphic strata. The fifth type comprises pyrophyllite occurrences in weathering crusts on metamorphic strata and metasomatite.

The formation conditions and distribution of raw pyrophyllite deposits were influenced by the geodynamic situations and geochemical conditions, such as character of tectonic dislocations, volcanism and chemical composition of hydrothermal solutions.

**Keywords:** pyrophyllite deposit, hydrothermal, foldbelts