Field Trip Guide

One-day field trip to the Mino Belt, a major structural unit of Paleozoic to Mesozoic age in Japan (November 1st)

International Biogeoscience Conference Nagoya 2013, Japan

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1. Introduction to the Mino Belt (Terrane)

The Mino Belt is a major geological unit in southwest-central Japan, and is composed of Permian to Triassic bedded cherts, limestones, basalts and Jurassic turbidite sandstones and shales (Wakita, 1988). The bedded cherts occur as blocks or lenses within the Jurassic turbidites. The Hida Belt placed to the north of the Mino Belt is a geological unit containing Permo-Triassic quartzo-feldspathic gneisses and schists (Kunugiza et al., 2006). This belt is considered to be the eastern extension of the collision zone between the North and South China blocks (Kunugiza et al., 2006). Due to the opening of the Sea of Japan, it was detached from the Asian continent. These older rocks are likely to be one of the sources for Jurassic terrigenous sediments (turbidite



Fig.1. Simplified geological map of Japan. Light blue zones correspond to Jurassic accretionaly complexes including the Mino Belt. From "2.0 billion-years of Japanese Islands, Iwanami Shoten Publishers".

sandstones and shales) in the Mino Belt (Adachi, 1976). Precambrian gneiss clasts and detrital zircon and monazite grains in the terrigenous sediments are considered to have originated from a Precambrian continent in Korean Peninsula (Adachi and Suzuki, 1993; Suzuki et al., 1997).

Taira et al. (1992) and Maruyama and Seno (1986) interpreted the Paleozoic-Mesozoic geological history of central-southwest Japan in the context of the processes of steady-state accretion of oceanic crust including bedded cherts and microcontinents. It is thought that the Mino Belt represents an accretionary prism formed at an ancient subduction zone (Matsuda and Isozaki, 1991). Matsuda and Isozaki (1991) argued that the Triassic bedded cherts were deposited in pelagic regions far from continents and accreted at an ancient subduction zone and admixed with Jurassic turbidites (sandstones and shales) composed of terrigneous materials.

Currently, the steady-state accretion model, featuring an ancient subduction zone facing the open ocean, where deep-sea siliceous sediments and occasionally seamounts with coral reefs were accreted, seems to be the most widely accepted formational model for the Mino Belt and more broadly, the entire Japanese Islands. This model is closely related to the origin of radiolarian bedded cherts in the Mino Belt. In other words, this accretion model depends on the premise of a deep-sea and pelagic origin of radiolarian bedded cherts, which has been argued based mainly on the following observations: 1) the lack of coarse-grained terrigeneous detrital materials, 2) lack of calcareous fossils (meaning deposition below the CCD), 3) assumed very low sedimentation rate, and 4) presence of radiolarian oozes in central Pacific regions remote from lands. However, De Wever and Baudin (1996) noted that radiolarian bedded cherts do not always indicate deep-sea and pelagic sedimentation. As described in the next section, some geochemical data of the Permo-Triassic bedded cherts in Japan are not consistent with their deep-sea and pelagic origin, as represented by the paper published by Sugisaki et al. (1982) in Nature that is entitled "Triassic bedded cherts in central Japan are not pelagic". Indeed, the observations listed above do not always indicate exclusively the deep-sea and pelagic origin of bedded cherts. The depth of the CCD could change dynamically in response to the pH and temperature of the ocean. Additionally, the sedimentation rates of marine sediments are not simply a function of distance from lands.

2. Radiolarian Bedded Chert

Radiolarian bedded chert, common in the circum-Pacific orogenic belt (e.g., Hein and Parrish, 1987), is a sedimentary rock characterized by rhythmic alternation of silica-rich chert beds several cm thick and a much thinner shale layer. They originated from marine sediments composed mainly of opaline biogenic silica, with lesser amounts of clastic lithogenic materials and authigenic components, and occasionally hydrothermal solution (Shimizu et al., 2001; Yamamoto, 1983).

Nisbet and Price (1974) proposed, based on detailed sedimentological work, that the rhythmic alternation of chert and shale represents turbidite-induced sedimentation. Another model is that the alternation represents cyclic change of surface productivity. Namely cyclic blooming of radiolaria (depending on blooming microalgae) with relatively constant clay sedimentation rate produces rhythmic alteration (e.g. Hori et al., 1993). In either case, the present distinct alteration of chert and shale is likely biased by later diagenesis (redistribution of Si)(De Wever et al., 1995; Tada, 1991). One major assertion for the depositional environment is that they were deposited in pelagic and deep water as described earlier.

Most Japanese geoscientists appear to assume as an axiom that the radiolarian bedded cherts represent a deep and pelagic depositional facies (Isozaki, 1997; Kato et al., 2002; Hori et al., 2000). Results of some earlier geochemical studies, on the other hand, are not consistent with pelagic origin of radiolarian bedded cherts. Compared with modern pelagic sediments characterized by high Mn and Co concentrations $(MnO/TiO_2 = 0.97 \pm 0.72, Co/TiO_2 = 37 \pm 7$ for Pacific ocean floor on the east of the Ogasawara Trench; MnO/TiO₂ = 2.11 ± 0.60 , Co/TiO₂ = 196 ± 34 for Northern Central Pacific basin), radiolarian bedded cherts in the Mino belt are depleted in both elements (MnO/TiO₂ = 0.25 ± 0.19 , Co/TiO₂ = 32.9 ± 14.5 for the Kamiaso Chert), close to those of hemiplegic sediments where Mn-oxides accumulation is limited by the suboxic sedimentary environment (Sugisaki et al., 1982; Yamamoto, 1983). A suboxic and non-deep-sea-floor depositional environment for radiolarian bedded cherts, particularly Triassic ones, is also supported by rare-earth element abundances and Sr isotopic data from the Southern Chichibu Terrane (the outer zone of southwest Japan; for details, see Kunimaru et al. (1998). This is supported by recent data on Sr-isotopes of limestone in the Chichibu Belt (similarly interpreted as Jurassic accretionary prism), south of the Mino Belt that range 0.7061 to 0.7079 (n=41) (Suzuki et al., 2011). These values, except for 5 samples, are lower than the contemporaneous Panthalassic Ocean values. Such low values were interpreted to require the contribution of hydrothermal solution and deposition in a semi-closed ocean basin convenient for achievement of isotopic equilibrium between seawater and hydrothermal water.

The major problem in using these geochemical redox proxies related to the site of deposition (i.e. pelagic vs. hemi-pelagic) is that the modern marine environment could not always be equivalent to ancient marine sediments. MnO/TiO_2 and Co/TiO_2 values are indeed useful indicators of redox environment of modern marine sediments that are a function of distance from lands. However, if the redox regime of the ancient ocean was different from the modern one, these proxies may not always be simply applicable.

3. Manganese Nodules and Bands

In the Mino Belt, manganese ores of small scale occur locally. Some of them that have been subjected to supergene enrichment have been mined since World War II; the primary mineralogy of these ores is believed manganese carbonate ($MnCO_3$). Although these mines are now closed, we can see centimeter to decimeter-scale nodules and beds in which manganese carbonate mineral (rhodochrosite) is highly concentrated at several localities in the Mino Belt. Representative localities are in the Hisuikyo and in the Unuma district. In nodules and beds, beautiful authigenic rhodochrosite crystals up to a few mm in diameter can be identified. The crystals overgrow siliceous tests of radiolarian and sponge spicules. From these nodules and beds, very well preserved radiolarian fossils have been identified.

Nodular ores dispersed in Jurassic siliceous shales in the Unuma district were once misunderstood to be equivalent to ferromanganese nodules composed of oxides distributed mainly on the pelagic ocean floor. However, in addition to their mineralogy, their lack of concentric laminae and cores are in conflict with deep-sea ferromanganese nodules. Recently, Nakada et al. (2013) proposed that the nodules were formed by direct precipitation of manganese carbonates. The layered manganese carbonate (called manganese bands), on the other hand, may be better explained by a model proposed by Sugitani (1989) and Sugisaki et al. (1991), who suggested that the manganese carbonate bands could have originated from the surface (or near



Fig. 3 Photomicrograph of authigenic rhodochrosite crystals in Jurassic siliceous shale.

surface) Mn-rich oxidized layer that is formed by dissolution of MnO₂ particles within sediments under suboxic conditions, and upward migration of Mn^{2+} , and re-oxidation and re-precipitation. If such a Mn-rich oxidized layer was, for example, buried and the reduction of Mn⁴⁺ to Mn²⁺ was coupled with concurrent high alkalinity, manganese carbonate could be precipitated. Carbon isotopic data of rhodochrosite and associated calcite of manganese bands and nodules suggest that CO₂ produced by respiration of organic matter (associated with the reduction of Mn-oxides?) was involved in the carbonate precipitation, although the degree of contribution of organic matter-derived CO₂ varies significantly between different deposits. In the case of Kamiaso (Hisuikyo), the δ^{13} C values tend to be lighter than -24 per mil, down to -37.5 per mil, implying the contribution of CO₂ formed by methane oxidation.



Fig. 4 Photomicrographs of rhodochrosite crystals in Triassic bedded chert at Hisuikyo Outcrop. Spherical grains are scattered within chert (left). Rhodochrosite grains contain well-preserved radiolarian tests (right).

4. Sites to visit

4.1. The Hisuikyo Outcrop in Hichiso Town

Caution: The outcrop of bedded chert is very slippery, especially in wet conditions.

The Hisuikyo outcrop is famous for massive development of potholes on an uplifted riverbed composed of nearly vertically dipping Triassic radiolarian bedded cherts. You will find lots of potholes from the meter to decameter size. The bedded cherts are various in color; white, grey, green, brick-red and black. Most chert beds range from a few to 15cm in thickness, whereas shale-partings are less than 0.5cm. Thickness of the outcrop in appearance is up to 100m. However, detailed radiolarian paleontology revealed that the succession is composed of repeated sections deposited during the same time (Kido, 1982). The sections are superimposed by repeated thrust faults. These thrust faults are though to have been formed during accretion at the subduction zone. In addition to the beautiful coloration of the bedded chert, you will find beautiful folding and the local development of carbonaceous cherts and manganese bands (bright green chert). Dr. Sugisaki (an emeritus professor of Nagoya University and my former supervisor) and his colleagues performed pioneering geochemical studies on bedded cherts in this area and claimed that the Triassic bedded cherts are NOT pelagic. The results include a Nature paper published in 1982 (Sugisaki et al., 1982).

4.2. Hichiso Precambrian Museum

This municipal museum specializing in geology was established in more than 20 years ago, and is dedicated to the discovery of the oldest rock in Japan by Dr. Mamoru Adachi in 1970 (Adachi, 1971), an emeritus professor of Nagoya University. He was involved in all the processes of establishment of this museum, including naming, probably unique in the world. The oldest rock in Japan is a pebble of gneiss whose metamorphic age was considered to be ca. 2.0 Ga. This pebble was discovered within Jurassic conglomerate. Dating of this pebble was made by the Rb-Sr method in the Geological Survey of Japan (Shibata and Adachi, 1974). Later, older ages (2.71, 3.05 and 3.56 Ga) were obtained for rounded zircon in granitic pebbles, by the new dating method called CHIME (U-Th-total Pb Chemical Isochron Method) developed by an emeritus professor of Nagoya University, Dr. Kazuhiro Suzuki (Suzuki and Adachi, 1991). Dr. Adachi suggested that some pebbles in this conglomerate such as gneiss and orthoquartzite were equivalent to Precambrian rocks in Korea. Namely, at the time of deposition of the Jurassic conglomerate (and shale-sandstone), the Japanese archipelago was attached to the Eurasia continent. The Sea of Japan is known to be an example of a pull-apart basin.

The collection of this museum includes Acasta gneiss, Amitsoq gneiss and some Pilbara rocks. This is outstanding for such a small municipal museum in Japan. Dr. Adachi made a significant contribution to the collection of these rocks, including his own field trip in the Pilbara. Counterparts of the specimens in this museum are exhibited also in the Nagoya University Museum. You may find me (K.S) sampling at Mt. Tom Price (Pilbara, WA) 25 years ago in an exhibited picture.

4.3. The Unuma Outcrop

Along the Kiso River, beautiful outcrops of Triassic to Jurassic seidimentary rocks in the Mino Belt are well exposed. Many important works on radiolarian biostratigraphy and structural geology of the Mino Belt have been made on rocks in this district. In particular, the Unuma Outcrop in Kakamigahara City is famous for its manganese carbonate nodules (see chapter 3. Manganese Nodules and Bands) and beds in Jurassic siliceous shales and for the succession of the Triassic radiolarian bedded chert that records an oceanic anoxic event. At one outcrop, the ca. 10m thick succession of bedded chert records sedimentation of radiolarian oozes. The lower unit ca. 1m thick is composed mainly of grey to black bedded cherts with partially shale-dominant sub units. This lithology drastically changes to the brick-red bedded cherts with a transitional phase of 30cm thick purple-red bedded chert. The drastic change of bedded chert lithology corresponds to geochemical and petrographic features summarized below (Sugitani and Mimura, 1998).

- 1) The lower grey to black unit is enriched in organic carbon and sulfur, both of which are quite low in concentrations or even under the detection limits in the upper unit.
- 2) The upper reddish cherts lack visible organic matter and sulfide. They contain disseminated oxide particles.

- 3) Some trace elements such as Ni, Cu and Zn also tend to be significantly higher in the lower unit.
- 4) Manganese contents tend to be higher in the upper reddish unit ($MnO/TiO_2 = 0.15 \sim 0.49$) compared with the lower grey-black unit (0.03-0.18), reflecting the contrasting sedimentary environment.



Fig. 5 Photomicrographs of radiolarian bedded cherts from the Unuma Outcrop. Left: black chert enriched in carbonaceous matter. Right: red chert. The matrix contains minute hematite particles.

Nakao and Isozaki (1994) and Kubo et al. (1996) claimed that the grey-black bedded cherts were deposited under a euxinic environment developed in the world ocean (superanoxia: Isozaki, 1997). These authors claimed that the superanoxia started from the end-Permian regression and continued until the Middle Triassic; seawater stratification resulting from the worldwide regression and the development of anoxic deep water facilitated the deposition of carbonaceous cherts. This is somewhat of an overestimation, because the end-Permian sea-level regression had already recovered in Early Triassic time (Embry, 1988) and indeed the brick-red bedded chert unit is known to occur below the grey-black chert unit at the different area of the Mino Belt. Sugitani and Mimura (1998) attributed the deposition of grey-black chert to the Middle Triassic



Fig. 6 SiO₂/TiO₂-element/TiO₂ plots for raw data of selected elements showing enrichment in cherts relative to shales on TiO₂-normalization basis. Open circles; shales, closed ones; cherts. From Takiguchi et al. (2006). Quadrangles indicate areas in which shales are plotted.

regression and argued that MnO/TiO₂ values in the reddish unit did not change significantly during later diagenesis and reflect primary values. The values are lower than modern pelagic sediments and (>1) close to hemipelagic values, which is consistent with the distribution pattern on Fe_2O_3/TiO_2 VS $Al_2O_3/(Al_2O_3+Fe_2O_3)$ that suggests sedimentation in hemipelagic region (Murray, 1994).

Takiguchi et al. (2006) performed successive collection and analysis of 70 brick-red cherts and shales from the succession described above and provided new perspectives to radiolarian bedded chert compositions. In order to reveal pre-diagenetic, primary

geochemical signatures related to marine biogeochemical cycles, composite data of chert-shale couplets in addition to raw data were examined. The results show that Mn, Cu, Sr, Ba and P were supplied significantly by non-lithogenic excess fractions. Positive correlation with SiO₂/TiO₂ suggests that accumulations of Ba, Sr, Mn and Cu were closely related to sedimentation of biogenic silica; Mn and Cu were probably incorporated into oxide, whereas Ba was incorporated into barite.

The carbonaceous black cherts at this outcrop may be worth examining in detail from the point of view of the microbial ecology of the ancient seafloor. The cherts exhibit various types of probable microbial (bacterial and algal) remains, including carbonaceous spheroids comprising colony-like clusters and organic-walled unicellular spheroids (see below). These objects have never been given much attention and thus their origins are uncertain to date. If the microbial remains include benthic cyanobacterial communities like Silurian chert from Poland (Kremer and Kazmierczak, 2005), the depth of deposition should be shallower than 200m, providing crucial counterevidence to the deep sea and pelagic origin of the Triassic bedded chert in the Mino Belt.



Fig. 7 Photomicrographs of carbonaceous black cherts from the Unuma Outcrop exhibiting probable microbial remains. See text for interpretation.

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Appendix I Geological Map of the Kamiaso area (a part of Mizutani and Koido (1992))



- Paleogene rocks Gp: granite porphyry, Gr: granite Permian rocks gs: greenstone (Permian), Is: limestone (Permian) Permian to Early Jurassic rocks ch: chert with siliceous claystone sh: siliceous shale
- ss: sandstone and shale
- cg: conglomerate and coarse-grained sandstone





Neogene rocks

Tt: gravel and sand, Mn: sandstone and mudstone, Mh: andesite volcaniclastics <u>Mesozoic rocks</u>

Kt: Toishi-type siliceous claystone, Kc: chert, Ki: siliceous mudstone, Km: mudstone and alteration of mudstone and sandstone, Ks: massive sandstone and alteration of sandstone and mudstone,