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The redox state of granitoids relative to tectonic setting and earth history: The magnetite–ilmenite series 30 years later

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ABSTRACT: The redox state variation of orogenic granitoids along convergent plate margins is examined in the Phanerozoic Circum-Pacific Belt and in some Cryptozoic terranes. The Phanerozoic granitoids of the NW and NE Pacific Rims can be divided into reduced ilmenite series occurring in the accretionary terranes with compressional tectonic setting, and oxidised magnetite series intruding crystalline basements under extensional to intermediate regional stress regime. The ilmenite-series granitoids have negative but the magnetite series have positive $\delta^{34}S$ values, which show a positive correlation with magnetic susceptibility of the granitoids. The negative $\delta^{34}S$ sulphur originated in biogenic sulphur from accreted pelitic sediments and positive $\delta^{34}S$ values show that sulphate sulphur migrated from seawater through subduction processes. The whole rock $\delta^{18}O$ values are higher than 8 permil in the ilmenite series, but lower than 8 permil in the magnetite series, and as a whole show negative correlation with the magnetic susceptibility of the granitoids. The higher $\delta^{18}O$ values reflect those of accreted sediments, whilst the lower $\delta^{18}O$ values represent magmatic values of an oxidised mafic protolith at depth.

The predominance of ilmenite-series granitoids of the NW Pacific rim can be explained by well-developed accretionary terranes in which mafic magmas from depth mingled with felsic magmas from the accretionary complex to form granodioritic magmas, whilst that of magnetite-series granitoids is postulated to be oxidised igneous sources for the magma generation and an extensional and/or intermediate tectonic setting for the magma ascent. The absence of the accretionary wedges by tectonic erosion and/or no fore-arc sedimentation also helped to form magnetite-series granitoids. Potassic granitoids are generally of oxidised type. A-type granites in late orogenic environments also belong to the magnetite series. Adakitic high-Sr/Y granitoids are oxidised in the Mesozoic–Cenozoic but are reduced in the Archaean TTG, reflecting the redox state of the then-current sea-floor environment. The oldest magnetite-series granite so far known is the 3105 Ma-old biotite granite of the Nelspruit batholith, South Africa.

KEY WORDS: Accretionary wedge, Archaean, ilmenite series, magnetite series, O-isotope, Phanerozoic, S-isotope.

Orogenic magmatism along convergent plate boundaries is the most important process producing granitoids and creating continental crust. The granitoids were simply classified into magnetite-series and ilmenite-series (Ishihara 1977), based upon the presence and absence of the rock-forming mineral magnetite, reflecting the oxygen fugacity of the granitic magmas. Free oxygen is most available on the earth's surface; therefore the redox state of granitoids is related not only to igneous processes in the lithosphere but also to biogenic evolution in the hydrosphere and atmosphere of the Earth. The formation of the magnetite-series granitoids required an oxidised mafic source, whilst the ilmenite series could have been formed by assimilation of organic carbon from the accreted sediments in lower-middle crust processes (Ishihara & Matsuhisa 1999) or through subduction processes (Takagi 2004) during the Phanerozoic.

These orogenic granitoids are important sources for metallic mineral resources, as their redox state primarily controls the types of metals concentrated in given ore deposits (Ishihara 1977; Blevin & Chappell 1992). In this paper the genesis of these granitoids is considered in terms of the magnetite/ilmenite-series classification for the Phanerozoic Japanese islands and Circum-Pacific region (Ishihara 1998), as well as some Cryptozoic terranes. The Japanese islands are composed of two basic basement units: the Hida meta-igneous crystalline terrane, which is a part of the Sino–Korean Paraplatform, and accretionary terranes of Palaeozoic to Tertiary ages (Fig. 1).

1. History of the discovery

Molybdenum (Mo) and tungsten (W) are known to be most closely associated with granites in space and time. A quantitative expression of the ore deposits in the 1960s (i.e., production and remaining ore reserves) in the major Mo and W mineralised region of Southwest Japan, indicated that many molybdenites recorded in W deposits are just mineral occurrences and were absent in many of tungsten deposits in the Sanyo Province; thus an obvious paired zoning, Mo in the north and W in the south, was delineated (Fig. 2).

Moreover, 98% of the Mo ores and 45% of the W ores are hosted in the granites, i.e. they are endogranitic, implying that the host granites must be different. Granitoids of the Sanyo W Province were studied in 1970, and their modal analyses indicated almost no opaque minerals in those from the Sanyo W Province, in contrast to abundant opaques in the Sanin Mo province. Wet chemical analyses of major elements indicated similar contents for most of the components, but a clear difference in the ferric/ferrous ratio (Ishihara 1971). It was obvious from these data that the difference between the

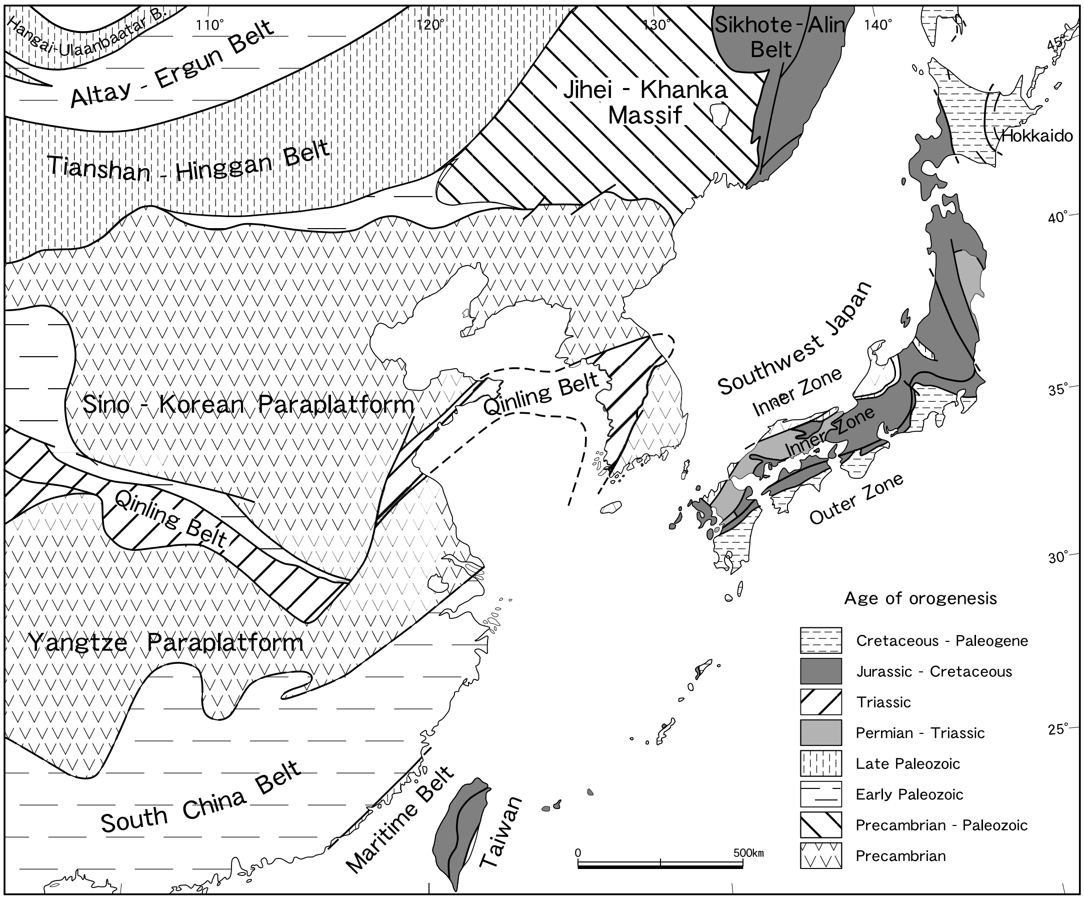

Figure 1 Straigraphic division of East Asia (from Teraoka & Okumura 2003). Typical accretionary terranes of Jurassic to Palaeogene age occur in the Sikhote Alin, Japan and Taiwan. The Palaeozoic Altay-Ergun, Tianshan-Hinggan and South China Belts are mainly composed of accretionary terranes.

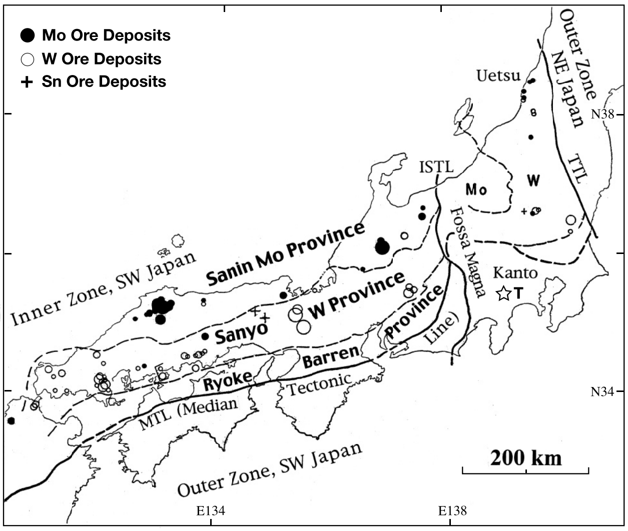

Figure 2 Late Cretaceous–Palaeogene Mo, W and barren metallogenic provinces in the Inner Zone of SW Japan (Ishihara, 1971), where magnetite/ilmenite-series granitoids were first identified. Open star with T, Tanzawa tonalite pluton.

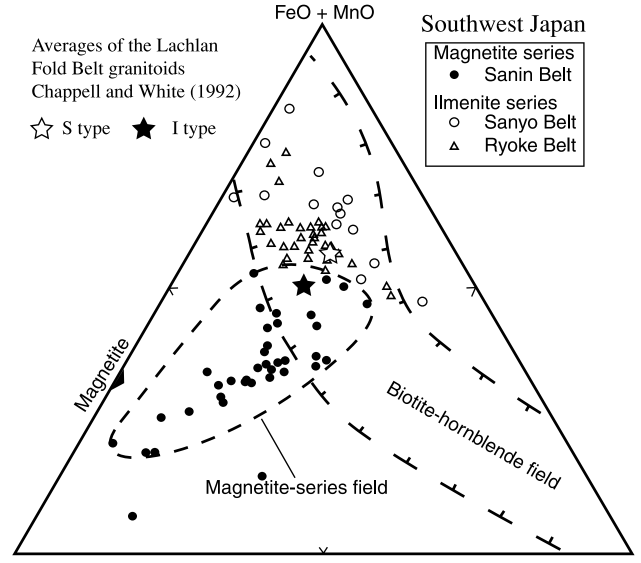

Figure 3 Bulk femic compositions of late Cretaceous–Palaeogene granitoids of the Inner Zone of SW Japan. Revised from Ishihara (1971). Note that the granitoids of Sanin Mo province plot towards the magnetite-haematite side line, while the averaged S and I types of the Lachlan Fold Belt (Chappell & White 1992) plot in the ilmenite-series field.

granitoids in the two provinces is the content of magnetite. This varying content, easily detected by magnetic susceptibility, was confirmed in the following years by using the Bison apparatus on the powdered samples (Kanaya and Ishihara 1973; Ishihara 1979).

The granitoids studied are mostly hornblende-biotite granodiorite or biotite monzogranite. Bulk analyses of the magnetite-free Sanyo and Ryoke granitoids plot in the biotite composition field of Heinrich (1946) in the FeO+MnO–Fe_2O_3+TiO_2–MgO diagram (Fig. 3). Average compositions of S and I type granitoids of the Lachlan Fold Belt (Chappell & White 1992) also plot in the same field, indicating the general

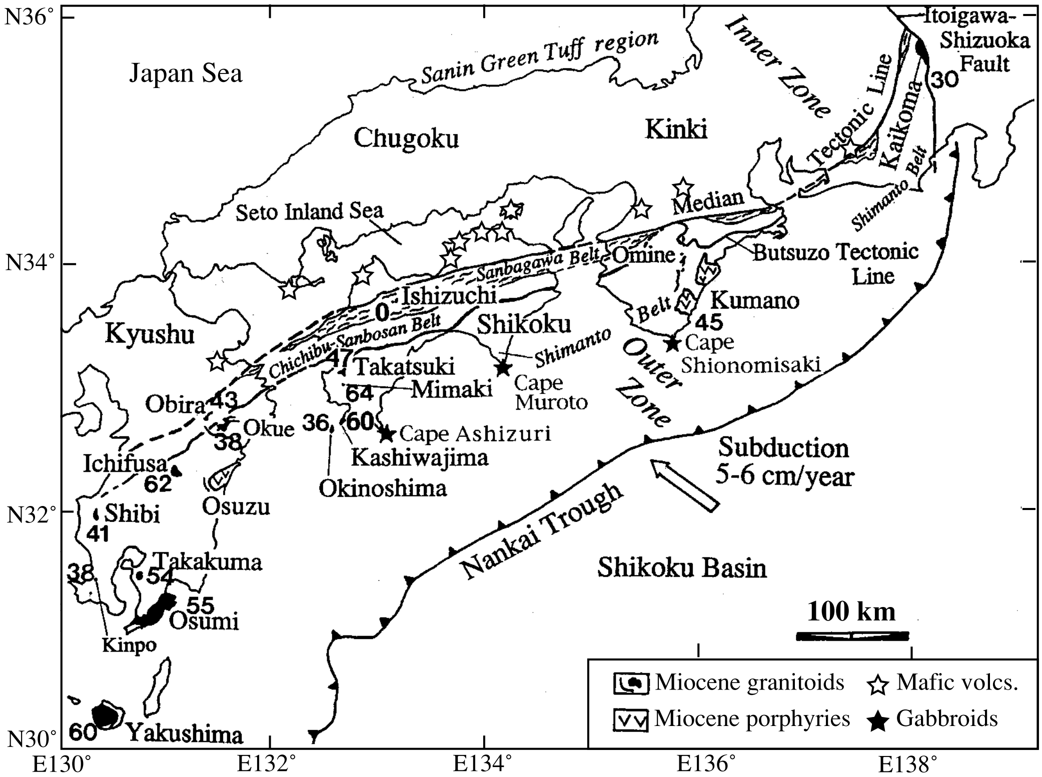

Figure 4 Distribution of Miocene granitoids and gabbroids in the Outer Zone of SW Japan. Numerals indicate percentage of accretionary wedge component in the granitoids, as calculated from the whole rock $\delta^{18}O$ values of Ishihara and Matsuhisa (1999). Mafic volcanics (basalts and high-Mg andesites) and gabbroids occur only at both sides of the ilmenite-series granitoids belt, implying that the mafic magmas were mingled with the wedge-source magmas to form the granitoids. The magnetite-series counterparts occur along the Sanin Green Tuff Belt along the Japan-Sea coast.

reduced nature of the Lachlan granitoids, especially the S-types.

The granitoids of the Sanin Province, in contrast, plot towards the magnetite–haematite side, implying that they contain haematitised magnetite, a feature confirmed by microscopic observation (Tsusue & Ishihara 1974). We now have good quality aeromagnetic data, which are useful in discriminating the two series of granitoids in regions where little or no overlapping of later magnetite-series igneous activity is known.

2. Granitoids in orogenic belts

Along the convergent plate boundary of the NW Pacific Rim, Phanerozoic granitic magmatism occurred in two contrasting basements: (1) the accretionary sedimentary unit and (2) the old crystalline unit. The former comprises sedimentary terrains formed by accretionary wedges accreted just prior to granitic intrusion. Their ages vary from the late Palaeozoic to Tertiary, culminating in the Jurassic (Isozaki 1998), and represented in the islands of Japan, Far East Russia, and the NE Pacific Rim. The sedimentary rocks are regionally un-metamorphosed or metamorphosed, and involved in the magma generation of ilmenite-series granitoids. These terranes have been intruded by granitoids from Triassic to Tertiary in age.

The old crystalline units are represented by the Sino–Korean Paraplatform, which is composed of Precambrian gneisses and granitoids seen in North China and the Korean peninsula (Fig. 1). This basement was intruded by Palaeozoic to Cretaceous granitoids in which the peak magmatism is Jurassic (Yanshanian and Daebo cycles) in the continental region. In Japan, similar granitoids occur in the Hida terrain (formerly called Funatsu Granite). Miocene magmatism of the Green Tuff region, Japan, is much younger, but may be the same in the basement setting, intruding mainly Cretaceous crystalline rocks.

In the NE Pacific rim, the major accretionary terranes are also Jurassic in age, intruded by the Jurassic–Cretaceous Coast Plutonic complex in Canada, and by Cretaceous and Tertiary plutonic rocks in the inland areas (Nokleberg *et al.* 2000; Hart *et al.* 2004). In the coastal Andes, on the other hand, the basement setting appears to be of crystalline type, because the Mesozoic to Cenozoic granitoids often intrude Precambrian crystalline rocks and late Palaeozoic granitoids, as well as into Jurassic and younger coeval volcanic rocks (Ishihara *et al.* 1984; Jaillard *et al.* 2000).

3. Granitoids with accretionary components – ilmenite series

The ilmenite-series granitoids are most widely distributed in the islands of Japan as well as in East Asia, in contrast to the predominance of magnetite-series granitoids in the East Pacific Rim (Ishihara 1977). The granitoids occur in major parts of the Inner Zone of SW Japan, i.e. late Cretaceous Sanyo and Ryoke Belts, and in the Outer Zone of the late Cretaceous Abukuma Belt, Tertiary Hidaka Belt and Miocene SW Japan, the last of which is the best preserved and discussed in the following paragraphs.

In the Sikhote Alin Belt (Fig. 1), Mesozoic granitoids are largely of ilmenite series associated with Sn and F mineralisations (Sato *et al.* 2002). In the South China Belt, Jurassic granitoids are mainly ilmenite series associated with W-mineralisations whereas magnetite series increase toward the Cretaceous granitoids (Ishihara & Wang 1999).

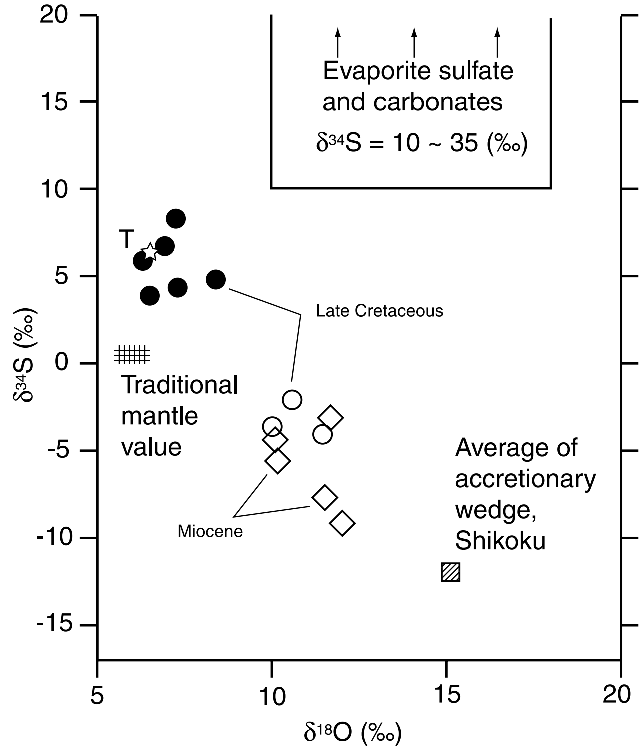

Figure 5 Whole rock δ^{34}S versus δ^{18}O values of the late Cretaceous to Miocene granitoids in SW Japan. (star with T) Tanzawa tonalite; (solid symbols) magnetite series; (open symbols) ilmenite series. Note that the SW Japan granitoids have no relationship with the sulphate–sulphur of evaporite and carbonates, which is common in the Cino-Korean Paraplatform (Ishihara *et al.* 2002a), but with that of the biogenic sulphur from the accretionary complexes.

3.1. Outer zone granitoids of SW Japan

The Miocene ilmenite-series granitoids occur mostly in the Cretaceous–Tertiary accretionary complex as isolated plutons ranging from 426 km^2 (Osumi body) to small stocks (Fig. 4). The average composition of the whole zone would be approximately monzogranite–granodiorite. These granites have high sulphur contents, locally up to 3550 p.p.m. (Ishihara *et al.* 1999), mostly occurring as pyrrhotite, but also as rare arsenopyrite and chalcopyrite. Their δ^{34}S values vary from -3 to -13 permil (Fig. 5), in contrast to the positive δ^{34}S values of the magnetite series (Sasaki & Ishihara 1979). Thus, the isotopic values are positively correlated with magnetic susceptibility (Ishihara & Sasaki 1989). The negative S isotopes are a characteristic product of biogenic sulphur in the euxenic environment on ocean floors where anaerobic bacteria live. An average δ^{34}S value of the Cretaceous–Tertiary accretionary wedges is $-13{\cdot}7$ permil. Thus, the Miocene granitoids have received sulphur from the intruded accretionary wedges.

In the largest Osumi pluton, the δ^{34}S values are fairly constant ($-8{\cdot}3$ to $-7{\cdot}0$‰) as compared to the large variation in the S content (70 to 1360 p.p.m., Ishihara *et al.* 1999), indicating that biogenic sulphur from the accretionary sediments was incorporated in the granitic magmas from the beginning of the magma generation and was well homogenised in the granitic body.

The Miocene granitoids have high δ^{18}O values of 9–13 permil (Fig. 5). Thus, they are negatively correlated with the δ^{34}S values. ^{18}O is concentrated by very low temperature fractionation, such as precipitation of cherts and illite on the ocean floor. The δ^{18}O values of the Outer Zone granitoids are much higher than that of typical Miocene low-K tonalite at Tanzawa in the southern Fossa Magna (T in Fig. 5), both occurring near the volcanic fronts. Both isotopic systems suggest that significant sedimentary components were involved in the genesis of the ilmenite-series granitoids.

The Tertiary granitoids are seen, together with coeval gabbroids, in the Hidaka accretionary wedges in the axial zone of Hokkaido, whilst the Miocene granitoids occur sporadically in the Cretaceous–Palaeogene Shimanto accretionary wedge of the Outer Zone of SW Japan (Fig. 4). Miocene gabbroids

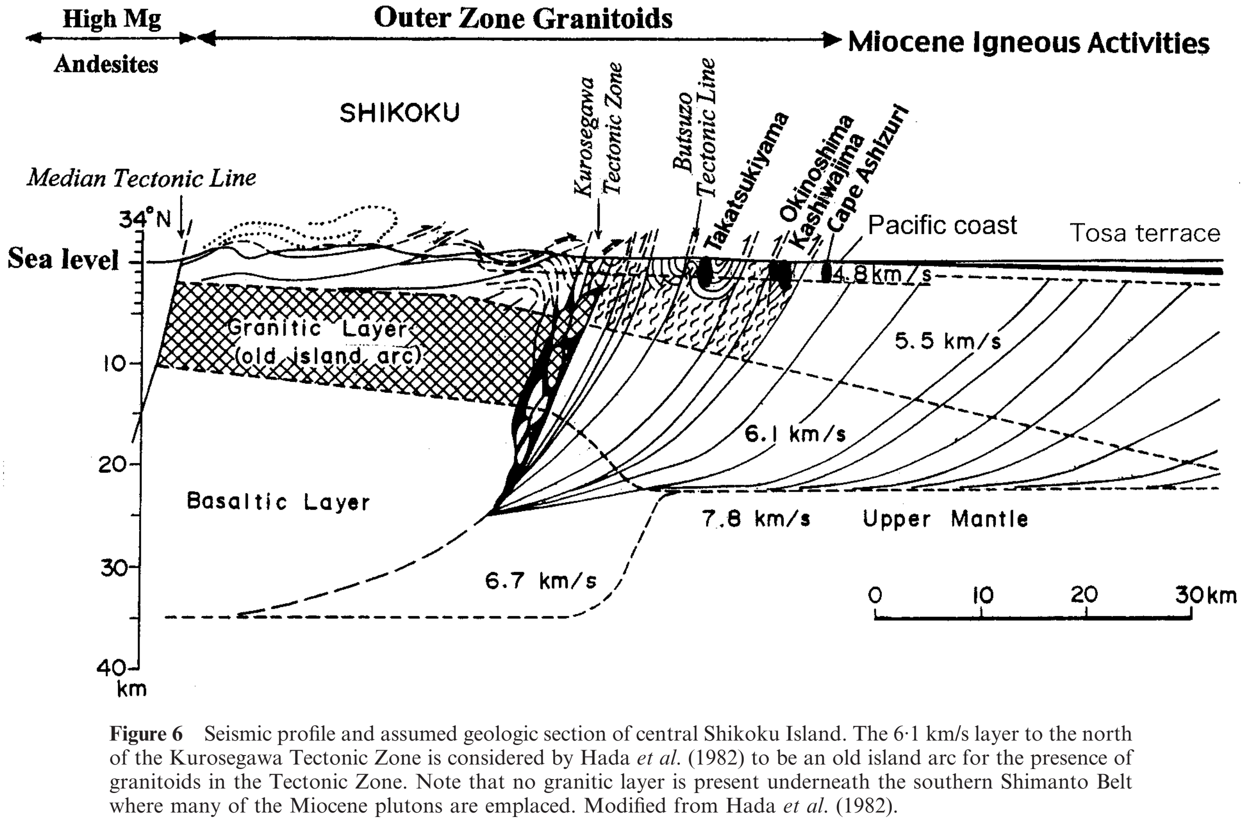

Figure 6 Seismic profile and assumed geologic section of central Shikoku Island. The 6·1 km/s layer to the north of the Kurosegawa Tectonic Zone is considered by Hada *et al.* (1982) to be an old island arc for the presence of granitoids in the Tectonic Zone. Note that no granitic layer is present underneath the southern Shimanto Belt where many of the Miocene plutons are emplaced. Modified from Hada *et al.* (1982).

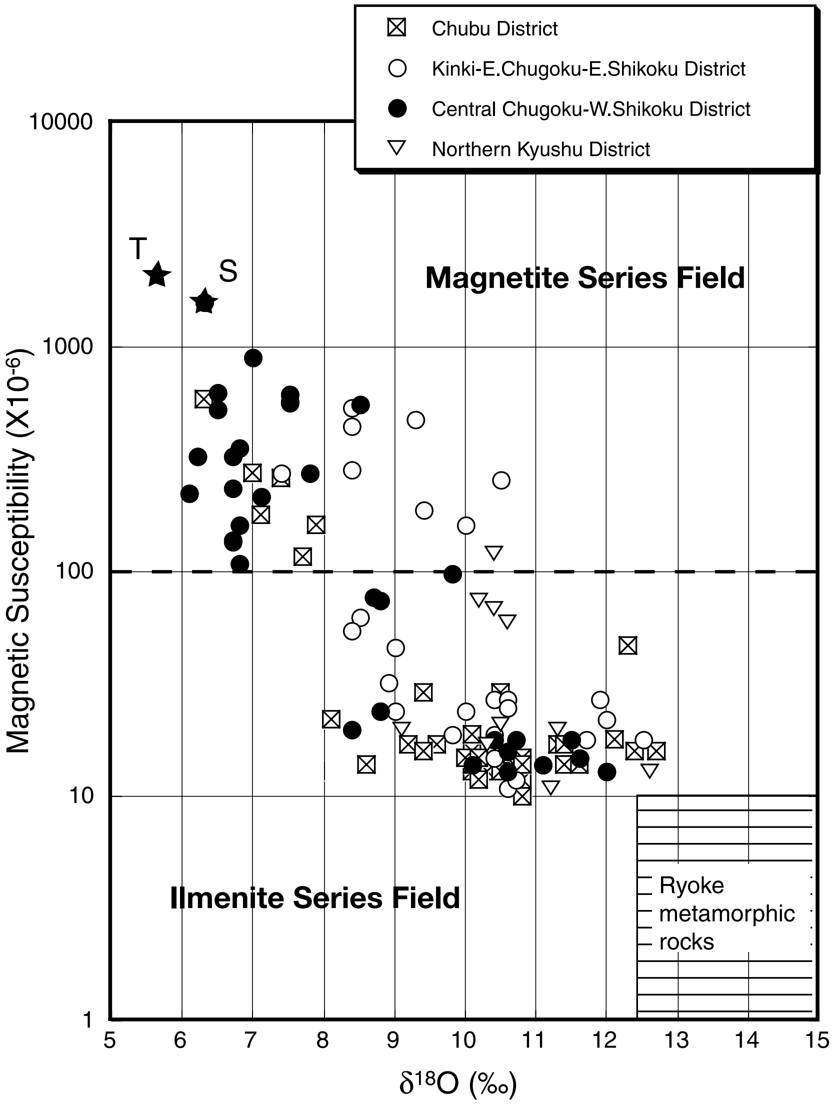

Figure 7 Magnetic susceptibility versus δ^{18}O values of the late Cretaceous–Palaeogene granitoids, SW Japan. The granitoids plot between the gabbroids of the Miocene Tanzawa body (star with T) and those of the Palaeogene body in Shimane Prefecture (star with S), and Jurassic accretionary wedges of the Ryoke metamorphic rocks. The original data from Ishihara and Matsuhisa (2002). Several granitoids which have possibly interacted with meteoric water in the Sanyo Belt are excluded.

occur at three cape areas: Cape Ashizuri, Cape Muroto and Cape Shionomisaki. To the north of the Median Tectonic Line (Fig. 4), high Mg andesites occur sporadically. These mantle-derived mafic rocks do not occur with the granitoid zone, but mingling of the mafic and felsic magmas is observed (e.g., Okueyama, Takatsukiyama and Cape Ashizuri). These observations indicate that the gabbroids and andesites must have provided heat and materials to the lower part of the accretionary complex from the upper mantle, and their mingling and mixing resulted in the generation of the ilmenite-series granodiorite–granitic magmas.

Seismic data for central Shikoku (Fig. 6) indicate that a basaltic layer of 6·7 km/s does not exist below the accretionary wedges of the Shimanto Supergroup; the latter is comprised of 6·1–4·8 km/s layers, probably the metamorphic and non-metamorphic accretionary complex, directly overlaying a 7·8 km/s unit, probably upper mantle peridotite. A 6·1 km/s layer to the north of the Kurosegawa Tectonic Zone is considered to represent an old island arc crust, given the nature of granitoids occurring in the tectonic zone (Hada *et al.* 1982). Severe crustal shortening has been observed in the accretionary wedges along the fore-arc side. This geologic setting was formed by southeastward migration of SW Japan, related to repeated openings of the marginal basin, the last of which formed the Japan Sea in the late Miocene. Miocene gabbroids, with the very low initial ^{87}Sr/^{86}Sr ratio of 0·7036 (Shibata and Ishihara 1979), may have originated in ultra-mafic to mafic materials in the upper mantle or underplated lower crust amphibolites (Kawate and Arima 1998). Any felsic magmas generated in this zone must have originated in the accretionary wedges, in the absence of any other felsic protolith below the Shimanto Supergroup.

Sulphur is a minor but oxygen is a major component in these granitoids. Assuming the granitoids were formed by mixing of the two end-members, namely the arc front gabbro-basalt and the accretionary wedge sediments, the observed δ^{18}O values can be converted to mass fraction (wt.%) of the accretionary sediments by simple mass-balance calculation (Ishihara & Matsuhisa 2002), as shown in Figure 4. The maximum is 67%, with mostly 50–30% of the sediments input in those granitoids intruding the accretionary terrane of Shikoku and Kyushu. A value of less than zero was obtained at the Ishizuchi-yama body occurring in the Sanbagawa meta-igneous metamorphic belt (Fig. 4).

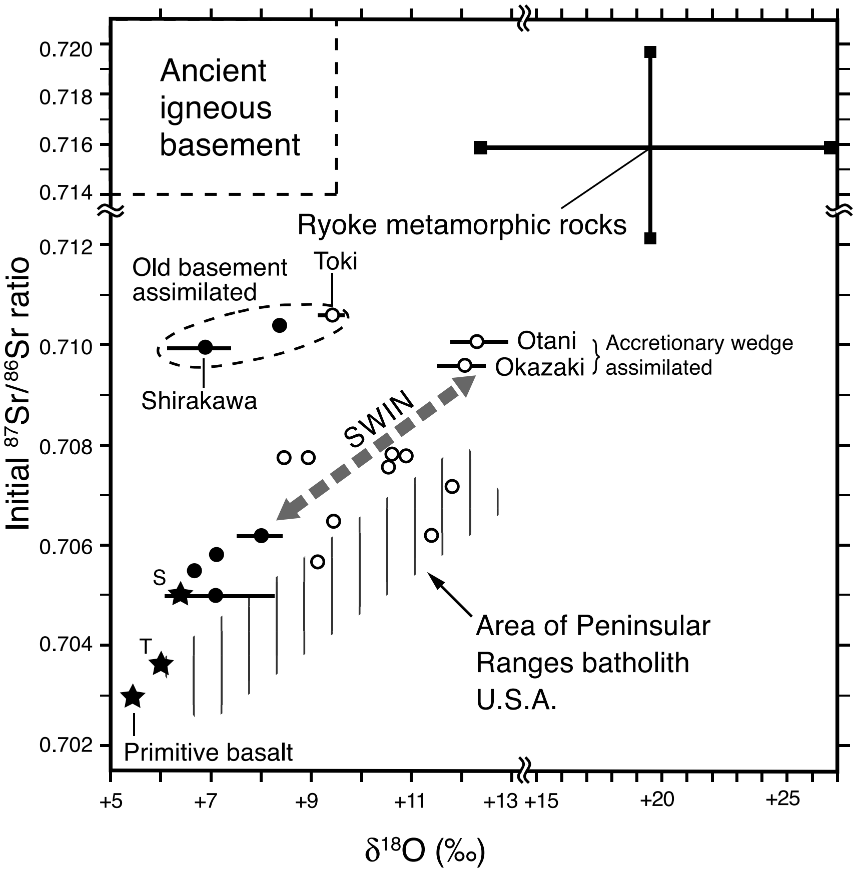

Figure 8 Initial ^{87}Sr/^{86}Sr ratio versus δ^{18}O ratios of the late Cretaceous–Palaeogene batholith of the Inner Zone of SW Japan (SWIN). Revised from Ishihara & Matsuhisa (2002). The original data for the Peninsular Range batholith are taken from Taylor (1986). (solid circle) magnetite series; (open circle) ilmenite series; (star with S) Palaeocene gabbro in Shimane Prefecture; (star with T) Miocene gabbro in Tanzawa; (primitive basalt) Quaternary tholeiitic basalt of Hachijo-jima (Matsuhisa *et al.* 1973).

3.2. Inner zone batholith of SW Japan

An older cycle of Cretaceous–Palaeogene granitoids occurs in the Inner Zone of SW Japan. The Inner Zone granitoids are mostly ilmenite series on the fore-arc side, and magnetite series on the back-arc side, similar to the asymmetric zoning of the Miocene granitoids. They are mostly granodiorite and monzogranite of calc-alkaline series. Alkaline rocks are absent, but adakitic magnetite-series quartz diorite-granodiorite stocks occur very locally in the early stage of the granitic activities at the northern margin of the W province (Kiji *et al.* 2000).

Whole rock δ^{18}O values of these granitoids are generally high in the ilmenite-series granitoids to the south, but low in the magnetite-series granitoids to the north. The ilmenite/magnetite-series boundary is located at around 8 permil (Ishihara & Matsuhisa 2002). The whole rock values are negatively correlated with magnetic susceptibility of the granitoids. All the data fall in an area between primitive gabbroids and the Ryoke metamorphic rocks (Fig. 7).

Gabbroids are rather dominant in the southernmost Ryoke Belt, where mingling of mafic and granitic magmas is often observed (Yokoyama 1984; Ishihara 2003). The Inner Zone granitoids were formed by mixing of mafic magmas, originated at depth, with felsic magmas derived from the Jurassic accretionary complex, and some older continental blocks. A mass-balance calculation on the δ^{18}O values between the gabbroids and the Ryoke metamorphic rocks indicates up to 32% of the metamorphic rocks mixed into the granitic magmas (Ishihara and Matsuhisa 2002). In this regard, the Ryoke metamorphic and granitic rocks presently exposed may represent a deeper facies of the Miocene Outer Zone granitoids of SW Japan.

The Inner Zone granitoids are different from the Miocene Outer Zone granitoids, based upon sporadic occurrences of high initial ^{87}Sr/^{86}Sr rocks, particularly around the Hida massif. The high initial ^{87}Sr/^{86}Sr rocks are observed in both ilmenite and magnetite series (Fig. 8), and are independent of the reducing agents. The observation indicates the presence of old, high Rb blocks of continental fragments, beneath the upper Palaeozoic to Jurassic accretionary wedges. The figure also indicates that the Inner Zone granitoids are more mature than the primitive arcs of the southern Fossa Magna as represented by the Tanzawa pluton (T, Fig. 8) and the Peninsular Range Batholith, reflecting the absence of old continental fragments in the latter regions.

In conclusion, the major part of the SW Japan granitoids, i.e., the ilmenite-series granitoids, were formed from the melting of accretionary wedges under the influence of heat and mafic and adakitic magmas from depth. Due to the opening of marginal basins, compressional tectonic setting occurred repeatedly from the late Cretaceous onwards, and mafic ascending magmas along the frontal zone were forced to interact with felsic magmas generated from the accretionary wedges. Along the back-arc side, on the other hand, intrinsically oxidised gabbroids and granitoids may have been intruded without crustal assimilation and solidified as the magnetite-series in the extensional tectonic setting, related to the opening of the marginal basin, and to the lack of organic carbon in the basement.

4. Granitoids in crystalline basements – magnetite series

The Quaternary volcanoes of the islands of Japan, composed of I-type magnetite-series rocks, occur along the volcanic front which cuts through various crystalline basements consisting of Mesozoic metamorphic, granitic and sedimentary rocks, overlain by the Neogene volcano-sedimentary rocks of the Green Tuff Belt. Miocene plutonism occurred in the same basement within the back-arc side of NE Japan and along the Japan Sea coast of SW Japan. It is possible that the crystalline basement provided no reducing agents such as organic carbon for magma generation.

4.1. Granitoids related to marginal basins

The Miocene plutonic rocks are of oxidised type, except where granitoids locally interacted with wall-rock sediments (e.g., Tokuwa granodiorite, Shimizu 1986; Chichibu mine stock, Ishihara *et al.* 1987). The magmatism appears to have occurred along rift zones formed by the opening of the Japan Sea and sheared fractures in the Fossa Magna (cf. Fig. 2). Therefore, the tectonic setting is considered generally extensional-intermediate, which allowed oxidised mafic to intermediate magmas to ascend without interaction with upper crustal rocks.

Palaeogene magnetite-series granitoids are also present in the Mo province of the Inner Zone of SW Japan (Fig. 2). They occur essentially in the pre-Jurassic metamorphic and granitic basement of the Hida Belt, which corresponds to the eastern edge of the Sino–Korean Platform (Fig. 1), and also in the Sangun metamorphic rocks. The Hida metamorphic rocks locally contain graphite-rich gneiss layers (e.g., Sennotani, Genda, Amo mines), but are largely meta-igneous in composition. Their tectonic setting is unclear but may be extensional, due to the opening of the proto-Japan Sea. Late Cretaceous granitoids of the Gyeongsang basin, South Korea, intruding Cretaceous non-marine sediments and overlying volcanic rocks at the southeastern edge of the Sino–Korean Platform, are mostly of magnetite series (Jin *et al.* 2001). A-type granites at Namsan, in the Gyeongsang Basin (Koh *et al.* 1996), which is late orogenic A-type and equivalent to the post-orogenic PA type (Hong *et al.* 1996), are strongly oxidised magnetite series.

4.2. Early Cretaceous Kitakami granitoids

Early Cretaceous granitoids occur along a narrow fault-bounded zone of the Kitakami Belt (Fig. 9). Compositionally calcic, they comprise some gabbroids, much quartz diorite, tonalite and granodiorite with some granite. High-Sr/Y adakitic tonalites and granodiorites are abundant in Zone II (Tsuchiya & Kanisawa 1994), but K-alkaline rocks also occur in the western part. These plutonic rocks are of oxidised type, having high values of magnetic susceptibility; highest in the K-alkaline rocks, high in the high Sr/Y granitoids, and lowest in the low Sr/Y granitoids (Fig. 10).

Country rocks for the early Cretaceous granitoids are continental margin sediments with some older metamorphic and granitic blocks in the southwestern Kitakami Mountains, and the Jurassic-Cretaceous accretionary wedges in the northeastern Kitakami Mountains. Yet the majority of the granitoids are of magnetite series with only local reduction due to assimilation of the basement sediments (Ishihara *et al.* 1985). The granitoids are associated with coeval volcanic rocks along the eastern coastal zone of the mountains where the granitoids are most magnetic. These granitoids are similar to those of the Peninsular Range Batholith, where coastal volcano-plutonic complexes are more magnetic than those inland (Gastil *et al.* 1990), but different from the granitoids of northern Chile, where the magnetic susceptibility of the I-type magnetite series increases towards the continent (Ishihara *et al.* 1984).

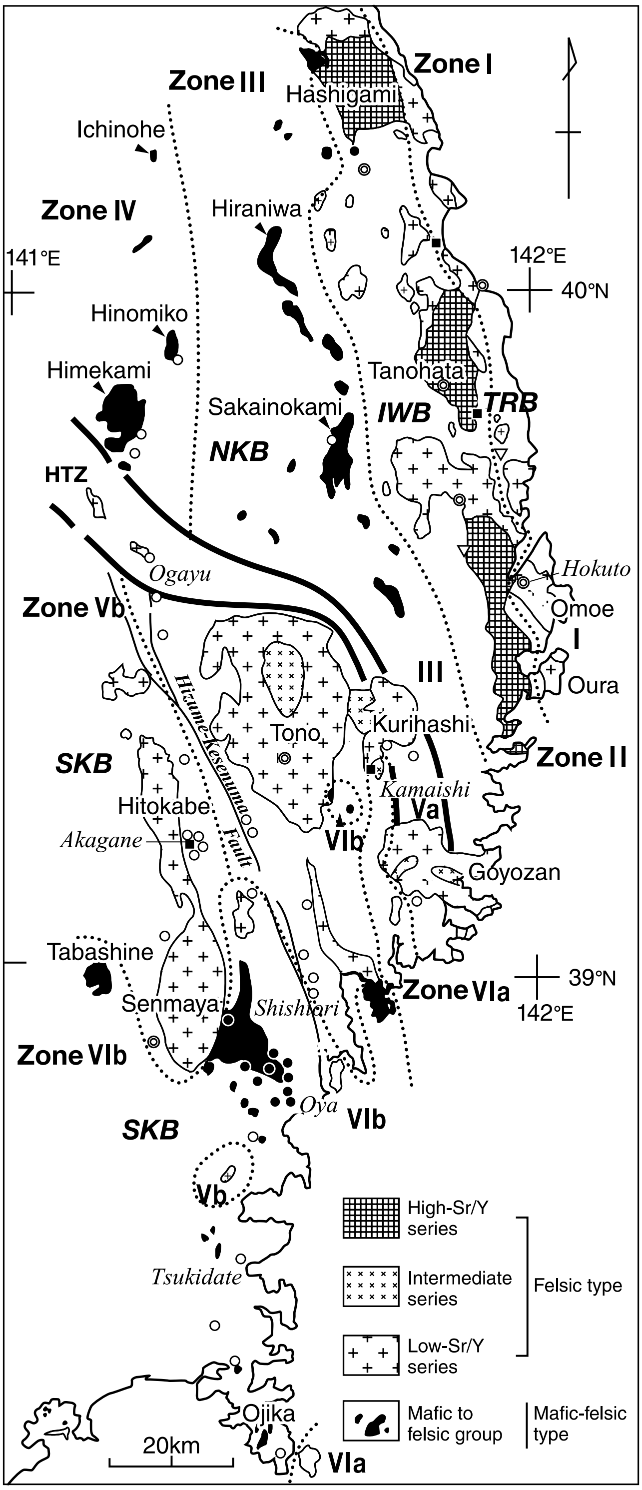

Figure 9 Distribution of the Cretaceous granitoid series and the studied ore deposits in the Kitakami Mountains (simplified from Ishihara & Muakami 2004). Adakitic rocks occur typically in Zone II and partly in Zone Va. Zone IV plutons are alkaline, whilst Zone VIb plutons are K-subalkaline. ◎ W and Mo deposits; ■ Skarn-type Fe and Cu-Pb-Zn deposits; ● high sulphide-type Au deposits; ○ low sulphide-type Au deposits; ∇ volcanogenic deposits. (HTZ) Hayachine Tectonic Zone; (SKB) Southern Kitakami belt; (NKB) Northern Kitakami belt; (IWB) Iwaizumi belt; (TRB) Taro belt.

Due to the mixed occurrence of gabbroid and granitoids of K-alkalic, high-Sr/Y and low-Sr/Y series, the Kitakami

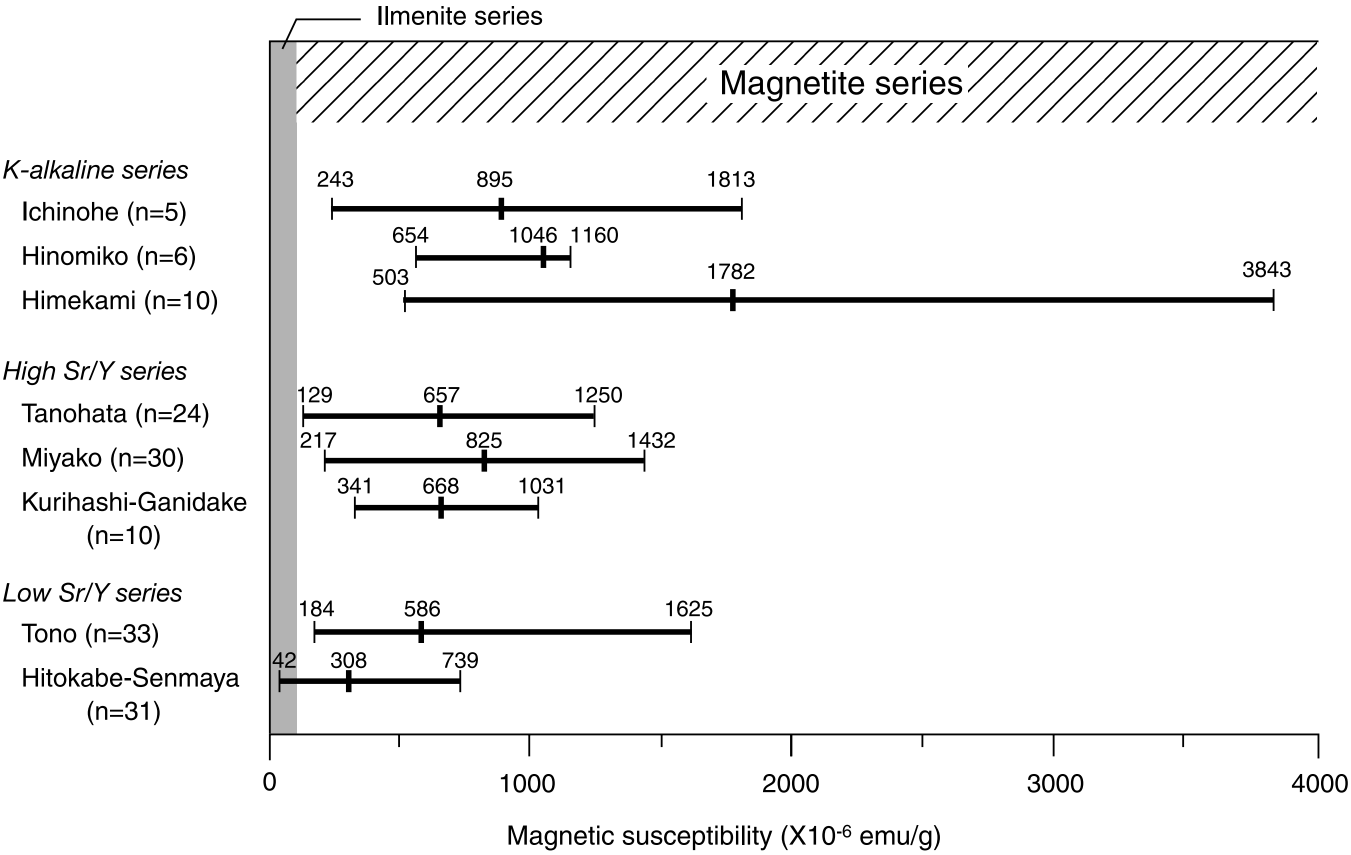

Figure 10 Range and average of magnetic susceptibility of the K-alkaline, high-Sr/Y and low Sr/Y granitoids in the Kitakami Belt, Japan. Original data from Geological Survey of Japan (1974).

plutonic rocks are considered to be a mixture of various magmas originating in the subducted slab, the upper mantle, and the lower crust (Tsuchiya & Kanisawa 1994; Ujiie-Mikoshiba *et al.* 2004; Ishihara & Murakami 2004). N–S and NNW-trending faults cut the accretionary complexes. The Kitakami block can be considered to have an intermediate status in the tectonic setting when the magmas intruded. Reducing agents from the accretionary wedges reacted only locally with the magmas of the marginal facies.

Similar magmatic arcs are predominant along the East Pacific Rim. Quartz diorite to granodiorite of the Coast Plutonic Complex, Canada, belong mostly to the magnetite series (J. Roddick & L. Carmel, personal com. 2001). Quartz diorite to granite of the Sierra Nevada batholith is dominantly magnetite series (Bateman *et al.* 1991). The coastal plutonic rocks in Peru (Ishihara *et al.* 2000) and northern Chile (Ishihara *et al.* 1984) are also mainly quartz diorite to granodiorite in composition. They generally belong to the magnetite series, interpreted to reflect the absence of the accretionary wedges due to tectonic erosion or little fore-arc sedimentation occurring from the Jurassic onward.

5. The redox state of granitoids in early Earth history

Phanerozoic adakitic plutons in the Kitakami Belt (Tsuchiya & Kanisawa 1994), and small copper-related porphyries in the Philippines (Sajona & Maury 1998), Erdenet, Mongolia (Morozumi 2003), Tongshankou, China (Wang *et al.* 2004) and northern Chile (Oyarzun *et al.* 2001) are oxidised, magnetite series. Archaean TTG suites are mostly high-Sr/Y adakitic series, and are often considered products of slab-melting, reflecting hotter oceanic crust in the Archaean (Martin 1986; Drummond & Defant 1990). The TTG suites in the Kaapvaal Craton of South Africa are all identified as ilmenite or intermediate series based on magnetic susceptibility (Ishihara *et al.* 2000, 2001), reflecting the generally reduced nature of the early (>3·2 Ga) Archaean hydrosphere and

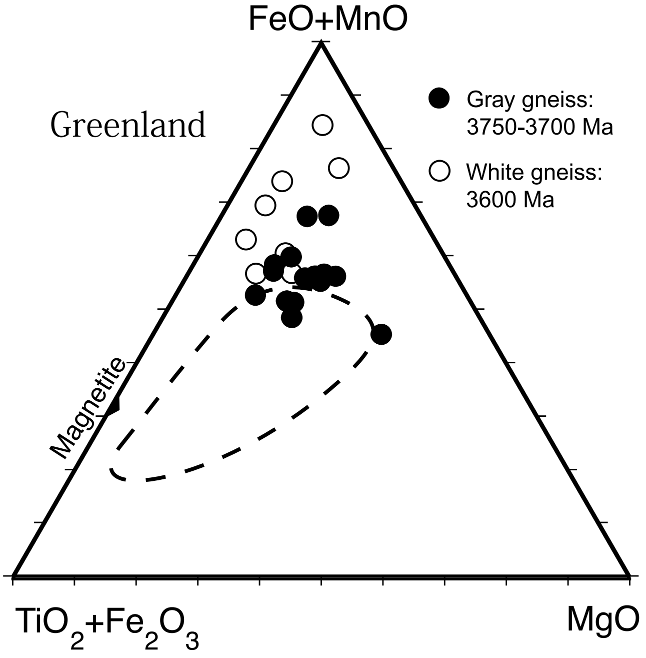

Figure 11 Bulk femic compositions of the Archaean granitic gneisses from Greenland. The grey gneiss plots in the ilmenite-series field, whilst the white gneiss is extremely reduced and also depleted in MgO. Data sources: Nutman *et al.* (1984); Nutman & Bridgwater (1986); Nutman *et al.* (1996). Broken line circle, see Fig. 3.

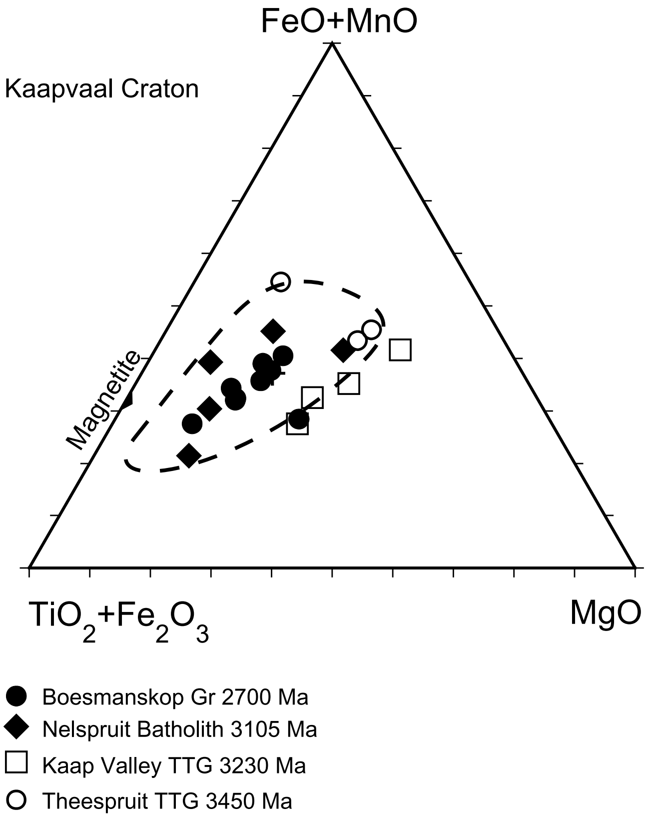

Figure 12 Bulk femic compositions of the Archaean granitoids from the Barberton Mountains, South Africa. Data sources: Viljoen & Viljoen (1969); Hunter (1974). The broken circle shows the representative area of the magnetite-series granitoids of the Sanin Province, Japan.

lithosphere (Huston & Logan 2004), and different source materials for the TTG magmatism (Smithies 2000; Smithies *et al.* 2003).

Some of the oldest Archaean granitoids are gneisses of the Central Dome of W. Greenland (Nutman & Bridewater 1986). Gray granitic gneiss (3750–3700 Ma) plot in the very reduced area of the FeO+MnO–Fe_2O_3+TiO_2–MgO diagram (Fig. 11), whilst the younger white granitic gneisses (3600 Ma) are slightly oxidised and MgO rich, but still largely reduced.

In South Africa, TTG suites occur closely associated with greenstones. The oldest TTG suites of the Barberton region (older than 3450 Ma) such as Rooihoogkte, Theespruit and other bodies, as well as the younger 3230 Ma Nelshoogte body, are reduced, ilmenite series (Ishihara *et al.* 2002b). The younger 3230 Ma Kaap Valley TTG pluton, and TTG and calc-alkaline granitoids of the Johannesburg Dome pluton (3340–2950 Ma) correspond to the ilmenite to intermediate series based on measurement of the magnetic susceptibility (Ishihara *et al.* 2002b).

Chemically, the Theespruit TTG plot in the least oxidised field (Fig. 12), whilst the Kaap Valley pluton falls in the ilmenite to intermediate series and is characterised by a high MgO content. The TTGs originated in reduced oceanic crust, but the Kaap Valley magmas may have had a high mantle component in the source materials.

The oldest known oxidised granite in South Africa is the biotite granite of the 3105 Ma Nelspruit batholith belonging to the late-tectonic cycle (Robb *et al.* 1983). Here, 86% of the 284 samples taken from the 100–230 km batholith give magnetic susceptibility values indicative of the magnetite series (Ishihara *et al.* 2002b). Euhedral magnetite is common and the coexisting biotite has a high Mg/Fe ratio (Ishihara *et al.* 2004). This granite and the post-tectonic K-alkaline granite are clearly the most oxidised in the FeO+MnO–Fe_2O_3+TiO_2–MgO diagram (Fig. 12). The Nelspruit granite is considered to have been generated from older Archaean continental crust (Anhaeusser & Robb 1980), implying that an oxidised crust existed before 3105 Ma ago in the Kaapvaal Craton.

Oxidised granitoids become common in the late Archaean and Proterozoic, especially after 2700 Ma. Good examples are those of the Eastern Goldfield Province, eastern Yilgarn Craton (Smithies & Witt 1997; Smithies & Champion 1999). Here the granitoids plot in the oxidised granitoid field in the FeO+MnO–Fe_2O_3+TiO_2–MgO diagram (Fig. 13). The felsic alkaline granites are even more oxidised than the typical

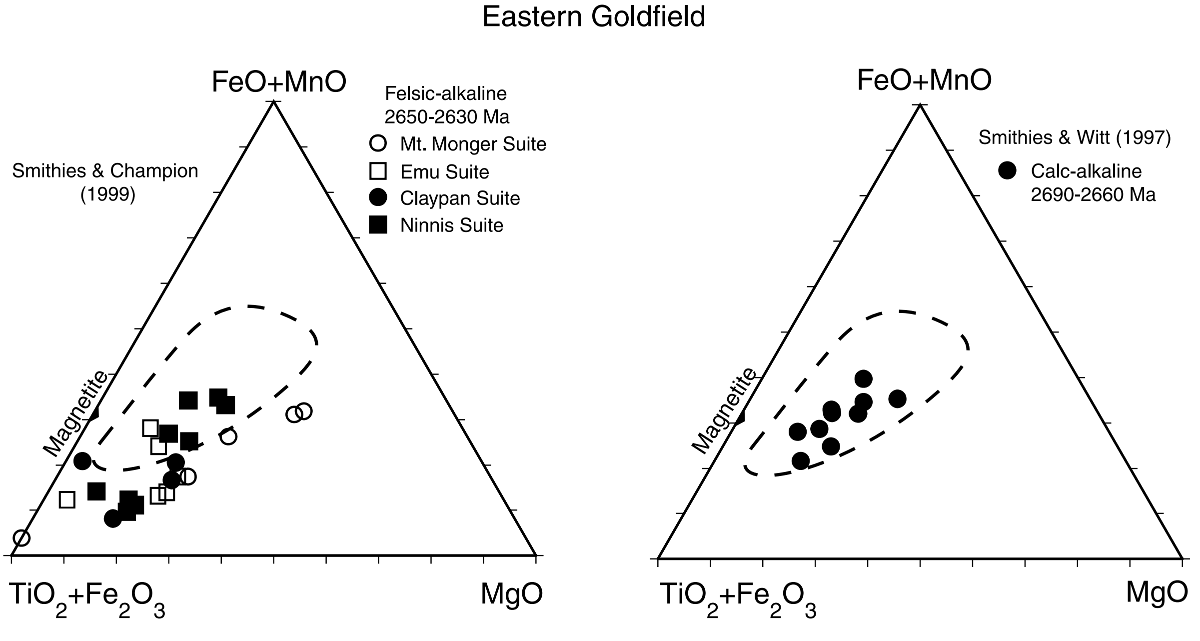

Figure 13 Bulk femic compositions of the Archaean granitoids, Eastern Goldfield, Yilgarn Craton, Western Australia. The felsic alkaline granitoids are extremely oxidised. Data sources: Smithies & Witt (1997); Smithies & Champion (1999). The broken circle shows the representative area of the magnetite-series granitoids of the Sanin Province, Japan.

magnetite-series, suggesting the presence of haematitised magnetite in the alkaline granites. The earth lithosphere appears to have become oxidised by this time, reflecting the increase of oxygen on the Earth's surface.

6. Concluding remarks

The orogenic belts of NW and NE Pacific Rims are characterised by granitic magmatism intruded into accretionary sediments and older cratons. Ilmenite-series granitoids were formed by mafic magmas from the upper mantle mixed with the accretionary sediments within the continental crust, as best shown by the Miocene and late Cretaceous granitoids of SW Japan. The mafic magmas may have been of oxidised type, but their original nature has been completely erased by reduced felsic magmas generated within the accretionary prism.

Miocene granitoids of the Green Tuff region are generally of magnetite series, because they were originally oxidised magmas and had little chance to mix with basement rocks, due to the development of vertical faulting, rather than horizontal compression, during the ascent and emplacement of the granitic magmas. The Cretaceous granitoids of the Kitakami Mountains, part of which occur within the Jurassic–Cretaceous accretionary complexes, can be explained by the same vertical-faulting tectonic setting. The magnetite-series occurring in the Sino–Korean Paraplatform had little chance of mixing with reducing agents in the source region, because carbon was concentrated in limited horizons as graphite gneisses.

The redox state of the granitoids varies in magma types. K-alkaline granitoids are generally oxidised. Anorogenic A-types are low in both fH_2O and fO_2 by definition (Loiselle & Wones 1979). Those having A-type chemistry in orogenic belts (the PA type of Hong *et al.* 1996), are strongly oxidised. The so-called adakites are oxidised in the Phanerozoic orogenic belt, but are reduced in the Greenland and Archaean Kaapvaal cratons, reflecting the reduced state of atmosphere, hydrosphere and lithosphere at that time. The first oxidised-type granite (*senso stricto*) appeared in the 3·1 Ga Nelspruit batholith in the Barberton region, South Africa.

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