

Magnetic Properties of Red Cherts with Special References to the Associated Greenstones, in Southwest Japan: A Rock Magnetic Approach

By

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Abstract

An experimental approach to the study of Fe-Ti minerals originally contained in Paleozoic to Mesozoic red cherts from the Tamba, Mino and Shimanto terrains in Southwest Japan has been made. The main purpose of the study is to establish a foundation for the paleomagnetic reliability of cherts to support paleomagnetic results which were already reported by the author and his collaborators. (SHIBUYA and SASAJIMA, 1980; KATSURA et al., 1980).

Thermomagnetic analyses combined with some heating experiments under an appropriate vacuum condition, lend an effective way to recover the original ferromagnetic mineral assemblage of these cherts. As the results, the possible ferromagnetic minerals (β phase) of the red cherts, which are found in stratigraphic sequences that contain greenstones, show an affinity with that of tholeiitic basalt ($x=0.62\pm 0.05$), suggesting that the primary ferromagnetic minerals in the red cherts were probably derived from related submarine basaltic tuffs.

If we accept a view that red cherts underwent submarine weathering or hydrothermal alteration almost the same time as the greenstones associated with them, a closed system with respect to Fe-Ti minerals and consequently blocking of their remanent magnetization as well, was maintained after an uncertain diagenetic event: this condition presumably related to the time of crystallization of major silica of the chert.

1. Introduction

One of the most important current problems in paleomagnetism in Japan is whether or not the outer zone of the Japanese islands belonged to a microcontinent which departed from somewhere near the paleoequator during the Late Mesozoic (SASAJIMA, 1981; SHIBUYA and SASAJIMA, 1980; KATSURA et al., 1980; HATTORI and HIROOKA, 1979; NUR et al., 1979). By summarizing Japanese paleomagnetic studies so far available, the writer substantiates that during the period from the Permian to the Triassic Honshu island lay near the paleoequator and then moved northwards until middle Cretaceous when it arrived at the eastern margin of the Asian continent, with a latitude about that of present Honshu; drift is estimated to have, most probably, occurred during middle to late Jurassic times (SASAJIMA, 1981).

Very recently, paleomagnetic results obtained from various kind of Mesozoic rocks in Southwest Honshu have further confirmed a low paleolatitudinal location for Honshu (SHIBUYA and SASAJIMA, 1981; HIROOKA et al., 1981).

The determination of remanent magnetization of bedded red cherts was introduced for paleomagnetic purpose because it has been found to be highly reliable (KATSURA et al., 1980; SHIBUYA and SASAJIMA, 1981). It is necessary to elucidate the rock magnetic properties of red cherts as a foundation to support their paleomagnetic reliability.

No rock magnetic study on red cherts has so far been published, partly because they have not ever been used for paleomagnetic purpose and partly because the constituent ferromagnetic minerals are so fine-grained that they can't be identified with neither a microscope using the highest magnification nor with the electron probe microanalyzer.

Thermomagnetic analyses, combined with heating experiments of red cherts, are presented in this paper with special references to pillow basalts and greenstones which have a close stratigraphic relationship to them. Most chert samples dealt with in these experiments are the same as those for which paleomagnetic results have already been reported, so that the results obtained may be accepted as an important contribution to paleomagnetic studies. The main aims of this study are the clarification of the ferromagnetic mineral sources, which are responsible for the NRM (natural remanent magnetization) in red cherts.

2. Sample and Experiments

Brief geologic records of the red cherts used in this study are listed in Table 1,

Table 1. Geologic notes of the samples used

Rock kind/sample no.	Locality	Age estimation	Reference
red chert/I32C	Inuyama, Gifu Pref., Mino Belt	Mid. Triassic	Yao et al. (1980)
red shale/HYG111	ditto	Mid. Jurassic	ditto
red chert/I10a	ditto	Low. Jurassic	ditto
red chert/2702	Omori, Kyoto Pref., Tamba Belt	Low.-Mid. Permian	Ishiga and Imoto (1980)
red chert/2712	ditto	ditto	ditto
pillow basalt	ditto	144 ± 7Ma (K/Ar, unpublished)	ditto
red chert/TB126	Ashimi, Kyoto Pref., Tamba Belt	Low.-Mid. Permian	Shimizu (1979)
red chert	Misoidani, Wakayama Pref., Shimanto	Up. Cretaceous	
pillow basalt/407-38	Reykjanes ridge, Iceland	39 Ma	Day et al. (1979)
basalt/K4	Kannabe, Hyogo Pref.	Recent	

together with those of pillow basalts dealt with in the heating experiments.

2-1) *Thermomagnetic analysis*

Thermomagnetic analysis of ferromagnetic minerals contained in rocks were carried out by means of sensitive silica-spring type Curie balance prior to the heating experiments. ADE-HALL et al. (1976 a) concluded with some reservation that thermomagnetic tests are more reliable than the electron probe microanalyses for determining the x-value of titanomagnetites contained in various basalts. The present writer holds the same view as the result of his experience, and therefore Curie point measurements have been applied to trace the change of chemical composition during various heat treatments of ferromagnetic and paramagnetic minerals contained in the rocks.

A member of the solid solution series between magnetite and ulvospinel (β phase) is defined by 'x' in the relationship $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$. Similarly, a solid solution member between hematite and ilmenite (α phase) is defined by 'y' in the relationship $\text{Fe}_{2-y}\text{Ti}_y\text{O}_3$. Fine-grained specimens about 20–100 mg in weight were used for Curie point analyses; the bulk precision of measurements seems to be lower than that of the usual measurements because of the low concentration of ferromagnetic minerals in case of the cherts. In order to increase the resolution power of measurement a special effort has been paid to separate the finest-grained ferromagnetic minerals from cherts but these attempts failed, except for a few cases.

2-2) *Result*

About two-thirds of whole rock measurements failed to certify any definite ferromagnetic Curie points in their thermomagnetic curves, which usually appeared to be paramagnetic in nature. Black, brown, gray, amber and green cherts were all involved in this paramagnetic category, excepting a few red cherts which were presumed to contain certain titanomagnetites (β phase) from the obvious Curie point. Some thermomagnetic results of ferromagnetic separates are shown in Fig. 1. They can be definitely identified as titanomagnetite phases, and exceptionally titanomaghemite phases in some pillow basalts; these conclusions were consistent with reflection microscopic observations using the highest magnification ($\times 1000$). In these cases it was possible to separate a ferromagnetic mineral fraction, but only a small amount, from a comparatively large volume of ball-milled fine rock-power.

Another ferromagnetic mineral which was almost certainly identifiable in the thermomagnetic curves was a titanhematite phase (including hematite) with a Curie point between 680–650°C. In this case its natural remanent magnetization (NRM) showed, in general, rather strong intensity (Jn) and a high stability (SHIBUYA and SASAJIMA, 1980). Such examples are shown in Fig. 2.

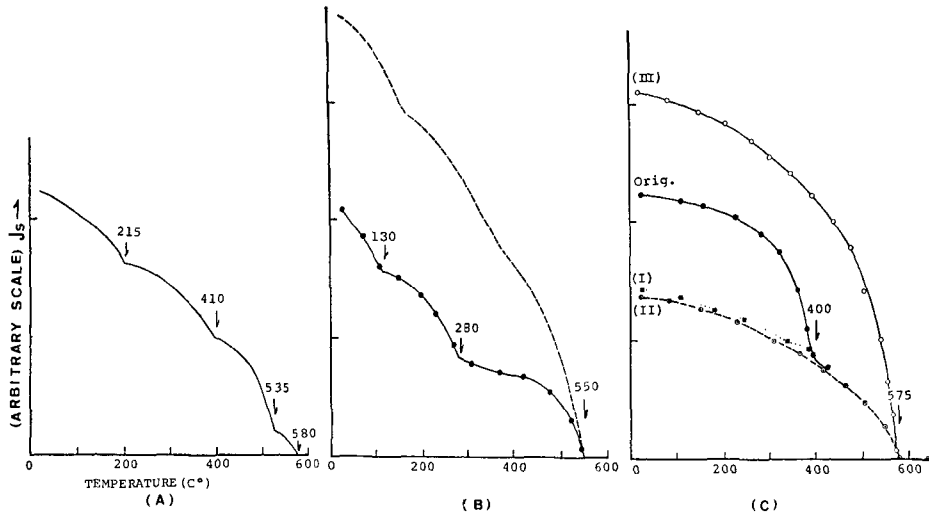


Fig. 1. Examples of thermomagnetic analysis of some red cherts and pillow basalt:
 (A) Red chert (sp. 32c) from Inuyama area; applied field H , 4.5 KOe in air.
 (B) Red chert (sp. 10a) from Inuyama area; $H=5.0$ KOe, under vacuum $P=5 \times 10^{-3}$ Torr.
 (C) Pillow basalt (Ts 919) from Tokushima, Shimanto terrain; $H=2.0$ KOe, $P=2 \times 10^{-3}$ Torr. (I) cooling process after the initial heating up to 420°C , (II) cooling process after an instantaneous heating at 660°C , (III) cooling process after 10 minutes heating at 660°C ; the possible production of magnetite reduced from the unmixed hematite which was resulted from the previous heat treatment at 600°C , may be inferred. The original ferromagnetic mineral (Orig) can be regarded as a titanomagnhemite of which transformation temperature seems to be 400°C .

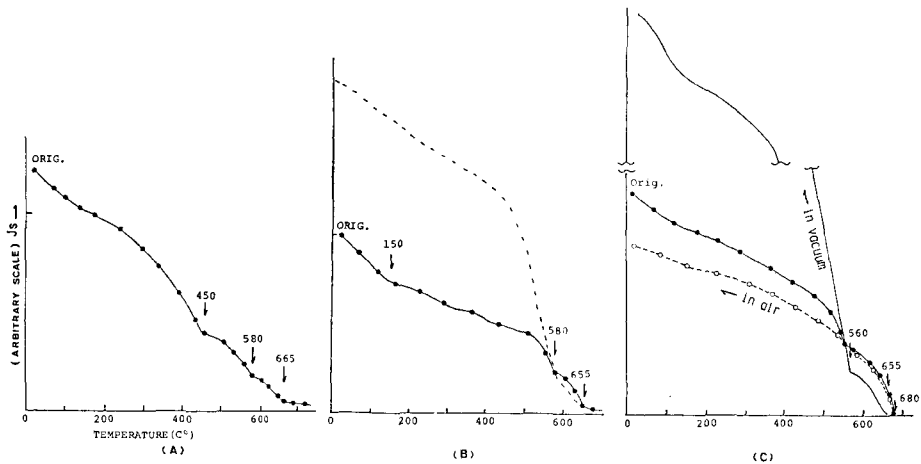


Fig. 2. Thermomagnetic curves of some red cherts showing coexistence of titanhematite (hematite) with titanomagnetite (magnetite) phases.
 (A) Specimen (2702) from Omori, Tamba terrain; $H=4.5$ KOe in air.
 (B) Specimen (TB 126) from Ashimi, Tamba terrain; $H=4.5$ KOe, $P=10^{-3}$ Torr.
 (C) Specimen (2712) from Omori, Tamba terrain; $H=3.0$ KOe, $P=6 \times 10^{-3}$ Torr and in air, respectively. J_s at room temperature became five times as large as that of the original after measurement in vacuum.

As seen in Fig. 2 the titanhematite phase is accompanied frequently by some titanomagnetite phases. The other type of ferromagnetic minerals common in red cherts is inferred to be pure hematite, although we could not identify its existence directly in thermomagnetic curves. As reported in the previous papers (SASAJIMA and TORII, 1980; SHIBUYA and SASAJIMA, 1980), it is possible to identify the positive existence of hematite in rocks indirectly, by the production of magnetite during the cooling process of thermomagnetic measurement. Such an unexpectedly reductive condition was considered to result from vapour of the rotary pump (with or without diffusion pump), especially without the cold trap of liquid nitrogen (SHIVE and DIEHL, 1977). Such indirect but powerful evidence of the existence of hematite was discovered in all the red cherts studied. Some typical examples are shown in Fig. 3. As shown in Fig. 3 A, the reaction from hematite to magnetite appears sometimes at about 450°C (SHIVE and DIEHL, 1977). It was experimentally determined that the production of magnetite is approximately dependent on the logarithm of time at a constant heating temperature of 460°C. As shown in both diagrams of Fig. 3 the cooling curve of thermomagnetic analysis after the heating at higher than 600°C under vacuum ($\approx 10^{-3}$ Torr of Pirani type vacuum gauge) always exhibits

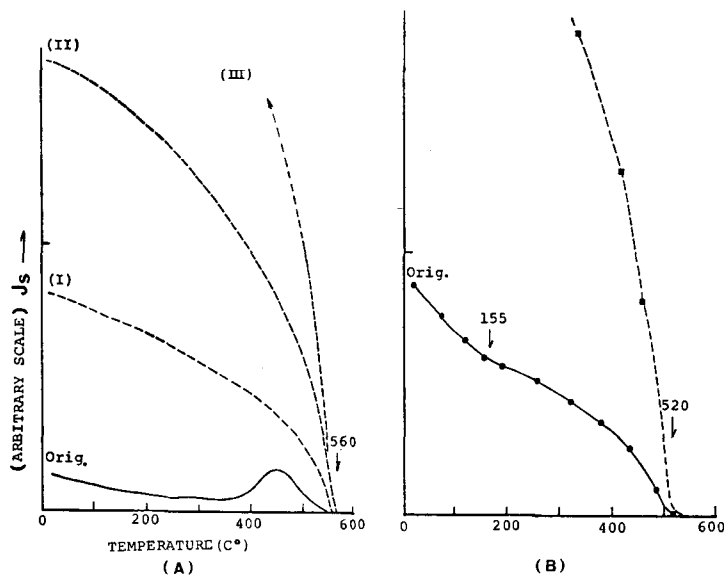


Fig. 3. Thermomagnetic measurements demonstrating the reductive production of magnetite from titanhematite (hematite) contained in red cherts.

- (A) Specimen (HYG 136) from Inuyama area; $H=2.5$ KOe, $P=10^{-2}$ Torr, (I) after heating at 560°C for 3 minutes, (II) after heating at 650°C for 25 minutes, (III) after heating at 650°C for 60 minutes.
- (B) Specimen (HYG 134) from Inuyama area; $H=4.5$ KOe, $P=6 \times 10^{-3}$ Torr, (I) after heating at 710°C for 10 minutes.

an abrupt increase in magnetization at a little higher temperature than the Curie point of magnetite (575°C).

Further clear evidence of existence of hematite crystals in red chert was first afforded by the use of the Analytical Transmission Electron Microscope (SASAJIMA et al., 1980). The size of platy crystals was about $330 \times 1,100 \text{ \AA}$ in a cross section and there was no measurable amount of impure elements, except the major element of iron with the analytical precision of 3 %. Based on the regular crystal growth of several euhedral hematites which conform to the surrounding microcrystalline quartz, such hematites seem likely to have crystallized nearly syngenetically with the majority of microcrystalline quartz. The hematite crystals sparsely dispersed in microcrystalline quartz are supposed to be biogenetic in origin mainly from its pure composition. The size of the single crystal is magnetically larger than those of superparamagnetic criterion and the single-domain size for hematite (BANERJEE, 1971).

Thus hematite crystals in red cherts are regarded as the ferromagnetic component responsible for their stable NRM as a whole.

2-3) *Heating experiments combined with thermomagnetic analysis, and the results obtained*

An appropriate weight of pulverized specimen (10-20 mg) was sealed in silica ampoule under a vacuum of rotary oil pump with or without the diffusion pump and without the cold trap of liquid nitrogen. The individual values of vacuum condition were ranged from 10^{-2} to 10^{-5} Torr with a Pirani ionization type vacuum gauge. It was expected through a cursory examination that such vacuum states would be fortuitously favourable to the present purpose of the experiments. However, for estimating the more accurate oxygen pressure realized under such conditions, the following calibration was undertaken.

2-3-a) *Calibration of the actual vacuum state*

As a pilot test, a pellet with appropriate weight of reagents, Fe_2O_3 , TiO_2 and sponge Fe-metal were prepared to synthesize two ferromagnetic minerals with respective composition of $0.65 \text{ Fe}_2\text{TiO}_4 \cdot 0.35 \text{ Fe}_3\text{O}_4$ and $0.87 \text{ FeTiO}_3 \cdot 0.13 \text{ Fe}_2\text{O}_3$ which were expected to coexist under the heating condition of $\log P_{\text{O}_2} = -9$ (atm) at $1,100^\circ\text{C}$ (KATSURA et al., 1976). A pellet of about 3 mg was sealed under a vacuum produced by oil pumping (3.0×10^{-3} Torr) and fired for 46 hours at $1,100^\circ\text{C}$. The black minerals obtained were determined their Curie points by thermomagnetic analyses as 195°C for the major phase, and -32°C and 450°C for the minor phases. X-ray crystallographic analysis of the same specimen showed the coexistence of a spinel member (β phase) which lattice parameter, $a = 8.40 \text{ \AA}$ for the minor component and a hexagonal member (α phase) with $a = 5.077 \text{ \AA}$ and $c = 13.851 \text{ \AA}$, giving $0.62 \text{ FeTiO}_3 \cdot 0.38 \text{ Fe}_2\text{O}_3$ for the majority. The two corresponding data do not neces-

sarily give consistent results expected from the starting material. It seems probable that the major hexagonal phase apparent in the X-ray chart represents the average of the two phases with 195° and -32°C Curie points.

The common processes of a run of heating experiments are as follows; a) thermomagnetic behavior under a strong magnetic field (J_s - T relation) is obtained always in the heating process, in order to avoid some discrepancy due to the cooling lag, b) a red chert specimen sealed in silica ampoule is offered directly to thermomagnetic measurement and at first heating up to 600°C , at which temperature the specimen is held for an appropriate time before quenching to room temperature, c) in a series of heating runs higher than 700°C , the ampoule is heated in a self-controlled electric furnace until the planned time, when the specimen is quenched by pouring into the cold water bath, d) subsequently a J_s - T curve is obtained in the heating process, e) after every step-up of the temperature the Curie point measurement is repeated.

After a successive heatings some reaction products appeared, white to pale gray in colour, coating the inner wall of silica ampoule. The chemical composition of the products was examined by the use of a 200 KV Analytical Transmission Electron Microscope. No appreciable element concentration over the 3 % precision limit was detected except Si, thus it was identified as tridymite, proving that it had no influence on the Curie point change concerned in this experiment (KITAMURA; personal communication, 1981).

The coexisting α and β phases in equilibrium can be plotted on the KATSURA et al. diagram (KATSURA et al., 1976); the diagram shows the relationship of two coexisting phases of the ulvospinel-magnetite series and the ilmenite-hematite series as functions of temperature and oxygen pressure ($-\log P_{\text{O}_2}$) (Fig. 4). This diagram was extended to the higher temperature range and improved on the previous BUDINGTON and LINDSLEY thermobarometer (1964).

If we assume the equilibrium coexistence of α and β phases in the above experiment, they can be plotted on the KATSURA et al. diagram, obtaining approximate values of 940°C and $\log P_{\text{O}_2} = -9$ (atm). This $\log P_{\text{O}_2}$ value is slightly higher than that for natural basalt, which is estimated to be between $-10 \sim -12$ (atm) assuming $1,100^\circ\text{C}$ (HAGGERTY, 1976). Alternatively, if we assume complete equilibrium at $1,100^\circ\text{C}$, the two phases synthesized cannot be fitted into the KATSURA diagram, but a rough estimation gives about -6 (atm) for the $\log P_{\text{O}_2}$ with some tolerance. As a result, we have not succeeded in establishing that the exchange reaction equilibrium between α and β phases does hold good under the present conditions of the heating experiments. However, it seems probable that results of the present heating experiments can be compared semi-quantitatively on KATSURA et al. diagram.

2-3-b) *Reproducibility test of the experiments*

The reproducibility of the experiments under a similar condition seems satis-

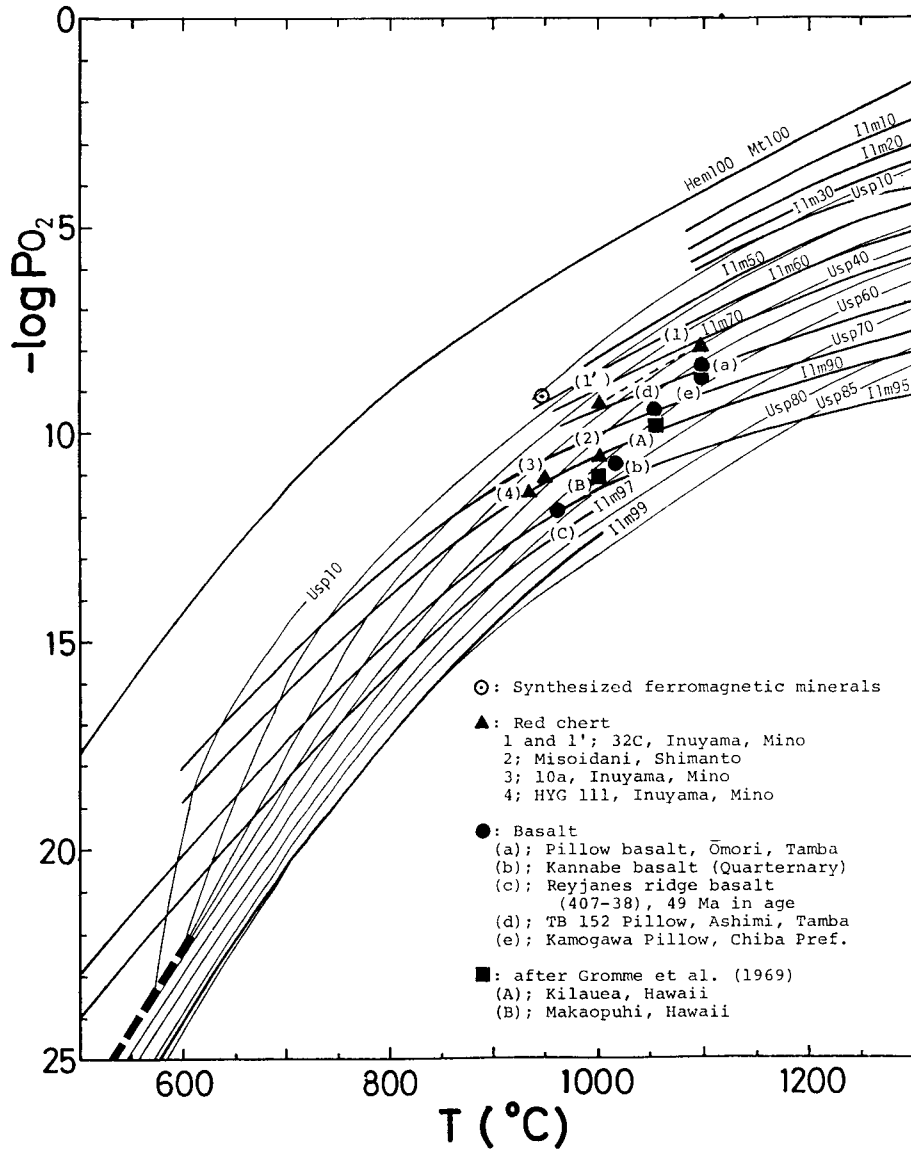


Fig. 4. Results of heating experiments of red cherts and basalts plotted on KATSURA et al. diagram (1976), for convenience sake.

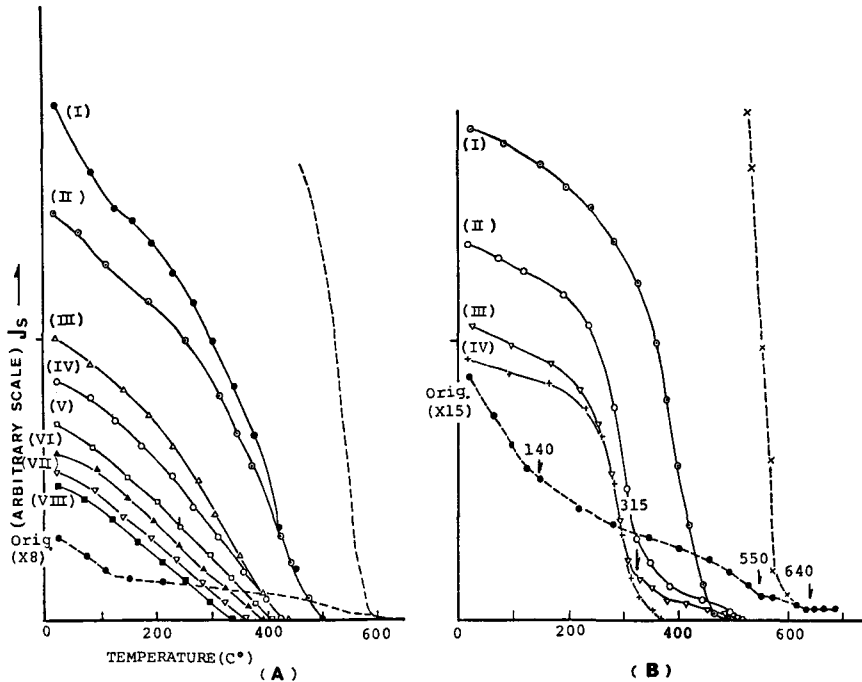


Fig. 5. Example of the reproducibility test of heating experiments on the same chert sample (sp. 32C); equilibrated phases in (A) and (B) show almost the same Curie point.
 (A) $H=4.5$ KOe, $P=1 \times 10^{-5}$ Torr, (I) at 700°C for 30 minutes, (II) at 750°C for 1 hour, (III) at 850°C for 4 hours, (IV) at 900°C for 7 hours, (V) at 950°C for 6 hours, (VI) at 950°C for 12 hours, (VII) at 1000°C for 6 hours, (VIII) at 1000°C for 30 hours.
 (B) $H=4.5$ KOe, $P=10^{-2}$ Torr, (I) at 800°C for 5 hours, (II) at 900°C for 15 hours, (III) at 1000°C for 12 hours, (IV) at 1100°C for 11 hours.

factory for the scope of this study though actual Po_2 of each silica ampoule was not strictly controlled. An example of such a duplicate test is shown in Fig. 5.

2-3-c) Time dependence

An example of the time dependent decrease of the Curie point by heat treatment at the same temperature is illustrated in Fig. 6 (TB 126 red chert). The strong field magnetization (J_s) decreases gradually from that of the initial Curie point of 550°C , corresponding to a decrease in its Curie point, although the original J_s before the first heating could not measure directly because of its less weakness compared with the sensitivity of the Curie balance. In the inset of Fig. 6 the relation of the decreasing Curie point to the logarithmic time of heating at 660°C is shown; it seems to show an approximate exponential relationship. It is suggested from Fig. 5 and 6 that the hematite (or titanhematite) contained in the specimen was reduced to Ti-poor magnetite, at least during the first heat treatment at 660°C for 15 min. or so.

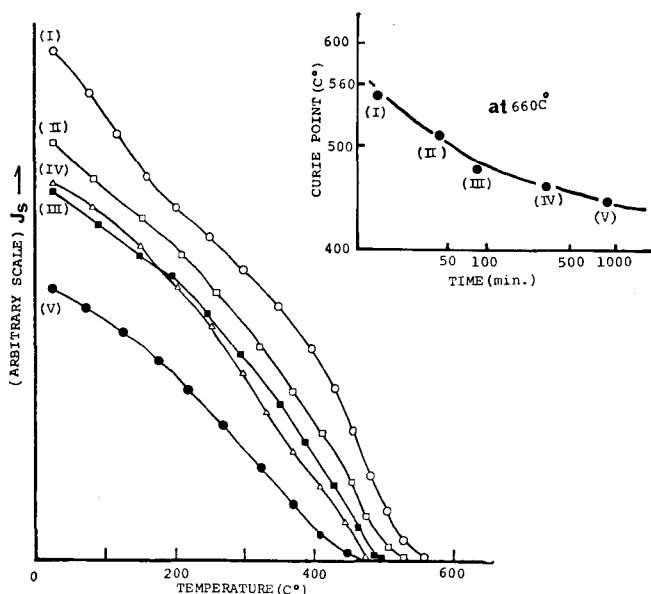


Fig. 6. Relationship between the heating duration at 660°C and corresponding decrease of the Curie point (TB 126); (I) 15 minutes, (II) 45 minutes, (III) 90 minutes, (IV) 300 minutes, (V) 900 minutes.

2-3-d) *Curie point decrease dependent on the vacuum gauge values*

SHIVE and DIEHL (1977) pointed out that the magnetite produced from hematite by the reductive agents of the rotary pump was caused by surface phenomenon and was therefore limited to about 5 % of all the hematite at the maximum. As already mentioned in the earlier the first step of heating leads to that reaction, however, the second step may cause reductive mixing of multiphase Fe-Ti minerals, such as the pseudobrookite series, and titanhematite and hemoilmenite phases. The dependence of the rate of decrease of the Curie point on indicated gauge values was tested experimentally without confirming a definitive dependence, although in a few cases a positive dependency was recognized.

For a better account of a systematic decrease in the Curie point the reaction of pseudobrookite and chlorite (KEENE and KASTNER, 1974) was tested in similar conditions. The results obtained are shown in Fig. 7 and 8. The chlorite specimen in Fig. 8 was chosen from chlorite schists in the Sambagawa metamorphic zone. A prominent increase in the J_s after about 600–700°C heat treatment seems to be due partly to a reduction of paramagnetic minerals into ferromagnetic ones, presumably to a Ti-poor titanomagnetite phase. The equilibrated Curie point at 1,000°C may be controlled mostly by the Ti-content in the original member of the pseudobrookite series and chlorite group, respectively. When a member of the pseudobrookite

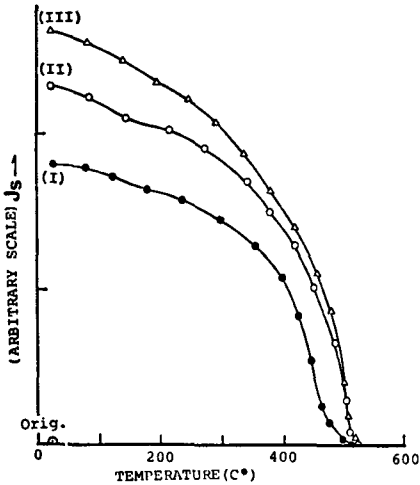


Fig. 7. Ti-poor titanomagnetite produced from a paramagnetic pseudobrookite (Orig.) clearly appears at 730°C for 5 hours heating (I), and then homogenization is advanced by much higher temperature treatments; (II) at 900°C for 8 hours, (III) at 1000°C for 19 hours. Sample locality is Vasko, Hungary (Krantz).

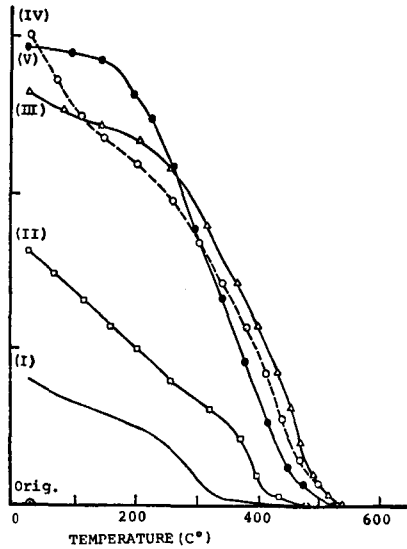


Fig. 8. Production and homogenization processes of a titanomagnetite phase from a chlorite specimen (Orig.) are shown during successive heat treatments; $H=3.5$ KOe, $P=6.3 \times 10^{-5}$ Torr, (I) at 710°C for 1 hour, (II) at 850°C for 1.6 hours, (III) at 900°C for 13 hours, (IV) at 1000°C for 4 hours, (V) at 1000°C for 14 hours. Sample from Sambagawa chlorite schist.

series and/or chlorite group occurs in red chert or pillow basalt, the reactions mentioned above would be expected to occur during the progress of the heating experiments.

Some of typical results of experimental runs are illustrated in Fig. 9. As shown in the figure, the equilibrated Curie points of red cherts at 1,000°C range from 210 to 340°C, with an average of 270°C, being correlative to the titanomagnetite, $x=0.48$ in average. On the average, this homogenized titanomagnetite is slightly Ti-poor compared with the average titanomagnetite composition of pillow basalts, $x=0.62$ (PETERSEN, 1976; JOHNSON and HALL, 1978).

3. Discussion

Although there have been controversial arguments concerning the origin of chert in general, some of cherts are considered to have been derived from the diagenetic alteration of volcanic materials (CALVERT, 1971; WOLF, 1971). According to STEINMANN (1927) cherts were deposited in deep sea basins, characterized by strong tectonic mobility which facilitated intrusion and extrusion of basic and ultra-

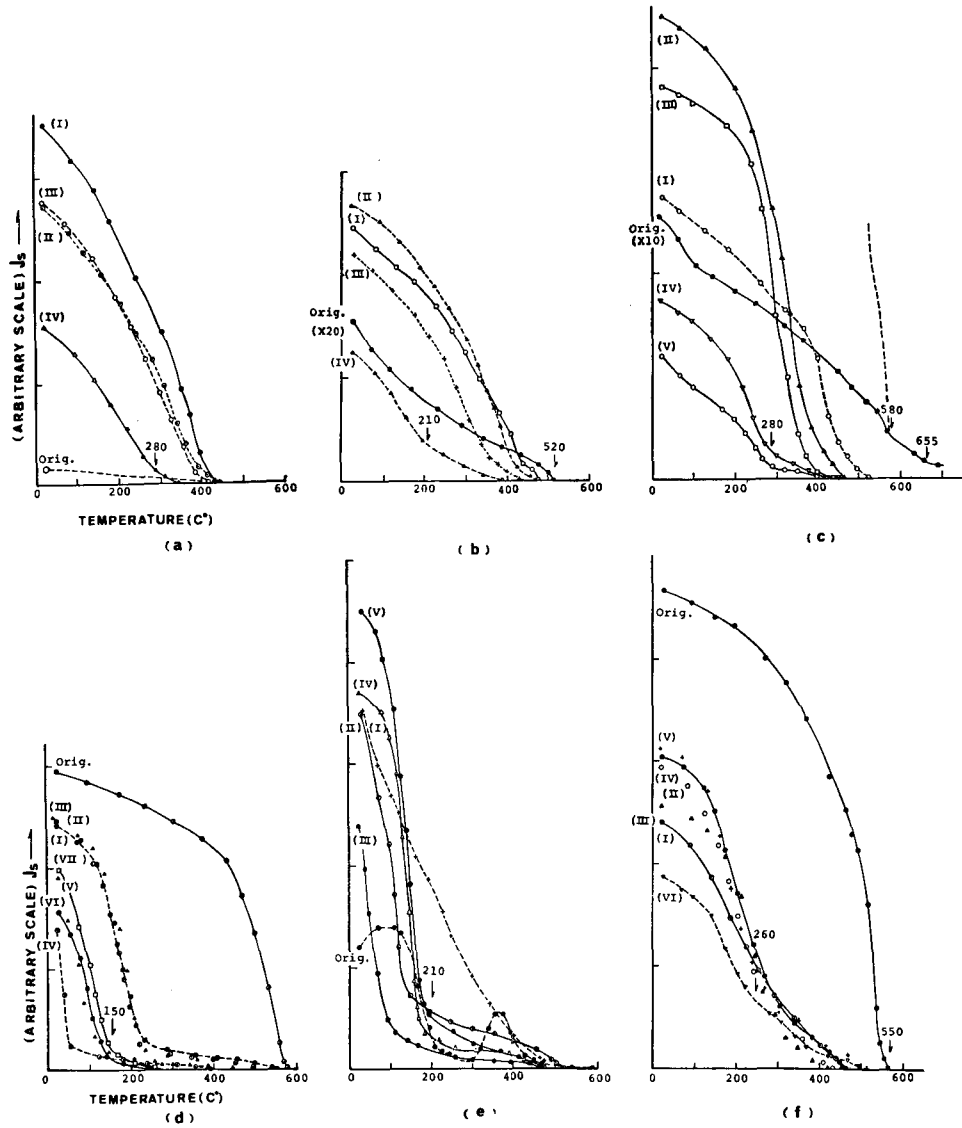


Fig. 9. Examples of thermomagnetic runs which show the recovering process of the original titanomagnetite phases contained in red cherts and basalts by a series of heat treatments.

- (a) Red chert (sp. 10a) from Inuyama area, $H=3.5\text{KOe}$, $P=3.5 \times 10^{-3}\text{Torr}$, (I) at 700°C for 2 hours, (II) at 800°C for 7 hours, (III) at 850°C for 9 hours, (IV) at 950°C for 9 hours.
- (b) Red chert from Misoidani, Shimanto terrain, $H=4.0\text{KOe}$, $P=5 \times 10^{-5}\text{Torr}$, original intensity is multiplied by 20, (I) at 700°C for 1.5 hours, (II) at 750°C for 8.5 hours, (III) at 850°C for 25 hours, (IV) at 1000°C for 6 hours.
- (c) Red chert (HYG 111) from Inuyama area, $H=3.5\text{KOe}$, $P=5 \times 10^{-3}\text{Torr}$, original intensity is multiplied by ten, (I) at 710°C for 20 minutes, (II) at 800°C for 1.5 hours, (III) at 800°C for 16 hours, (IV) at 900°C for 2 hours, (V) at 950°C for 12 hours.

basic magma. Based on a review of the worldwide distribution of radiolarian cherts, GRUNAU (1965) emphasized chert-ophiolite association; in the other words, in ophiolite sequences, intermediate igneous rocks, tuffs and tuffaceous breccia are usually found together with radiolarian cherts.

Mineralogical analyses of cherts are found sporadically in literature but accurate colour descriptions of cherts in relation to chemical analyses and mineral contents are practically non-existent. GRUNAU presented an interesting result showing ferric-ferrous contents in relation to colour of cherts in his Fig. 6. This diagram clearly shows that light red hues become gradually darker with increasing ferric iron (hematite) content, and that a comparatively high ferrous and low ferric iron content produces dark green colours. However, an astonishing fact is that cherts having almost the same ferric/ferrous iron content can be either red or green. This fact was also substantiated by SUYARI and CHIBA (1977) in some cherts distributed in Southwest Japan. Red chert samples from Inuyama and Tamba were analysed by the X-ray diffraction method. Data show that the cherts consist predominantly of quartz, and therefore can be ascribed to 'true chert' defined by CALVERT (1971). Exceptionally, a chert specimen (TB 2720) comprised diffraction presumed to be due to prehnite besides those of predominant quartz.

Most cherts, especially red cherts in Southwest Japan are closely related to greenstones including pillow basalts, pillow breccia and aquagene tuff, in stratigraphic sequences (e.g. SAKAI and KANMERA, 1981; ISHIGA and IMOTO, 1980; SHIMIZU, 1979). SUZUKI and HADA (1979) especially pointed out direct evidence supporting a close relationship between red cherts and greenstones both of which were contained in the tectonic melange of the Shimanto Belt, South Shikoku. They concluded that the basaltic rocks are petrochemically analogous to oceanic islands and seamounts. Based on a large number of chemical analyses, including trace transition metals, KAWABE et al. (1979) were led to the conclusion that the volcanic rocks in Tamba and Mino had chemical affinity with ocean floor basalt or ocean island basalt. On the contrary, IJIMA et al. (1978) suggested that the Triassic bedded cherts of Central Japan were deposited in a relatively shallow-water environment, such as marginal sea.

SUYARI and CHIBA (1977) who studied the chemical composition of Triassic and

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- (d) Alkaline basalt from Kannabe, Hyogo Prefecture, $H=3.5$ KOe, $P=4 \times 10^{-3}$ Torr, (I), (II) and (III) at 875°C for 2, 5 and 10 hours respectively, (IV) at 980°C for 8.5 hours, (V) at 940°C for 8 hours, (VI) at 980°C for 3 hours, (VII) at 1020°C for 5 hours.
 - (e) Ocean ridge basalt from Reykjanes, Iceland (sp. 407-38), $H=4$ KOe, $P=6 \times 10^{-5}$ Torr, (I) at 590°C for 10 minutes, (II) at 710°C for 6 hours, (III) at 850°C for 4 hours, (IV) at 850°C for 13 hours, (V) at 1000°C for 16 hours.
 - (f) Pillow basalt from Omori, Tamba terrain, $H=3$ KOe, $P=3.1 \times 10^{-3}$ Torr, (I) at 750°C for 8.5 hours, (II) at 850°C for 25 hours, (III) at 950°C for 9 hours, (IV) at 1000°C for 14 hours, (V) at 1050°C for 7 hours, (VI) at 1100°C for 9 hours.

Cretaceous bedded cherts in Shikoku, Southwest Japan suggested average chemical composition of spilites broadly accounts for the abundance ratios of Fe_2O_3 , FeO , TiO_2 , MnO , Al_2O_3 and P_2O_5 in the cherts, disregarding excess SiO_2 and easily soluble, variable MgO , CaO , Na_2O and K_2O . If we compute a supposed titanomagnetite phase, to be produced from Fe_2O_3 , FeO and TiO_2 , of which molar ratio is given from the average chemical compositions of the Japanese red cherts (SUYARI and CHIBA, 1977; SUGISAKI, 1981, personal communication), it is found that titanomagnetite is of $x=0.22$ and it gives the saturation magnetization of 0.33 emu/gr for the bulk red chert. It should be noted that the given J_s value is nearly comparable with those oxidized submarine basalts with relatively higher oxidation grades (DAY et al., 1979; JOHNSON and HALL, 1978; ADE-HALL et al., 1976a).

The results of heating experiments on cherts, (Fig. 5 and 9) have broadly substantiated the conclusions mentioned above, suggesting that the red pigments in red cherts were initially derived from basaltic aquagene ash. Neutron activation analyses of the rare-earth elements in red cherts showed no significant difference between those from the Tamba, Mino and Shimanto belts (MASUDA and SASAJIMA, 1982), basically supporting the previous view of a marginal sea origin suggested by SHIMIZU and MASUDA (1977). It is encouraging for the study of paleomagnetism of red cherts that TIPPIT et al. (1981) have shown that the sediment ages of red chert of the Samail ophiolite are similar to those of basalt flows intercalated the chert. From this evidence it is suggested that the stable remanent component of red cherts resides in titanhematite (SHIBUYA and SASAJIMA, 1981) and was acquired preferentially during the period of submarine volcanic activity, as the result of hydrothermal alteration (Van ANDELL and BALLARD, 1979). SHIBATA and MIZUTANI (1980) have compared Rb-Sr and K-Ar wholerock ages with radiolarian age for the same siliceous shale, accompanied by chert layers, giving an age of about 20 Ma younger for the Rb-Sr closed system than for the radiolarian age.

Since VINCENT et al. (1959) studied the heating changes of some natural titaniferous magnetites microscopically, magnetically and by X-ray, a few similar experiments have also been reported (PUCHER, 1969; SERGEYEVA, 1968). These studies that on heating titanomagnetite containing ilmenite lamellae up to 950°C, some interchange of ions between phases occurs; i.e. $\text{Fe}_3\text{O}_4 + \text{FeTiO}_3 - \text{Fe}_2\text{TiO}_4 + \text{Fe}_2\text{O}_3$, the ilmenite lamellae taking Fe_2O_3 into solid solution.

FRÖLICH et al. (1965) discussed how impurity cations may effect the Curie point of titanomagnetite; Cr^{3+} , Co^{2+} , Mg^{2+} and Al^{3+} have the effect of depressing the Curie point by an increasing amount, in this order. Furthermore, CREER and STEPHENSON (1972) exactly determined the effects of Al and Mg impurities on titanomagnetites. It should be noted that in titanomagnetites Ti has a greater mobility than Fe (PETERSEN, 1970). The reduction of the Curie point (Ti-composi-

tion change in β phase) is due partly to the oxygen fugacity change of β phases resulting from increased temperature (CARMICHAEL and NICHOLLS, 1967; GROMME et al., 1969; KATSURA et al., 1976; KONO and TANAKA, 1977).

The mineral assemblages of chert is considered to be rather simpler than in igneous rocks, so that result of the heating experiments in vacuum is expected to be clearer than that of basic igneous rocks. In interpreting the present heating experiments of red cherts, we may safely take the view that only oxide minerals (ferromagnetic and paramagnetic) are capable of playing effective roles in changing of the Curie point. Only a limited number of oxide minerals contribute to the reduction in the Curie point as the result of heat treatment. Minerals which are mainly responsible for the reduction in the Curie point are the exsolved products of initial Ti-rich titanomagnetite and ilmenite (CARMICHAEL and NICHOLLS, 1967; BUDDINGTON and LINDSLEY, 1964; HAGGERTY, 1976; JOHNSON and HALL, 1978), and their alteration products, due to submarine weathering or hydrothermal alteration (KENT et al., 1978; BUTLER et al., 1976). They are as follows: (1) a member of the paramagnetic pseudobrookite series, (2) hematite and/or a low-Ti titanhematite phase, (3) exsolution lamellae of ilmenite and spinel ($\text{Mg Al}_2\text{O}_4$) in ferromagnetic minerals, (4) unmixed rutile (TiO_2) and sphene (CaTiSiO_5) which were possibly contained in original ferromagnetic minerals from igneous rocks, (5) chlorite contained in cherts, if any, forms low-Ti magnetite in reductive conditions (Fig. 8).

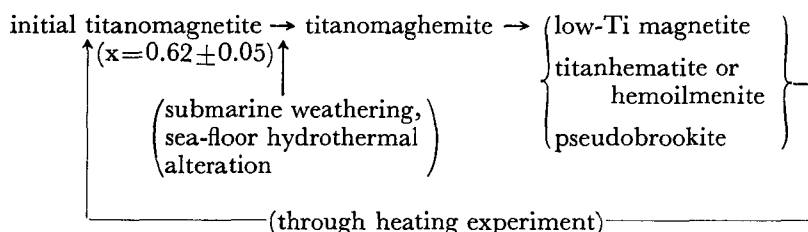
During the course of heating experiments we have recognized some irregular behaviors in the depression of the Curie point with progressively higher temperatures or increased heating times (Fig. 9). They may be due to some kind of thermal threshold constrained specifically by the different minerals mentioned above. It is almost substantiated that low-temperature alteration of titanomagnetite involves the diffusion of some of the Fe^{2+} cations away from the original lattice site into the surrounding silicate during oxidation to Fe^{3+} (JOHNSON and MELSON, 1977; SASAJIMA, 1961). This could result in an increase in Ti/Fe ratio of the remained titanomagnetite phases (MARSHALL and COX, 1972; GROMME and MANKINEN, 1976; JOHNSON and HALL, 1978). If this is true, mixing and homogenization of Fe-Ti oxides due to heat treatment may expectedly advance Ti-enrichment.

It is incorrect to plot such β phase on to the KATSURA et al. (1976) diagram based on its Curie point on the assumption that the β phase is in equilibrium with a coexisting α phase. However, for conventional purposes it may be instructive to plot the results obtained on the diagram, in order to compare their situations semi-quantitatively (Fig. 4).

Needless to say, the complicated reactions which actually occur between magnetic oxide minerals during high-temperature heating cannot be entirely understood merely in terms of the Curie measurements concerned. However, results of heating

experiments on red cherts showing a successive decrease in Curie point are accounted for shortly by the remixing of breakdown components of secondary titanomaghemite (O'REILLY and READMAN, 1971; KEEFER and SHIVE, 1981) which was primarily derived from titanomagnetite in volcanic, fine-grained clastics or tuffs, and underwent low temperature oxidation or hydrothermal alteration in a submarine environment.

In this simplified inference we assume an ideal closed system with respect to Fe-Ti oxides after their breakdown. The following framework is a schematic expression of the transformation of Fe-Ti oxides in nature and synthesis:



The Curie points of tholeiitic basalts are considered to be within the range, $x=0.62 \pm 0.05$, that is, between the Curie points of 80°C and 180°C (PETERSEN, 1976; JOHNSON and HALL, 1978). As shown in Figs. 5 and 9 the Curie points of red cherts equilibrated at 1,100°C approximate to those of pillow basalts, taking into consideration the fact that cherts are generally composed of some additional, biogenic hematite, which is responsible for raising the Curie point of the cherts compared with basalts. Of course, a possible correlation of the Curie points of red chert with those of intermediate rocks cannot be ruled out.

4. Conclusive Remarks

From the preceding discussion of the present magneto-mineralogic studies and the geological information on red cherts, the following conclusions can be drawn: 1) a strange reductive condition of thermomagnetic measurement under the evacuation with a rotary oil-pump tied up with a diffusion pump, is approximately estimated to be $\approx 10^{-9}$ atm. in actual oxygen pressure, irrespective of the value indicated by a Pirani gauge as ranging between 10^{-3} — 10^{-5} Torr, 2) ferromagnetic minerals of bedded red cherts in Southwest Japan are composed of titanhematite and some biogenic hematites in general and sometimes titanomagnetite, 3) the thermomagnetic change of red cherts due to progressive heat treatment in vacuo can be generalized as follows; a) at the first heating, up to about 600°C, weakly paramagnetic original chert transforms to a strong ferromagnetic substance, due mainly to a reduction of a small amount of titanhematite (hematite) into Ti-poor titanomagnetite (magnetite), b) almost

syngenetic or subsequent, reductive change from paramagnetic minerals (pseudo-brookite and/or chlorite) into Ti-poor titanomagnetites occurs at the second or third successively higher temperature treatment, c) mixing or homogenization of aforesaid ferromagnetic minerals with rutile (TiO_2), spinel (MgAl_2O_4) and possibly sphene (CaTiSiO_5) proceeds at much higher temperatures resulting in a corresponding decrease in their Curie points, 4) the Fe-Ti oxides contained in red cherts are related most probably to the submarine basalts although a possible relation to intermediate volcanic rocks cannot be completely ruled out, 5) the geologic association between red chert and greenstone in Southwest Japan suggests a mutual affinity in initial Fe-Ti minerals, then to put it shortly, 6) if we accept a view that red cherts underwent submarine weathering or hydrothermal alteration at the same time as the greenstones associated with them, a closed system with respect to Fe-Ti minerals and consequently blocking of their remanent magnetizations as well, was maintained after an uncertain diagenetic event which was presumably related to the major silica crystallization (lithification).

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