

Chloritized granitic rock in the Nagato Tectonic Zone, southwest Japan: an example of a static metasomatic rock in the serpentinite mélangé zone

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Abstract Chloritized granitic rock occurs in the serpentinite mélangé of the Nagato Tectonic Zone, southwest Japan. The rock occurs as a small block of ca. 1m in diameter in the sheared serpentinite matrix and is difficult to distinguish from massive serpentinite. It consists mostly of chlorite with basal spacing of 14Å and FeO content <0.3 wt. %. It is homogeneous under a microscope with plane-polarized light. Twinning with Carlsbad and polysynthetic textures are remarkable under crossed polars, suggesting that pseudomorphs were parentally K-feldspar and plagioclase, respectively. Rare relict minerals are apatite and biotite. Grain sizes of pseudomorphs after feldspars and quartz are similar to those in normal granitic rock. The relict minerals and grain sizes suggest that they were replaced almost totally by FeO-free chlorite from a granitic rock.

Although quartz and feldspar were well preserved in a large granitic and gneissose blocks from the serpentinite mélangé, replacement by FeO-free chlorite is observed along the twin plane of plagioclase in the rocks. Preservation of twinning texture in the chloritized granite implies that the metasomatism took place under static conditions without deformation.

Key words: Nagato Tectonic Zone, serpentinite mélangé, Chloritization, Granite, Pseudomorph

Introduction

The chemical composition of a rock often changes radically during low-grade metamorphism or hydrothermal alteration. Rocks having undergone such changes are known as metasomatic rocks. A metasomatic rock usually has no source rock corresponding in chemistry. However, we can sometimes identify their original rocks by macroscopic to microscopic textures. For example, a silicified wood and pyritized fossil can change their chemical compositions completely while still retaining wood and fossil structures (e.g. Akahane *et al.*, 1999; Briggs *et al.*, 1996). In such cases, the original rock will not be identified by chemical analyses but by macroscopic and microscopic observations. In many cases, the metasomatic processes take place under static conditions, namely, deformation-free. Another

metasomatic process occurs when a single mineral is replaced as in carbonatization (Nakamura and Kato, 2004) and sericitization of volcanic rock and serpentinitization of peridotite. Chloritizations of volcanic rocks are also reported from altered igneous rocks (Greenough, 1985). In the serpentinitization of peridotite, chemical composition is not so severely altered, but it also belongs to one of the metasomatic rocks.

In the metasomatic rocks, the outer shapes of phenocrysts or porphyroblasts are occasionally observed as pseudomorphs. As far as we know, however, the preservation of a clear twin texture has not been reported in the metasomatic rocks. In this paper, we present chloritization of exceptionally preserved twinning texture including outer shapes, clearly showing that the rock was derived from a granitic rock.

Nagato Tectonic Zone

The Nagato Tectonic Zone crops out intermittently as a narrow belt with an extension of about 35 km with a maximum width of 2 km, trending from NNE to SSW in western end of the Chugoku district, southwest Japan (Fig. 1). The zone is in fault contact with the post-Triassic formations and the Mine Formation of Triassic age and upper Paleozoic formations. It is unconformably overlain partly by the Toyoura Formation of Jurassic age and the Kanmon Group of Cretaceous age. From south to north, the main localities of the zone are the Toyogatake district, the Nishiichi district, the Dai district and the Misumi district (Murakami and Nishimura, 1979).

The main rock types of the Nagato Tectonic Zone are the Sangun metamorphic rocks, upper Paleozoic formations (unidentified age to Permian), serpentinite and amphibolite (Murakami and Nishimura, 1979). The serpentinite is highly sheared and includes various types of blocks such as orthogneiss, gabbro, granodiorite, trondhjemite and diabase. The blocks are mostly more than several meters in diameter and preserve the original minerals and texture. Chlorite rocks develop at the boundaries between serpentinite and blocks. Such a chlorite rock from the serpentinite

massif has been described as a blackwall (e.g. Frost, 1975; Leach and Rodgers, 1978). Since minerals in large blocks in the serpentinite mélange are well preserved, their ages were obtained by various methods. Kawano *et al.* (1966) reported the K-Ar age, 424 Ma, of muscovite in a gneiss enclosed in the sheared serpentinite at the Dai district. Hornblende age in amphibolite in the same area was obtained as 373 Ma by K-Ar method (Shibata and Murakami, 1975). Muscovite in a granitic rock from the Nishiichi district was 371 Ma (Murakami *et al.*, 1977). Shibata and Nishimura (1989) reported a Rb-Sr muscovite-whole rock age of 303 Ma for the Sangun pelitic schist in the Toyogatake district.

Petrography of the Chloritized Rock

The chlorite rock was found as a block in a small serpentinite quarry of about 30 meters across in the Dai district (Fig. 1). The block is about 1 meter in diameter and has been left on the sheared serpentinite. The rock is faintly dark green and more transparent than the surrounding serpentinite. The block is composed almost wholly of colorless chlorite and is traversed by veins consisting of serpentine and/or chlorite.

Under a microscope with plane-polarized light, the rock is homogeneous locally with dusty

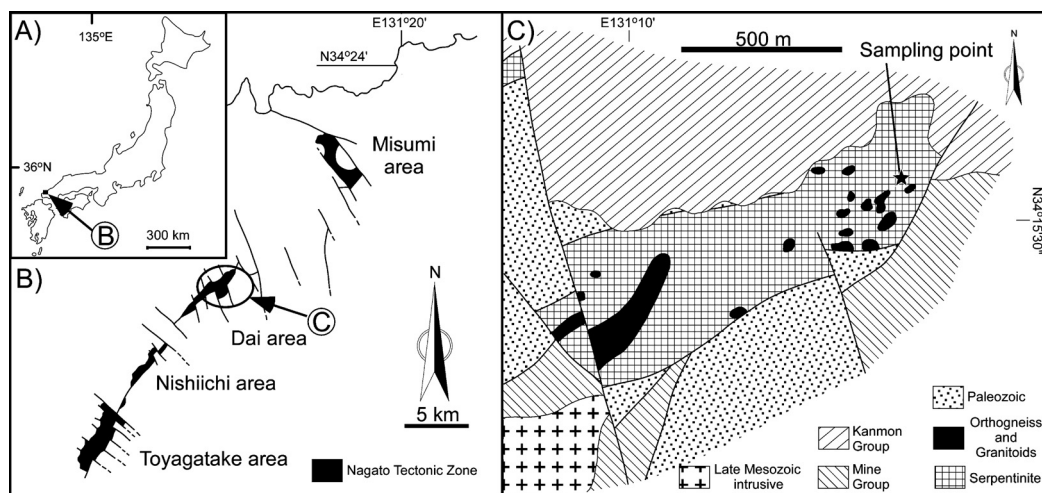


Fig. 1. Geological sketch map of the Nagato Tectonic Zone. (after Murakami and Nishimura, 1979) a and b: outcrops of the Nagato Tectonic Zone, c: sample locality of the chlorite rock in the Dai District.

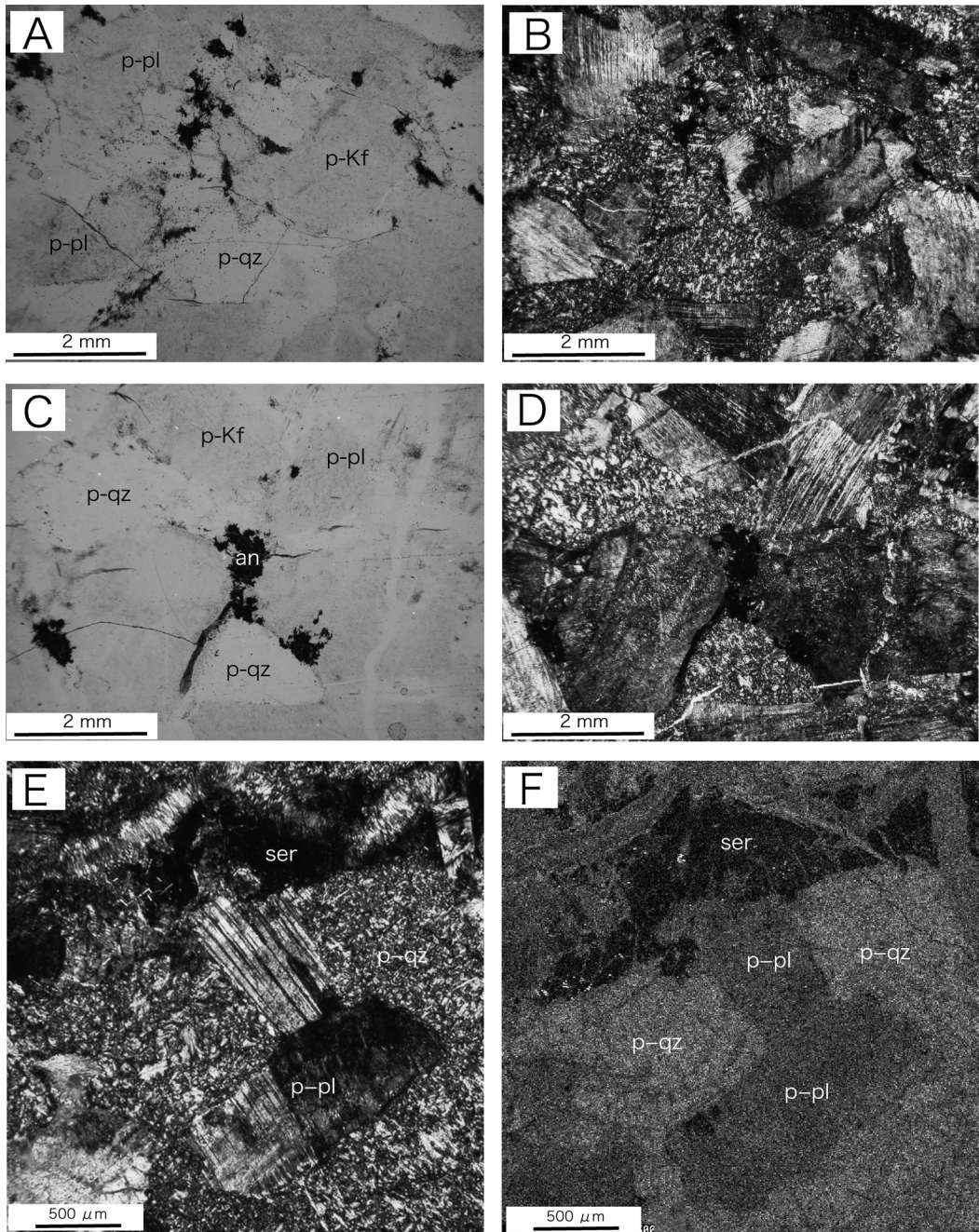


Fig. 2. Microphotographs of chloritized rock in thin section. A and B; chlorite showing twinning textures under plane-polarized light and crossed polar, respectively. C and D: *ibid.* E; chlorite rock with twinning texture under crossed polar. F: concentration map of Ca in the same area as photo E. Abbreviations, p-qz: pseudomorph after quartz, p-pl: pseudomorph after plagioclase with polysynthetic twin, p-Kf: pseudomorph after K-feldspar with Carsbad twin, an: ankerite or dolomite, ser: serpentine.

parts (Fig. 2 A and C). Under the microscope with crossed polars, the granitic texture appears (Fig. 2 B, D and E). Textures of polysynthetic and Carlsbad twins are remarkably well preserved in the rock. In normal granitic rocks, polysynthetic twinning is common and representative in plagioclase, whereas Carlsbad twinning is prevalent in monoclinic K-feldspar (orthoclase). Hence, it is reasonable to assume simply at first that the pseudomorph with polysynthetic twinning corresponds to that of plagioclase, whereas the pseudomorph with Carlsbad twinning to that of K-feldspar. Grain sizes of the pseudomorphs are 0.5–2 mm, similar to those in granitic rocks. If the parental rock for the chlorite rock was a granitic rock, cryptocrystalline aggregate

without any twinning texture (Fig. 2) should correspond to quartz. As rare minerals, apatite, biotite, pyrophanite, ankerite and zircon were also found. Biotite with size around 0.1 mm is found in the chlorite matrix (Fig. 3A). It is surrounded by chlorite with a greenish color. Greenish chlorite without a biotite core sometimes occurs in the colorless chlorite matrix. The grain size of greenish chlorite is around 1 mm in length. Apatite is found as anhedral grains of 0.2 mm diameter. Pyrophanite, MnTiO_3 , occurs as an aggregate and apparently forms a pseudomorph probably of ilmenite (Fig. 3C). Carbonate minerals, dolomite and ankerite, are fine-grained and form an aggregate. They appear like opaque minerals under plane-polarized light. Zircons usually

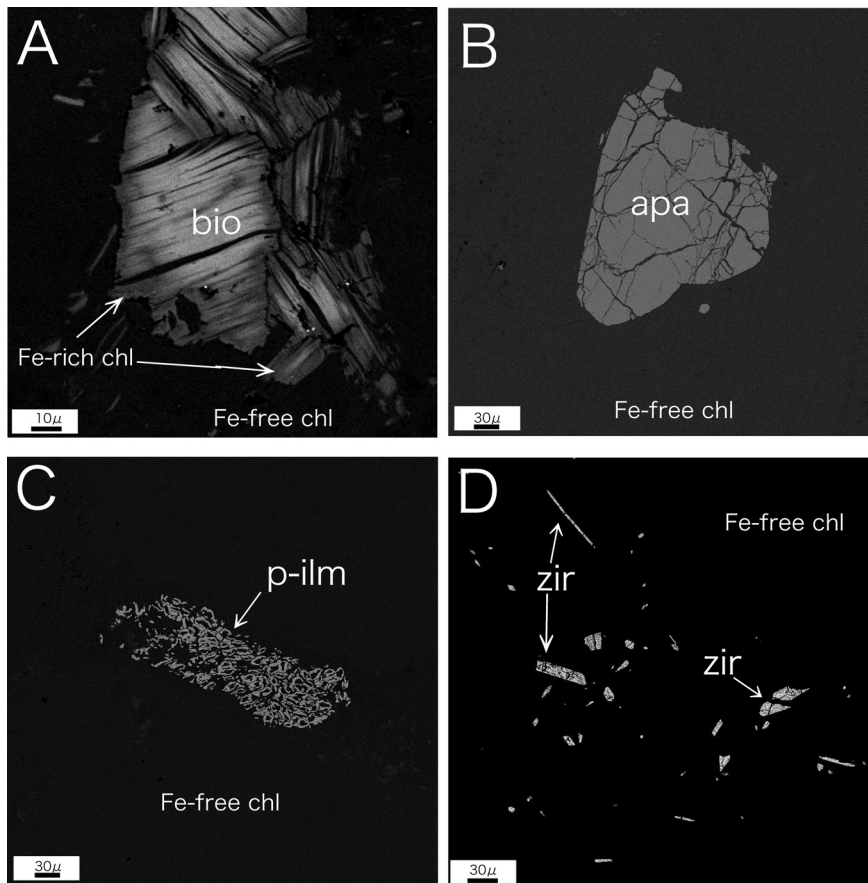


Fig. 3. Back-scattered electron image of minerals in Fe-free chlorite matrix. A: relict biotite (bio) surrounded by Fe-rich greenish chlorite. B: relict apatite. C: aggregate of pyrophanite showing pseudomorph after ilmenite. D; various types of zircon grains concentrated in a part.

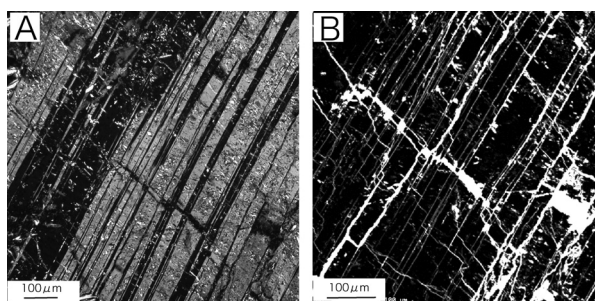


Fig. 4. Partly chloritized plagioclase in a large granitic block occurring in a sheared serpentinite. A: microphotograph of plagioclase with polysynthetic twin (crossed polars). B: concentration of Mg showing crystallization of chlorite (white) along twin planes and fractures.

occur as fine-grained crystallites up to ca. $100\ \mu\text{m}$ in length (Fig. 3D). They vary in shape; acicular, euhedral and fragmented, and are concentrated in a part (Fig. 4). Zoning and heterogeneous patterns are not observed in the BSE image of zircon. Monazite rarely occurs forming an aggregate.

The microscopical features and minerals clearly show that the protolith of the chlorite rock was evidently a granitic rock and was transformed into a monomineralic rock by a metasomatic process. The chlorite rock seems to have been protected from any deformation after chlorite crystallization, suggesting that the original granitic rock was metasomatized statically. As shown in the map in Fig. 1, there are many tectonic blocks larger than several meters across. Chlorite formation occurs at the boundary between the block and serpentinite, but the original minerals are more or less preserved in these large blocks. At a marginal part of a granitic block, replacement of plagioclase by chlorite was observed (Fig. 4). The replacement occurs along the twin plane and fractures. It is probable that preservation of twin textures in the chlorite rock was due to the replacement by chlorite progressing in each twin plane.

Chemical Compositions of Minerals

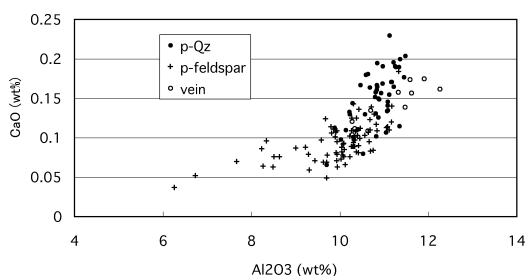
The chemical compositions of minerals were analyzed by electron microprobe analyzer, JEOL 8800, located in the National Museum of Nature

and Science. The analytical conditions were 15 kV and a current of 20 nA with a beam diameter of about $2\ \mu\text{m}$. The following synthetic and natural materials were used as standards: wollastonite for Si and Ca, anatase for Ti, corundum for Al, Mg_2SiO_4 for Mg, Fe_2SiO_4 for Fe, rhodonite for Mn, albite for Na and adularia for K. Chemical compositions of chlorite and other representative minerals are listed in Table 1.

Chlorite is confirmed to have a basal spacing of $14\ \text{\AA}$ by X-ray diffractometry. It is almost Fe-free with less than 0.3 wt% as FeO content. The Al_2O_3 content is mostly around 10 wt%, very low as a chlorite composition reported (Deer et al., 1962). Although the CaO content in normal chlorite should be usually negligible, it is recognizable at around 0.15 wt% in a quartz pseudomorph, whereas around 0.1 wt% in plagioclase and K-feldspar pseudomorphs are present (Table 1). Mapping of the rock by Ca shows that the plagioclase pseudomorph is clearly poorer in CaO content than that of the quartz pseudomorph (Fig. 2 F). Al_2O_3 content is slightly higher in the quartz pseudomorph than that in feldspar (Fig. 4). Chlorite around biotite differs in chemical composition from the Fe-free chlorite mentioned above. It is usually Fe-rich and varies in FeO content up to 19 wt%. The Al_2O_3 content is also up to 19 wt%. Biotite is a less resistant mineral against alteration of granite (e.g. Wilamowski, 2002). The chlorite around biotite is negligible in CaO content ($<0.03\ \text{wt}\%$), similar in composition to those around altered biotite in a granitic

Table 1. Chemical composition of various chlorites and other representative minerals. P-mineral: pseudomorph after the mineral.

Mineral Texture (Pseudomorph)	chlorite pseudomorph (quartz)		chlorite pseudomorph (plagioclase)		chlorite pseudomorph (K-feldspar)		chlorite vein -		biotite relict -		chlorite pseudomorph (biotite)		pyrophanite pseudomorph (ilmenite)	
	wt%	1 σ	wt%	1 σ	wt%	1 σ	wt%	1 σ	wt%	1 σ	wt%	1 σ	wt%	1 σ
SiO ₂	37.65	0.64	38.27	1.02	38.09	1.17	37.21	0.88	39.53	0.42	33.47	2.77		
Al ₂ O ₃	10.80	0.43	9.86	1.46	9.86	1.10	11.12	0.71	12.53	0.25	11.96	4.30		
TiO ₂									1.51	0.20	0.41	0.24	54.53	0.66
FeO	0.11	0.03	0.25	0.11	0.20	0.04	0.15	0.04	14.72	0.86	10.59	4.66	<0.10	
MnO	0.08	0.02	0.09	0.02	0.07	0.02	0.10	0.03	0.18	0.08	0.25	0.07	45.60	0.47
MgO	38.86	0.32	39.28	0.68	39.31	0.63	38.93	0.50	17.36	0.79	31.32	5.48		
CaO	0.15	0.04	0.10	0.02	0.09	0.03	0.14	0.03						
K ₂ O									9.90	0.35	0.03	0.02	9.90	0.35
Total	87.66	0.67	87.88	0.76	87.68	0.84	87.68	0.81	95.73	0.83	88.03	0.76	100.13	0.71

Fig. 5. Diagram showing compositional variation of CaO and Al₂O₃ contents of chlorites in pseudomorphs after quartz and feldspar and in vein.

rock. Pyrophanite is almost pure with FeO content less than 0.1%. This mineral has not been found as an igneous stage mineral in granitic rock. The outer shape of the aggregate suggests that it was replaced from ilmenite.

Discussion

Replacement of a rock by a single species of mineral is not uncommon, well-known examples are: silicification, pyritization, carbonatization, sericitization, serpentinization and chloritization. In most of the cases, metasomatic replacement has been explained as interaction between rock and seawater and/or hot water, but the mechanism remained incompletely understood. In the chloritized rock studied here, the petrographical texture of pseudomorphs with twinning and pres-

ence of relict minerals indicate that the rock in the serpentinite mélangé was originally a granitic rock. Chloritization of feldspar was described from altered sandstones through SEM observation. Pervasive replacement of detrital feldspar by chlorite was confirmed in variously replaced feldspar (Marad and Aldaham, 1987). The authors concluded that the replacement is due to dissolution of feldspar.

The microscopic observation of chloritization of feldspar reported here is unusual in that almost complete preservation of the twinning texture of igneous feldspar in the chloritized rock occurs. Most of the original minerals were replaced by Fe-free and Mg-rich chlorite. Green Fe-rich chlorite, which was present prior to the Mg-rich chloritization, has not been replaced. Furthermore, biotite, partly replaced by greenish chlorite, also survived at the time of Mg-rich chloritization. Apatite will be preserved as a mineral of the igneous stage. There is a transfer of elements from the original rock to the outer side: removal of Na, Si, K and Fe to the outside, whereas addition of Mg from the outer side. As the rock is enclosed in the serpentinite, there is abundant Mg to supply to the original granitic rocks as discussed in a chlorite rock, blackwall, occurring at the boundary between serpentinite and enclosed block (e.g. Frost, 1975; Leach and Rodgers, 1978). In spite of the difficulty to find where the Na and K elements were moved, it is

reasonable that transfers of the elements were induced by fluids migrating through the serpentinite. Although it is also hard to explain the mechanism, it is clear that the replacement occurred under static conditions without deformation. Preservations of twinning and partly replaced plagioclase by chlorite (Fig. 2 and 4) show that the replacement started from the twin plane in spite of the differences of crystal structure. Chlorite and serpentine veins developed in the chloritized blocks. Although timing of vein is clearly later than the chloritization of granitic rock, it is hard to discuss the timing of serpenitization and/or shearing of the serpentinite blocks.

The most unusual observation is the presence of relict biotite. Biotite is the first mineral replaced by chlorite in an altered granite. As the biotite is surrounded by normal Fe-rich greenish chlorite, preservation of biotite may imply that the biotite was protected by the Fe-rich chlorite during the crystallization of Fe-free chlorite.

Dubińska *et al.* (2004) reported zircon crystals in a chlorite rock occurring at the boundary between serpentinite and rodingite. They concluded that the zircons were formed by a metasomatic process at around 300°C during serpentinitization. In the chlorite rock studied here, fine-grained zircons with acicular, euhedral or fragmented textures are concentrated in a part (Fig. 3D). It suggests that an original zircon grain was fragmented and dissolved. The presence of some euhedral zircon may show that they were newly formed at the time of chloritization. Elementary Zr is generally considered to be an immobile element. Dissolved Zr may recrystallize in situ as zircon. Ilmenite and monazite are commonly observed in granitic rocks. In the chlorite rock, ilmenite (FeTiO_3) was replaced by pyrophanite (MnTiO_3), whereas monazite was recrystallized into a newly formed aggregate. A newly formed Ti-phase, pyrophanite, is in agreement with the observation that the mobility of Ti is very low during serpenitization (e.g. Schandl *et al.*, 1989). REEs may be also immobile elements. So far it is hard to discuss the age of chloritization; whether it occurred at the serpenitization stage or before

shearing stage. Age analyses of fine-grained zircon and monazite may reveal the timing of the chloritization.

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