

Geikielite, baddeleyite and zirconolite in dolomitic marble from the Neichi mine, Miyako City, Iwate Prefecture, Japan

By

Akira KATO and Satoshi MATSUBARA

Department of Geology, National Science Museum, Tokyo 169, Japan

Abstract Microprobe study on geikielite in dolomitic marble from the Neichi mine, Iwate Prefecture, described by Watanabe *et al.* (1963) informed it to be zoned with low MgO rim. The analyses of core and rim are: MgO 20.10, 15.23; FeO 12.69, 15.98; MnO 6.04, 8.66; CaO 0.40, 0.29; TiO₂ 61.44, 59.31; totals 100.67, 99.47%, respectively. Their empirical formulae (basis: O = 3) are: (Mg_{0.65}Fe_{0.23}Mn_{0.11}Ca_{0.01}) Σ _{1.00}Ti_{1.00}O₃ and (Mg_{0.51}Fe_{0.30}Mn_{0.17}Ca_{0.01}) Σ _{0.99}Ti_{1.01}O₃, respectively. Manganese and iron are remarkably high relative to the associated spinel and forsterite. Also, baddeleyite, zirconolite and zircon are found as its close associates, the second being the first find in Japan. All of them are so close to their ideal formulae as represented by zirconolite. The chemical analysis gave CaO 16.41, TiO₂ 45.87, FeO* 0.76, ZrO₂ 36.56, total 99.60%. The empirical formula (basis: O = 7, FeO* as Fe₂O₃) is Ca_{1.00}(Ti_{1.07}Fe_{0.04}) Σ _{2.01}Zr_{1.02}O₇, thus, the material is extremely poor in the non-essential components, which are always contained in zirconolites of igneous origin.

Introduction

At Kamineichi, Miyako City, Iwate Prefecture, dolomite was mined till 1965 under the name Neichi mine, where some borates like kotoite, suanite, szaibelyite, ludwigite and warwickite are described by Watanabe *et al.* (1963), who found geikielite, too. However, it was determined after the microscopic and X-ray powder studies only at that time. The present work purported to determine the chemical composition. During the analytical survey baddeleyite, zirconolite and zircon were found, the second one being the first occurrence in Japan.

The chemical analyses of geikielite informed its high contents of MnO, which are zonally concentrated outward. The chemical compositions of these zirconium minerals and the associated spinel and forsterite were also determined. The last two ferromagnesian minerals are rather low in MnO, which is preferentially incorporated into geikielite. This nature is also found in magnesian ilmenites found nearby two dolomite quarries, where no zirconium minerals have been found. It is worthy of note that a similar manganoan geikielite is found in from Pakistan, where no zirconium mineral is found (Cressey, 1986).

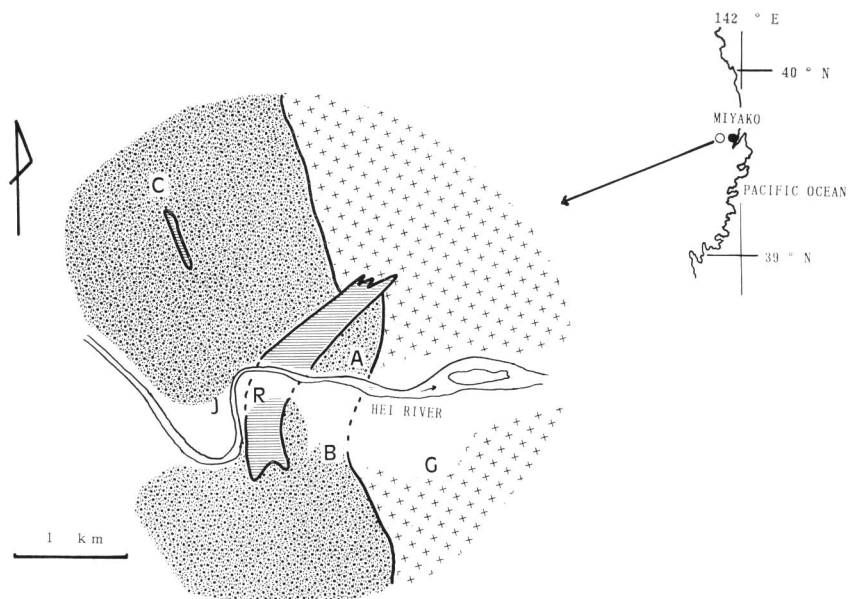


Fig. 1. Index map of the localities of quarried dolomite and limestone bodies. A: Kamineichi (Neichi mine). B: Nejou (No. 2 Kadogami mine). C: Kebaraichi (No. 1 Kadogami mine). J: Jurassic accretional complex including the dolomite and limestone bodies. G: Miyako granodiorite. R: rhyolite and dacite dikes.

Occurrence

At about 6 km west of Miyako station of JR Higashi Nihon Co. Ltd., a plutonic body called Miyako granodiorite intrudes Jurassic accretional complex involving a few dolomite and limestone bodies (Fig. 1). Both of plutonic and complex units were later intersected by a dacite dike, which involves abundant xenoliths of granodiorite, metamorphosed sedimentary rocks as well as recrystallized carbonate rocks.

The material containing geikielite collected by the late Dr. T. Watanabe, is a piece of white recrystallized carbonate rock with granular aggregates of greenish grey forsterite, which is to some extents replaced by serpentine. Along the boundary of forsterite aggregate and carbonate very minute black tablets of geikielite are sprinkled to form spotty aggregates accompanied by light purple octahedra of spinel. The size of geikielite and spinel is the order of 0. n mm.

Under the microscope, opaque hexagonal tablets of geikielite contact with needles of zirconolite at one end of it. As stated later, zirconolite is compositionally very close to the theoretical formula, $\text{CaTi}_2\text{ZrO}_7$, and the colour in thin section is exceptionally very light yellow brown, which is far lighter than the deep orange-brown colour of zirconolite containing various kinds of vicarious components (Fowler and Williams, 1986). According to the proposal of Bayliss *et al.* (1989), the usage of name zirconolite

must accompany any suffix to express the symmetry. However, the present zirconolite is determined by the chemical analysis only impeding the usage of appropriate suffix. Therefore, the name zirconolite without any suffix is used hereafter to indicate crystalline $\text{CaTi}_2\text{ZrO}_7$ with unknown symmetry. Baddeleyite is exclusively found as idiomorphic inclusions within geikielite tablets. Zircon is dimensionally too small to be microscopically observed. Spinel is more densely distributed in the parts rich in geikielite tablets. Forsterite occurs as subround grains of a millimeter order and is minutely veined by serpentine. The feature of serpentinization of forsterite is similar to that in ultrabasic rocks in itself, but magnetite is lacking in the present case.

Chemical Compositions of Geikielite, Zirconolite, Forsterite and Spinel

The chemical analyses of these minerals were made after the employment of Links Systems energy-dispersive X-ray spectrometer as given in Table 1.

Geikielite is chemically zoned due to the outward decreasing of MgO and increasing (FeO+MnO) contents as seen in the back-scattered electron image (Fig. 2), and at least two zones are visible with a rather sharp boundary, although less obvious compositional variations are extant within both zones. The highest MnO content obtained exceeds that of geikielite in marble from Pakistan (Cressey, 1986).

Zirconolite is characterized by an extreme proximity to theoretical $\text{CaTi}_2\text{ZrO}_7$ without compositional inhomogeneity (Fig. 3), though one of analyses gives very

Table 1. Chemical analyses of geikielite (Nos. 1 (core) and 2 (rim)), zirconolite (Nos. 3 and 4), spinel (No. 5) and forsterite (No. 6) from Kamineichi, Miyako City, Iwate Prefecture.

Weight percentages:

	1.	2.	3.	4.	5.	6.
TiO ₂	61.44	59.31	45.72	45.87	0.29	—
ZrO ₂	—	—	36.70	36.56	—	—
SiO ₂	—	—	—	—	—	41.68
Al ₂ O ₃	—	—	—	—	69.83	—
MgO	20.10	15.23	0.39	—	26.22	55.19
FeO*	12.69	15.98	1.50	0.76	2.78	1.87
MnO	6.04	8.66	—	—	0.44	0.63
CaO	0.40	0.29	15.83	16.41	—	0.33
total	100.67	99.47	100.14	99.60	99.56	99.70%

Empirical formulae: (basis: O = 3 (geikielite), O = 7 (zirconolite), and O = 4 (spinel, forsterite)) (FeO*: total iron. Calculated as FeO in geikielite and forsterite, and as Fe₂O₃ in zirconolite)

Geikielite (No. 1) $(\text{Mg}_{0.65}\text{Fe}_{0.23}\text{Mn}_{0.11}\text{Ca}_{0.01})_{\Sigma 1.00}\text{Ti}_{1.00}\text{O}_3$

Geikielite (No. 2) $(\text{Mg}_{0.51}\text{Fe}_{0.30}\text{Mn}_{0.17}\text{Ca}_{0.01})_{\Sigma 0.99}\text{Ti}_{1.01}\text{O}_3$

Zirconolite (No. 3) $(\text{Ca}_{0.96}\text{Mg}_{0.03}\text{Fe}_{0.00}\text{Ti}_{1.94}\text{Fe}_{0.06})_{\Sigma 2.00}\text{Zr}_{1.01}\text{O}_7$

Zirconolite (No. 4) $\text{Ca}_{1.00}(\text{Ti}_{1.96}\text{Fe}_{0.03}\text{Zr}_{1.00})_{\Sigma 2.96}\text{O}_7$

Spinel (No. 5) $(\text{Mg}_{0.94}\text{Fe}_{0.06}\text{Mn}_{0.01})_{\Sigma 1.01}(\text{Al}_{1.98}\text{Ti}_{0.01})_{\Sigma 2.00}\text{O}_4$

Forsterite (No. 6) $(\text{Mg}_{1.96}\text{Fe}_{0.04}\text{Mn}_{0.01}\text{Ca}_{0.01})_{\Sigma 2.02}\text{Si}_{0.99}\text{O}_4$

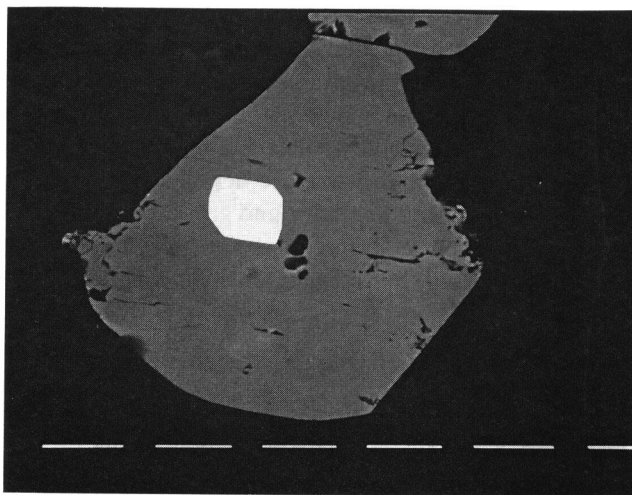


Fig. 2. Back scattered electron image of baddeleyite crystal (white) and zoned geikielite (dark grey to grey). A bar indicates 10 μm .

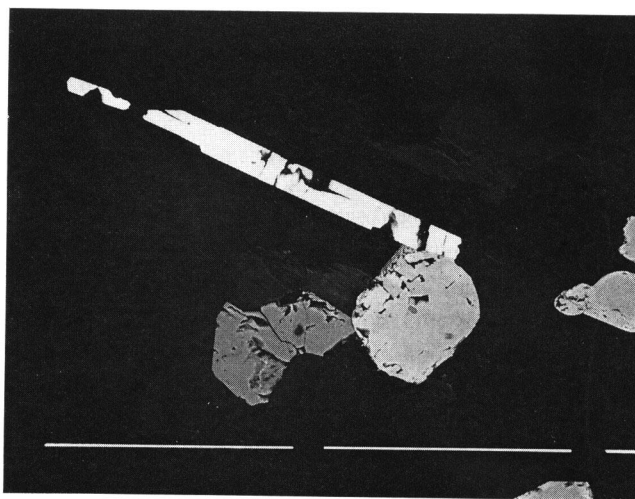


Fig. 3. Back scattered electron image of zirconolite (white) and geikielite (grey). A bar indicates 10 μm .

small amount of iron. The chemical analyses of baddeleyite and zircon indicated that both of them are essentially pure except for the presence of very small amount of HfO_2 in both. Therefore, they were not given in the table.

All the compositions of examined forsterite grains are very close to forsterite end member, or exceeding 95 mole %, as commonly seen in this mineral of pure skarn origin. Those of spinel in direct contact with geikielite have higher $\text{Mg}/(\text{Mg}$

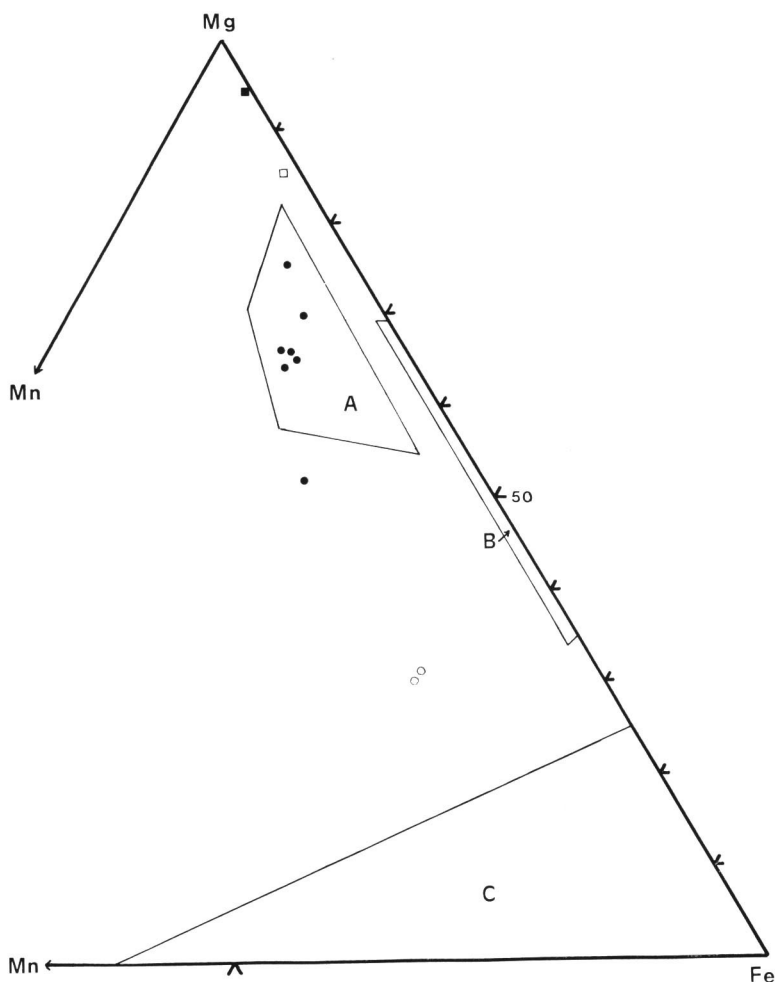


Fig. 4. The Mg (MgTiO_3)-Fe(FeTiO_3)-Mn (MnTiO_3) diagram. Solid circle: geikielite from Kamineichi. Open circle: magnesian ilmenite from Nejou. Solid square: spinel associated with geikielite from Kamineichi. Open square: spinel associated with magnesian ilmenite from Nejou. A: Jacupiranga carbonatite; B: Kimberlites; C: Lamprophyres, Granite, Basalts, Carbonatites (after Mitchell, 1978)

+Fe+Mn) ratio, too, though slightly lower than forsterite.

The relationship between the chemical composition and mode of occurrence of geikielite is demonstrated by Mitchell (1978), who analysed geikielite in jacupirangite and plotted the composition in MgTiO_3 - FeTiO_3 - MnTiO_3 triangular diagram, after the exclusion of Fe_2O_3 molecule. The plots for the present analyses are incidentally included within the area for the materials from Jacupiranga carbonatite. The dif-

ference between two is the absence of Fe_2O_3 molecule in the present analyses, in which the ratio $(\text{Mg} + \text{Fe} + \text{Mn}) : \text{Ti}$ is nearly unity. The present analyses are plotted on the MgTiO_3 - FeTiO_3 - MnTiO_3 triangular diagram (Fig. 4), where the linings of areas after Mitchell (1978) are given for comparison. Also, this diagram includes several points for magnesian and manganoan ilmenites from a dolomite quarry nearby the Neichi mine in order to consider the origin of geikielite and ilmenite in recrystallized dolomite.

Consideration of the Chemical Composition and Genesis

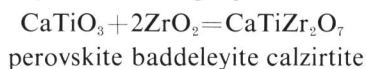
Above analyses prove that geikielite has a strong affinity to Mn^{2+} under such a skarn-forming condition. As already referred to, geikielite in marble from Pakistan has very high MnO content (Cressey, 1986), where no zirconium mineral appears in the description. The presence of zirconium at the site of formation of geikielite gives no influence to such a behaviour of geikielite to take up Mn^{2+} preferentially. Although some borates are found in the mine, none of them is found in the examined materials. Therefore, the relation to borate-bearing parts in the quarry is unknown. However, in the borate-bearing assemblages represented by kotoite-marble (Watanabe *et al.*, 1963), titanium appears as an essential constituent of warwickite, $(\text{Mg}, \text{Fe}^{2+})_3\text{Ti}[\text{O}|\text{BO}_3]_2$. The origin of this mineral was discussed by Watanabe (1954), who described it from Hol Kol mine, North Korea, where it was derived from geikielite due to the reaction with a boron-bearing substance coming from a granitic intrusion and dolomite. The exclusive occurrence of geikielite in marble and that of warwickite in kotoite-marble validate his conclusion at this locality, too.

The association of zirconium oxides and silicate with skarn minerals has been reported from Fuka, Okayama Prefecture, by Henmi *et al.* (1988), where calzirtite, baddeleyite and zircon are found in so-called contaminated rock derived from a peculiar alkali-rich magma generated after the effect of contamination with limestone. Although all of them have a fair proximity to their theoretical formulae, respectively, such minor fractions of FeO^* , Al_2O_3 , MgO , MnO , etc. are lodged in them in detectable amounts by microprobe. They consider the presence of magmatic fluid at the time of formation of zirconium minerals, and the entrance of such minor components to be one of the reflections of the co-existence with a magma. While, the present zirconium minerals are all closer to their theoretical compositions than those from Fuka. This is explained by the scanty of such minor cations capable of entering the structure of zirconolite in the marble.

The compositional comparison with zirconolite of different origin delivers another conclusion. Zirconolite in nepheline syenite of Malawi has been recently described (Platt *et al.*, 1987). It has a compositional zoning and the core is slightly enriched in MnO up to 0.54% in weight. This may imply the absence of any phases more capable of taking up Mn^{2+} than zirconolite in the mineral association. The chemistry of zirconolite attracts our special attention due to the usage as disposal of radioactive wastes (Ringwood, 1985).

The comparison with the other geikielite localities is also presented here. It is the creation of series of mineral associations including titanium and zirconium oxides in the increasing order of degree of participation of zirconium minerals. That is, at first, the association of geikielite and perovskite in marble from Pakistan represents the association without any trace of zirconium mineral. Secondly, the association of zirconolite and baddeleyite in the present case corresponds to the incipient participation of zirconium minerals. Thirdly, that from Fuka may be dealt with as more zirconium-bearing due to the appearance of calzirtite in place of zirconolite. Note that the variation of zirconium contents in the concerned oxides is not gradual but stepwise. This is a mineralogical support accounting for the difference of site preference between titanium and zirconium as indicated in zirconolite-2M (Mazzi and Munno, 1983). Although the detailed informations are not always complete, the mineral associations including zirconium oxides from Tazheran massif, Transbaikal (Konev *et al.*, 1970) are considered to represent the most zirconium-rich association of oxides. According to them, the occurrence of calzirtite, baddeleyite, geikielite, perovskite and zircon is known as the associated minerals of tazheranite, a new mineral corresponding to cubic zirconia stabilized by CaO. As compared with this case, the present baddeleyite was formed under a lower temperature condition. One of the authors (A. K.) visited this locality and could observe the mode of occurrence of tazheranite. In this locality, the contents of mineral associations in skarns are so diverse in every observation points.

On account of extreme purity of the present zirconium minerals, the role of minor constituents cannot be discussed on the examined materials. At Fuka, Henmi *et al.* (1988) refer to the appearance of perovskite in the associated minerals with calzirtite and baddeleyite. The compositional relation among ideal perovskite, calzirtite and baddeleyite is given by the following equation:



Their description refers to slight compositional deviations from the ideal compositions on baddeleyite and calzirtite. Provided that these three were formed under an equilibrium condition, their association might have been favoured by the presence of minor vicarious constituents serving to stabilize them.

The Possible Source of Titanium

The occurrence of related titanium mineral is also found in nearby two dolomite quarries at Kebaraichi and Nejou, Miyako City, respectively (Fig. 1). In both localities, realized titanium mineral is magnesian and manganoan ilmenites. In Table 2 the materials from Nejou are given in favour of the higher MnO contents. At the former locality, ilmenite forms a black smear-like band of about a centimeter wide in a marble containing spinel, forsterite and brucite collected from a marginal part of a large dolomite lense. While in the latter, ilmenite is a subordinate constituent of

Table 2. Chemical analyses of ilmenite (No. 1), spinel (No. 2) and forsterite (No. 3) from Nejou, Miyako City, Iwate Prefecture.

Weight percentages:

	1.	2.	3.
TiO ₂	56.51	—	—
SiO ₂	—	—	41.40
Al ₂ O ₃	—	68.12	—
MgO	8.26	24.00	51.99
FeO*	25.40	6.69	5.25
MnO	8.99	0.66	1.29
total	99.16	99.47	99.93 %

Empirical formulae: (basis: O=3 (ilmenite), O=4 (spinel, forsterite))

Ilmenite (No. 1) (Fe_{0.51}Mg_{0.29}Mn_{0.18})Σ_{0.98}Ti_{1.01}O₃

Spinel (No. 2) (Mg_{0.88}Fe_{0.14}Mn_{0.01})Σ_{1.03}Al_{1.99}O₄

Forsterite (No. 3) (Mg_{1.87}Fe_{0.11}Mn_{0.03})Σ_{1.01}Si_{1.00}O₄

a spinel-rich marble composed of clinohumite, forsterite, phlogopite, and calcite besides fine magnetite grains derived from serpentinization of forsterite, which contains higher content of fayalite molecule than that in the Neichi mine, and the aggregates of them are devoid of any banded texture, suggesting the disappearance of the original texture. Ilmenites from these localities have similar composition to each as well as the associated spinel, in which higher FeO contents than that in spinel from the Neichi mine are of note alike forsterite.

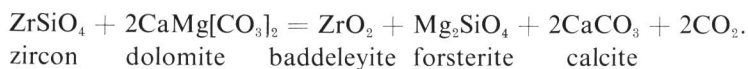
From these evidences, the most probable origin of the described assemblage is considered to be a kind of residual clay developed on carbonate beds. The source of titanium in the residual clay was ilmenite possibly from granitic rocks or their pegmatites. The ilmenite suffered a prolonged weathering, by which the loss of iron took place, as exemplified by the case of formation of pseudorutile (Grey and Reid, 1975) or of "kleberite" (Bautsch *et al.*, 1978), the Fe/Ti ratio being 2/3 and 1/6, respectively. One of the most significant factors responsible for the difference is the degree of weathering, which extracts iron relative to titanium. If a residual clay containing such a material with higher Fe/Ti ratio, or in a less weathered state, was metamorphosed, the product was to contain a magnesian ilmenite after the supply of magnesium from the surrounding dolomite in the same manner as the case of formation of warwickite as just referred to. If the material with lower Fe/Ti ratio, or in a more weathered state, was metamorphosed, the amount of incorporated magnesium forming an oxide phase with (Mg+Fe+Mn): Ti=1 should have been larger than the previous case. Thus, in the product the quantity of magnesium could exceed relative to iron, leading to the formation of ferroan geikielite.

As to the alteration of ilmenite, Haggerty (1976) introduces the decomposition of ilmenite solid solution to anatase plus hematite with the preferred dissolution of Fe₂O₃ and ilmenite unaltered. If such an aggregate is subjected to thermal metamorphism under the existence of dolomite which can be a source of magnesium, the

metamorphism enables the formation of geikielite solid solution or magnesian ilmenite. The existence of core portion enriched in geikielite molecule can be explained by the earlier formation of core after the reaction of anatase with magnesium from dolomite than that of rim probably derived from the reaction of hematite, ilmenite solid solution and available magnesium from dolomite.

Suppose that particles of decomposed ilmenite were deposited on dolomite beds, they will be a simple dust-like substance of invisible size unless metamorphosed. But, if metamorphosed, the products are to have visible dimensions. The particles might have been accompanied by aluminous sediments, which served as the source of spinel. If decomposed ilmenite grains were deposited on argillite beds, the product of thermal metamorphism will not have any independent titanium mineral but titanium-bearing biotite in its place. In case of limestone, no independent titanium mineral is formed unless the temperature condition allowed the formation of such an oxide as perovskite, provided that a silica-poor condition was prevailing. In case of presence of silica, titanite will be formed in place of perovskite.

As to the origin of zirconium minerals, the observed evidence simply indicates that the existence of two phases, baddeleyite and zircon, both being extremely pure. The most probable state prior to the formation of them is the presence of zircon, which had a remote composition from the end member as is seen in materials from granitic to syenitic pegmatites. The thermal treatment of such pegmatitic zircon informs that incipient substantial changes including the enhancement of crystallinity take place under the temperature condition as low as about 700°C (Lima de Faria, 1964). Provided that such a reactive zircon was extant in dolomite before thermal metamorphism, the generation of baddeleyite is accounted for by the following equation:



As to the formation of near end member zirconolite, the most acceptable explanation is to expect the presence of such a complex oxide as srilankite, ideally ZrTi_2O_5 (Willgallis *et al.*, 1983), which was combined with calcium subsequent to the formation of zoned geikielite. This mineral is found in gem gravels from Sri Lanka, where they include zirconolite, baddeleyite, geikielite, spinel and perovskite.

In order to interpret the sequence of observed oxide assemblage concluded by the formation of zirconolite, it is highly expected that the described assemblage is the product of progressive contact metamorphism, where the formation of principal constituents had been initiated by that of geikielite. It was formed after the supply of magnesium from the surrounding dolomite which was thermally dissociated to leave calcite under lower temperature condition than calcite dissociation, and, then, the increasing temperature favoured the formation of zirconolite after the supply of calcium from the surrounding calcite. Since the both cases are the reactions of solid phases with carbonates liberating carbon dioxide, it is reasonable that the order of two reactions is in accordance with that of dissociation temperatures dolomite to

calcite, or low to high.

References

- Bautsch, H.-J., G. Rohde, P. Sedlacek & A. Zedler, 1978. Kleberit, ein neues Eisen-Titanium Oxide aus Tertiär Sande. *Zeit. geol. Wiss.*, **6**: 661–671.
- Bayliss, P., F. Mazzi, R. Munno, and T. White, 1989. Mineral nomenclature: zirconolite. *Min. Mag.*, **53**: 565–569.
- Cressey, G., 1986. Geikielite and perovskite in serpentine brucite marble from Baltistan, Northern Area (Kashmir), Pakistan. *Min. Mag.*, **50**: 345.
- Fowler, M. B. & C. T. Williams, 1986. Zirconolite from the Glen Dessarry syenite; a comparison with other Scottish zirconolites. *Min. Mag.*, **50**: 326–328.
- Grey, I. R. & A. F. Reid, 1975. The structure of pseudorutile and its role in the natural alteration of ilmenite. *Amer. Miner.*, **60**: 898–906.
- Haggerty, S. E., 1976. Opaque mineral oxides in terrestrial igneous rocks. In *Oxide minerals, Short course notes*, Min. Soc. Amer., **3**: 101–276.
- Henmi, C., I. Kusachi & K. Henmi, 1988. Zirconium minerals from Fuka, Bicchu-cho, Kawakami-gun, Okayama Prefecture. *Abst. Autumn Meeting of Mining Soc. Japan, Assoc. Petro. Miner. Econ. Geol. Japan, and Miner. Soc. Japan, Tokyo*, 12. (In Japanese.)
- Konev, A. A., Z. F. Ushchapovskaya, A. A. Kashaev & V. S. Lebedeva, 1969. Tazheranite, a new calcium-titanium-zirconium mineral. *Doklady Akad. Nauk SSSR*, **186**: 917–920 (In Russian.)
- Mazzi, F. & R. Munno, 1983. Calciobetafite (new mineral of the pyrochlore group) and related minerals from Campi Flegrei, Italy; crystal structures of polymignyte and zirkelite: comparison with pyrochlore and zirconolite. *Amer. Miner.*, **68**: 262–276.
- Mitchell, R. H., 1978. Manganoan magnesian ilmenite and titanian clinohumite from the Jacupiranga carbonatite, Sao Paulo Brazil. *Amer. Miner.*, **63**, 544–547.
- Platt, P. G., F. Wall, C. T. Williams, & A. R. Woolley, 1987. Zirconolite, chevkinite and other rare earth minerals from nepheline syenites and peralkaline granites and syenites of the Chilwa Alkaline Province, Malawi. *Min. Mag.*, **51**: 253–264.
- Ringwood, E. A., 1985. Disposal of high-level nuclear wastes: a geological perspective. *Min. Mag.*, **49**: 159–176.
- Watanabe, T., 1954. On the occurrence of warwickite ($\text{Mg, Fe}_3\text{TiB}_2\text{O}_8$) at Hol Kol: a study of boron metasomatism. *Jour. Fac. Sci. Univ. Tokyo, Ser. II*, **9**: 337–344.
- Watanabe, T., A. Kato & T. Katsura, 1963. Kotoite, $\text{Mg}_3(\text{BO}_3)_2$, from the Neichi mine, Iwate Prefecture, Japan. *Proc. Japan Acad.*, **39**: 176–181.
- Willgallis, A., E. Siegmann & T. Hettiaratchi, 1983. Srilankite, a new Zr-Ti-oxide mineral. *Neues Jahr. Miner. Monat.*, 151–157.