

Aluminum Phosphates from Inokura, Imaichi City, Tochigi Prefecture, Japan

By

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Abstract Turquoise and planerite from a clay deposit at Inokura, Imaichi City, Tochigi Prefecture, occur in veins in argillized dacite and acidic tuff partially stained by goethite. Their chemical analyses indicate the former to be differentiated into two variants, Fe-free Cu-deficient and Fe³⁺-rich Cu-deficient ones, and the latter to be a Zn- and Ba-bearing one. Their average figures are, respectively; CuO 5.54, 5.72, 3.35; ZnO –, –, 1.21; BaO –, –, 0.36; Al₂O₃ 37.77, 29.95, 37.76; Fe₂O₃ –, 9.52, 0.70; P₂O₅ 33.69, 33.41, 35.52; totals 78.42, 78.60, 78.90 wt%. Their empirical formulae taking the rests as due to water are: (Cu_{0.56}□_{0.44})Al_{5.99}(PO₄)₃(PO₃OH)(OH)_{8.09}·5.14H₂O, (Cu_{0.61}□_{0.39})(Al_{4.99}Fe_{1.01})_{Σ6.00}(PO₄)₃(PO₃OH)(OH)_{5.22}·5.48H₂O, and (Cu_{0.34}Zn_{0.15}Ba_{0.02}□_{0.49})(Al_{5.92}Fe_{0.07})_{Σ5.99}(PO₄)₃(PO₃OH)(OH)_{7.99}·4.87H₂O, respectively, calculated on the basis of P=4, where the half-empty formula is taken as the basis. Preferential incorporation of Zn into planerite rather than turquoise is demonstrated. The Fe-rich turquoise veins are developed in goethite-stained parts. Wavellite and cacoxenite are found as coatings on fracture walls. Turquoise of both types and planerite will be precipitates from hydrothermal solutions containing Cu²⁺ and PO₄³⁻, where Al³⁺ might have been supplied from the clay minerals in wall rocks due to the loss of Al³⁺ in kaolinite to form quartz. Diminishing Cu²⁺ content in the solution favoured the precipitation of planerite rather than turquoise. Fragments of altered wallrocks enclosed within the veins of Fe³⁺-rich turquoise consist of pyrophyllite, kaolinite, quartz, and wavellite, indicating prolonged mineralization of phosphates. Also, altered wallrocks involve minor aggregates of chalcopyrite and sphalerite, bornite, covellite, and djurleite, but it seems that they are not direct sources of copper in turquoise and planerite and of zinc in the latter.

Introduction

Despite the extensive development of clay deposits of hydrothermal origin in volcanic and pyroclastic rocks younger than Miocene in Japan, the reports dealing with phosphates, which are found in some foreign clay deposits are so few. KATO (1965) alluded to a beryllium-bearing variscite pseudomorphing apatite from the present locality formerly worked under the name Onuki mine, and KAMITANI (1977) reported the occurrence of augelite from the Hinomaru-Nako orebody, Yamaguchi Prefecture, where MATSUBARA *et al.* (1993) note the occurrence of trolleite, svanbergite, and gorceixite. The first work is a trigger of the present study to note the first occurrences of turquoise and planerite at this locality (MATSUBARA *et al.*, 1987). Just after

this planerite has been reported from Toyoda, Kochi City (MATSUBARA *et al.*, 1988), where the mineral owes the phosphate ion to nearby apatite rock by the attack of sulphate ion liberated from pyrite.

The present description is for the chemical study on turquoise and planerite. The former includes visually distinguishable two chemical types, Fe-free Cu-deficient one and Fe-rich Cu-deficient one, and the latter has rather uniform composition with ZnO (ca. 1 wt. %) and BaO (ca. 0.3 wt. %), which is also found in Macedonian turquoise (SKLAVOUNOS *et al.*, 1992). Veins of turquoise of both types and of planerite are nearly monominerallic but involve minor quartz and nacrite. Also, wavellite is found in veins cutting argillized rocks and cacoxenite occurs as thin coatings on fracture walls in goethite-stained rocks.

The product of the initial stage of phosphate mineralization at this locality is apatite and the subsequent ones are wavellite, turquoise, planerite, and cacoxenite from PO_4^{3-} -bearing solutions with variable Cu^{2+} contents that favoured the formation of turquoise or planerite, and supply of Al ion from the clay minerals and Fe^{3+} ion from the goethite-stained wallrocks, respectively. Aggregates of chalcopyrite with minor sphalerite frequently found in argillized rocks apart from the phosphate-bearing veins include bornite, covellite, and djurleite in part, all being possibly of secondary origin. But no direct proof that they were direct sources of copper and zinc contained in turquoise and planerite was found.

Occurrence

The clay deposit has been worked for kaolinitic clay for more than 40 years in an open pit located about 4 kilometers northeast of Fubasami station, Nikko Line, Eastern Japan Railway Company Ltd. The ores are represented by kaolinite ores produced due to the argillization of dacite and dacitic tuff. Less argillized dacite retains the original texture composed of phenocrysts of quartz of a few millimeters size and of plagioclase, which is completely altered into kaolinite plus quartz. The groundmass is also converted into the aggregate of quartz and kaolinite with minor pyrite. The argillized tuff is a light cream coloured fine-grained one composed of quartz and kaolinite of variable ratio with or without goethite stains, which vary from a feebly developed smear to heavy soakings along fractures. Also, goethite cements fractured argillized rocks into a vein-like form with maximum thickness exceeding a centimeter.

Heavier argillization makes kaolinite (including dickite and nacrite)-dominant aggregates in which coarser-grained kaolinite flakes and pyrite grains are contained. It is such an aggregate that Be-bearing variscite was found (KATO, 1965), though the situation relation to the turquoise and planerite veins could not be known. The variscite was referred to as redondite at that time, but this has been later re-named as Messbach-type variscite (SALVADOR & FAYOS, 1972). Turquoise has two visually distinguishable modes of occurrence in close relation to the chemical characteristics.

Fe-free and Fe^{3+} -rich ones. The veins of the former are thin filmy ones cutting argillized dacitic tuff. They have a light green colour and monominerallic in appearance, except for some thin white aggregates of pure nacrite of a millimeter order. The veins have clear walls and no apparent branches. The goethite stain in the wallrock is absent or very poor if present. While, the veins of Fe^{3+} -rich turquoise have a light greenish blue colour and the width is more than a centimeter. They are exclusively developed in goethite-stained parts with sharper walls but involve fragments of wallrocks imparting a branch-rich feature. Two kinds of wallrocks are realized among the enclosed fragments. One of them is a simple involvement of altered wallrocks composed of kaolinite and quartz, but the other has a more or less waxy appearance and consists of quartz, pyrophyllite, kaolinite, and wavellite. The main parts of veins consist of aggregates of very fine grains of turquoise with small amounts of nacrite and quartz, which form thin bands in the petering parts. The walls are generally smooth unless rich in fragments. In the wider parts, small voids exclusively walled by turquoise are developed. Under the electron microscope, the walls are composed of gyroidal aggregates of minute parallelogram-shaped tablets as indicated in Fig. 1, where a perfect cleavage is seen on the parallelogram, corresponding to $\{001\}$ very probably.

In the open pit, the development of turquoise veins of both types and of planerite veins is very restricted, where no primary copper sulphides are found nearby, although the development of staining of goethite without turquoise seems to be rather extensive.

Planerite occurs as thin filmy coating on fracture walls intersecting argillized dacite

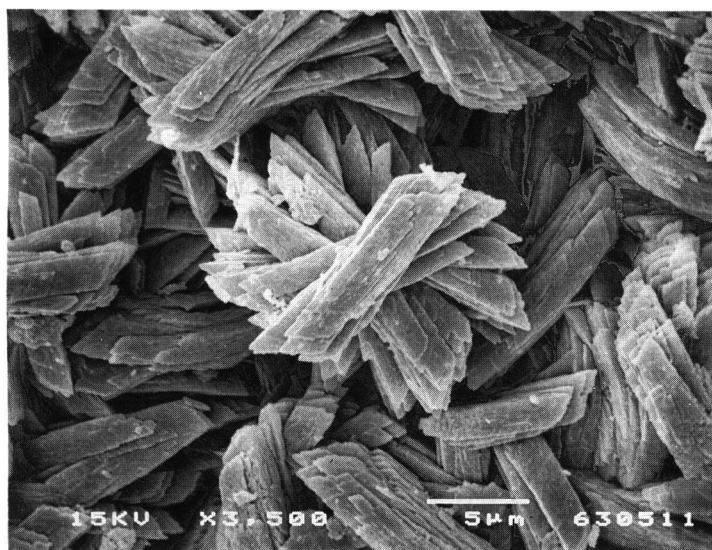


Fig. 1. Electron microscope images of gyroidal aggregates of idiomorphs of turquoise demonstrating the parallelogram-shaped outline and the perfect cleavage. A bar indicates 5 μm .

generally retaining the original texture, though notably disseminated by pyrite grains of submillimeter order without any goethite stain. Along the fracture walls pyrite is the unique associate with planerite. It forms a millimeter order aggregates of cubo-octahedral crystals with denser distribution than within the wallrocks of planerite vein. The colour of planerite is similar to that of Fe-rich turquoise but devoid of greenish tint.

Wavellite forms white film in altered tuff with goethite stain. The films are nearly monominerallic. It also occurs as a minor constituent of fragments of an altered wall-rock enclosed within the Fe-rich turquoise veins.

If minute fractures are developed in goethite-stained silicified wallrocks, the walls are frequently covered by very thin films of cacoxenite or overlain by tiny yellow brown rosettes composed of radially aggregated extremely minute hexagonal prisms of cacoxenite. Among phosphates hereby described, cacoxenite has the most extensive distribution in the open pit. A part of them looks like a stain of goethite, but cacoxenite has a rather velvety luster. Both of films and rosettes of cacoxenite are apparently monominerallic.

Chemical Compositions of Turquoise and Planerite

Chemical analyses of turquoise and planerite were made by using Links Systems Energy Dispersive X-ray Spectrometer as given in Table 1. As already stated, the present turquoise is differentiated into two variants due to Fe_2O_3 contents, both with Cu-deficiency. Their empirical formulae were calculated after the reference to the half-empty formula of turquoise series, $(\text{M}^{2+}_{0.5}\square_{0.5})\text{M}^{3+}_6(\text{PO}_4)_3(\text{PO}_3\text{OH})(\text{OH})_8 \cdot n\text{H}_2\text{O}$, where $\text{M}^{2+} = \text{Cu, Zn, Fe and Ca}$; $\text{M}^{3+} = \text{Al, Fe}$, a modified general formula of the series proposed by FOORD and TAGGERT (1988). All the differences coming from the

Table 1. Chemical analyses of Fe-free turquoise, Fe-rich turquoise, and planerite from Inokura, Imaichi City, Tochigi Prefecture, Japan

Weight percentages: (*: total Fe)							
	CuO	ZnO	BaO	Al_2O_3	* Fe_2O_3	P_2O_5	Total
1.	5.53	—	—	37.77	—	33.69	78.42
2.	5.72	—	—	29.95	9.52	33.41	78.60
3.	3.35	1.21	0.36	37.76	0.70	35.52	78.90

Empirical formulae: (basis: P=4; rest = H_2O)

- $(\text{Cu}_{0.56}\square_{0.44})\text{Al}_{5.98}(\text{PO}_4)_3(\text{PO}_3\text{OH})(\text{OH})_{8.08} \cdot 5.14\text{H}_2\text{O}$
- $(\text{Cu}_{0.61}\square_{0.39})(\text{Al}_{4.99}\text{Fe}_{1.01})_{\Sigma 6.00}(\text{PO}_4)_3(\text{PO}_3\text{OH})(\text{OH})_{8.22} \cdot 5.48\text{H}_2\text{O}$
- $(\text{Cu}_{0.34}\text{Zn}_{0.15}\text{Ba}_{0.02}\square_{0.49})(\text{Al}_{3.92}\text{Fe}_{0.07})_{\Sigma 5.99}(\text{PO}_4)_3(\text{PO}_3\text{OH})(\text{OH})_{7.99} \cdot 4.87\text{H}_2\text{O}$

1. Fe-free turquoise. Average of two analyses.
2. Fe-rich turquoise. Average of three analyses.
3. Planerite. Average of five analyses.

low totals are ascribed tentatively to H_2O , and this treatment invites no inconvenience. The upper limit of n is about 5.5. Their general formula is interpreted as the substitution of 2H for Cu in currently accepted formula of turquoise, $CuAl_6(PO_4)_4(OH)_3 \cdot nH_2O$, where $n=4 \sim 5$.

The chemical analyses of planerite present the degree of Cu-deficiency to be moderate. Also, the lower Fe_2O_3 contents, existence of ZnO more than 1% in weight and minor BaO are indicated. All of the chemical analyses have the relation $\square > (Cu, Zn)$ even in the analysis with the highest CuO content, and are identified as planerite after FOORD and TAGGERT (1988), although they use the name "half-empty" planerite-turquoise series for the material with the same degree of vacancy of that site. The present usage is in conformity with our previous one to the material from Toyoda, Kochi City (MATSUBARA *et al.*, 1988). The low totals of the analyses are also treated as due to H_2O . The amounts are approximately coincident with those of planerite analyses (FOORD, pers. comm.). All of the present analyses include ZnO (>1.5 wt.%) and

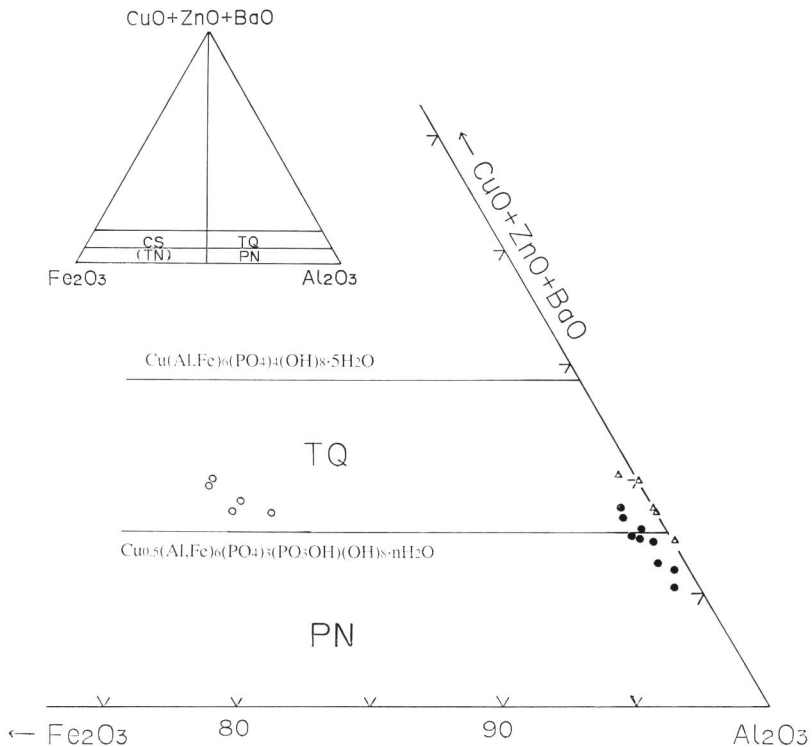


Fig. 2. Chemical compositions of turquoise and planerite plotted on $(CuO+ZnO+BaO)-Al_2O_3-Fe_2O_3$ diagram.

Open triangle: Fe-free turquoise. Open circle: Fe-rich turquoise. Closed circle: planerite. TQ: turquoise (including faustite). PN: planerite CS: chalcosiderite (TN): tinctite (not a precise Fe^{3+} analogue of planerite) (See the chapter of X-ray powder study).

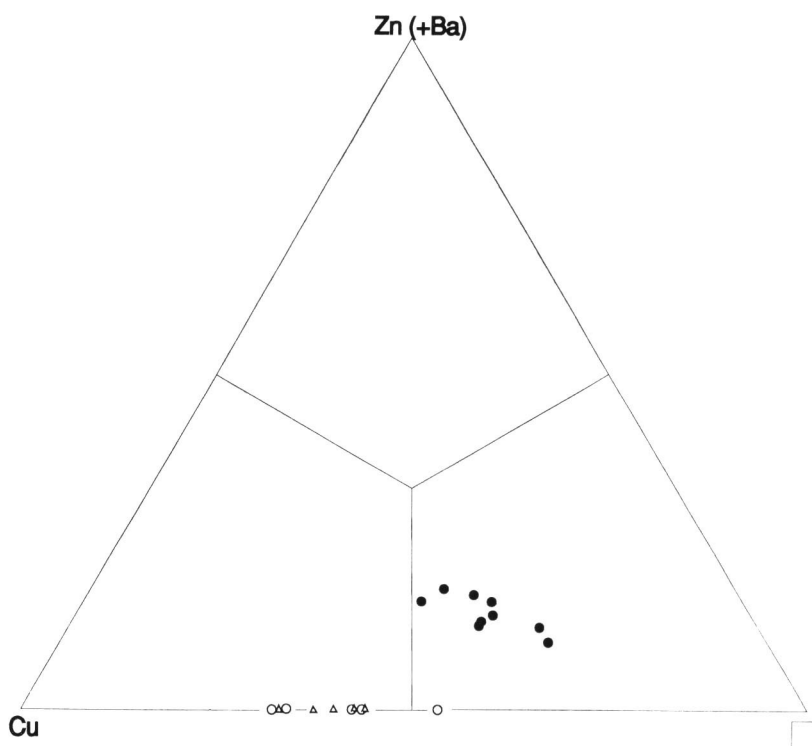


Fig. 3. Mole ratio of Cu, Zn(+Ba), and vacancy in turquoise and planerite. Note the higher ZnO contents in planerite. The symbols are the same as in Fig. 2.

BaO (<0.5 wt. %). The significant substitution of Zn for Fe^{2+} is known in aheylite from Bolivia up to 4.5 wt. %, or $\text{Fe}^{2+} \geq \text{Zn}$, planerite (up to 0.9 wt. %) and turquoise (up to 0.14 wt. %) (FOORD, pers. comm.).

The chemical analyses of turquoise and planerite are at first plotted on $(\text{CuO} + \text{ZnO} + \text{BaO}) - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3$ diagram to demonstrate the separation of compositional areas of Fe-free turquoise, Fe-rich turquoise, and planerite (Fig. 2), where those of the first and third minerals overlap. But if the contents of divalent cations including vacancy are considered as given in Fig. 3, the plots are to demonstrate an evident tendency that zinc is preferentially incorporated into planerite and excluded by turquoise of both types. According to FOORD (pers. comm.), except for faustite the most zinchophile phase among the members of turquoise series is aheylite, in which the maximum ZnO content is nearly the same as FeO content, and planerite has the subsequent importance. It seems that there is an evident difference in the ability to admit Zn between turquoise and planerite, that of the former being low.

As to the existence of BaO, SKLAVOUNOS *et al.* (1992) report BaO 0.35 wt. % in turquoise from Vathi, Macedonia, where the origin is ascribed to the circulation of

hypergene metalliferous solutions through an altered trachyte hosting the mineral. Here, the primary copper mineral is given as chalcopyrite accompanied by supergene enrichment zone including chalcocite and covellite, though the former might be djurleite, and all of them are formed in the altered trachyte. The turquoise analyses give near ideal CuO contents, minor As_2O_5 , UO_2 , and ThO_2 . The presence of these ingredients are the chemical differences from the present turquoise.

X-Ray Powder Study

The X-ray powder study using diffractometer method is made on the Fe-rich

Table 2. X-ray powder patterns of turquoise and planerite.

1.		2.		3.		1.		2.		3.	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
				9.09	50						
6.80	50	6.78	45	6.73	50	2.516	10				
6.21	26	6.20	30	6.17	70	2.478	2			2.47	20
6.05	10	6.04	10	6.00	40	2.440	1	2.436	4	2.44	10
		5.71	5	5.77	20	2.390	2	2.390	5	2.40	20
4.78	20	4.77	25	4.80	60	2.355	8	2.358	12	2.35	40
4.60	2	4.61	8	4.65	20	2.302	10	2.300	15	2.32	40
				4.49	10	2.244	10	2.239	10	2.23	40
				4.18	10			2.194	2	2.19	20
4.15	2			4.06	10	2.131	4	2.130	10	2.12	40
3.70	100	3.693	100	3.68	100	2.062	12	2.061	15	2.07	50
3.50	5	3.501	15	3.51	10	2.011	9	2.010	15	2.02	60
3.43	30	3.432	45	3.44	70	1.987	2	1.984	4	1.994	10
3.29	30	3.283	40	3.28	70			1.967	2	1.966	10
3.27	10				70			1.960	2		
3.09	20	3.089	45	3.10	40					1.934	20
3.02	20	3.017	10	3.05	20	1.902	12	1.900	18	1.903	40
2.902	50	2.899	55	2.91	80	1.850	9	1.847	20	1.845	40
				2.89	10	1.841	9				
2.864	5	2.861	15	2.84	20					1.824	40
2.727	1			2.74	20					1.814	10
2.609	1			2.62	10	1.792	4	1.794	5	1.784	20
		2.579	5	2.58	10	1.721	4	1.720	8	1.727	20
2.536	8	2.531	20	2.52	20						

1. Fe-rich turquoise. Inokura, Imaichi City, Tochigi Prefecture, Japan. Co/Fe radiation. Diffractometer method. The present study.
2. Planerite. Inokura, Imaichi City, Tochigi Prefecture, Japan. Co/Fe radiation. Diffractometer method. The present study.
3. Turquoise. Campbell County, Virginia. JCPDS Card No. 6-214.

turquoise and planerite (Table 2). The two patterns are essentially same. Some diffraction peaks with overlapped indices make it meaningless to derive the unit cell parameters.

It is worth mentioning that the patterns are also similar to that of tenticite after SAKURAI *et al.* (1992), who derived an orthorhombic cell from the pattern in favour of the original description including the morphological study under the microscope. Their chemical formula corresponds approximately to Fe^{3+} analogue of Cu-free planerite, unless minor difference in water contents between them is considered. But tentative calculation failed to account for the existence of any crystallographic relation between them.

Consideration on the Geneses of Phosphates

The geneses of realized phosphates, turquoise of Fe-free and Fe-rich types, planerite, wavellite, and cacoxenite are here considered.

Generally turquoise accompanies no copper sulphides and native copper as its direct associates and this is also the case at the present locality, too. The manner of primary mineralization of copper and zinc in this deposit is represented by the dissemination of chalcopyrite and sphalerite in silicified pyroclastic rocks. Prior to the formation of these sulphides, silicification and argillization had already influenced the dacite and dacitic tuff. Seeing from the mode of dissemination of sulphides, which is scarcely controlled by any fractures, the fracturing of argillized rock took place after the formation of sulphides. While, the principal part of goethite is controlled by fractures. Then the sequence of argillization and silicification of dacite and dacitic tuff, dissemination of chalcopyrite and sphalerite, fracturing, precipitation of goethite, and formation of turquoise and planerite will be constituted.

As to the formation of turquoise and planerite, a solution at least loaded by Cu^{2+} , Al^{3+} and PO_4^{3-} came along fracture of argillized rocks, in which the association of quartz+kaolinitic clay+sericite±pyrite derived from dacite had been stable under a rather reducing condition and pyrite is taken place by goethite under an oxidizing one. In case of oxidizing condition, goethite is an alternative fixer of Fe. The solution precipitated Fe-free turquoise in argillized rocks, whereas Fe-rich one was formed instead after the incorporation of Fe^{3+} through the partial solution of goethite possibly due to phosphoric acid. As an ingredient of solution zinc might have been contained, though always less dominant than Cu^{2+} . Seeing from the separate occurrences of turquoise veins of both types and of planerite from the copper sulphides and sphalerite, it is unlikely that such secondary sulphides of copper and turquoise have the same genetic histories but the solution had inherited the role of transportation of Cu and Zn ions even after the formation of sulphides of them, where the addition of PO_4^{3-} to the solution took place and any solution containing Cu^{1+} or Cu^{2+} must have been circulating. That copper ions had been fixed under the presence of chalcopyrite corresponds to the ordinary case of secondary enrichment of copper seen

in superficial parts of chalcopyrite-bearing copper deposits of various types, where the most common anion is SO_4^{2-} derived from the decomposition of sulphides under atmospheric condition. The formation of such secondary copper sulphides is to be accomplished by the reaction of a solution containing copper ions only, whereas that of turquoise requires the participation of phosphate ion at least. Therefore, the parental solution producing turquoise must have been discrete from that reacting with chalcopyrite to form secondary copper sulphides, which were produced after the formation of turquoise through an ordinary supergene process, where an oxidizing condition was prevalent, and that this was favoured by the pre-existence of goethite.

As to the genesis of wavellite, MATSUBARA *et al.* (1988) explained it on the material from Toyoda, Kochi City, where it was found in solution voids and in veinlets cutting chert-dominant sedimentary rocks comprising thin seams of fluorapatite and of pyrite-bearing mudstone. The weathering process led to the oxidation of pyrite to produce SO_4^{2-} , which reacted with the seams of fluorapatite to generate PO_4^{3-} , and this reacted with mudstone from which Al^{3+} was derived. Although the genesis of country rocks to phosphate-bearing veins are not same, the genesis of present wavellite is considered as follows after the reference to the case of Toyoda. Any ascending solution containing PO_4^{3-} reacted with the wallrocks of fractures, which were conduits to that solution. A part of wallrocks must have been solved by the PO_4^{3-} -bearing solution inviting the decomposition of the clay minerals in the wallrocks to liberate Al^{3+} .

Cacoxenite has owed the formation to the existence of available Fe^{3+} ion. The mineral is exclusively found in argillized and silicified rocks suffering from a remarkable staining of goethite. The extensive development of goethite-stained rocks in the open pit informs that any solution containing PO_4^{3-} enabled the cacoxenite formation if it circulated along minute fractures developed within the rocks.

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