

NINGYOITE IN URANIUM DEPOSITS OF SOUTH-CENTRAL BRITISH COLUMBIA: FIRST NORTH AMERICAN OCCURRENCE

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ABSTRACT

Ningyoite has been found in the uranium deposits of southern British Columbia, where it constitutes the major uranous (U^{4+}) phase present. It occurs as accretionary stars, crystal mats and aggregate masses of spindle- or lozenge-shaped crystals that rarely exceed 2 mm in length. Occasionally it is present as single crystals in cleavage cracks of saléeite. The mineral forms in pyritiferous organic-rich fluvial sediments (Tye deposit) or carbonaceous sandy mudstones (Blizzard deposit). In transmitted light ningyoite is greenish brown and displays a slight pleochroism. Extinction of the spindle-shaped grains is parallel and the mean index of refraction is between 1.60 and 1.70. Ningyoite is orthorhombic a 6.75(1), b 12.00(1), c 6.38(1) Å, V 516.78 Å³, $Z = 3$, diffraction aspect C^{***} . Electron-microprobe analysis failed to detect rare-earth elements in ningyoite from British Columbia. Rare-earth elements were detected in only some ningyoite aggregates from the type locality in Japan. It is proposed that the formula for ningyoite be written $Ca_{2-x}U_x(PO_4)_2 \cdot nH_2O$, where $x \leq 1$. Optimum conditions for the formation of ningyoite are attained when weakly alkaline groundwaters leaching granitic basement complexes and containing high concentrations of U and PO_4 infiltrate pyritiferous, organic-matter-rich sediments.

Keywords: ningyoite, saléeite, uranium, phosphorus, groundwaters, Blizzard deposit, Tye deposit, British Columbia.

SOMMAIRE

La ningyoite est l'espèce minérale uranifère (U^{4+}) dominante dans les gîtes d'uranium de la Colombie-Britannique méridionale. On la trouve en accréions stellaires, en tapis et en agrégats de cristaux fusiformes ou losangiques de longueur généralement inférieure à 2 mm. Parfois on la trouve en cristaux uniques dans les fentes de clivage de la saléeite. La ningyoite a été précipitée dans les sédiments fluviaux pyritifères et riches en matière organique (gisement Tye) et dans les boues arénacées carbonacées (gisement Blizzard). En lumière transmise, elle est

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d'un brun verdâtre, légèrement pléochroïque. L'extinction est parallèle, et l'indice moyen de réfraction se situe entre 1.60 et 1.70. La ningyoite est orthorhombique, a 6.75(1), b 12.00(1), c 6.38(1) Å, V 516.78 Å³ pour $Z = 3$; aspect de diffraction C^{***} . La microsonde n'a décelé aucune terre rare dans les échantillons canadiens, quoique les terres rares aient été trouvées dans certains agrégats de ningyoite de la localité-type japonaise. Nous proposons la formule $Ca_{2-x}U_x(PO_4)_2 \cdot nH_2O$, $x \leq 1$. La formation de la ningyoite est favorisée par l'infiltration, dans des sédiments riches en matière organique et en pyrite, d'eau légèrement alcaline, enrichie en U et PO_4 par lessivage des complexes granitiques du socle.

(Traduit par la Rédaction)

Mots-clés: ningyoite, saléeite, uranium, phosphore, eau météorique, gisement Blizzard, gisement Tye, Colombie-Britannique.

INTRODUCTION

Until recently the calcium uranium phosphate mineral ningyoite had not been found in uranium deposits outside Japan. Investigations of the mineralogy of the Blizzard and Tye basal-type uranium deposits in south-central British Columbia (Fig. 1) have shown that this mineral is the only uranium-bearing mineral in the Tye deposit; with the exception of very small amounts of pitchblende, it is the only uranous phase in the Blizzard deposit. Recently, ningyoite has been identified in some of the uranium deposits of the U.S.S.R. (Belova *et al.* 1978a, b), although its paragenesis and the types of deposits in which it occurs have not been adequately described.

Ningyoite was first discovered in uranium deposits of the Ningyō-Tōgē area, Tottori Prefecture, Japan (Muto *et al.* 1959), where it occurs as acicular or elongated lozenge-shaped crystals that form aggregates in voids or surround diagenetic pyrite and detrital quartz and feldspar grains (Fig. 2). The mineral is found in the unoxidized zone of uranium deposits that have formed in paleochannels within Miocene fluvial conglomerates, sandstones and mudstones overlying a Cretaceous granitic complex. Pyrite,

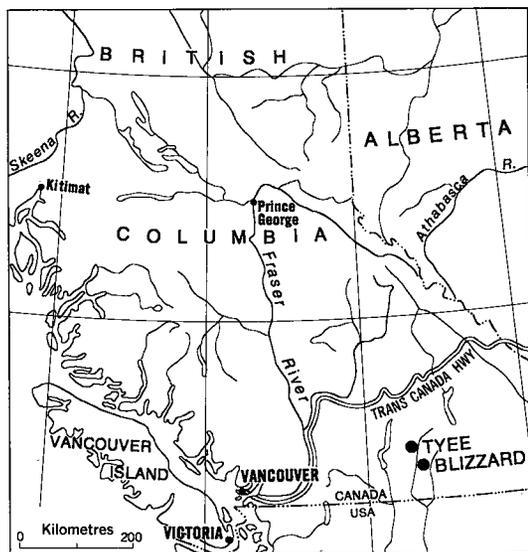


FIG. 1. Location of Blizzard and Tyee uranium deposits, British Columbia.



FIG. 2. Back-scattered electron image of uranium ore (polished section) from the Ningyô-Tôgê mine, Tottori Prefecture, Japan. Aggregates of spindle-shaped ningyoite crystals (white) replacing pyrite (grey in white rosettes) in a matrix of fragmented quartz (grey) and carbonaceous material (black). (Sample ROM 23237-3, courtesy of Royal Ontario Museum).

marcasite, gypsum and small amounts of sphalerite are the only authigenic minerals associated with the ningyoite. Pitchblende and coffinite are deposited adjacent to the zones of ningyoite mineralization. In a number of the Ningyô-Tôgê deposits, ningyoite is the main ore-bearing mineral, whereas in many other deposits in Japan it is of lesser importance. The initial description of ningyoite in Japanese deposits has been followed by reports on the paragenesis of uranium minerals in the Ningyô-Tôgê area (Muto 1961, Watanabe 1976), the precipitation environment of ningyoite (Muto 1962, Kajitani 1970) and the thermochemical stability of the mineral (Muto 1965).

The present paper describes the occurrence, mineralogy and paragenesis of ningyoite from two uranium deposits in south-central British Columbia. To the authors' knowledge, this is the first reported occurrence of this mineral in North American uranium deposits.

OCCURRENCE

The Blizzard and Tyee uranium deposits are located in the Okanagan region of south-central British Columbia, 60 and 30 km southeast of Kelowna, respectively (Fig. 1). At present, the Blizzard deposit is the only economic uranium deposit in the region.

Uranium mineralization in the Blizzard and Tyee deposits occurs as grain coatings and void fillings of ningyoite, saléeite, autunite and pitchblende in a Miocene continental conglomerate-sandstone-mudstone sequence. The deposits were formed in paleochannels overlying Tertiary faults and small graben structures within a Cretaceous-to-Tertiary quartz monzonite-syenite-granodiorite intrusive complex (Christopher & Kalnins 1977, Boyle 1979). Ningyoite is the only uranium-bearing mineral identified in the Tyee deposit, where it occurs in close association with marcasite and humic materials in polymictic conglomerates. In the Blizzard deposit, which consists principally of a cyclic assemblage of sandstones, siltstones and mudstones, ningyoite is concentrated principally in siltstones and sandy mudstones. It may also form at sandstone-mudstone interfaces in association with saléeite and organic matter. Pitchblende has been identified in only a few samples from the Blizzard deposit; ningyoite is, therefore, the main uranium (4+) mineral.

PHYSICAL AND OPTICAL PROPERTIES

Ningyoite occurs as spindle- or lozenge-shaped

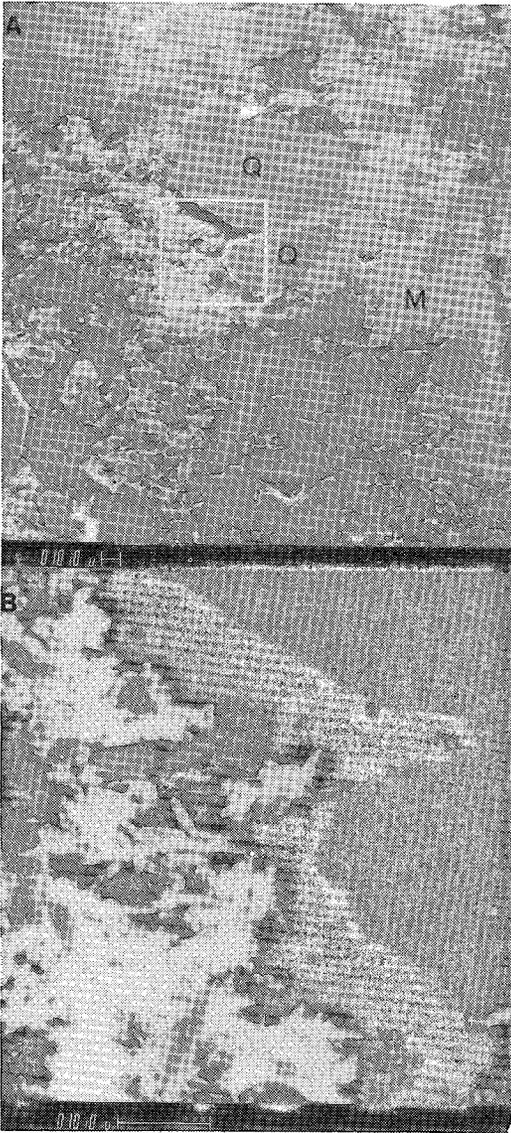


FIG. 3. Scanning-electron images of uranium ore (polished section) from the Tyee deposit. A. Star-shaped concretions and accretionary masses of ningyoite surrounding quartz (Q) and marcasite (M) grains in voids filled with carbonaceous matter (C). Note absence of ningyoite in areas occupied by massive marcasite (back-scattered electron image). B. Detail of area outlined in A, showing accretionary masses of spindle-shaped crystals of ningyoite surrounding and consuming euhedral crystals of marcasite (secondary electron image).

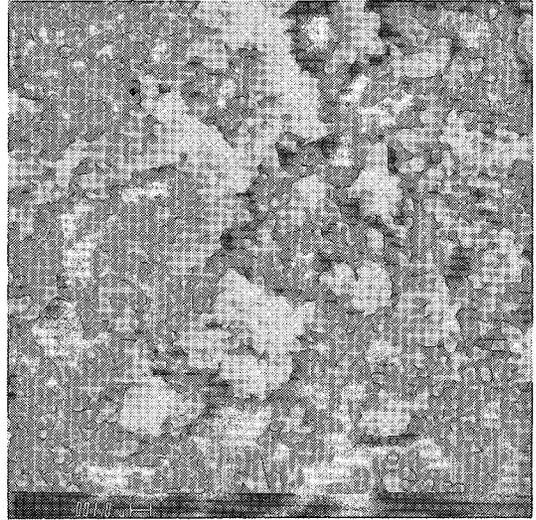


FIG. 4. Secondary electron image of uranium ore (grain mounting) from the Blizzard deposit. Spindle-shaped crystals of ningyoite growing as rosettes.

crystals forming stars (Fig. 3), crystal mats (Fig. 4) or accretionary masses (Figs. 3, 4) and occasionally as single crystals in cleavage cracks of saléeite (Fig. 5). Crystals rarely exceed 2 micrometres in length. In transmitted light (in air) the mineral is greenish brown and displays a slight pleochroism. Extinction of the spindle-shaped grains is parallel, in agreement with Muto *et al.* (1959). The indices of refraction could not be determined precisely owing to the extremely fine-grained nature of the mineral, but the mean index of refraction appears to be between 1.60 and 1.70. Belova *et al.* (1978a) obtained a mean index of refraction of 1.64. An accurate determination of specific gravity could not be made, as it was impossible to produce a pure concentrate of the mineral from its ore. The mineral did, however, sink in methylene iodide and must therefore have a specific gravity greater than 3.30.

X-RAY POWDER DIFFRACTION

The X-ray powder pattern of ningyoite from the Tyee deposit is presented in Table 1. Indexing was based on the electron-diffraction study of Belova *et al.* (1978a), who obtained systematic extinctions for ningyoite (hkl with

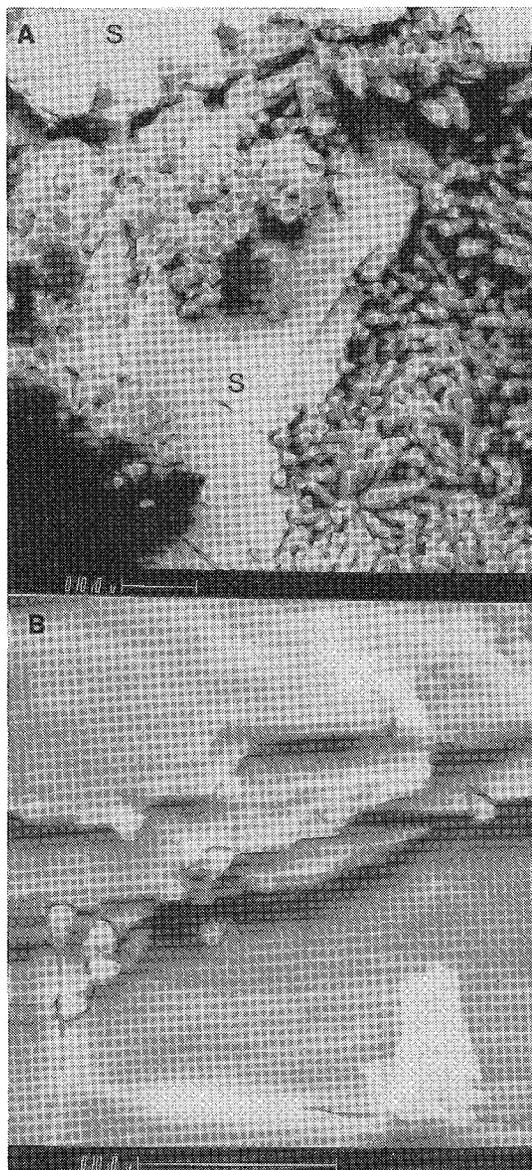


FIG. 5. Secondary electron image of uranium ore (grain mounting) from the Blizzard deposit. A. Spindle-shaped crystals of ningyoite surrounding and growing on saléite (S). B. Ningyoite crystals growing in cleavage cracks in saléite.

$h+k = 2n$, $0kl$ with $k = 2n$, $h0l$ with $h = 2n$, $hk0$ with $h+k = 2n$) that characterize a C-centered orthorhombic cell (diffraction aspect C^{**}). The unit-cell refinement was based on 14 lines between 6.02 and 1.432 Å for which

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR NINGYOITE, TYEE DEPOSIT, B.C.

Test.	$d_{\text{meas.}}$	$d_{\text{calc.}}$	hkl	Test.	$d_{\text{meas.}}$	$d_{\text{calc.}}$	hkl
5	6.02	6.00	020	4	1.719	1.720	260
9	4.35	4.37	021	4	1.691	1.694	062
		4.33	111			1.688	400
*6	3.44	3.44	130	1/2	1.674	1.671	332
10	3.00	3.00	040	1	1.657	1.661	170
9	2.81	2.82	022			1.661	261
*1	2.71	2.81	112	*3	1.594	1.596	004
1	2.35	2.71	041	2	1.536	1.540	114
*3	2.32	2.34	132			1.534	313
8	2.13	2.32	202	1/2	1.518	1.514	262
		2.13	151	1	1.501	1.499	080
		2.13	003	1/2	1.475	1.473	172
		2.01	023	1/2	1.460	1.448	422
*4	2.01	2.00	113			1.448	134
		2.00	060	1	1.432	1.433	441
5	1.843	1.845	152	1	1.363	1.363	370
1/2	1.814	1.818	312	1/2	1.342	1.342	510
		1.810	133			1.340	281
1	1.735	1.735	043	2	1.304	1.304	154

- 114.6 mm Debye-Scherrer powder camera, Cu radiation Ni filter ($\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$), lines belonging to marcasite and quartz deleted.
- Intensities estimated visually (intensities marked with * are enhanced by marcasite overlap).
- Indexed with $a=6.75 \text{ \AA}$, $b=12.00 \text{ \AA}$, $c=6.38 \text{ \AA}$ on a C-centered orthorhombic cell; space-group choices are C_{2mm} , $C222$, C_{2m2} , C_{2m2} (Belova et al. 1978a); C_{2mm} is also possible.

unambiguous indexing was possible. The resultant cell parameters (Table 2; a 6.75(1), b 12.00(1), c 6.38(1) Å, V 516.78 Å³) are in general agreement with those derived by Muto *et al.* (1959) and Belova *et al.* (1978a).

COMPOSITION

The problems of separating a mineral of this grain size (1-2 μm) from its ore have been outlined in some detail by Muto *et al.* (1959). Tedious procedures of separation by these workers resulted in a concentrate that was only 60-70% ningyoite. The present authors could do no better than this, and wet chemical analysis was therefore considered to be unreliable. By using a selective acid leach to take up most of the ningyoite from its concentrate, Muto *et al.* (1959) were able to propose a chemical formula for ningyoite represented by $\text{Ca}_{1-x}\text{U}_{1-x}\text{RE}_{2x}(\text{PO}_4)_2 \cdot 1-2\text{H}_2\text{O}$, where x varies from 0.1 to 0.2. The distribution of rare-earth elements in ningyoite from Japan best corresponds to the apatite type described by Goldschmidt & Thomasson (in Muto 1962); total concentrations in the order of 2 to 5% of REE have been recorded (Muto 1962).

Examination of material from the Tyee, Blizzard and Ningyô-Tôgé deposits was carried out by electron microprobe and scanning electron microscope using an energy-dispersion spectrometer. Polished sections were used for Tyee and Ningyô-Tôgé material in both the microprobe and SEM; grain mounts were used for Blizzard material in the SEM.

Energy-dispersion spectra for ningyoite from the Tyee and Ningyô-Tôgé deposits invariably show the presence of Fe and S (Fig. 6). This

TABLE 2. CELL PARAMETERS OF NINGYOITE

	This Study	Muto et al. (1959)	Belova et al. (1978a)
Symmetry	Orthorhombic	Orthorhombic	Orthorhombic
Space Group Choices	Cmm, C222 Cmm2, Cm2m C2mm	P222	Cmm, C222, Cmm2, Cm2m, C2mm
a (Å)	6.75(1)	6.78(3)	6.77
b (Å)	12.00(1)	12.10(5)	12.10
c (Å)	6.38(1)	6.38(3)	6.37
$a:b:c$	0.563:1:0.532	0.560:1:0.527	0.559:1:0.526
V (Å ³)	516.78	523.40	521.82
Z	3	3	3

appears to be due to the presence of finely occluded marcasite that has been incompletely replaced by ningyoite. X-ray-diffraction powder patterns of ningyoite from Tye show the presence of marcasite (see footnotes, Table 1). Belova *et al.* (1978b) have described a ferruginous variety of ningyoite from deposits in the U.S.S.R. The Fe supposedly replaces Ca in the structure, but concentration levels are not given and the calculated unit-cell parameters do not differ from those of nonferruginous ningyoite. Energy-dispersion spectra of ningyoite

from the Blizzard deposit, which contains only minor amounts of pyrite and marcasite, do not display peaks for Fe and S (Fig. 6c).

The presence of rare earths in Japanese ningyoite was confirmed by the occurrence of Ce peaks in the spectra of some ningyoite aggregates (Fig. 6b, d). However, the distribution of Ce is very erratic; it commonly occurs with Ti, but not Ce, also appears in the spectra of some ningyoite specimens from Tye. An unidentified Ti-bearing phase associated with ningyoite, marcasite and clays was found in a

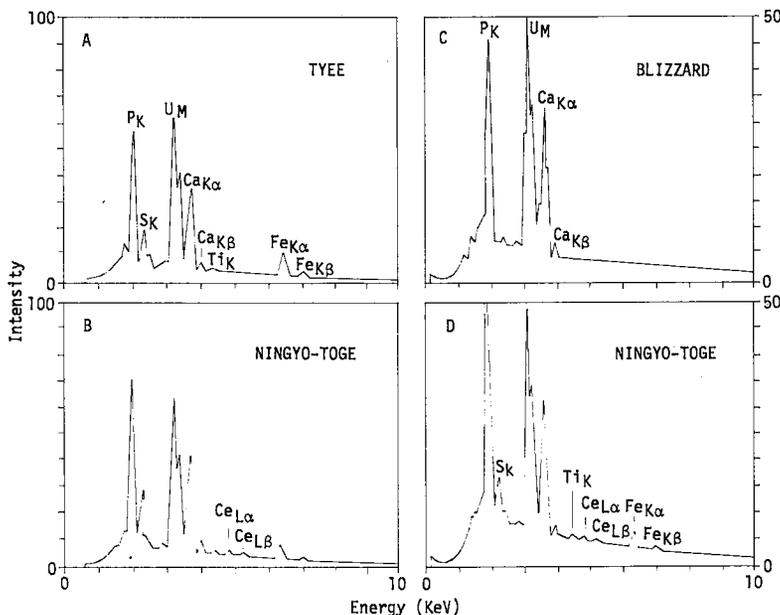


FIG. 6. X-ray energy-dispersion spectra for ningyoite. A. Tye deposit, British Columbia. B. Ningyô-Tôgê mine, Japan. C. Blizzard deposit, British Columbia. D. Ningyô-Tôgê mine, Japan. A and B were obtained using a microprobe, C and D using a scanning electron microscope (spectra acquired for 100 seconds in each case).

few locations in the Tye ore during microprobe examinations, and detrital ilmenorutile has been identified by powder XRD in poorly mineralized samples from this deposit. It would appear that Ti in the spectra for Tye ningyoite is due to the presence of a Ti-bearing mineral, possibly ilmenorutile, in the same way that Fe and S are due to finely occluded marcasite. Blizzard ningyoite, which in some places does not form intergrowths with other minerals (Fig. 4), contains only the elements Ca, U and P (Fig. 6c).

Because of the foregoing observations, it is probable that the rare earths reported in Japanese ningyoite are also due to the presence of an incompletely replaced mineral in a finely divided state. This mineral is probably apatite, as stated by Muto (1961, 1962). Comparison of energy-dispersion spectra (Fig. 6) indicates that Japanese ningyoite contains more P and Ca relative to U than British Columbia ningyoite. Inclusions of apatite in the Japanese ningyoite would contribute Ca and P as well as Ce to the spectrum.

The authors propose that rare earths and Fe are not essential constituents of ningyoite and that the formula may be written as $\text{Ca}_{2-x}\text{U}_x(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$, where $x \leq 1$.

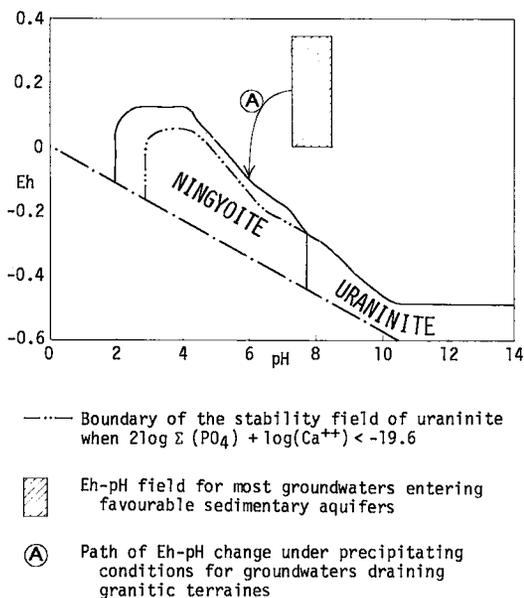


FIG. 7. Eh-pH diagram showing the stability fields of ningyoite; $(\text{Ca}^{2+}) = 10^{-8}$, $(\Sigma\text{PO}_4) = 10^{-7}$, $(\Sigma\text{U}) = 10^{-6}$ (from Kajitani 1970).

PARAGENESIS

The conditions under which ningyoite may form are still not clearly understood. At present it is one of three uranium (4+) minerals that constitute economic concentrations of uranium in sandstone-type deposits, the other two being uraninite and coffinite.

A considerable amount of information on the origin of ningyoite can be gleaned from its relationships with other minerals and from its habitat within the host sediments. Ningyoite is present only in sediments where a sufficient quantity of reducing agents such as pyrite, marcasite and organic matter occur. Its deposition, however, spans a wide range of reducing conditions under which uraninite or coffinite also may form. In the Tye deposit, ningyoite occurs in sediments containing as much as 45% marcasite and 4% organic carbon. In the Blizzard deposit, the mineral occurs in organic-matter-rich sandy mudstones or at limonitized sandstone-mudstone interfaces where the oxidation of pyrite to limonite and the partial humification of organic matter are sufficient to precipitate the mineral.

The availability of phosphorus plays a key role in the formation of ningyoite, although opinions differ as to the origin of the phosphate. Muto (1961, 1962) stated that ningyoite is formed by the replacement of detrital apatite in fluvial sediments because (1) apatite is present in less-uraniferous ore but is rarely found in high-grade ores and (2) the rare-earth distribution in ningyoite resembles that of apatite. Similarly, Katayama (in Muto 1962) suggested that replacement of detrital apatite is the principal mode of ningyoite formation, because uranium concentrations decrease with strontium and yttrium almost linearly, and apatite is not detected in the ores. Kajitani (1970), on the other hand, postulated that the phosphate is of organic origin, having been remobilized from Neogene lake and bog deposits and reprecipitated in fluvial sediments as ningyoite.

Present-day groundwaters draining the intrusive rocks that underlie the mineralized areas in British Columbia contain U concentrations generally in excess of 10 ppb (Boyle & Ballantyne 1980) and also exhibit abnormally high concentrations of phosphate (80 to 2,000 ppb; unpubl. data). This feature, and the fact that ningyoite deposits appear to form only in fluvial paleochannels overlying granitic basement complexes, suggest that most of the phosphate is introduced together with uranium by groundwater infiltration. In addition, the high concen-

trations of phosphate in these deposits are more than can be accounted for by the simple replacement of apatite. We would agree that, under the conditions of precipitation observed, the small amounts of detrital apatite that may have been present might have contributed to the formation of ningyoite, but this would be only a minor source of phosphate. The absence of rare earths in ningyoite from British Columbia and the fact that we have not seen ningyoite replacing apatite would mitigate against a detrital origin for phosphate.

The relative stability fields of ningyoite and uraninite in situations where $(Ca^{2+}) = 10^{-3}$, $(\Sigma PO_4) = 10^{-7}$ and $(\Sigma U) = 10^{-6}$ are shown in Figure 7. The stability field of ningyoite over the pH range of 3 to 7.8 is replaced by that of uraninite in cases where $2 \log \Sigma(PO_4) + \log(Ca^{2+}) < -19.6$ (Kajitani 1970). Because of the increased solubility of phosphate compounds in alkaline solutions (Muto 1965), ningyoite is not stable in alkaline reducing environments with pH greater than 7.8. The Eh-pH path taken by groundwaters during their evolution within favorable host sediments is, therefore, as important as the availability of phosphate. Groundwaters draining granitic terranes are generally neutral to weakly alkaline and have low buffering capacities. It is reasonable to assume that optimum conditions for the formation of ningyoite are attained where weakly alkaline groundwaters, leaching granitic basement complexes and containing high concentrations of U and PO_4 , infiltrate pyritiferous, organic-matter-rich sediments. Ningyoite may form after marcasite in highly reducing sediments rich in humic acids (e.g., the Tyee deposit, Fig. 3), or when slightly oxidizing groundwater conditions, favoring the formation of uranyl minerals like saléite, yield to more reducing conditions as a result of 1) the oxidation of pyrite to limonite and 2) the decomposition of vegetable matter (e.g., the Blizzard deposit, Fig. 5). Acid conditions are suggested by the oxidation of pyrite to limonite (Blizzard deposit) and the presence of humic acids in both the British Columbia and Japanese ningyoite deposits. Muto (1965) has shown that ningyoite is a low-temperature mineral that will not stably precipitate at temperatures much above 25°C.

ACKNOWLEDGEMENTS

The authors thank Mr. D.A. Walker for assisting in the scanning-electron-microscopy studies and Dr. A.G. Plant for assisting in the electron-microprobe studies. Samples of ningyoite from

Japan were kindly supplied by Dr. R.I. Gait of the Royal Ontario Museum. Drill cores from the Blizzard and Tyee deposits were kindly supplied by Norcen Energy Resources and Tyee Lake Resources, respectively. We also thank Dr. R.W. Boyle and Dr. A.G. Plant for reviewing the manuscript.

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Received September 1980, revised manuscript accepted January 1981.