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 saléite. The mineral forms in pyritiferous organic-rich fluvial sediments (Tyee 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) Å, b 12.00(1) Å, c 6.38(1) Å, V 516.78 Å³, Z = 3; aspect of diffraction 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_{x-1}U_x(PO_4)_2·nH_2O, where x ≤ 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, saléite, uranium, phosphorus, groundwaters, Blizzard deposit, Tyee deposit, British Columbia.

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 Tyee basal-type uranium deposits in south-central British Columbia (Fig. 1) have shown that this mineral is the only uranium-bearing mineral in the Tyee 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 Ningyo-Tôge area, Tottori Prefecture, Japan (Muto et al. 1959), where it occurs as acicular or elongated lozenge-shaped crystals that form aggregates in voids or surrounding 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,
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, saléite, 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 saléite 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 (backscattered 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 saléite (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
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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.

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 Caₙ₋ₓ(U₀.₅₋ₓREₓ)(PO₄)ₓ·1–2H₂O, 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 Ningyō-Tōge deposits was carried out by electron microprobe and scanning electron microscope using an energy-dispersion spectrometer. Polished sections were used for Tyee and Ningyō-Tōge 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 Ningyō-Tōge deposits invariably show the presence of Fe and S (Fig. 6). This
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 Tyee 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. Ti, but not Ce, also appears in the spectra of some ningyoite specimens from Tyee. An unidentified Ti-bearing phase associated with ningyoite, marcasite and clays was found in a

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**Fig. 6.** X-ray energy-dispersion spectra for ningyoite. A. Tyee deposit, British Columbia. B. Ningyō-Tōgē mine, Japan. C. Blizzard deposit, British Columbia. D. Ningyō-Tōgē 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 Tyee ore during micro-probe 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 Tyee 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 \( \text{Ca}_{x-n} \text{U}_x (\text{PO}_4)_n \cdot n\text{H}_2\text{O} \), where \( x \leq 1 \).

**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 Tyee 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 & Ballyntyne 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 \((\text{Ca}^{2+}) = 10^{-3}, (\Sigma \text{PO}_4) = 10^{-7}\) 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 \(2 \log (\Sigma \text{PO}_4) + \log (\text{Ca}^{2+}) < -19.6\) (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 salée, 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.

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