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OCCURRENCE OF EPIGENETIC PHOSPHATE MINERALS IN A PHOSPHATIC IRON-FORMATION, YUKON TERRITORY

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ABSTRACT

A phosphatic iron-formation in the Richardson Mountains, Yukon, shows evidence of an unusual postdepositional history that led to the development of a spectacular suite of phosphate minerals. Four major epigenetic fracture-filling mineral associations were formed, each categorized by the persistent occurrence or dominance of one or two characteristic elements in one or more minerals. Each association is related to a particular host rock: Ca-rich association with phosphate mudstone, Ba-rich with conglomeratic slump deposits, Fe–Mg-rich with siderite sandstone, and Na-bearing with phosphate sandstone. Simple mineral associations (three minerals or fewer) are related to particular host rocks or represent local accumulations of a restricted number of elements. The phosphate mineralization in the Big Fish River and Boundary Creek areas is largely confined to recrystallized spherulitic replacements of ammonites and pelecypods and oblate concretionary phosphate nodules. The minerals in both comprise pyrite, wolfeite, satterlyite, maricite, vivianite–baricite, varulite, and their alteration products.

Keywords: phosphatic iron-formation, phosphate minerals, paragenesis, Yukon Territory, epigenetic mineralization.

SOMMAIRE

Les roches d'une formation de fer phosphatée située dans les montagnes Richardson (territoire du Yukon) ont évolué d'une façon assez particulière après leur dépôt, ce qui a mené au développement d'une suite spectaculaire de minéraux phosphatés. On observe quatre associations importantes de minéraux épigénétiques comme remplissage de fractures; dans chacune, on trouve un ou deux éléments chimiques caractéristiques dans au moins une espèce minérale. De plus, chaque association se relie à un type de roche encaissante, comme suit: association riche en calcium: mudstone phosphaté; association riche en baryum: dépôts d'effondement conglomératiques; association riche en Fe + Mg: grès sidéritique; association sodique: grès phosphaté. Les associations minérales simples, de trois minéraux ou moins, se relient à une lithologie particulière ou représentent l'accumulation locale d'un nombre restreint d'éléments. Dans les régions de la rivière Big Fish et du crique Boundary, la minéralisation phosphatée est surtout présente en recristallisations sphérolitiques d'ammonites et de pélécypodes, et en concrétions sous forme de nodules aplatis. Dans les deux cas, on trouve pyrite, wolféite, satterlyite, maricite, vivianite–baricite, varulite, ainsi que leurs produits d'altération.

(Traduit par la Rédaction)

Mots-clés: formation de fer phosphatée, minéraux phosphatés, paragénèse, territoire du Yukon.

INTRODUCTION

Rocks of the Rapid Creek Formation (unofficial name, used informally) are located in the northern Richardson Mountains, Yukon Territory. This sequence has aroused great interest among mineralogists in recent years because it contains a spectacular development of phosphate minerals. Attention was first drawn to this area when Campbell (1962) identified lazulite, a hydrous, magnesium, iron, aluminum phosphate, in samples recovered by B. Cameron from the bed of Blow River near the mouth of Rapid Creek (Fig. 1).

Regional geological mapping carried out by Young (1972) revealed the existence of an extensive iron-formation in the region. In the process of staking claims for Welcome North Mines, several macroscopic, well-crystallized phosphates were noted by A. Kulan, leader of the field party. Kulan was joined by members of the staff of the Royal Ontario Museum, who helped with the identification of the minerals found there. Since then, J. A. Mandarino and B. D. Sturman have identified seven new mineral species. As well as new minerals, a number of other rare phosphates occur in the area in exceptionally well-crystallized forms.

Until now, no effort had been made to correlate the mineral occurrence of the area with its geological setting. Robertson (1980) at-

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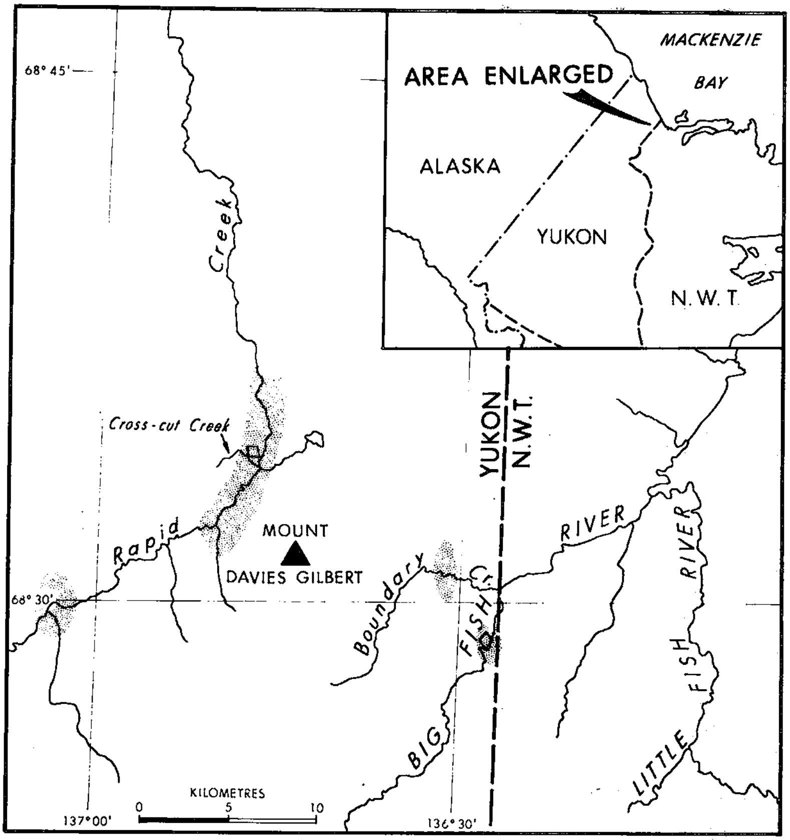

FIG. 1. Location map; the stippled areas indicate localities where phosphate minerals and rock exposures are best developed. The location of measured sections illustrated in Figure 2 are indicated with a diamond symbol.

tempted to provide an understanding of the stratigraphy and petrography of the newly named Rapid Creek Formation that contains these rare minerals (unpubl. data). This paper describes the mineral occurrence and its relationship to the stratigraphy. A detailed description of the sedimentology and petrography of the Rapid Creek Formation is presently in progress.

GEOLOGICAL SETTING

The Rapid Creek Formation (Fig. 2) is lowermost Albian (upper Lower Cretaceous) in age and consists of highly phosphatic ironstones deposited on the flank of the penecontemporaneous Cache Creek High. Age-equivalent strata include an unnamed thick sequence of flysch in the adjacent Blow Trough to the west and the Arctic Red Formation to the east. Albian rocks are missing owing to erosion in the south and are deeply buried to the north.

Rapid Creek strata were deposited in a shallow marine environment without current activity, probably just below storm-wave base. Fluctuations in sea level, tectonic instability, or a progradational sediment system caused the formation of coarsening-upward sequences that were capped by conglomeratic slump deposits in the lower part of the formation in the Rapid Creek area. The upper part of the section is a monotonous sequence of shale, mudstone and minor sand lenses; the sequence represents relatively stable conditions. In the Big Fish River and Boundary Creek areas, differential deposition of autochthonous minerals produced gradational mudstone–shale couplets.

The rocks of the Rapid Creek Formation are texturally similar to other Phanerozoic phosphate and iron deposits. They are broadly categorized as shale, mudstone, siltstone and sandstone and are composed of four basic components: pellets and granules, detrital quartz grains, skeletal fragments, and siderite mud

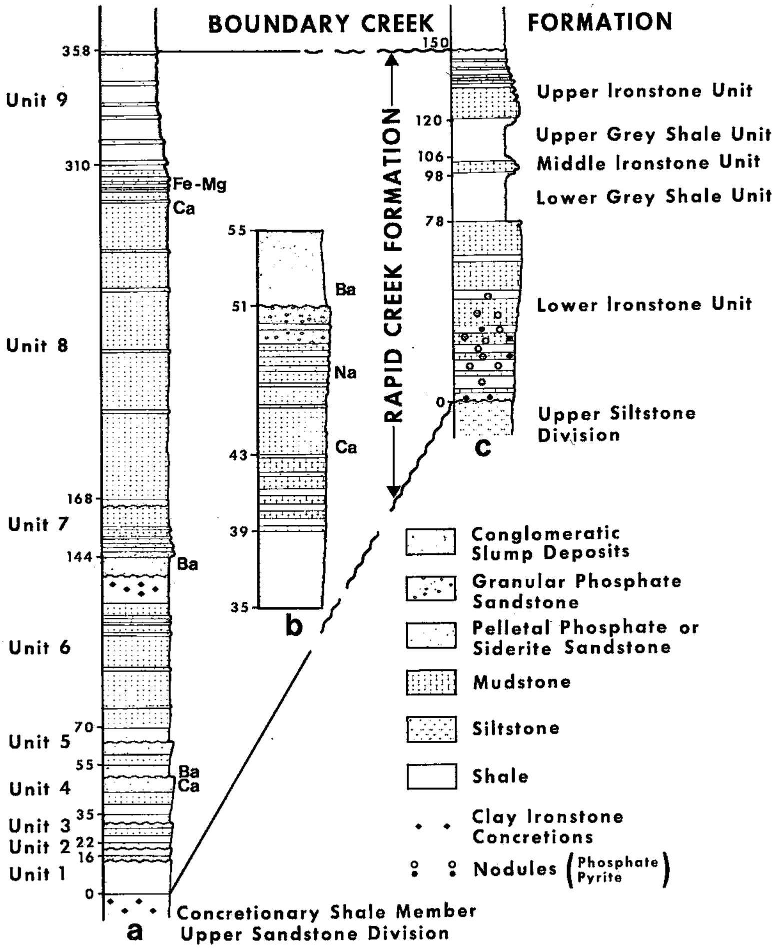

FIG. 2. Measured sections of the Rapid Creek Formation. Section A was measured along Cross-cut Creek (see Fig. 1) and demonstrates the relationship of each of the four major epigenetic-mineral associations to rock type (see Table 1 for association designations). Section B is the thickest and best-developed coarsening-upward sequence in the Cross-cut Creek section. Much of the material for which this locality is noted was mined by A. Kulan from this unit. Section C was measured along Big Fish River. Major amounts of nodular phosphate minerals occur only in the lower 40 m of the lower ironstone unit (section thicknesses are in metres).

matrix. Mixed phosphate–siderite pellets, granules, and matrix constitute a grain-size spectrum from sandstone to mudstone and account for the major part of the formation. The rocks were originally composed of detrital quartz, clay minerals, autochthonous siderite, pyrite, a mixed Ca–Fe–Mg phosphate of uncertain identity or apatite and an unidentified Fe–Mg phosphate. Metamorphism altered the phosphate mineral(s) and remobilized the siderite. In the nonpelletal phosphate mudstone, the primary Ca–Fe–Mg phosphate altered to carbonate-apatite, which occurs with siderite as pseudomorphs (after gypsum?) in star-shaped concretionary bodies. In the coarser-grained rocks, the primary Ca–Fe–Mg phosphate altered to satterlyite, which later altered to arrojadite. Gormanite–souzalite was a common alteration mineral (or replacement) in both fine- and coarse-grained rocks.

MINERAL ASSOCIATIONS

Phosphates also occur in coarsely crystalline segregations; these are most commonly epigenetic fracture fillings (veins) but also include vugs, concentrations along bedding-plane partings, fillings in fault breccias, and isolated nodules. The various phosphate minerals in this area, their compositions and characteristic associations are outlined in Table 1. Nodules (Fig. 3) are restricted to the Big Fish River and Boundary Creek areas and are described separately. In the Rapid Creek area, veins are abundant and divisible into two groups: simple and complex.

Simple veins

Simple veins contain only one or two phosphate minerals and are relatively small (less than 2 m long and 5 cm wide). The occurrence of some simple veins is restricted to a specific rock type whereas others occurs in a number of rock types. Most simple veins have no preferred orientation relative to bedding.

Almost all bedding planes between phosphatic beds have some vivianite–barićite and metavivianite mineralization along them. In many places, this mineralization is up to 3 mm thick and laterally continuous up to 5 m. Where vivianite–barićite is present, it is usually highly altered to a yellow, friable mass, whereas metavivianite retains its deep green color even where intensely altered. This mineralization accounts for most of the color on outcrop surfaces.

TABLE 1. MINERALS, COMPOSITIONS, AND CHARACTERISTIC ASSOCIATIONS

Mineral	Composition	Characteristic Associations[1]
Apatite	$Ca_5(PO_4)_3(OH,F,Cl)$	Ca
Arrojadite	$K(Na,Ca)_5(Fe,Mn,Mg)_{14}Al(PO_4)_{12}(OH)$	Fe-Mg, N
Augelite	$Al_2PO_4(OH)_3$	U
Barićite[2,3]	$(Mg,Fe,Mn)_3(PO_4)_2 \cdot 8H_2O$	U, N, Na, Fe-Mg, Ca
Brazilianite	$NaAl_3(PO_4)_2(OH)_4$	Na, Ba
Carbonate-apatite[4]	$Ca_5(PO_4,CO_3)_3(OH,F)$	N, U
Childrenite	$(Fe,Mn,Ca)AlPO_4(OH) \cdot H_2O$	U, Ca, Fe-Mg
Collinsite[5]	$Ca_2(Mg,Fe,Mn)(PO_4)_2 \cdot 2H_2O$	Ca, Fe-Mg
Destinezite	$Fe^{3+}{}_2PO_4SO_4(OH) \cdot 5H_2O$	U
Dypingite	$Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$	Surface Alteration
Gorceixite	$BaAl_3(PO_4)_2(OH)_5 \cdot H_2O$ (?)	Ba
Gordonite	$MgAl_2(PO_4)_2(OH)_2 \cdot 8H_2O$	U
Gormanite[6,7]	$(Fe,Mg,Mn,Ca)_3(Al,Fe^{3+})_4(PO_4)_4(OH)_6 \cdot 2H_2O$	Fe-Mg, U
Kryzhanovskite	$(Fe,Mg,Mn,Ca)(Fe^{3+}Al)_2(PO_4)_2(OH)_2 \cdot H_2O$	Fe-Mg
Kulanite[8,9]	$Ba(Fe,Mg,Mn,Ca)_2(Al,Fe^{3+})_2(PO_4)_3(OH)_3$	Ba
Lazulite	$(Mg,Fe,Mn)Al_2(PO_4)_2(OH)_2$	Na, Ca, Ba, Fe-Mg
Ludlamite	$(Fe,Mg,Mn)_3(PO_4)_2 \cdot 4H_2O$	Fe-Mg, U
Marićite[10]	$NaFePO_4$	N
Messelite[11]	$Ca_2(Fe,Mg,Mn)(PO_4)_2 \cdot 2H_2O$	Ca, Fe-Mg
Metavivianite	$Fe_3(PO_4)_2 \cdot 8H_2O$	U, Na, Fe-Mg, N
Nahpoite[12]	Na_2HPO_4	N
Nesquehonite	$MgCO_3 \cdot 3H_2O$	Surface Alteration
Penikisite[13,14]	$Ba(Mg,Fe,Ca)_2Al_2(PO_4)_3(OH)_3$	Ba
Satterlyite[15]	$(Fe,Mg,Fe^{3+},H,Na,Mn)_2PO_4(OH)$	N
Souzalite[16]	$(Mg,Fe,Mn)_3Al_4(PO_4)_4(OH)_6 \cdot 2H_2O$	Fe-Mg, U
Varulite	$(Na,Ca)(Mn,Fe)_2(PO_4)_2$	N
Vivianite[17]	$(Fe,Mg,Mn,Ca)_3(PO_4)_2 \cdot 8H_2O$	U, N, Na, Fe-Mg, Ca
Wardite	$NaAl_3(PO_4)_2(OH)_4 \cdot 2H_2O$	U, Na, Ba
Whiteite	$Ca(Fe,Mn)Mg_2Al_2(PO_4)_4(OH)_2 \cdot 8H_2O$	Ca
Wicksite[18]	$NaCa_2(Fe,Mn)_4MgFe^{3+}(PO_4)_6 \cdot 2H_2O$	N
Wolfeite	$(Fe,Mn,Mg)_2PO_4(OH)$	N

[1] N = nodules; U = alone; Na = Sodium-bearing association; Ca = Calcium-rich association; Ba = Barium-rich association; Fe-Mg = Iron-magnesium-rich association; [2] Sturman & Mandarino (1976); [3] solid solution series with vivianite; [4] Dahlite, the hydroxyl-bearing member of the carbonate-apatite group, is probably the mineral present in this area, but possitive identification was not made, thus the group name has been used; [5] solid solution series with messelite; [6] Sturman *et al.* (1981a); [7] solid solution series with souzalite; [8] Mandarino & Sturman (1976); [9] solid solution series with penikisite; [10] Sturman *et al.* (1977); [11] solid solution series with collinsite; [12] Coleman & Robertson (1981); [13] Mandarino *et al.* (1977); [14] solid solution series with kulanite; [15] Mandarino *et al.* (1978); [16] solid solution series with gormanite; [17] solid solution series with barićite; [18] Sturman *et al.* (1981b). NOTE: Iron without superscript is Fe^{2+}.

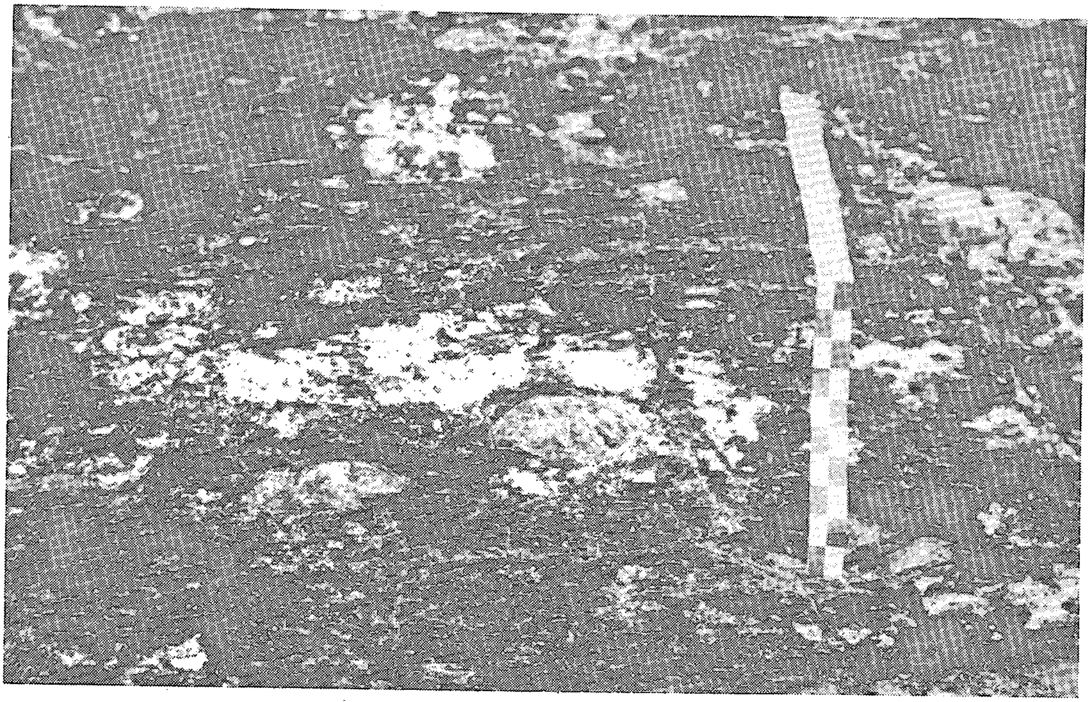

FIG. 3. Phosphate nodules in the Big Fish River area are abundant in parts of the section, as shown here, but are more easily obtained from talus slopes rather than 'plucking' them from outcrop (scale bar is divided in centimetres). The white patches in this photograph show where dypingite has formed as an encrustation.

Only two samples containing carbonate-apatite have been observed by the writer. Carbonate-apatite is the sole macroscopic mineral present and occurs as a botryoidal crust, lining cavities in a solution breccia. Since both samples were found in talus, the association of this mineral with rock type is not known. Gypsum is relatively uncommon and occurs as a late-stage mineral in fractures that were probably generated by near-surface weathering. These veins have been found cutting all rock types but are generally more abundant in nonphosphatic shale and mudstone.

Augelite-bearing veins are found associated with faults and either line the walls of solution cavities or fault breccias or are superimposed on other veins that have been transected by faults. Augelite crystals generally decrease in size away from the fault zones, which indicates their genetic relationship with faults. Childrenite, wardite and gormanite–souzalite are the most common minerals in simple veins. Childrenite veins are smaller than the other two, being less than 1 mm wide, whereas wardite veins are usually more than 3 mm wide. Gormanite–souzalite veins are intermediate in size.

In the Big Fish River area, asbestiform ludlamite occurs along bedding-plane partings. Occasionally, fibres of ludlamite are curved into an S form, which indicates slippage along the bedding plane during mineralization. Arrojadite associated with vivianite–baricite and quartz constitutes the majority of the few veins present in the Big Fish River area. Any of the three components can dominate the vein or occur by itself; however, vivianite–baricite generally is scarce, and arrojadite is more common than quartz. Quartz crystals in these veins are characteristically terminated by a single pyramid.

Complex veins

Most complex veins contain more than two phosphate minerals. As these veins are all perpendicular to bedding, vertical, and strike 100°, it appears that they are related to the same vein-forming event. The veins are up to 40 cm wide and 10 m long, and transect more than one bed and rock type; thus, they have no obvious association with any single rock-type. However, they usually occur in parts of the section that are dominated by one rock type. This accounts for the four chemical associations possessed by the minerals found in complex veins: Ca-rich (occurring with phosphatic mudstone), Na-bearing (with phosphate sandstone), Fe–Mg-rich (with siderite sandstone-dominated portions of the section), and Ba-rich (with conglomeratic slump deposits).

Mineral associations in complex veins are characterized by the dominance of one or two elements that are represented by one or more minerals. Minerals in the following descriptions are listed in what is considered to be an approximate paragenetic sequence based on observations of cross-cutting relationships. In many places, surface alteration has produced goethite or limonite pseudomorphs after siderite. All of the following associations can be found with a coating of dypingite or nesquehonite, which are also products of weathering, and thus excluded from the lists of minerals.

THE CALCIUM-RICH ASSOCIATIONS

Two calcium-rich associations are recognized: 1. quartz ± siderite ± lazulite ± apatite, and 2. quartz ± siderite ± lazulite ± whiteite ± collinsite–messelite ± childrenite ± vivianite–barićite. Of these two, the first is by far the most common association; it is generally found totally enclosed in phosphatic (either pelletal or nonpelletal) mudstone, which is both the source and the host rock. The abundance of these mudstones in the Rapid Creek area makes this association very common. In these veins, any of the four minerals can exist alone or dominate over the other three, but most contain equal proportions of quartz and siderite, slightly larger quantities of lazulite and very little apatite.

The second association, which is not as common, is related to phosphatic mudstone, has a more complex mineralogy, and does not appear to be represented by any one typical mineral-assemblage. All combinations of those minerals listed above are found, and examples have been noted in the field where several veins occur side by side, have the same general size, and yet contain radically different assemblages. One vein may contain whiteite and lazulite, a second whiteite and vivianite–barićite, and another only whiteite. The only generalization concerning these veins is that collinsite–messelite is a very minor component; it is well developed in only one place. Although it is rare, childrenite in this association is distinct from that found in the simple veins in that it is always cream-colored (a microprobe analysis indicates compositions similar to that of other childrenite samples).

SODIUM-BEARING ASSOCIATION

The sodium-bearing association, the second most common association, is characterized by quartz ± brazilianite ± lazulite ± siderite ± apatite ± wardite ± metavivianite. Whereas assemblages of the calcium-rich association commonly contain a high proportion of the calcium-rich mineral phase (whiteite, apatite or collinsite–messelite), this association rarely has more than a scattering of crystals of the sodium-rich phase (either brazilianite or wardite). Quartz and lazulite usually dominate in these veins. Apatite and metavivianite occur only rarely in patches.

Sodium-bearing associations occur most commonly in the pelletal phosphate sandstone-dominated section of strata. Because the length of the vein is generally greater than the thickness of a single bed, there must be some contribution to the bulk chemistry of the vein from other rock types.

IRON–MAGNESIUM-RICH ASSOCIATION

The iron–magnesium-rich association is the most variable of all. This is partly due to its complex mineralogy; quartz ± siderite ± arrojadite ± lazulite ± kryshanovskite ± gormanite–souzalite ± collinsite–messelite ± ludlamite ± vivianite–barićite ± metavivianite ± childrenite. In this association, lazulite and collinsite–messelite are very rare constituents; gormanite–souzalite is not common but, where present, is abundant relative to the other minerals. As in the calcium-rich association, no typical assemblage was observed by the writer. In general, one of the minerals arrojadite, kryzhanovskite or ludlamite dominates over all other minerals in a vein. Veins containing only arrojadite are quite common.

This association is found in strata dominated by siderite-rich phosphate and siderite sandstone in the upper portion of the section measured at Cross-cut Creek and in stratigraphically equivalent rocks on the east side of Rapid Creek.

BARIUM-RICH ASSOCIATIONS

The barium-rich association is relatively rare in the area. Two types are recognized on the basis of the barium-containing mineral present: 1. quartz ± siderite ± lazulite ± gorceixite ± aragonite, and 2. quartz ± apatite ± siderite

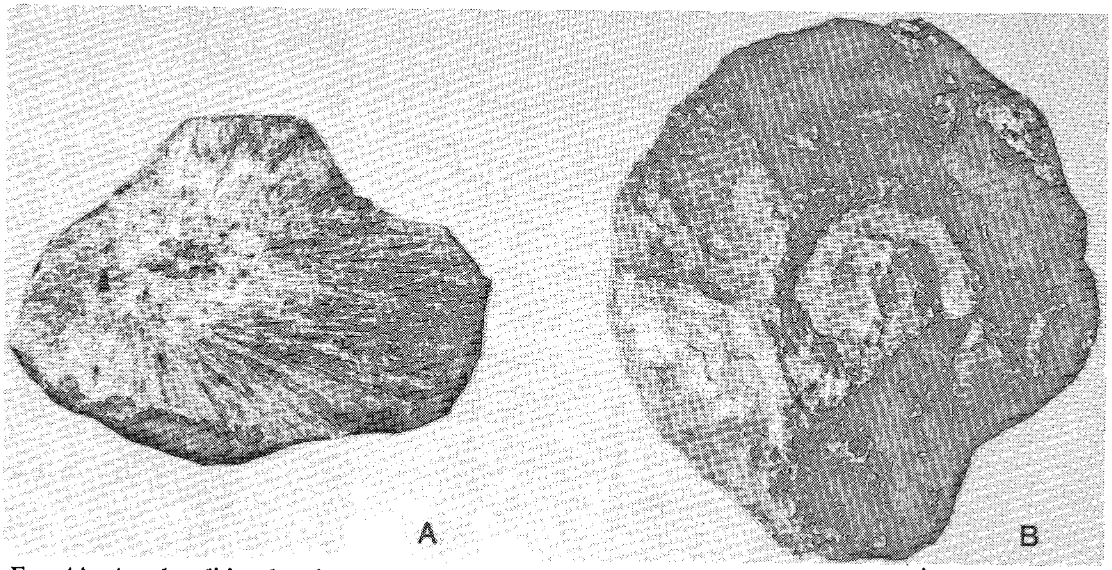

FIG. 4A. A spherulitic phosphate nodule (8 cm wide). This one is almost pure marićite with a quartz core. B. This unusual phosphate nodule (10 cm wide) strongly resembles an ammonite.

± lazulite ± kulanite–penikisite ± brazilianite ± wardite. Only two occurrences of the first association were observed, one in the conglomeratic slump deposit at the top of unit 4 in the measured section at Cross-cut Creek and the other within a brecciated fault-zone in another area, where only siderite and rare gorceixite crystals were observed.

In the first association, any of the first four minerals can dominate portions of the vein, and aragonite occurs in small spherulitic arrays atop quartz crystals. A similar association has been observed by H. G. Ansell (pers. comm. 1979) in the upper reaches of Rapid Creek. However, this association contains goyazite, a strontium aluminum phosphate related to gorceixite.

The second barium-rich association also is uncommon but generally occurs in conglomeratic slump deposits. Lazulite and apatite are usually not major constituents; brazilianite and wardite are also relatively scarce and are mutually exclusive. One occurrence of this association has been observed in pelletal phosphate sandstone beds immediately below a slump deposit. In it, lazulite is relatively abundant.

OCCURRENCES OF NODULES

Nodular phosphate segregations are restricted to the Big Fish River and Boundary Creek areas. In these areas, only the lower ironstone unit (Fig. 2) contains significant quantities of macroscopic phosphate minerals, which occur mainly in spherulitic nodules (Fig. 4a). There are three distinct types of nodules: 1) those that resemble ammonites or pelecypods in outline and show remnant ribs or costae (Fig. 4b), 2) those that resemble ammonites in outline only (Fig. 5a), and 3) those that bear no resemblance to ammonites or pelecypods (Figs. 5b, 5c). All types, where found *in situ,* show lamination of shale mudstone draped over the edges of the nodules.

Although the first type of nodule is very rare, sixteen specimens were submitted to J. A. Jeletzky for identification and confirmed as recrystallized replacements of ammonites and, more rarely, pelecypods. Nodules of the second type are most abundant in the Big Fish River area and have a peculiar raised three-armed stellate structure on one or, more commonly, both sides. On several specimens found *in situ,* the stellate pattern was observed on the basal side only. The third type of nodule is most abundant in the Boundary Creek area. A fourth type of nodule occurs only in the basal five metres of the Big Fish River measured section. Nodules of this type are irregular, lumpy and composed wholly of microcrystalline pyrite. A 4-cm-thick mudstone bed 73 m above the base of the lower ironstone in the measured section contains small (5–10 mm) structureless nolules composed of carbonate-apatite.

Despite external differences, the phosphate nodules of types 1, 2 and 3 are mineralogically

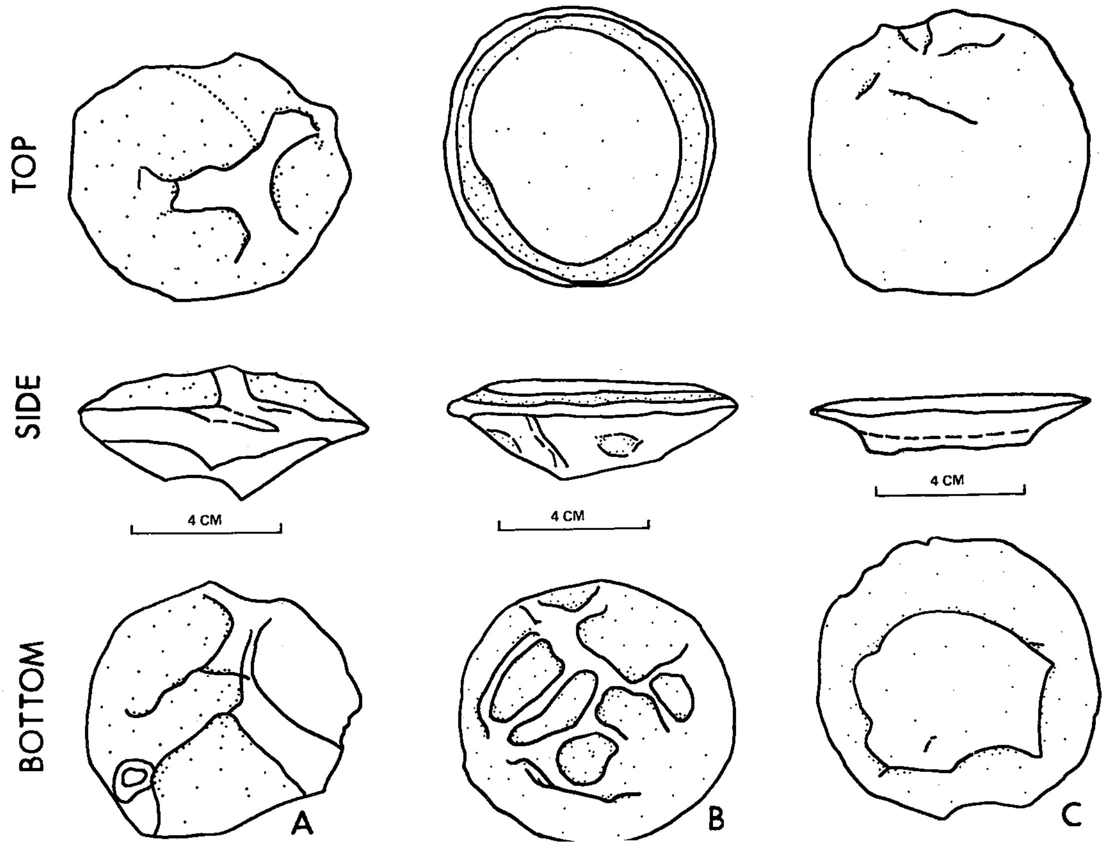

FIG. 5. Three common types of phosphate nodules. A is convex-convex in cross section and displays a peculiar three-armed stellate pattern of slightly raised ridges on both top and bottom. These ridges are not ribs or costae but rather correspond to the apex of the radiating bladed crystals in some of these nodules. B is plano-convex, having a featureless top and irregularly patterned bottom. C is plano-plano and featureless on top. The bottom of this specimen is partially obscured by adhering shale but is probably also smooth. The orientation of these specimens, although found in talus, is extrapolated from similar ones observed *in situ*.

similar. Many are monomineralic, but some contain a variety of minerals. Dominant minerals in these nodules include pyrite, wolfeite, satterlyite, marićite, vivianite–barićite and varulite; these are in part altered to ludlamite, metavivianite, carbonate-apatite, secondary pyrite and secondary vivianite–barićite. Quartz is a rare constituent. Nahpoite, a new mineral (Coleman & Robertson 1981), was found as a fine, white encrustation in fractures in marićite and is presumably an alteration of that mineral.

A brief study of the distribution of nodules was carried out to discover if any regularity exists in nodule mineralogy within single beds or from bed to bed. Unfortunately, many nodule interiors are too weathered to allow positive mineral identifications. In the Big Fish River area, many of them have been plucked from the outcrop surface by previous collectors. For these reasons, the results of this study are not definitive.

The procedure followed was to count the number of nodules of each mineral present along a single bed, usually 0.5 to 1 m thick, as far as it could be traced or reached and then, to move 2 to 3 m up the section and repeat the procedure. The results indicate that there is no significant difference in the mineralogical compositions of nodules in shale and in mudstone. The overall abundance is about the same in both types of rock and varies almost randomly in the section as a whole. Pyrite nodules dominate the lowermost portion of the section, but give way to phosphate nodules as

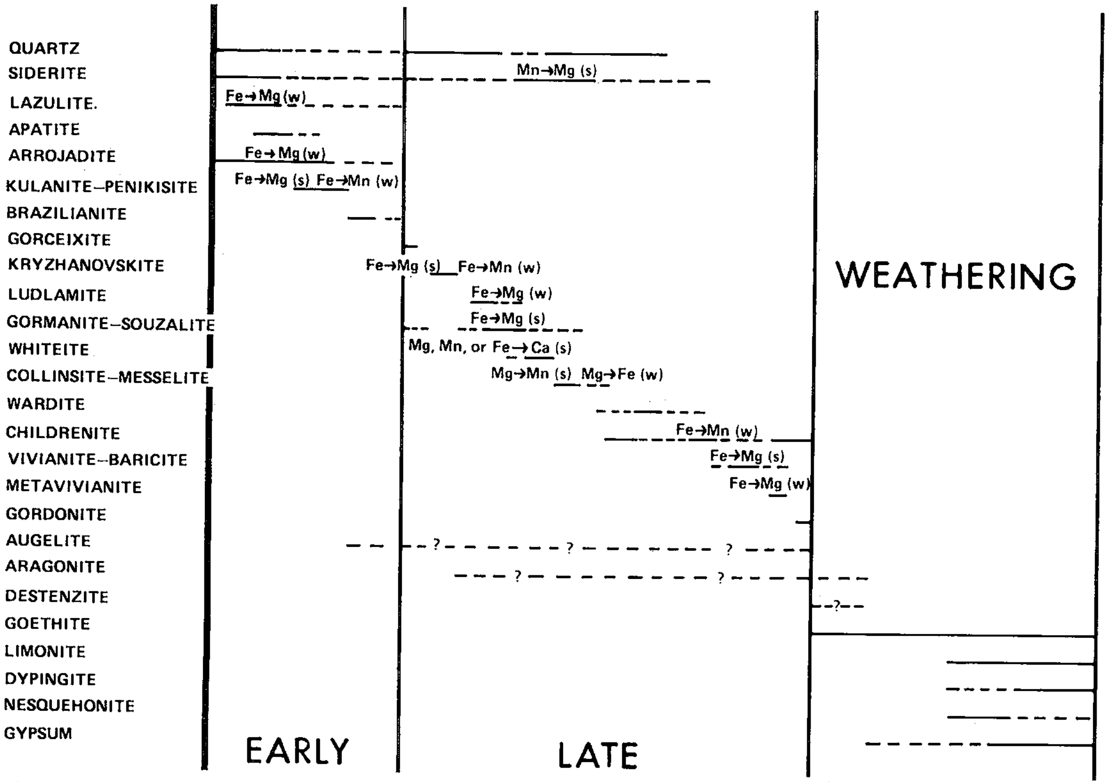

FIG. 6. A paragenetic sequence for vein minerals found in the Rapid Creek and Big Fish River areas. Elemental zoning, shown from centre to exterior, was determined by electron-microprobe analysis and is a summary of many determinations. Complete data are given in Robertson (1980).

one goes up the section to about 50 m from its base, where the nodules become less and less abundant until they are nonexistent 20 m further up. In the portion of the Big Fish River section studied in detail, wolfeite occurs in 1:1 to 2:1 ratios with pyrite, 20:1 with satterlyite and 30:1 with maricite. Vivianite–baricite nodules were not observed *in situ*.

At Boundary Creek, nodules consisting mostly of wolfeite make up 90% of the total. Pyrite nodules are fairly rare (1 in 20), and satterlyite nodules are almost as rare (1 in 10). Maricite and vivianite–baricite nodules were not observed *in situ* in this area.

DISCUSSION

A crude paragenetic sequence, based on cross-cutting relationships, was developed for all vein-phosphate mineral associations for both the Rapid Creek and Big Fish River areas (Fig. 6). Almost all mineralization occurs as undisrupted open-space fillings. This indicates that the mineralization is epigenetic and formed after the formation of the open fractures. Inverse spherulitic bundles in certain areas indicate that veins may have been widened during or after initiation of mineral precipitation. A high proportion of void space in many veins indicates that the mineralizing solutions were exhausted before the veins were completely filled.

Despite the common Fe-to-Mg zoning (Fig. 6), the paragenetic sequence overall is contrary to the normal pattern of mineral zonation. This is displayed particularly well by the kryzhanovskite–ludlamite–vivianite–metavivianite series, in which the individual minerals are Mg-rich, Fe-rich, Mg-rich, and Fe-rich, respectively, whereas each is zoned from Fe to Mg. Mn appears to act independently, being either enriched or depleted outward in different minerals. The pattern probably is related to local variation in the element's abundance.

The paragenetic sequence of vein minerals in this deposit is similar to the sequence for pegmatite phosphates developed by Moore (1973). Most of the minerals in Moore's sequence formed above 200°C, and several above 500°C.

There is no direct evidence of a high-temperature origin for the mineralization in the Rapid Creek Formation. The thickness of Upper Cretaceous and Tertiary strata in this area overlying the iron formation is approximately 2300 m (Young 1975), which would produce a temperature of 96°C with a geothermal gradient of 33°/km and a surface temperature of 20°C. Preliminary results from an investigation of the oxygen isotope geochemistry of vein siderite and quartz indicate that the temperature of formation was about 50°C. This suggests that the phosphate minerals of the Rapid Creek Formation, although more commonly found in higher-temperature circumstances, may also originate at quite low temperatures.

Definite mineral associations occur with specific host-rock types. This strongly suggests that the host rocks are also the source for the vein mineralization, but the exact nature of this relationship is masked by the fact that most veins intersect more than one rock type. The calcium-rich association occurs with pelletal and nonpelletal phosphate mudstones in which the dominant phosphate phase is carbonate-apatite. This phase probably contributed both Ca and P to the veins. Other elements might have been supplied by the solution or alteration of quartz, siderite and clay minerals. The sodium-bearing association occurs with phosphate sandstones. The amount of Na_2O in these rocks is not significantly different from other rock types. However, the phosphate sandstones are completely altered to satterlyite. If the alteration of a Na-rich phosphate that was the precursor to satterlyite was concomitant with vein formation, the Na released in the formation of satterlyite could be either transported to a nearby vein or used to crystallize a more Na-rich alteration mineral, such as arrojadite, which is abundant in some phosphate sandstones. This is supported by the observation that arrojadite is more abundant in phosphate sandstones in areas where there is little veining. Other elements were probably derived from the interbedded mudstone.

The iron-magnesium-rich association occurs with siderite sandstones. The abundance of siderite in the rocks accounts for the abundance of Fe-rich minerals in the veins. Sodium was probably supplied to the veins in the same manner as with the sodium-bearing association but, in this case, combined with Fe to form arrojadite rather than the Na–Al phosphates brazilianite and wardite.

The occurrence of barium-rich associations with conglomeratic slump deposits is a mystery. The amount of barium in a siltstone clast that hosts the best-developed barium-rich association is about average and, in fact, much lower than in some other samples. The amount of CO_2 in the mineralizing solution probably determined which mineral, gorceixite or kulanite–penikisite, formed in veins exhibiting the Ba-rich association. In kulanite–penikisite-bearing veins, CO_2 was probably used up in the formation of siderite, and excess Fe was left over to form the Ba–Fe phosphate. In gorceixite-bearing veins, Fe was used up in the formation of siderite. Excess CO_2 contributed to aragonite formation after the precipitation of an Fe-free Ba phosphate.

Veins showing a simple association probably represent isolated late-stage formation, where mineralogy is largely dependent on the selective leaching of host rocks or on local accumulations of only a few elements. An effort to determine which elements have been leached from at least one host-rock type (a bed of nonpelletal phosphate mudstone between two veins of the calcium-rich association), and to what extent, was inconclusive, suggesting that the primary lateral variation in composition of the bed was greater than any change induced by preferential leaching of elements used in forming the vein minerals.

The dominance of ferrous iron in these veins indicates reducing conditions during mineralization. Abundant ferric iron is present in only one mineral, kryzhanovskite. Although this mineral usually forms *via* the oxidation of phosphoferrite $(Fe^{2+},Mn)_3(PO_4)_2{\cdot}3H_2O$ (Moore 1971, 1973), B.D. Sturman (pers. comm. 1980) believes that it is a primary mineral in this deposit, which would indicate at least one short period of oxidation during mineralization.

The occurrence of the hydrated magnesium carbonates dypingite and nesquehonite is unusual because they are normally found in caves (Langmuir 1965) or as weathering products of serpentinite (Raade 1970). Their occurrence in this deposit is probably related to simultaneous weathering of siderite and vivianite–baricite. When siderite alters to goethite or limonite, it releases CO_2; the weathering of Mg-rich vivianite–baricite results in the crystallization of an Fe-rich yellowish compound, a process that releases Mg. Thus the progressive evaporation of the weathering solutions on an outcrop could produce nesquehonite and dypingite.

Microscopic examination of thin sections of phosphate nodules shows that the paragenetic sequence between constituent minerals is complex. Simply, the sequence of mineral formation is as follows: satterlyite, wolfeite, marićite, varulite, arrojadite, ludlamite, vivianite–barićite, metavivianite, goethite. Steps in this sequence are omitted in many samples. Examples of wolfeite altering directly to goethite or of satterlyite altering to vivianite–barićite have been noted; the position of carbonate-apatite in this series could not be determined.

Phosphate minerals were replaced paragenetically by quartz, pyrite and siderite. Quartz grains often contain tiny euhedral apatite crystals and occur near the centre of the phosphate nodules. This type of replacement, along with siderite replacement, was uncommon, but many nodules contain large euhedral crystals of pyrite. Pyrite nodules other than those at the base of the Big Fish River section are believed to be completely replaced phosphate nodules because several of these contain rare grains of satterlyite or vivianite–barićite.

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REFERENCES

CAMPBELL, F.A. (1962): Lazulite from Yukon, Canada. *Amer. Mineral.* **47**, 157-160.

COLEMAN, L.C. & ROBERTSON, B.T. (1981): Nahpoite, Na_2HPO_4, a new mineral from the Big Fish River area, Yukon Territory. *Can. Mineral.* **19**, 373-376.

LANGMUIR, D. (1965): Stability of carbonates in the system $MgO–CO_2–H_2O$. *J. Geol.* **73**, 730-754.

MANDARINO, J.A. & STURMAN, B.D. (1976): Kulanite, a new barium iron aluminum phosphate from the Yukon Territory, Canada. *Can. Mineral.* **14**, 127-131.

———, ——— & CORLETT, M.I. (1977): Penikisite, the magnesium analogue of kulanite, from Yukon Territory. *Can. Mineral.* **15**, 393-395.

———, ——— & ——— (1978): Satterlyite, a new hydroxyl-bearing ferrous phosphate from the Big Fish River area, Yukon Territory. *Can. Mineral.* **16**, 411-413.

MOORE, P.B. (1971): The $Fe^{2+}{}_3(H_2O)_n(PO_4)_2$ homologous series: crystal–chemical relationships and oxidized equivalents. *Amer. Mineral.* **56**, 1-17.

——— (1973): Pegmatite phosphates: descriptive mineralogy and crystal chemistry. *Mineral. Record* **4**, 103-130.

RAADE, G. (1970): Dypingite, a new hydrous basic carbonate of magnesium, from Norway. *Amer. Mineral.* **55**, 1457-1465.

ROBERTSON, B.T. (1980): *Stratigraphic Setting of some New and Rare Phosphate Minerals in the Yukon Territory.* M.Sc. thesis, Univ. Saskatchewan, Saskatoon, Sask.

STURMAN, B.D. & MANDARINO, J.A. (1976): Barićite, the magnesium analogue of vivianite, from Yukon Territory, Canada. *Can. Mineral.* **14**, 403-406.

———, ——— & CORLETT, M.I. (1977): Marićite, a sodium iron phosphate, from the Big Fish River area, Yukon Territory, Canada. *Can. Mineral.* **15**, 396-398.

———, MANDARINO, J.A., MROSE, M.E. & DUNN, P.J. (1981a): Gormanite, $Fe^{2+}{}_3Al_4(PO_4)_4(OH)_6 \cdot 2H_2O$, the ferrous analogue of souzalite, and new data for souzalite. *Can. Mineral.* **19**, 381-387.

———, PEACOR, D.R. & DUNN, P.J. (1981b): Wicksite, a new mineral from northeastern Yukon Territory. *Can. Mineral.* **19**, 377-380.

YOUNG, F.G. (1972): Cretaceous stratigraphy between Blow and Fish Rivers, Yukon Territory. *Geol. Surv. Can. Pap.* **72-1A**, 229-235.

——— (1975): Upper Cretaceous stratigraphy, Yukon Coastal Plain and northwestern Mackenzie Delta. *Geol. Surv. Can. Bull.* **249**.

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