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FORMATION OF A JAROSITE DEPOSIT ON CRETACEOUS SHALES IN THE FORT NORMAN AREA, NORTHWEST TERRITORIES*

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ABSTRACT

A 5800+ m^3 deposit composed primarily of jarosite, 54 km northeast of Fort Norman, N.W.T., is being precipitated as a yellow ochre from an acidic (pH 2.9), iron-bearing groundwater seep. Subsequent weathering of the surficial crust results in alteration of the jarosite to goethite and gypsum. The groundwater chemistry is attained through dissolution of dolomite followed by Ca + Mg for Na + K cation exchange, sulfide oxidation and gypsum precipitation during subsequent migration through a Cretaceous shale unit.

Keywords: jarosite, groundwater, pyrite oxidation, cation exchange, Great Bear Lake, N.W.T.

SOMMAIRE

Un gisement de plus de 5800 m^3, composé surtout de jarosite, est en train de se former par précipitation sous forme d'ocre jaune à partir d'une exsudation d'eau acidique (pH 2.9) ferrifère, 54 km au nord-est de Fort Norman, Territoires du Nord-Ouest. Un lessivage de la croûte en surface transforme la jarosite en goethite + gypse. Le chimisme de l'eau évolue par dissolution de la dolomite, suivie d'un échange cationique de Ca+Mg pour Na+K, oxydation des sulfures et précipitation du gypse au cours de sa migration à travers d'une unité de shale Crétacé.

(Traduit par la Rédaction)

Mots-clés: jarosite, eau sous-terraine, oxydation de pyrite, échange cationique, Grand Lac de l'Ours, Territoires du Nord-Ouest.

INTRODUCTION

The jarosite group of hydrous iron sulfate minerals commonly occurs as crusts or coatings related to oxidation of sulfide minerals. Brophy & Sheridan (1965) have listed reports on the occurrence of the various jarosite minerals in a number of different geological environments. One of the most common associations, other than with ore deposits, appears to be with the oxidation of pyrite and especially pyritiferous shales. A large number of investigations into the formation of jarosite by the oxidation of pyrite have been summarized by van Breemen (1973). He found that natrojarosite, the sodium member, forms only after depletion of all available potassium and, therefore, is rarer than the jarosite end-member.

Yorath & Cook (1981) have reported on the formation of jarosite due to the combustion of bituminous pyrite-bearing shale in the Smoking Hills Formation east of the Mackenzie Delta. Ross & Ivarson (1981) suggested that natrojarosite is generally more abundant than jarosite in the acidic sulfate soils of western and northern Canada. The occurrence of natrojarosite in polar regions has also been reported by Vennum (1980) and by Foscolos & Kodama (1981). In most instances, the jarosite group of minerals occurs as yellow mottles or stains within acidic sulfate soils, and is due to *in situ* weathering of exposed sulfides. This paper describes a major accumulation of jarosite, referred to informally as the Golden Deposit, precipitated from a groundwater seep in the Northwest Territories.

DESCRIPTION OF THE SITE

The Golden Deposit, located 54 km northeast of Fort Norman, N.W.T. (latitude 65°11′58″ N, longitude 124°38′15″ W, Figs. 1, 2), consists of a yellow ochre, which is precipitating from a seep of acidic, iron-bearing groundwater. The active area of deposition is 126 metres in length and 46.5 metres in width (Fig. 3a). Probing of the deposit with a metal rod indicates that it is at least 1 metre thick; deeper penetration was impossible owing to permafrost conditions. Groundwater discharges through small holes in the crust of the deposit (Fig. 3b) at a rate of approximately 2 to 3 L/min. Surrounding the area of active deposition is a low muskeg-type vegetation that covers older deposits produced by the same system.

The site is underlain by a thick sequence of pyrite-bearing Cretaceous marine shales (unit 'c' of Yorath & Cook 1981), which was deposited within the Great Bear Basin. Limestones and dolomites of Lower to

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FIG. 1. Location of the Golden Deposit, near Great Bear River, N.W.T.

Middle Devonian and Ordovician age are exposed within the Keele Arch, approximately 12 km west of the deposit.

MINERALOGY OF THE DEPOSIT

Samples of the yellow clay were collected from points of active discharge of groundwater and from the drier crust of the deposit. In addition, crystals encrusted on vegetation surrounding the exposed deposit were sampled. The mineralogy of samples for all three materials is given in Table 1.

Analysis by X-ray diffraction revealed that the yellow ochre collected at points of groundwater discharge contains primarily jarosite (66%) with $a = 7.303(2)$, $c = 17.09(1)$ Å, and a small amount of goethite (9%). Clay minerals carried in suspension comprise the remaining 25%. The crust, which covers most of the deposit (darker portions in Fig. 3), has been altered to goethite, with only minor jarosite remaining. In addition, some gypsum has formed during breakdown of the jarosite. The formation of goethite and gypsum is believed to be due to leaching by rain and snowmelt, such that:

$$KFe_3(SO_4)_2{\cdot}(OH)_6 + 4H_2O + 2Ca^{2+} \rightarrow 3FeOOH + 2\,[CaSO_4{\cdot}2H_2O] + K^+ + 3H^+ \qquad (1)$$

During midsummer, some of the vegetation growing along the perimeter of the exposed deposit was found encrusted in "salts", owing to evapotranspiration of the saline groundwater. Analysis of these "salts" by X-ray diffraction, at the Institute of Sedimentary and Petroleum Geology in Calgary, indicated that they are composed primarily of bloedite $Na_2Mg(SO_4)_2{\cdot}4H_2O$, with smaller concentrations of rozenite $FeSO_4{\cdot}4H_2O$, gypsum, silica and one other mineral. On the basis of X-ray diffraction and X-ray fluorescence data, this other mineral is tentatively reported as variscite $AlPO_4{\cdot}2H_2O$ (J. Wong and A.G. Heinrich, pers. comm.).

GROUNDWATER CHEMISTRY

A sample of the groundwater was collected from one of the discharge points in the middle of the deposit, for major-ion and a partial heavy-metal analysis (Table 2). Field measurements indicate that the groundwater is mineralized and acidic (pH 2.9).

All three major cations (Ca^{2+}, Mg^{2+}, Na^+) are present in significant concentrations, with magnesium dominant, whereas sulfate is the only abundant major anion present (Fig. 4). Potassium is present in low concentrations only. The lack of bicarbonate ions is due to the low pH. A typical recharge water for this area has also been plotted in Figure 4 for comparison. Major variations between the two plots indicate that groundwater discharging at the Golden Deposit has been substantially altered during subsurface flow.

The low concentration of chloride indicates that halite is not the source of the high concentration of sodium. We believe, therefore, that the sodium is derived from shale during cation exchange with calcium and magnesium. During the cation-exchange process, calcium and magnesium in solution would be adsorbed onto the clay-mineral surfaces, whereas sodium (and potassium) would be released into solution from the shale. The chemical data were analyzed using the PHREEQE computer program of Parkhurst *et al.* (1980). From this analysis, the high Mg^{2+}/Ca^{2+} ratio of 3.87 is attributed to calcium depletion due to gypsum saturation and precipitation.

Negative $\delta^{34}S$ values and $\delta^{18}O$ values close to zero (Table 3) indicate that the aqueous sulfate and the precipitated sulfates in the deposit are derived from the oxidation of sulfides rather than marine sulfates, which have $\delta^{34}S$ values between +15.1 and +32.6 ‰, and $\delta^{18}O$ values between +12.0 and +17.1 ‰ in this area (van Everdingen *et al.* 1982). Oxidation of sulfides is also suggested by high concentrations of trace metals in the groundwater relative to most groundwaters studied by Michel (1977) in the central Mackenzie Valley (Table 2). The exceptionally high value for iron suggests that pyrite is the dominant sulfide encountered during subsurface flow.

Yorath & Cook (1981) reported on the widespread existence of pyrite-bearing marine shales of Cretaceous age in the region. The presence of such a unit along the flow system would satisfy the requirements for cation exchange and provide a source of sulfide.

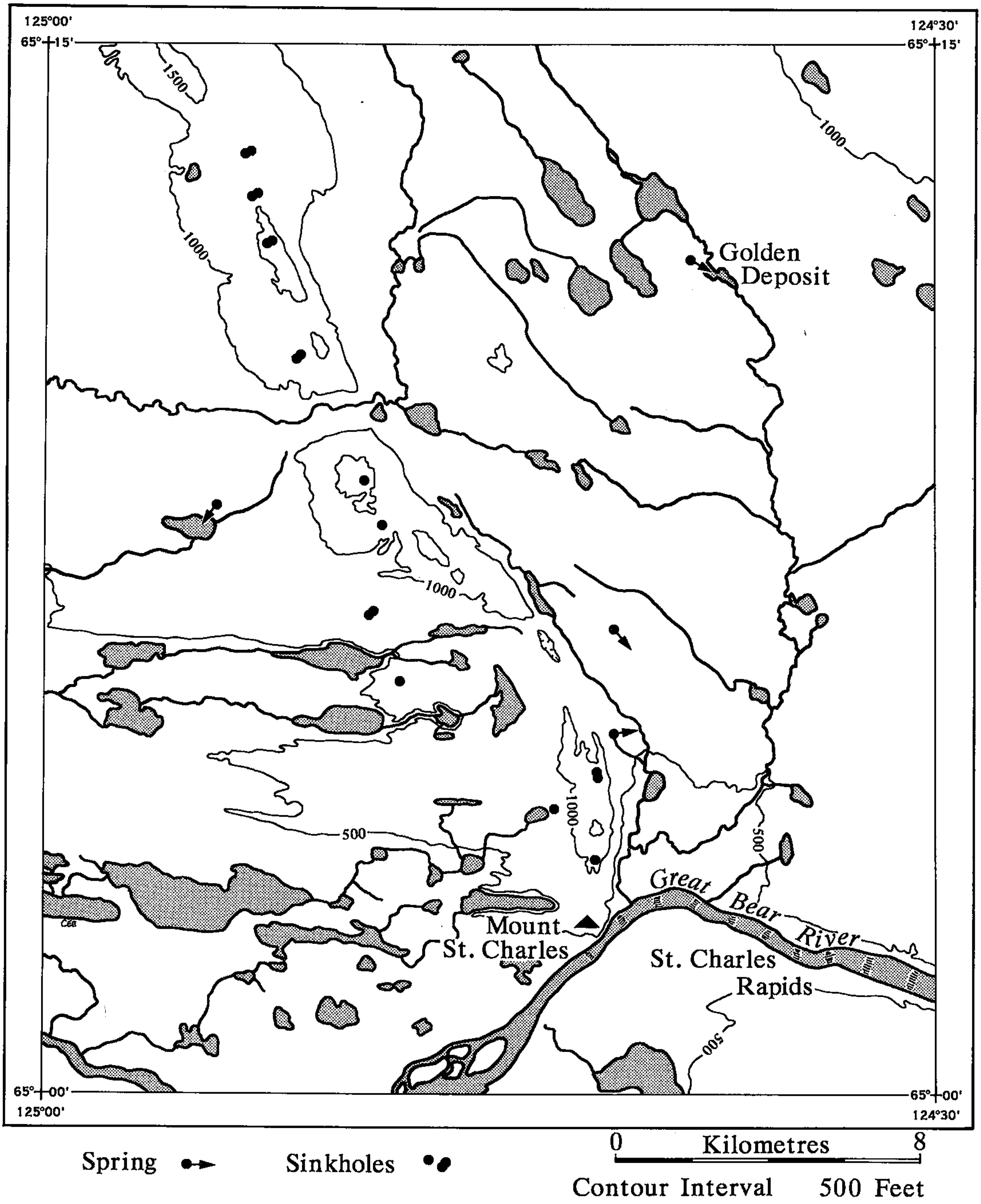

FIG. 2. Topography and location of springs and karst features (modified from van Everdingen 1981; elevation contours in feet).

FORMATION OF THE DEPOSIT

The Golden Deposit represents the accumulation of jarosite (and products of its weathering) precipitated from groundwater discharging at the site. It constitutes the largest concentrated occurrence of a jarosite-group mineral reported to date in Canada. Allen & Day (1935) have also described the deposi-

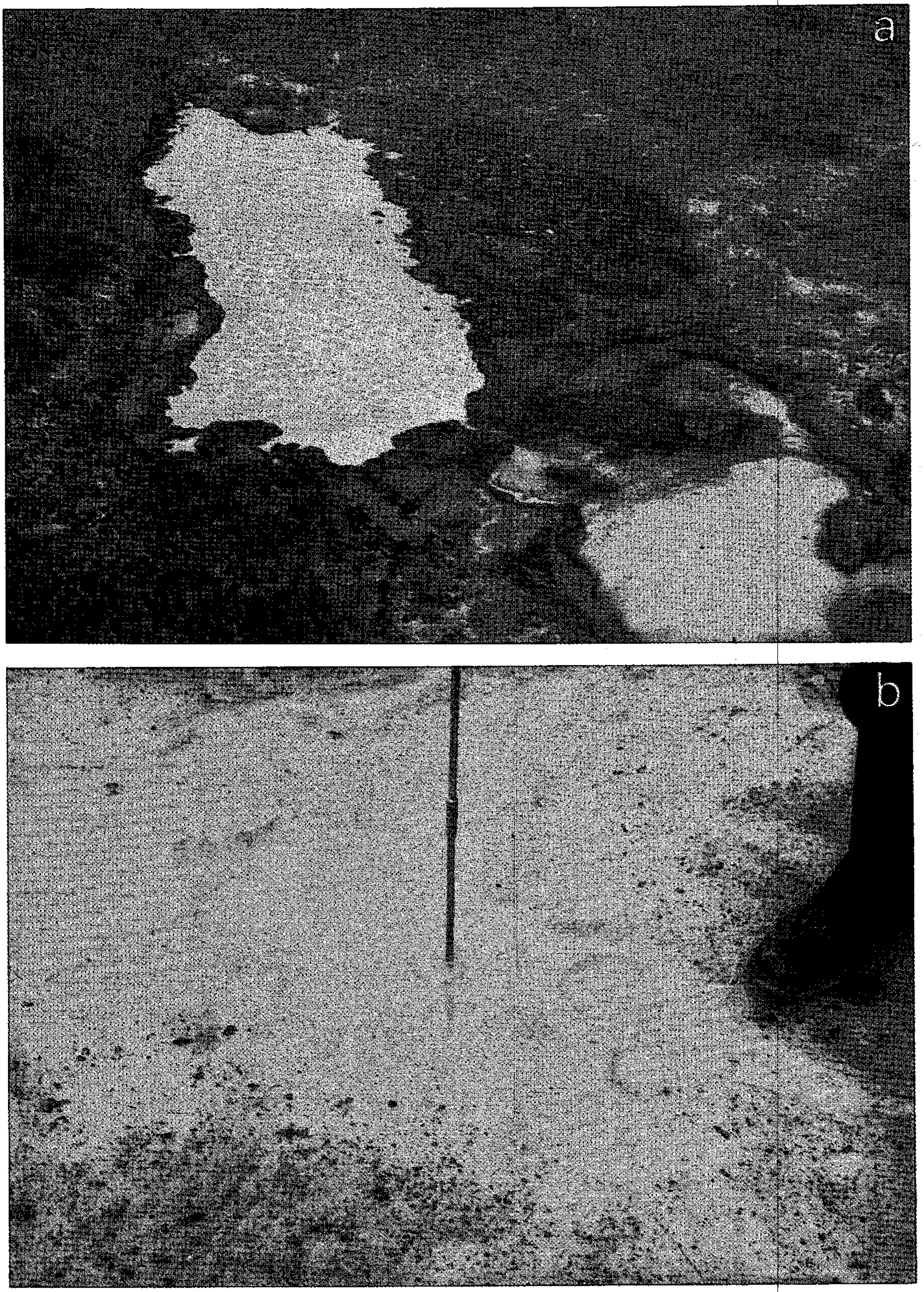

FIG. 3. a. Aerial photograph of the Golden Deposit and adjacent area. Deposit is 126 metres by 46.5 metres. b. Close up of an active discharge-point of groundwater within the Golden Deposit.

tion of jarosite from springs in Yellowstone National Park, Montana (Brophy & Sheridan 1965). Since the Golden Deposit jarosite is a product of dissolved constituents in the groundwater, it is important to examine the flow system and the evolution of the chemistry of the groundwater.

TABLE 1. MINERALOGICAL COMPOSITION OF THE GOLDEN DEPOSIT, N.W.T.

Mineral	Yellow Ochre at Discharge Points	Crust	Crystals on Plant
Jarosite	66	9	-
Goethite	9	56	-
Gypsum	-	8	4
Silicates[1]	25	27	8
Bloedite	-	-	56
Rozenite	-	-	18
Variscite[2]	-	-	14

Proportions in %. X-ray-diffraction analyses obtained at the Institute of Sedimentary and Petroleum Geology, Geological Survey of Canada, Calgary (J. Wong and A.G. Heinrich, analysts). [1] Clay minerals and silica. [2] Inferred; presence supported by results of X-ray-fluorescence scan.

TABLE 2. CHEMICAL COMPOSITION OF GROUNDWATER DISCHARGE AT THE GOLDEN DEPOSIT, NORTHWEST TERRITORIES

Temp (°C)[1]	3.7	Mn	6.5 (0.05)[2]
pH [1]	2.9	Cu	0.03 (0.005)[2]
Eh (mV) [1]	+683	Pb	0.12 (0.005)[2]
Conductivity (uS/cm)[1]	8900	Zn	0.17 (0.05)[2]
		As	0.0005 (0.0005)[2]
Ca	341	HCO_3	0.0
Mg	800	SO_4	5300
Na	500	Cl	24
K	7.0	F	0.15
Fe	220 (1.5)[2]	SiO_2	37

Compositions quoted in mg/L. Analyses performed at the Water Quality Branch, Inland Waters Directorate, Environment Canada, Calgary. [1] Field measurements. [2] Figures in parentheses represent values for approximately 90% of more than 100 analyzed samples of groundwater from the central Mackenzie Valley (data from Michel 1977).

The recharge area for the flow system is believed to be situated approximately 12 km west of the deposit, along a 300-metre-high ridge that trends northwest from Mount St. Charles and the St. Charles Rapids on Great Bear River (Fig. 2). Recharge, into sinkholes developed in dolomitic rocks of the Bear Rock and Franklin Mountain Formations exposed along the ridge, gives the groundwater an initial composition enriched in Ca^{2+}, Mg^{2+} and HCO_3^-. During subsequent flow through pyritiferous Cretaceous shales, cation exchange results in a loss of calcium and magnesium, and an addition of sodium and potassium to the groundwater. Biochemical oxidation of pyrite in the shales leads to high concentrations of iron, sulfate and hydrogen ion in the groundwater. The high concentration of sulfate in turn leads to precipitation of gypsum and a preferential loss of calcium over magnesium.

The oxidation of pyrite can be described by the reaction:

$$4FeS_2 + 10H_2O + 15O_2(aq) \rightarrow 4FeOOH + 8SO_4^{2-} + 16H^+ \qquad (2)$$

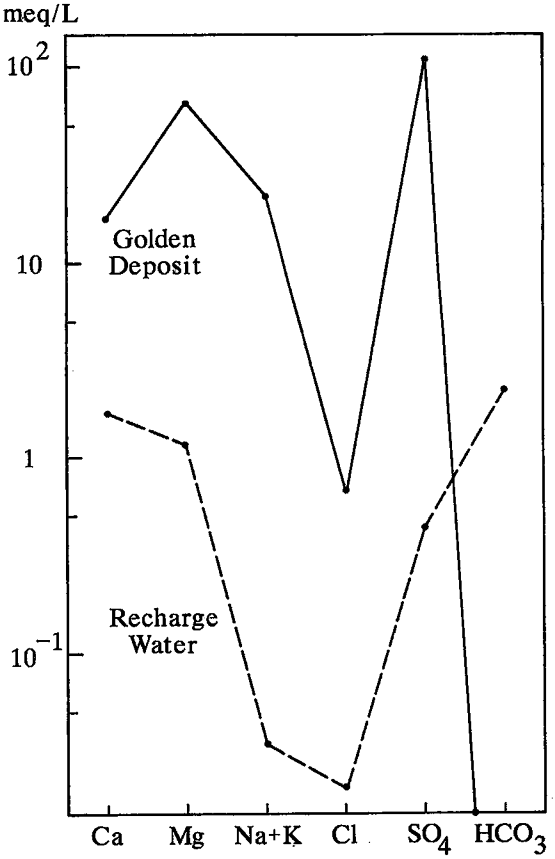

FIG. 4. Semi-log plot showing major-ion data for water samples from the Golden Deposit and a typical recharge water in the area (data from Michel 1977).

TABLE 3. ISOTOPIC DATA FOR SULFATE FROM THE GOLDEN DEPOSIT

Material	$\delta^{34}S$	$\delta^{18}O$
Groundwater	-22.8 ± 0.2°/oo	+0.5 ± 0.2°/oo
Yellow ochre at discharge points	-22.3	+2.4
Crust	-24.9	+4.4
Crystals on plants	-19.1	-0.8

Data from Shakur (1982), except for those on crust (from Stable Isotope Laboratory, Physics Dept. of the University of Calgary. $\delta^{34}S$ and $\delta^{18}O$ quoted with respect to CDT and SMOW, respectively.

(Stumm & Morgan 1970). Van Everdingen *et al.* (1985) have determined that over 50% of the oxygen in the sulfate of the Golden Deposit is derived from water molecules, and that *Thiobacillus ferrooxidans* likely plays a role in the oxidation process. With the development of acidic conditions (increasing $[H^+]$), bicarbonate ions are consumed to form carbonic acid H_2CO_3.

Subsequent combination of liberated iron and sulfate ions with potassium released during cation exchange leads to the production of jarosite. The overall reaction can be expressed as:

$$6FeS_2 + 2CaMg(CO_3)_2 + 4(Na,K)\cdot Clay + 20H_2O + 20O_2 \rightarrow 2KFe_3(SO_4)_2\cdot(OH)_6 + 2(Ca,Mg)\cdot Clay + 4H_2CO_3 + CaSO_4 + 7SO_4^{2-} + 20H^+ + Mg^{2+} + 2Na^+ \quad (3)$$

In addition to the formation of jarosite described in equation (3), small quantities of goethite are precipitated, and the total concentration of dissolved solids in the groundwater increases as the reaction proceeds to the right.

The formation of jarosite has resulted in only low concentrations of potassium being present in the discharging groundwater. This has led to the unusually high Na^+/K^+ ratio of 120.7. Even with the high concentration of sodium in the groundwater, no sodium was detected in the precipitate (analysis by microprobe). This supports the conclusion of van Breemen (1973), who noted that natrojarosite would form only after depletion of all available potassium.

Regardless of the actual iron sulfate mineral formed, it is important to recognize that the Golden Deposit is the result of a concentrated discharge of mineralized groundwater that has encountered a sulfide-bearing horizon during subsurface flow. The recognition and understanding of systems of groundwater flow and their related deposits, especially those that contain substantial concentrations of iron and other heavy metals, could become as important in the exploration of unexposed sulfide deposits as gossans are where the sulfides are exposed to surficial weathering.

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