

Niobium-Thorium-Strontium-Rare Earth Element Mineralogy and Preliminary Sulphur Isotope Geochemistry of the Eaglet Property, East-Central British Columbia (NTS 093A/10W)

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INTRODUCTION

The Eaglet fluorite property (MINFILE 093A 016) is located on the northeastern side of Quesnel Lake in east-central British Columbia in NTS area 093A/10W (Figure 1). The history, exploration activities, geological setting, petrography, mineralogy and estimated resource potential of the property have been previously described in Hora et al. (2008). That study identified several minerals not previously known from this fluorite deposit, including pyrochlore, thorite and rare earth element (REE)-enriched carbonate. In this paper, new data on the chemical composition, alteration and interrelationships of these unusual minerals have been collected. In addition, the sulphur isotope composition of celestite and common sulphide minerals was measured in several samples collected in the study area. Mineralogical and sulphur isotope studies were undertaken in Prague at the Institute of Geology, Academy of Sciences of the Czech Republic, using the methodologies described in Hora et al. (2008), and the Czech Geological Survey, Czech Republic.

NIOBIUM-THORIUM-TITANIUM-RARE EARTH ELEMENT MINERALOGY

Pyrochlore ($(\text{Na}, \text{Ca})_2(\text{Nb}, \text{Ca})_2\text{O}_6(\text{O}, \text{OH}, \text{F})$) is the dominant mineral in this group; it occurs as small ($\sim 50 \mu\text{m}$ in diameter) iso-

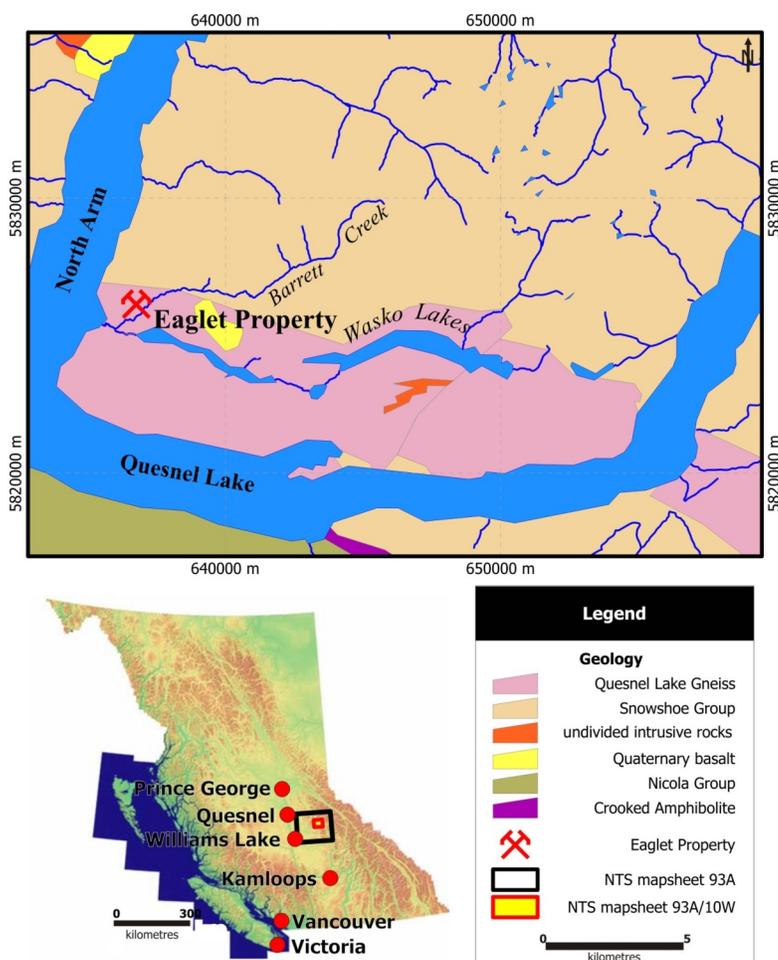


Figure 1. Location of study area, northeastern side of Quesnel Lake, east-central British Columbia.

metric grains, which commonly have partially preserved octahedron crystal habits. Pyrochlore also forms crystal-line aggregates up to $150 \mu\text{m}$ in width; these aggregates are commonly associated with zircon, kaolinite and uraninite in a matrix of K-feldspar. The most abundant elements measured by the electron microprobe are Nb, Ti (Figure 2) and U, which is as expected for pyrochlore. The pyrochlore from the Eaglet property (Table 1) also has relatively high FeO contents (up to 19.22%). Other notable observations include an inverse correlation between calcium and uranium abundances with niobium (Table 1); this is likely the result of alteration intensity (Figures 3a–d). The alteration and partial replacement of pyrochlore is especially well-de-

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veloped along crystal margins; its development imparts a light grey colour to the crystal margins. Uraninite and an unidentified highly hydrated mineral with 59.6% ThO₂ and 10.1% CaO occur as alteration products of pyrochlore. The identification of uraninite as an alteration product of pyrochlore is suggested by the unusual abundance of Nb, Ti, Fe and Ca (Table 1).

A carbonate mineral compound of La, Ce, Gd and Sm, probably bastnaesite ((La, Ce)CO₃F), commonly occurs in association with pyrochlore (Figures 3a–c). Bastnaesite frequently forms minor inclusions in pyrochlore (Figure 3c) and some individual bastnaesite grains range up to 10 µm in length. It is also found in cavities and fractures in other minerals such as pyrite.

Thorite (ThSiO₄) is another common mineral found in this mineral association from the Eaglet property; it occurs as isometric grains typically about 100 µm in diameter.

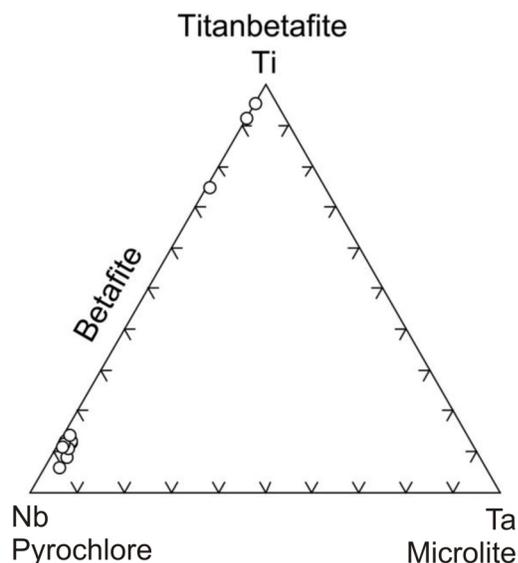


Figure 2. Ternary Ti-Nb-Ta diagram (from Godovikov, 1975) of Eaglet deposit minerals, east-central British Columbia. Points corresponding to titanbetafite were measured within one grain, whereas the cluster of points corresponding to pyrochlore represents 15 measurements in multiple adjacent grains.

Thorogummite ((Th, U)SiO₄(OH)₄; Figure 3f) commonly forms a reaction rim around a central core of thorite.

Titanbetafite, a titaniferous member of the pyrochlore family, is the least common mineral identified in samples examined from the Eaglet property (Figures 2, 3e); it is present as xenomorphic grains, which can reach up to 100 µm in length. The niobium content of titanbetafite is more variable than that of pyrochlore.

In conclusion, the Nb-Th-Ti-REE group of minerals exhibit extensive replacement reactions along their contacts with adjacent silicate minerals and alteration products. This finding suggests that the Nb-Th-Ti-REE group of minerals may represent an early stage of the mineralization process in the deposit.

SULPHUR ISOTOPE GEOCHEMISTRY

The presence of celestite (SrSO₄) has been recognized at the Eaglet property since the deposit's discovery. Although early exploration programs by Eaglet Mines Ltd. did not include analysis for strontium, the systematic inductively coupled plasma–mass spectrometry analytical work conducted later by Freeport Resources Inc. led to the discovery of the widespread distribution of celestite throughout the deposit. Values commonly in excess of 10 000 ppm Sr were reported from drillcore samples (Hora, 2005). A preliminary sulphur isotope study of celestite and several sulphide minerals (pyrite and molybdenite) was undertaken to provide a better understanding of the Eaglet deposit.

Celestite-enriched zones were separated from the samples by a combination of crushing and hand-picking; the samples were then homogenized in an agate mortar, dissolved in diluted HCl and the insoluble residuum filtered off. The dissolved sulphate was then precipitated as BaSO₄ by the addition of a solution of BaCl₂. The BaSO₄ was converted to SO₂ gas following the method outlined in Haur et al. (1973) with modifications described in Yanagisawa and Sakai (1983).

Sulphide minerals were hand-picked from crushed samples and oxidized to SO₂ following the procedure in Grinenko (1962). The sulphur isotope compositions of the prepared SO₂ gas samples were measured using a Finnigan

Table 1. Major-element content of representative minerals of niobium, thorium and uranium, Eaglet prospect, east-central British Columbia.

Oxide (%)	Pyrochlore			Titanbetafite		Thorite		Thorogummite		Uraninite
ThO ₂	0	0.01	0.37	0	0.04	73.73	71.69	66.35	66.18	0.38
TiO ₂	5.65	7.02	9.68	70.71	93.01					0.72
Nb ₂ O ₅	70.79	61.72	56.87	19.67	3.65					4.75
Ta ₂ O ₅	2.17	2.15	0.61	0.69	0.17					0
U ₂ O ₃	1.27	9.57	6.76	0	0	1.9	2.44	1.85	1.71	92.65
MnO	0.77	0	0.15	0.23	0.02					0
FeO	19.22	0.59	3.55	5.23	1.02	0.01	0.3	0.16	1.17	1.28
CaO	0.12	8.25	4.21	0.05	0.02	0.33	0.32	0.65	2.14	0.91
Na ₂ O	0	0.33	0.4	0.06	0.06					0
SiO ₂	0	0	2.58	0.42	0.04	18.33	18.19	17.07	15.07	0
Total	99.99	89.64	85.18	97.06	98.03	94.3	92.94	86.08	86.27	100.69
a.p.	4	5	11	12	13	15	16	17	18	x

Explanation: a.p., analytical points from Figure 2; x, not represented on Figure 2; empty spaces, elements not analyzed.

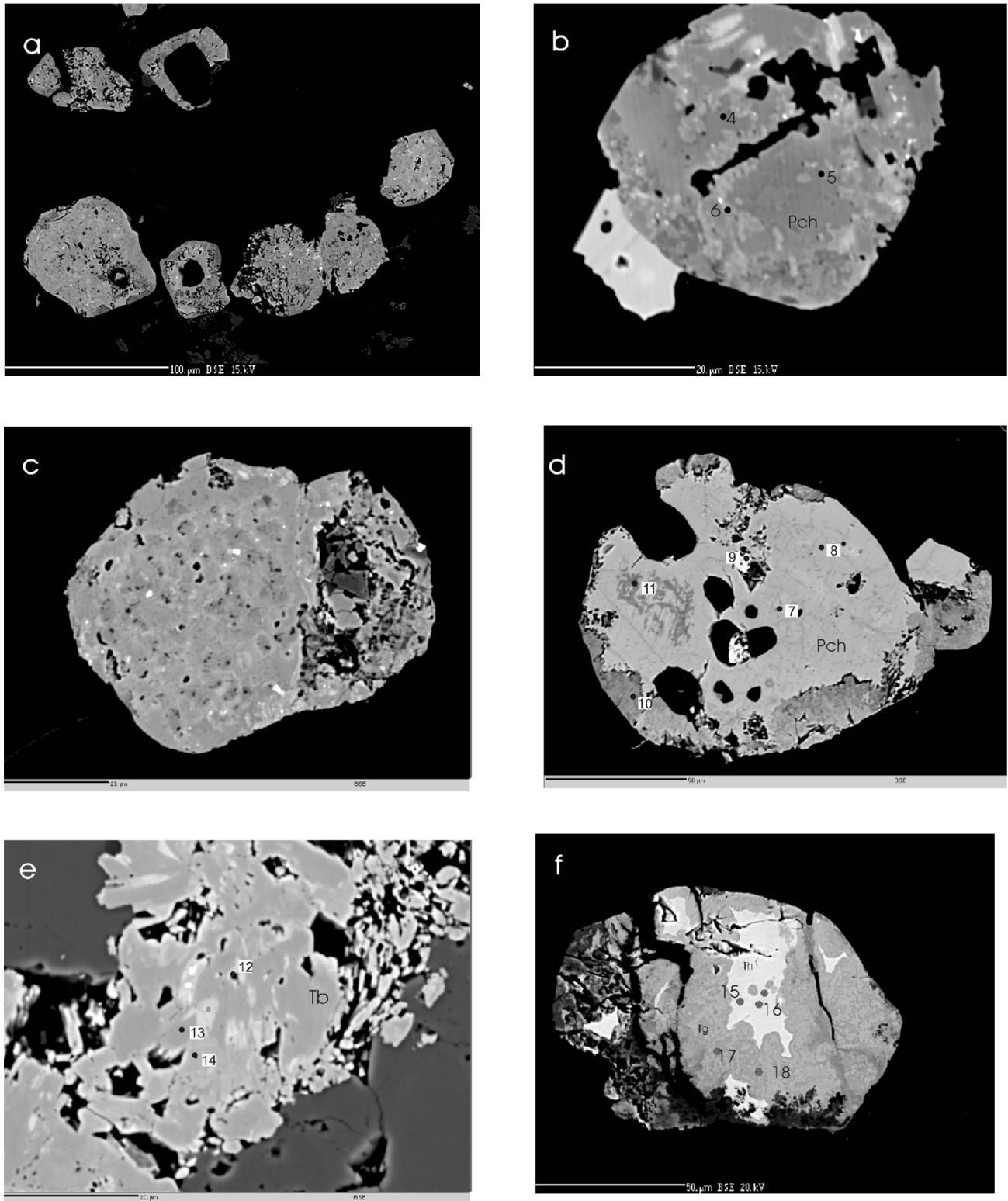


Figure 3. Scanning electron microscope photomicrographs showing **a**) partially replaced pyrochlore (Pch) crystals in host silicates with altered rims (dark shade); white dots are bastnaesite (scale bar 100 μm); **b**) corroded and altered crystal of pyrochlore; large white grain corresponds to bastnaesite; analytical points 4 and 5 (dark field), 6 (pale grey field) (scale bar 20 μm); **c**) typical occurrence of pyrochlore; small white grains correspond to bastnaesite (scale bar 20 μm); **d**) partially replaced pyrochlore rimmed by darker altered zones corresponding to altered pyrochlore; enclosed white grain (analytical point 9) is unidentified hydrated mineral close to thorianite; analytical points 7, 8, 9, 10 and 11 (scale bar 50 μm); **e**) titanbetafite (Tb) with variable contents of niobium; analytical points 12, 13 and 14 (scale bar 20 μm); **f**) thorite (Th) replaced by thorumgummite (Tg); analytical points 15, 16, 17 and 18 (scale bar 50 μm).

Table 2. Sulphur isotope data, Eaglet property, east-central British Columbia.

Sample no.	Mineral composition of the sample	$\delta^{34}\text{S}$ celestite (‰)	$\delta^{34}\text{S}$ sulphide (‰)
QL A-1	celestite, fluorite, quartz	6	
QL A-2	celestite, quartz, fluorite	7.06	
QL A-3	quartz, celestite, fluorite, feldspar	12.91	
QL A-4	celestite, quartz, fluorite, molybdenite	7.12	molybdenite: -4.81
QL A-5	celestite, fluorite, quartz, feldspar	6.87	
QL C-1	calcite, celestite, pyrite	9.86	pyrite: -4.84

MAT 251 mass spectrometer in the laboratories of the Czech Geological Survey, in Prague. Overall uncertainty in analytical measurements of ^{34}S from both sulphate and sulphide minerals is $\pm 0.2\%$. Analyses are reported relative to the Canyon Diablo troilite (CDT) standard.

RESULTS

The sulphur isotope analyses yielded the data presented in Table 2.

DISCUSSION

Measurements of ^{34}S from celestite that range between 6.00 and 12.91‰ (CDT) exclude the possibility of precipitation from metamorphic fluids mobilizing marine evaporites or of hydrothermal mobilization of sulphate minerals from evaporites of marine origin. Throughout the Earth's history, marine evaporites have had sulphate ^{34}S values greater than 10‰ (greater than 25‰ during the Late Proterozoic) and during the Mississippian, the presumed age of the Eaglet prospect host intrusion, ^{34}S values were greater than 20‰ (CDT). Only minor sulphur isotope fractionation is imparted during metamorphism of massive accumulations of evaporitic sulphate minerals or during hydrothermal mobilization of sulphate minerals followed by sulphate precipitation (in the order of a few sulphur isotopes per mil). The only exception is a high-temperature sulphur isotope exchange between sulphide and sulphate minerals, which can significantly alter the isotope composition of both minerals.

The sulphide minerals (pyrite and molybdenite) have ^{34}S values of -4.8‰ (CDT). The difference between the ^{34}S values of sulphide minerals and those of sulphate minerals is ~12–15‰. Isotope fractionation between sulphate and sulphide minerals can be used as a geothermometer (Ohmoto and Rye, 1979); when reduced and oxidized, sulphur minerals reach isotope equilibrium and the sulphide-sulphate fractionation reported here corresponds to temperatures of 450–540°C. More work is required to verify the occurrence of isotope exchange equilibrium in sulphide and sulphate minerals; in the absence of such verification, there are several ways to interpret the data:

the sulphate minerals (e.g., celestite) and sulphide minerals (pyrite and molybdenite) were formed independently, at different stages of the ore-forming process;

the sulphate minerals and sulphide minerals formed following the mobilization of sulphur from different crustal reservoirs; and

the sulphate minerals and sulphide minerals were influenced by high-temperature (~450–540°C) isotope exchange between reduced and oxidized sulphur species.

SUMMARY

In conclusion, the Nb-Th-Ti-REE group of minerals may represent an early stage of the mineralization process in the Eaglet deposit. The sulphur isotope studies allow for several interpretations of the results and more work is required to verify which interpretation applies to the Eaglet deposit.

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