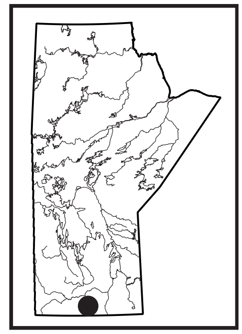
GS-11 Rare-earth element potential of the Gammon Ferruginous Member of the Upper Cretaceous Pierre Shale in southwestern Manitoba

by J.D. Bamburak, M.P.B. Nicolas, J. Hatcher[1] and X.M. Yang



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Summary

The Upper Cretaceous Gammon Ferruginous Member[2], with a maximum thickness of 56 m, was intersected in thousands of oil wells in southwestern Manitoba. More importantly, anomalous concentration and enrichment of rare-earth elements (REE) have been noted in Gammon Ferruginous outcrops present along the Manitoba escarpment and in the Pembina River valley, compared with other Cretaceous shale horizons. The highest REE values, in inorganic geochemical analyses, were found at the Spencer's Ditch locality near the escarpment edge; accordingly, this location was selected for additional investigation during 2013. This work revealed that the sample contains 0.225% light rare-earth elements (LREE) and 0.124% heavy rare-earth elements (HREE). The latter constitute 35.5% of the total rare-earth elements (TREE). Further, it was shown that the sample has 3178 ppm TREE or 3844 ppm total rare-earth oxides (TREO); and the HREE content is >1000 ppm, which accounts for >30% of TREE. These values are higher than those contained in some currently active rare-earth exploration areas. Mineralogical study of the sample indicated that apatite, which accounts for ~35% of the sample by volume in the –300/+100 µm size fraction, may be the mineral hosting most of the REE. The HREE may be contained in the accompanying zircon grains that make up ~0.02% of the mineral mass. Further investigation will include electron-microprobe analysis. This may lead to additional information about REE distribution of the Gammon Ferruginous Member that could result in the discovery of a new type of mineable sedimentary REE deposit in Manitoba.

Introduction

The Gammon Ferruginous Member of the Upper Cretaceous Pierre Shale (Figure GS-11-1) was named by Rubey (1930) for the numerous red-weathered ferruginous or sideritic concretions contained in the uniform, dark grey mudstone or silty shale that occurs along Gammon Creek on the northwest flank of the Black Hills in Wyoming (Twp. 57N, Rge. 67, 68W, Crook County). It is present in the subsurface in southwestern Manitoba and intermittently in outcrops along the Manitoba escarpment.

The potential for the Gammon Ferruginous Member to host an REE deposit has been noted in Manitoba Geological Survey (MGS) reports of the past few years by Bamburak and Nicolas (2009, 2010a, b), Nicolas and Bamburak (2009, 2011a, b, 2012a), Nicolas et al. (2010) and Bamburak et al. (2012). When present in Manitoba, the Gammon Ferruginous Member is unconformably bound between calcareous speckled shale at the top of the Boyne Member of the Carlile Formation and the interbedded bentonite and black shale beds at the base of the Pembina Member of the Pierre Shale (Figure GS-11-1). The stratigraphy of the Gammon Ferruginous Member was described in greater detail by Bamburak and Nicolas (2010a) and Bamburak et al. (2012).

As noted by Bannatyne (1970, p. 26, 52, 53), the Gammon Ferruginous Member that is indicated in numerous oil-well logs in the subsurface of southwestern Manitoba was up to 54.9 m in thickness. However, erosion during the Late Cretaceous resulted in the thinning and/or complete removal of the member, especially as seen in outcrop in the Pembina River valley and along the Manitoba escarpment (Bannatyne, 1970, p. 52, 53; McNeil and Caldwell, 1981, p. 65).

The Gammon Ferruginous Member outcrops at several sites in southwestern Manitoba and northeastern North Dakota, as shown in Bamburak et al. (2012). However, it was noted that the results of the previous inorganic geochemical analyses of the 3.2 m thick member at the Spencer's Ditch locality (Bamburak and Nicolas, 2010a, Figure GS-15-2b, locality 7; Bamburak et al., 2012, Figure GS-13-2, locality 7) returned the highest relative REE values (Bamburak and Nicolas, 2010b); accordingly, this location was selected for further investigation in 2013.

Previous work

Spencer's Ditch locality

Bamburak et al. (2012) indicated that bulk sampling of the 3.2 m thick Gammon Ferruginous Member at the Spencer's Ditch locality was done in 2012 by the Canadian Fossil Discovery Centre (CFDC). Three duplicate samples (of about 12 kg each) were collected from within

[1] Canadian Fossil Discovery Centre, 111-B Gilmour Street, Morden, MB R6M 1N8

[2] For the sake of consistency, the Manitoba Geological Survey has opted to make a universal change from capitalized to noncapitalized for the generic part of lithostructural feature names (formal stratigraphic and biostratigraphic nomenclature being the exceptions).

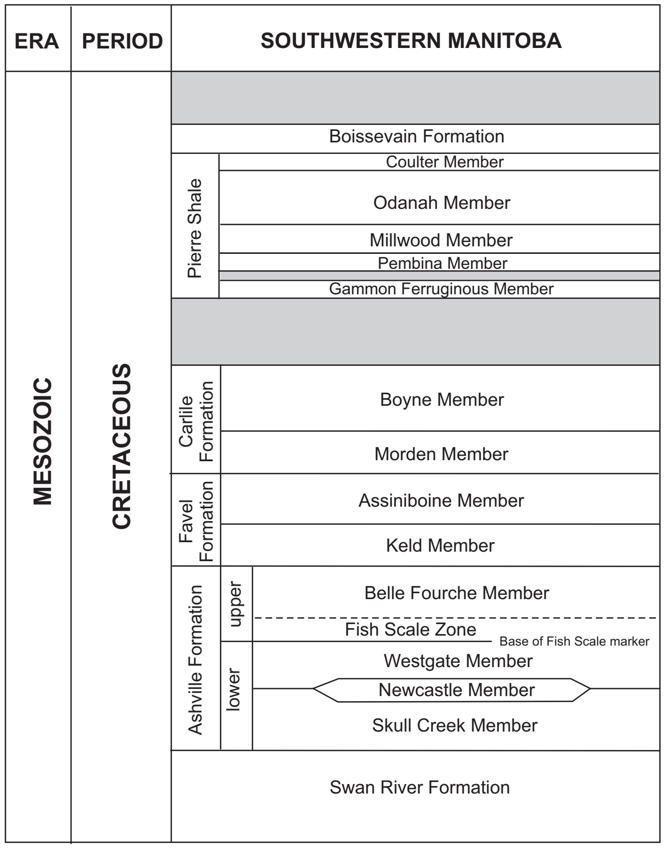

Figure GS-11-1: *Cretaceous stratigraphy of southwestern Manitoba (Nicolas and Bamburak, 2009).*

three contiguous beds: a lower 38 cm thick bed (samples 99-12-SD-001A, B); a middle 115 cm thick bed (samples 99-12-SD-002A, B); and an upper 167 cm thick bed (samples 99-12-SD-003A, B).

Current investigations

The current study of the potential for the Gammon Ferruginous Member to host REE mineralization first involved a preliminary comparison of the three outcrop samples from Spencer's Ditch using a portable X-ray fluorescence (XRF) unit, operated (without charge) by local prospector J. Brown. Next, follow-up discussions took place with the staff of the Saskatchewan Research Council (SRC) to establish a step-by-step process for conducting the investigations.

XRF analysis

In 2013, J. Brown performed several XRF analyses (at no cost) on three Gammon Ferruginous Member samples from Spencer's Ditch at the MGS Midland Rock and Core Storage facility. The tests indicated that the middle bed of the member was relatively enriched in REE compared to the upper and lower beds from the site. On this basis, the middle bed was selected for further testing.

Saskatchewan Research Council tests

Several attempts were made to find a lab prepared to conduct tests to evaluate the REE potential of a sample of Cretaceous shale/silt The most informed response was received from J. Zhang, Senior Metallurgist of Mineral Processing and Metallurgy at the Saskatchewan Research Council (SRC) in Saskatoon. The staged process, recommended by SRC to evaluate the REE potential of the shale/silt sample, is shown in Figure GS-11-2.

Sample preparation

In the first step of sample preparation (Figure GS-11-2), the 12 kg sample (99-12-SD-002B) was crushed in a jaw crusher and then dried in an oven at 70°C. The dried sample was homogenized (to permit representative splitting and assay) and then riffled to get a 500 g subsample. The subsample was split again to get a 100 g sample for analysis. The remaining 400 g sample was used in the ion-exchange test (see below).

Head assay

The head assay was carried out to understand the major composition of the sample and its abundance and distribution of REE. The head assay comprised a whole-rock analysis, followed by REE analysis using an inductively

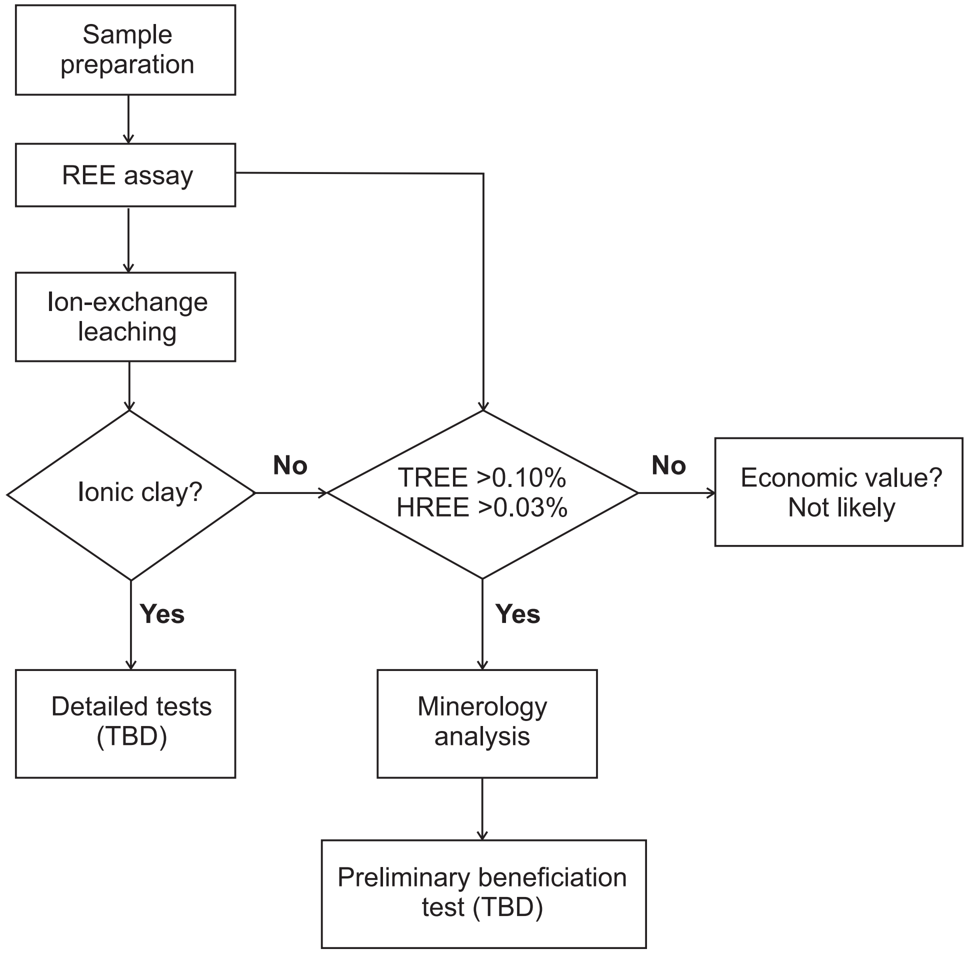

Figure GS-11-2: *Flow chart of rare-earth element (REE) evaluation procedures for the sample from the Gammon Ferruginous Member (J. Zhang, written communication, July 8, 2013).*

coupled plasma–mass spectrometry (ICP-MS) rare-earth package.

Whole-rock analysis

For the whole rock analysis, the sample was first fused with lithium metaborate and then digested in nitric acid for determination by inductively coupled plasma–emission spectrometry (ICP-ES). Results shown in Table GS-11-1 indicate that the major components of the Gammon Ferruginous Member sample are Al_2O_3, CaO, Fe_2O_3, P_2O_5 and SiO_2.

ICP rare-earth package

For the ICP-MS rare-earth package, a 0.1 g pulp was fused at 1000°C with lithium metaborate and then dissolved in dilute HNO_3. According to the SRC report (Zhang, 2013), the REE assay (Figure GS-11-2, Table GS-11-1) indicated that the sample contains 0.124% heavy rare-earth elements (HREE) and 0.225% light rare-earth elements (LREE). The HREE account for 35.5% of the total rare-earth elements (TREE).

Ion-exchange leaching

To determine whether the sample is an ion-absorption type of rare earth in clay (or ionic clay, see Figure GS-11-2; the major source of HREE can easily be processed), ion-exchange leaching was done on the sample. The first step of the test was to place the sample in 4% ammonium sulphate in a bottle, which was then rolled for 24 hours at room temperature (at pH 4.0) to produce a slurry with 40% solids. The slurry was filtered and then the leaching solution, washing solution and leached solids were analyzed for REE.

The test results (Table GS-11-2) indicate that less than 0.1% of each REE was leached. This leaching test suggests that there is no ion-absorption type of REE in the sample. However, the sample does contain 3178 ppm TREE or 3844 ppm total rare-earth oxides (TREO), and the HREE content is >1000 ppm, which accounts for >30% of TREE. According to Zhang (2013), "The abundance of rare-earth in the sample is higher than many samples from some active rare-earth exploration areas where the typical abundance of REE is in the range of 1000 ppm to

Table GS-11-1: Whole-rock analysis and rare-earth element (REE) content of sample 99-12-SD-002B, Gammon Ferruginous Member, Spencer's Ditch locality, southwestern Manitoba.

Parameter	Concentration (wt. %)
Whole-rock analysis:	
Al_2O_3	11.4
CaO	11.2
Fe_2O_3	5.77
K_2O	3.15
MgO	1.23
MnO	0.85
Na_2O	0.84
P_2O_5	8.13
TiO_2	0.45
SiO_2	39.4
LOI	13.6
Total	**95.14**
Light rare-earth elements:	
Sc	0.003
La	0.057
Ce	0.082
Pr	0.014
Nd	0.057
Sm	0.01
Eu	0.002
Heavy rare-earth elements:	
Gd	0.014
Tb	0.002
Dy	0.013
Tm	0.002
Y	0.089
Yb	0.006

2000 ppm." Comparative examples include the Brockman deposit in Australia, with a measure-in-pit resource of 4.29 million tonnes at a grade of 0.2% TREO (Chalmers, 1990; Long et al., 2010); the Narraburra deposit in Australia, with measured, indicated and inferred resources of 55 million tonnes at a grade of 0.03% TREO (Long et al., 2010); and the Zeus (Kipawa complex) deposit in Quebec, with measured, indicated and inferred resources of 2.270 million tonnes at 0.11% TREO (Knox et al., 2009; Long et al., 2010).

QEMSCAN® analysis

Because the sample was not an ion-absorption type of rare earth in clay, further detailed testing (as shown in Figure GS-11-2) was not required. However, since TREE was greater than 0.1% and the HREE was greater than

Table GS-11-2: Ion-exchange leaching results for rare-earth elements (REE) in the sample from the Gammon Ferruginous Member, Spencer's Ditch locality, southwestern Manitoba.

Element (ppm)	Sample type *(mass in grams)*			
	Feed (400)	**PLS** (717)	**Wash** (712)	**Residue** (393)
Sc	29	0	0.01	30
Y	804	0.16	0.03	820
La	510	0.15	0.02	520
Ce	687	0.04	0	700
Pr	118	0.01	0.01	120
Nd	520	0.02	0	530
Sm	88	0.01	0	90
Eu	20	0	0	20
Gd	128	0.01	0	130
Tb	20	0.01	0.02	20
Dy	118	0.01	0	120
Ho	0	0	0	0
Er	69	0.01	0	70
Tm	20	0	0	20
Yb	49	0.01	0	50
U	112	1.25	0.81	110
Lu	0	0	0	0
LREE	**2099**	**0.24**	**0.04**	**2140**
HREE	**1079**	**0.20**	**0.05**	**1100**
TREE	**3178**	**0.44**	**0.09**	**3240**

0.03%, mineralogical analysis to identify the major rare-earth minerals in the sample was a logical next step.

The modal mineralogy of the sample was determined using Bulk Mineralogical Analysis (BMA) in SRC's QEMSCAN system—an automated mineralogy and petrography solution that provides quantitative analysis of minerals, rocks and man-made materials. The BMA method traces a line across the particles and identifies the minerals present in each particle. During a typical run, from 50 000 to 60 000 particles are analyzed and the modal mineralogy is calculated from the robust dataset (S. Creighton, pers. comm., 2013).

The QEMSCAN system comprises a Quanta 650 field-emission scanning electron microscope (F-SEM) with a large specimen chamber capable of holding fourteen 30 mm diameter round blocks. Each block comprised a mounted (with epoxy resin) random aliquot of the –350/+200 and –200/+100 µm size fractions that had been sieved by SRC from the supplied sample. After curing, the blocks were ground flat and polished to obtain a surface suitable for X-ray analysis. The F-SEM is fitted with two light-element energy-dispersive X-ray spectroscopy (EDS) detectors with a maximum throughput of 1.3 Mcps. The mounted samples were analyzed with a 2.5 μm spot spacing for quantitative mineral abundances. To assist in mineral identification, an additional analysis was done on each size fraction using a spot spacing of 1.5 μm with a field size of 300 μm, and additional imaging of particles was completed to aid in identifying agglomerated mineral grains (Hunt, 2013).

According to Hunt (2013), the modal mineralogy of sample 99-12-SD-002B is mainly apatite (35.05%), fine-grained biotite (24.12%), K-feldspar (21.79%), quartz (5.84%), fine-grained agglomerated particles (3.42%) and kaolinite (3.30%), as shown in Table GS-11-3. Minor amounts (<2% each) of amphibole, anhydrite, muscovite, Na-feldspar, biotite/phlogopite, rutile/anatase, oolitic ironstone, barite, zircon and calcite are also present. The apatite grains (accounting for ~35% in volume of the sample) may be the mineral hosting most of the REE. Hunt (2013) commented that "Multiple generations of apatite were observed with evidence of a complex history of dissolution and re-precipitation or possible elemental zoning." In one case, compositional zoning was interpreted as being due to a variance in the abundance of Sr or REE. The other candidate that may have contributed to the HREE in the Gammon Ferruginous Member sample is zircon, which accounts for ~0.02% of the mineral mass (Table GS-11-3).

Table GS-11-3: Modal mineralogy of the –300/+250 μm and –250/+100 μm size fractions and weighted average of the sample from the Gammon Ferruginous Member, Spencer's Ditch locality, southwestern Manitoba.

Mineral	Mineral Mass (%)		
	–300/+250 μm	–250/+100 μm	Weighted average
Apatite	25.56	36.53	35.05
Biotite (fine-grained)	29.37	23.3	24.12
K-feldspar	24.55	21.36	21.79
Quartz	5.89	5.84	5.84
Fine-grained agglomerated particles	3.56	3.40	3.42
Kaolinite	3.56	3.27	3.3
Amphibole	2.00	1.83	1.85
Muscovite	1.81	1.6	1.63
Anhydrite	2.24	1.4	1.52
Na-feldspar	0.45	0.49	0.48
Biotite/phologopite	0.37	0.38	0.37
Rutile/anatase	0.26	0.25	0.25
Oolitic ironstone	0.11	0.19	0.18
Barite	0.24	0.19	0.18
Zircon	0.02	0.01	0.01
Calcite	0.01	0.01	0.01

Further work on the sample will likely involve electron-microprobe analysis of the apatite and zircon for major, trace and REE elements. Depending upon the results of this work, the following tests could be performed: acid leaching, floatation, gravity separation and magnetic separation.

Economic considerations

The identification of economic quantities of rare-earth elements, especially heavy rare-earth elements, within the Gammon Ferruginous Member of the Pierre Shale would mark the first time that this kind of deposit has been found in Manitoba. Further work is required, which may lead to the development of a new type of mineable sedimentary REE deposit in the province.

Acknowledgments

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