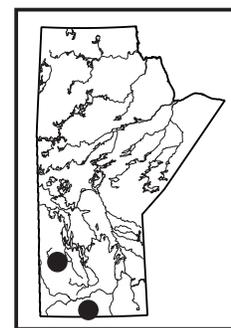


GS-15 Update on the rare-earth element potential of the Gammon Ferruginous Member of the Upper Cretaceous Pierre Shale in southwestern Manitoba

by J.D. Bamburak, T. Martins, M.P.B. Nicolas and X.M. Yang



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Summary

Anomalous concentration and enrichment of rare-earth elements (REE) in comparison to most other Cretaceous shale horizons have been noted in outcrops of the Gammon Ferruginous Member along the Manitoba escarpment and in the Pembina River valley of southwestern Manitoba, and have prompted additional work to address the potential for economic REE deposits in this unit. The highest REE values were obtained from inductively coupled plasma–mass spectrometry of samples from the Spencer’s ditch locality near the escarpment edge; subsequent testing revealed up to 3844 ppm total rare-earth element oxides. Apatite, which accounts for ~35% of the mineral mass (–300/+100 mesh size fraction), was identified in initial tests as the most likely host for most of the REE (heavy REE may also be contained in zircon grains, which make up ~0.01% of the mineral mass). Although the apatite was initially thought to be of magmatic origin, electron-probe microanalyses and petrographic examination of heavy mineral separates indicate that these grains may actually be biological apatite (or bioapatite), representing fossilized bone material. The discovery of an association of REE and fossil bone material may represent a useful diagnostic tool to identify, perhaps by using a portable X-ray fluorescence unit, potential fossiliferous bone beds similar to those known to contain exceptionally well-preserved marine reptile fossils in Manitoba. Further testing is underway to determine if there is any potential for economic REE mineralization within the Gammon Ferruginous Member, unrelated to the bone beds.

Introduction

The discovery of anomalous rare-earth element (REE) concentrations in the Gammon Ferruginous Member of the Upper Cretaceous Pierre Shale (Bamburak et al., 2013, Figure GS-11-1) resulted from bulk inorganic geochemical profiling of the Cretaceous shale sequence in 2009 (Bamburak and Nicolas, 2009). Since that initial discovery, investigation of its REE potential has been carried out yearly to assess its source and economic potential (Bamburak and Nicolas, 2009, 2010a, b; Nicolas and Bamburak, 2009, 2011a, b, 2012a, b; Nicolas et al., 2010; Bamburak et al., 2012, 2013).

Rare-earth element mineralization can be found in different types of deposits, including carbonatite, hydrothermal/magmatic Fe-REE, placer accumulations of heavy

mineral assemblages, alkaline and peralkaline related, and ion-adsorption deposits (residual deposits of REE-bearing clays). Since the REE anomaly in the Gammon Ferruginous Member was in a clastic sedimentary sequence, the placer accumulation or ion-adsorption deposits were the best models to follow for further investigation. Bamburak et al. (2013) had concluded that the ion-adsorption deposit was unlikely. In this report, the placer accumulation of heavy mineral assemblage model will be tested.

The Gammon Ferruginous Member outcrops at several sites in southwestern Manitoba and northeastern North Dakota. The detailed stratigraphy of the Gammon Ferruginous Member was described by Bamburak and Nicolas (2010a) and Bamburak et al. (2012). This report updates work carried out by the Manitoba Geological Survey (MGS) during the past year to characterize the REE mineralogy of the Gammon Ferruginous Member and to determine the nature and composition of potential REE hosts.

Previous work

Spencer’s ditch locality

Of all of the known sites of Gammon Ferruginous Member in southwestern Manitoba, the Spencer’s ditch locality in L.S. 15, Sec. 31, Twp. 3, Rge. 6, W 1st Mer. (abbreviated 15-31-3-6W1; UTM Zone 14U, 553843E, 5457258N; southwest corner of NTS 62G8; Figure GS-15-1) has the highest relative REE values, as noted by Bamburak and Nicolas (2010a, b), Bamburak et al. (2012) and Bamburak et al. (2013).

From a sample collected at the site, it was determined by portable X-ray fluorescence unit that the middle bed (sample 99-12-SD-002B) contained anomalous REE values thus it was selected for study at the Geoanalytical Laboratories of the Saskatchewan Research Council (SRC). Whole rock analysis of the sample indicated that the major components are Al_2O_3 , CaO , Fe_2O_3 , P_2O_5 and SiO_2 (Bamburak et al., 2013, Table GS-11-1). Using inductively coupled plasma–mass spectrometry, the REE assay indicated that the sample contains 0.124% heavy rare-earth elements (HREE), making up 35.5% of total REE, and 0.225% light rare-earth elements (LREE). The sample contains 3178 ppm REE or 3844 ppm total

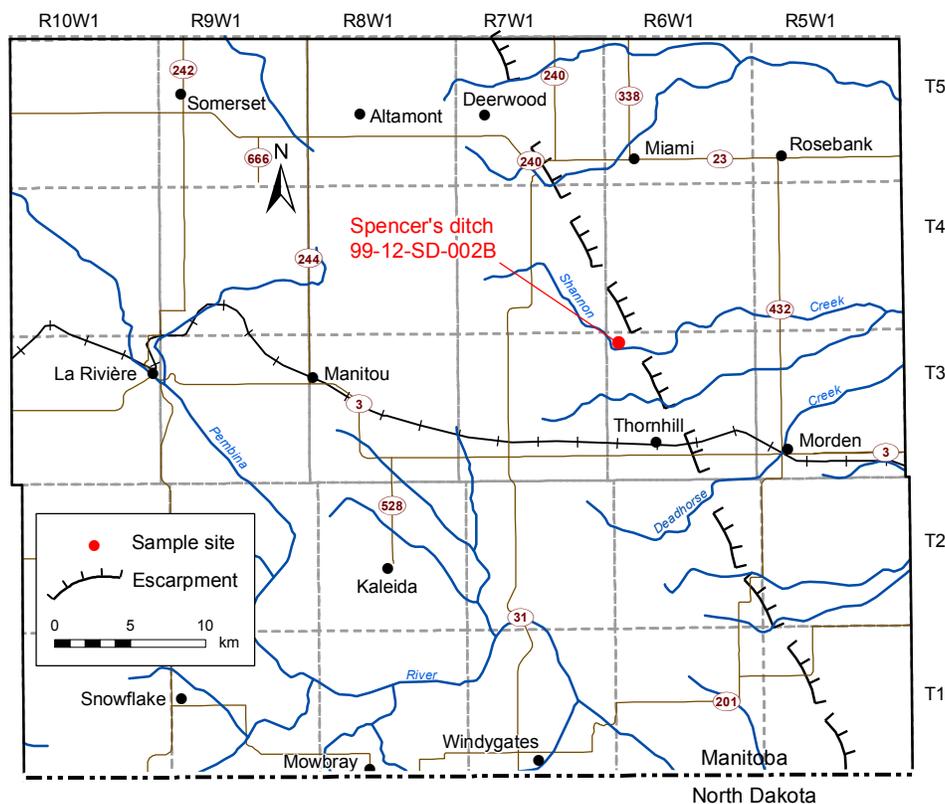


Figure GS-15-1: Location of Gammon Ferruginous Member sample 99-12-SD-002B collected at the Spencer's ditch site in the Pembina Hills area of southwestern Manitoba.

rare-earth element oxides; and the HREE content is >1000 ppm, which accounts for >30% of total REE (Bamburak et al. 2013, Table GS-11-2). These values are higher than those contained in some currently active rare-earth elements exploration areas (Long et al., 2010). The modal mineralogy of the sample was determined using bulk mineralogical analysis on SRC's QEMSCAN® system. The sample consists mainly of apatite (35.05%), a likely host for most of the REE, and ~0.01% zircon, which may have also contributed to the HREE (Bamburak et al., 2013, Table GS-11-3). It was also noted that multiple generations of apatite are present, with evidence of a complex history of dissolution and re-precipitation or possible elemental zoning.

Vermilion River locality 1b

In 2013, two samples (99-13-VR-001A and -001B) were collected from the Gammon Ferruginous Member above the contact with the Boyne Member of the Carlike Formation (Bamburak et al., 2013, Figure GS-11-1) at locality 1b, shown on Figure GS-15-2. The outcrop is situated in 2-22-23-20W1 (UTM Zone 14U, 416682E,

5649782N; northeast corner of NTS 62K16) on the Vermilion River (same location as outcrop section 76 of McNeil and Caldwell [1981]). Localized sample 99-13-VR-001A was collected just above the contact and channel sample 99-13-VR-001B was taken between 2 and 4 m above the contact. Testing of these samples is described below.

Current investigations

Electron-probe microanalyses of sample 99-12-SD-002B from Spencer's ditch

The main objective of electron-probe microanalyses, carried out at the University of Manitoba, was to understand if the apatite (contained in sample 99-12-SD-002B from Spencer's ditch, Figure GS-15-1) identified by the SRC is the principal carrier of the REE, as previously suggested by Bamburak et al. (2013). In an initial stage of this study, round mounts prepared and analyzed by the SRC were re-used in order to ensure that analytical results were obtained from the same mineral grains. However, the analyses performed on these mounts produced low sum totals (Martins et al., 2014¹), this may be as a result of

¹ MGS Data Repository Item DRI2014004, containing the data or other information sources used to compile this report, is available online to download free of charge at <http://www2.gov.mb.ca/itm-cat/web/freedownloads.html>, or on request from minesinfo@gov.mb.ca or Mineral Resources Library, Manitoba Mineral Resources, 360-1395 Ellice Avenue, Winnipeg, MB R3G 3P2, Canada.

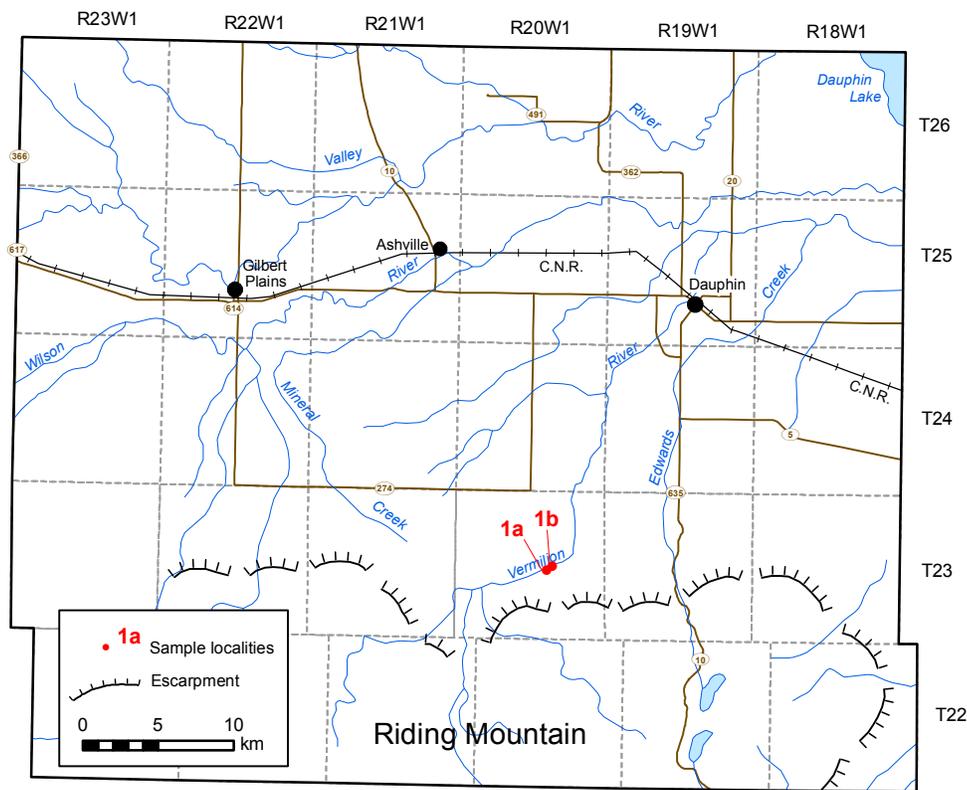


Figure GS-15-2: Gammon Ferruginous Member outcrop location on the north flank of Riding Mountain (modified from Bamburak and Nicolas, 2010a). Locality 1b corresponds to outcrop section 76 of McNeil and Caldwell (1981; Bamburak et al., 2012, Figure GS-13-1).

the grains being damaged by the electron beam in the initial analysis, as is evident in backscattered electron (BSE) images (Figure GS-15-3). This damage may have resulted from a number of factors, such as a defocusing effect, beam-sensitive samples, type of epoxy used in the round mounts or low connectivity related to the nature of the

mounts (when compared to a thin section). Regardless, in order to mitigate the analytical problems described above new mounts were prepared for this study.

Methodology

The grain separates were mounted in epoxy on glass slides, ground and polished to approximately 30–60 μm thick at the Midland Sample and Core Library laboratory. The selected size fractions for the grain mounts were 100–250 mesh and 250–300 mesh, in order to be consistent with the SRC study. All analytical measurements were performed in situ on carefully selected representative material. Two thin sections of the Gammon Ferruginous Member were studied initially using optical microscopy, BSE imaging and energy-dispersive X-ray spectrometry. These methods were employed to identify inclusions, contamination and chemical zoning in the grains. X-ray maps of selected apatite grains were also performed to further evaluate chemical zonation. The chemical compositions were determined by wavelength-dispersive X-ray spectrometry using a CAMECA SX 100 electron probe operated at an accelerating voltage of 15 kV and a beam current of 10 nA at the University of Manitoba. These analyses were carried out using a beam diameter of 20 μm to avoid sample damage. The following

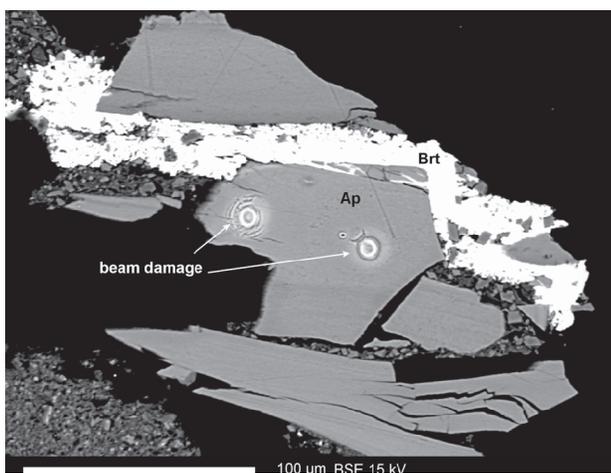


Figure GS-15-3: BSE imagery of a grain in round mount, damaged by the electron beam. Abbreviations: Ap, apatite; Brt, barite.

natural and synthetic standards were used for the analysis: apatite (F and P), albite (Na), diopside (Si), apatite (Ca), synthetic SrTiO_3 (Sr), fayalite (Fe), rare-earth orthophosphates (La, Ce, Pr, Nd, Y, Sc, Dy, Sm), barite (S), synthetic $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ (Ba), and andalusite (Al), spessartine (Mn) and tugtupite (Cl). The raw data were reduced and corrected using the ‘PAP’ method of Pouchou and Pichoir (1985).

Cathodoluminescence images of the apatite grains were also obtained at the University of Manitoba using a Technosyn cold cathode luminescence system.

Results

All values and characteristics of the apatite grains discussed in this report refer to the results obtained from thin sections only. The data obtained for round mineral mounts are available in Martins et al. (2014), but are not discussed here due to poor quality of the electron-probe data resulting from extensive beam damage to the samples.

Observations under the polarizing microscope were compromised due to the variable thickness of the thin sections. Nevertheless, it is possible to observe that the grains are subhedral to anhedral, usually appear cloudy or with inclusions of different materials or possibly voids (Figure GS-15-4a). The apatite grains vary in size from 80 to 250 μm in the mesh size 100–250, and from 150 to 400 μm in the 250–300 mesh. The BSE imagery and X-ray maps indicate that most of the apatite grains have little to no zoning (Figure GS-15-4b, c).

All of the oxide totals are low, with a highest total of 97.80 wt. % and a lowest of 72.77 wt. % (Table GS-15-1; Martins et al., 2014, Table 2). The highest total of rare-earth element oxides ranges from 0.50 to 2.11 wt. % (Martins et al., 2014, Table 2). The FeO content is quite high in some of the analyzed grains (up to 11.82 wt. %) and SO_3 content varies from 1.10 to 2.20 wt. % (Martins et al., 2014, Table 2).

Discussion

Given the low analytical totals for the major- and trace-element oxides, and some abnormally high values of certain elements, such as Fe, it was not possible to calculate chemical formulas from the mineral analyses using the ideal formula for fluorapatite: $\text{Ca}_5(\text{PO}_4)_3\text{F}$ (as defined by Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association; Pasero et al., 2010).

The extent of the damage caused in some of the grains (i.e., volatilization under the electron beam) is very unusual for magmatic apatite, especially with the operating conditions described earlier. Textural evidence of primary porosity is observed under the optical microscope (Figure GS-15-4a) and in BSE imagery (Figure GS-15-5),

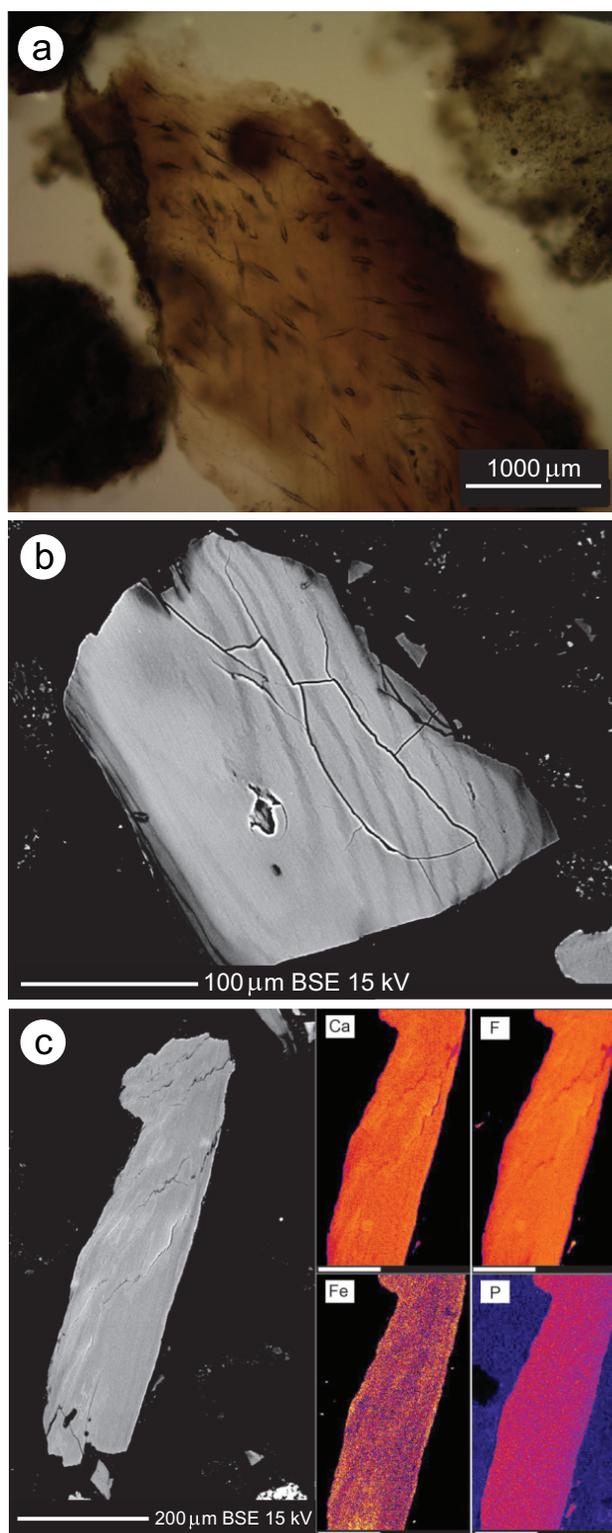


Figure GS-15-4: Microphotographs of different apatite grains analyzed as part of this study: **a)** cloudy apatite grain under the optical microscope (plane-polarized light); **b)** BSE image of a grain with apparent chemical zoning; none of the analyzed elements showed meaningful variation (Martins et al., 2014, analytical results in columns J and K); **c)** BSE image of apatite grain with X-ray maps; insets of the same grain showing no significant internal variation for elements Ca, F, Fe and P (scale bar insets are 100 μm).

Table GS-15-1: Selected results of electron-probe microanalyses (EPMA) of studied apatite grains. Abbreviation: REEO, rare-earth element oxides.

Oxides (wt. %)	Sample number						
	S1-Ap1_C	S1-Ap3_C	S1-Ap7_C	S2-Ap2_C	S2-Ap3_C	S2-Ap4_C	S2-Ap9_C
Na ₂ O	1.12	1.14	1.35	1.23	1.07	0.95	1.12
Al ₂ O ₃	0.66	2.17	1.04	2.27	1.56	0.54	2.66
SiO ₂	0.02	0.04	0.02	0.00	0.05	0.00	0.02
P ₂ O ₅	35.77	36.24	36.53	36.68	34.93	35.64	35.46
SO ₃	2.20	1.77	1.75	1.27	1.35	2.17	1.67
CaO	50.92	49.01	34.35	43.97	47.34	50.69	48.69
FeO	0.93	1.34	11.82	3.41	0.85	0.78	0.80
MnO	0.07	0.17	0.05	0.13	0.15	0.10	0.18
SrO	0.27	0.33	0.19	0.24	0.26	0.25	0.27
BaO	0.07	0.08	0.17	0.24	0.08	0.04	0.13
La ₂ O ₃	0.14	0.17	0.32	0.52	0.32	0.10	0.13
Ce ₂ O ₃	0.19	0.00	0.40	0.59	0.47	0.25	0.00
Pr ₂ O ₃	0.19	0.19	0.22	0.10	0.00	0.00	0.25
Nd ₂ O ₃	0.02	0.00	0.60	0.42	0.34	0.17	0.27
Sm ₂ O ₃	0.17	0.03	0.17	0.00	0.03	0.20	0.10
Dy ₂ O ₃	0.18	0.23	0.00	0.08	0.12	0.00	0.01
Y ₂ O ₃	0.13	0.27	0.47	0.80	0.52	0.22	0.18
F	3.94	4.62	2.39	3.67	4.38	3.89	4.92
Total	96.99	97.80	91.84	95.62	93.82	95.99	96.86
ΣREEO+Y ₂ O ₃	1.02	0.89	2.18	2.51	1.80	0.94	0.94

Notes: Cl was sought but it was below detection limit. Abbreviations: C, core of apatite; REEO, rare-earth element oxides; S1, thin section 1 with 100–250 mesh; S2, thin section 2 with 250–300 mesh.

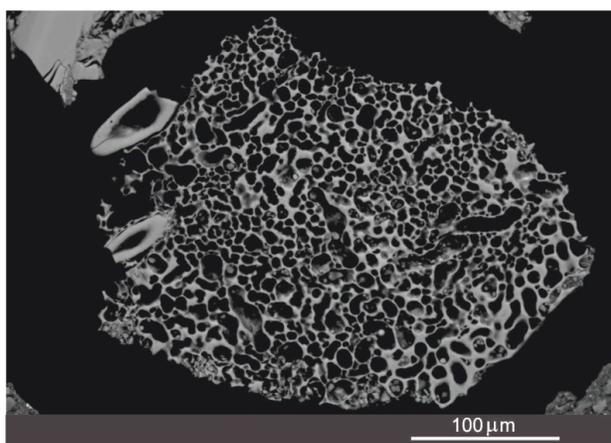


Figure GS-15-5: BSE imagery of apatite grain from the Gammon Ferruginous Member showing evidence of primary porosity.

which is uncommon in magmatic apatite. Taking these aspects into account, the apatite recovered from the Gammon Ferruginous Member is interpreted to be biological apatite, representing fossil bone rather than magmatic apatite.

According to Dorozhkin and Epple (2002), in biological systems, calcium orthophosphates occur as the principal inorganic constituent of bones, teeth, fish enameloid and some species of shells, as well as pathological calcifications (e.g., dental and urinary calculus and stones, atherosclerotic lesions). Structurally, they occur mainly in the form of poorly crystallized nonstoichiometric sodium-, magnesium- and carbonate-containing carbonated hydroxyapatite (often called biological apatite or dahllite). Comparison of images of calcined porous bone provided by Dorozhkin and Epple (2002) to some of this study's images (Figure GS-15-4b) supports the authors' contention that the analyzed material is biological apatite (e.g., fossilized bone).

The literature provides many examples of highly enriched REE in fossilized bone or bone beds. For example, the Pleistocene Ologesailie Formation of southern Kenya has total REE concentrations in fossil bones ranging from 33 to 48 175 ppm (Trueman et al., 2006). Another example is the Monte San Giorgio beds at Ticino, Switzerland (240 Ma), where the Meride Formation has an average total REE concentration of 2200 ppm and the Besano Formation has variable REE contents, from very low

(300–800 ppm) to very high (>10 000 ppm; Kocsis et al., 2010). Although most trace elements are probably only adsorbed onto the surface of fossil bones (e.g., Shaw and Wasserburg, 1985), it is observed that these concentrations may increase significantly (up to thousands of ppm) in fresh bones and teeth during diagenesis. These authors attribute the increase in REE to the diffusion and adsorption onto crystallite surfaces, possibly during transformation of bone material, and state that the increase in trace-element content is unequivocally diagenetic in origin (Trueman, 2007).

When comparing this study's results to those from magmatic apatite, the highest total of rare-earth element oxides (0.50–2.11 wt. %) is high when compared to fluorapatite from the Paint Lake carbonatite in Manitoba (0.17–0.46 wt. %, T. Martins and A. Chakhmouradian, unpublished data, 2010), but is similar to the range of values reported for fluorapatite from carbonatite in the Eden Lake complex in Manitoba (1.12–3.51 wt. %, Chakhmouradian et al., 2008). On the other hand, the reported total values are not as high as fluorapatite from Lovozero, Kola Peninsula, Russia (1.24–10.09 wt. %, T. Martins and A. Chakhmouradian, unpublished data, 2010) or the Misery syenitic intrusion, Quebec (2.28–10.74 wt. %, Petrella et al., 2014). Iron content is quite high in some of the analyzed grains (up to 11.82 wt. %), which is quite uncommon for apatite (e.g., Chang et al., 1998). The highest reported values of Fe in apatite are from the Fresia and

Carmen magnetite-apatite deposits in Chile, which contain up to 1.21 wt. % FeO (Treolar and Colley, 1996). Sulphur contents are higher in the analyzed grains than those reported for other apatite (Chang et al., 1998, report SO₃ values ranging from 0.01 to 0.37 wt. %). However, higher contents of S are also found at Eden Lake, Manitoba, for example, with fluorapatite containing up to 1.35 wt. % of SO₃ (Chakhmouradian et al., 2008).

Taking all of this into consideration, the concentrations of rare-earth element oxides in the Gammon Ferruginous Member are comparable to examples from elsewhere in the literature (as indicated above) and could be explained by biological apatite, which contains up to 2.96 wt. % of rare-earth element oxides plus Y₂O₃ in the present case.

Heavy mineral separation of Vermilion River sample (99-13-VR-001B, locality 1b)

As indicated earlier, two Gammon Ferruginous Member samples were collected on the Vermilion River at locality 1b (Figure GS-15-2). Both samples were submitted to Activation Laboratories Ltd. (Actlabs) for REE evaluation (Code 8 – REE assay package). Results of these analyses are shown in Figure GS-15-6. Except for lanthanum, the values for sample 99-13-VR-001B are slightly less than those for sample 99-13-VR-001A.

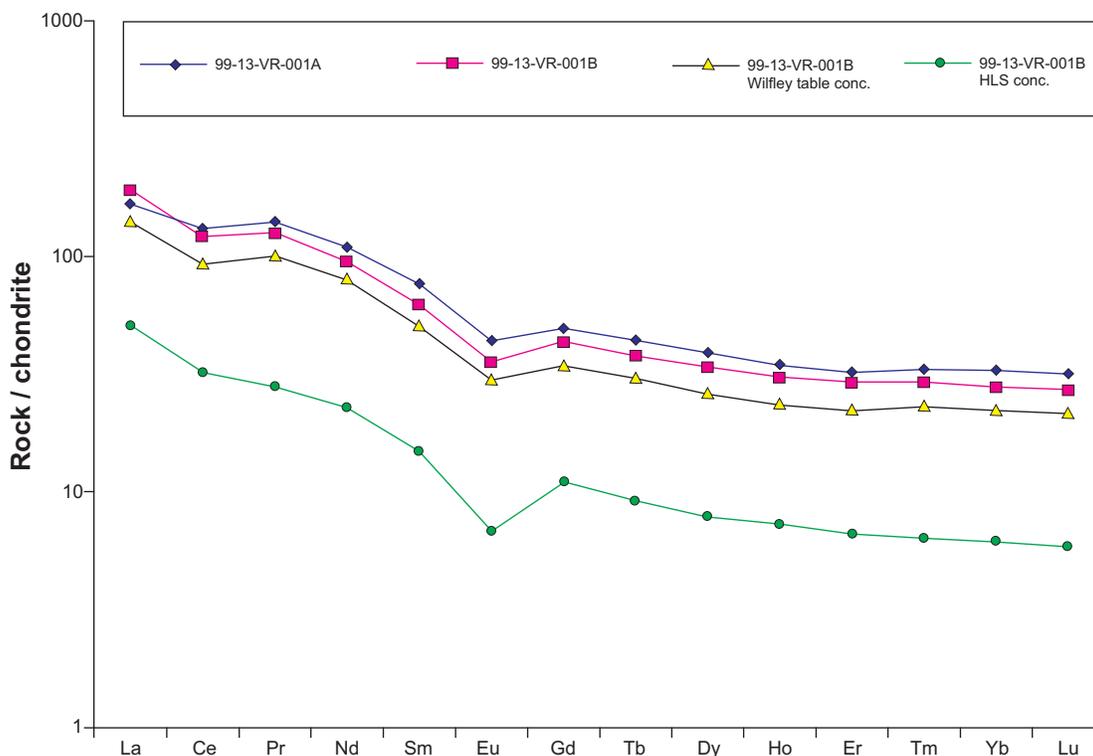


Figure GS-15-6: Chondrite-normalized rare-earth element (REE) diagram for samples 99-13-VR-001A and B. Also shown are the results of heavy mineral concentration (conc.) of sample 99-13-VR-001B using the Wilfley table and heavy liquid separation (HLS). Normalized values are from Sun and McDonough (1989).

To determine whether sample 99-13-VR-001B might contain other REE-bearing minerals, such as zircon (specific gravity [sg] of 4.6–4.7), xenotime (sg of 4.4–5.1) or monazite (sg of 4.6–5.7), two heavy mineral concentrates were prepared at Actlabs from sample 99-13-VR-001B using the Wilfley table and heavy liquid separation (HLS), using methylene iodide (sg of 3.3). However for both methods, it was found that the concentrates contained only a small fraction of the total REE contained in the unconcentrated sample. J. Steyn, Metallurgy Manager of Actlabs, speculated that this was probably due to small grain size and resulting encapsulation in lighter minerals. Figure GS-15-6 shows that the REE values obtained in Wilfley table concentrate were slightly lower than those from the bulk analysis, and that the values for the HLS concentrate were substantially lower. This would indicate that some of the REE are contained in the light-fraction material (sg <3.3), possibly biological or magmatic apatite. The light fraction will be examined to determine if either is present. It should be noted that at Spencer's ditch, the highest REE values were obtained within a bone bed in the *Xiphactinus* Kill Zone quarry within the middle Gammon Ferruginous Member (Bamburak et al., 2012, Figure GS-13-4).

Sampling of Vermilion River localities 1a and b in 2014

In 2014, a total of 12 samples of the Gammon Ferruginous Member (99-14-VR-001B to 99-14-VR-001M) were collected at 0.5 m intervals over the 5.8 m thickness of the member at Vermilion River localities 1a and 1b (Figure GS-15-2). One sample of the underlying Boyne Member of the Carlile Formation (99-14-VR-001A) and 11 samples of the overlying Gammon Ferruginous Member (99-14-VR-001B to 99-14-VR-001L) were taken at locality 1b. At locality 1a, one sample of the Gammon Ferruginous Member (99-14-VR-001M) was collected. The overlying Pembina Member of the Pierre Shale (99-14-VR-001N) was also sampled at locality 1a. The samples will be submitted to Actlabs for REE evaluation to provide complete information for the entire thickness of the Gammon Ferruginous Member at localities 1a and 1b.

Possible sources of REE enrichment

Trace-element studies in biological apatite indicate that the geochemical composition of modern biominerals can be used as a fingerprint to identify their sources (e.g., Trueman et al., 2006). Changes in the geochemistry of fossil bones can provide context to different depositional environments and reflect the regional geochemistry of a certain period. According to Trueman (2007), the most important control on the trace-element composition of a fossil bone is the trace-element composition and chemistry of the pore water and diagenetic fluids in the burial

environment. This pore water and diagenetic fluid can be controlled by different environmental variables, such as country rock, weathering rates, hydrology, climate, pH, redox conditions and suspended particles. Also, Herwartz et al. (2011) agrees that trace elements present in diagenetic fluid at the time of recrystallization may be incorporated into the apatite crystal lattice.

It is possible that fluids enriched in rare-earth element oxides passing through the Gammon Ferruginous Member could have entered the biological apatite bone structure during diagenesis. Selective REE enrichment of the Gammon Ferruginous Member, as compared to the other overlying and underlying strata, may be due to its high biological apatite content and the ability of this material to incorporate REEs. At the moment the source for these fluids is uncertain.

Conclusions

In Bamburak et al. (2013), it was reported that the Gammon Ferruginous Member is not an ion-adsorption deposit. The results of this study suggest that the analysed material is bioapatite, and the results from the heavy mineral separation test indicate that only a small fraction of the REE is present in the heavy mineral concentrates. Taking all this into consideration, it seems that most of the REE concentration is associated with the bone beds as biogenic apatite, however this does not exclude the possibility that some of the apatite could also be of magmatic origin. As described above, there are other examples of bone beds with high enrichment in REE but, to the authors' knowledge, there is no active exploration associated with these types of REE enrichment.

Economic considerations

The origin of the REE mineralization within the Gammon Ferruginous Member of the Pierre Shale seems to be associated with the bone beds and at the present time the origin of the REE fluid that caused this enrichment is uncertain. However, systematic testing of Cretaceous stratigraphic units, using portable XRF units to detect anomalous concentrations of REE, might be a useful tool to find bone beds, which might yield significant fossil finds of marine reptiles, such as the mosasaurs and plesiosaurs on display at the Canadian Fossil Discovery Centre (CFDC) in Morden. The significant fossil discoveries that can occur using this methodology would further enhance the recognition of the CFDC in the scientific community and on the world stage. Greater recognition can directly result in more successful funding requests by the CFDC to expand its museum and services, attraction of world-class scientists and technical people to work and live in the local community, and help grow the centre as a major must-see attraction in Manitoba. All of these have direct economic benefits to the local community, and to Manitoba as a whole.

Although the original purpose of this project, begun several years ago, was to describe the potential for economic REE mineralization within the Gammon Ferruginous Member of the Pierre Shale, the determination that REE seem to have only accumulated in the bones of Cretaceous creatures reduces the possibility of making an economic discovery. However, to confirm or reject this hypothesis, additional analytical testing will be done on the outcrop samples collected in 2014 in the Vermillion River area.

Acknowledgments

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