GS-14 Evaluation of Manitoba bentonites in the catalysis of RNA synthesis by montmorillonite (parts of NTS 62G1, 8, 10, K3, N1)

by M.F. Aldersley[1], J.D. Bamburak, P.C. Joshi[1], J. Thompson[1,2], J.W. Delano[3] and J.P. Ferris[1]

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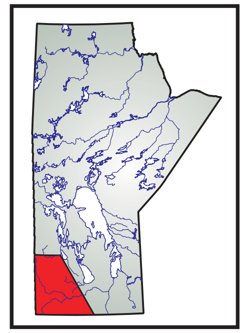

Summary

Bentonite, an altered volcanic ash, is found in the Phanerozoic succession around the world. Bentonite is unique compared to other rock-forming components in that it can catalyze the oligomerization of activated nucleotides to form RNA. It is proposed that the origins of life on Earth (and possibly on Mars) were facilitated by the storage of the genetic code within RNA, catalyzing first life on Earth. However, not all bentonites are equally catalytic and ongoing studies are being conducted on bentonite samples collected worldwide by the Rensselaer Polytechnic Institute of Troy, New York, to determine the best catalysts. The initial work identified 12 excellent and good catalysts located mainly in the northern United States. Follow-up investigations have led to southern Manitoba, where one excellent catalyst and one good catalyst have been recognized from the Odanah Member of the Pierre Shale. Additional testing will be done in an attempt to recognize if the Odanah Member bentonite consistently provides good to excellent catalytic properties and to determine if these properties may be attributed in part to the underlying Paleozoic basement rock.

Introduction

The RNA world hypothesis for the origins of life proposes that RNA stored the genetic code and catalyzed the first life on Earth (Bernal, 1949). Evolution of the RNA world resulted in the formation of the DNA/protein world present on the Earth today. So far, there is no prebiotic route to RNA but it has been possible to generate RNA oligomers by the montmorillonite-catalyzed reaction of activated monomers (Ferris and Ertem, 1992). Reactions in the terrestrial environment forming oligonucleotides having 40 or more bases is generally one of the key requirements for the RNA world scenario for the origin of life on Earth. This proposal requires that RNA both store genetic information and catalyze chemical reactions. The identification of phyllosilicates, including montmorillonite, on Mars raises the possibility that such processes may have taken place there, too (Bishop et al., 2008; Wray et al., 2008).

Montmorillonite clay minerals, which occur in altered volcanic ash, are generally classified as bentonite in Phanerozoic sedimentary strata. Montmorillonite is a phyllosilicate, chiefly containing the elements silicon, aluminum, magnesium, iron and oxygen (Figure GS-14-1), where cations are found within its highly organized negatively charged layers. Because of its unique structure, montmorillonite is different from most rock-forming components in that it can catalyze the oligomerization of activated nucleotides to form RNA (Aldersley et al., 2009a,

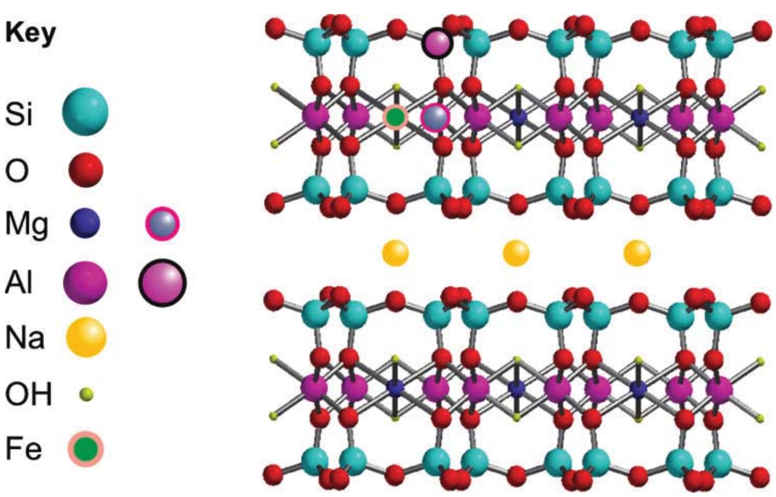

Figure GS-14-1: *The structure of montmorillonite (from Joshi et al., 2009 and Aldersley et al., 2009a).*

[1] Department of Chemistry and Chemical Biology and the New York Center for Astrobiology, Rensselaer Polytechnic Institute, Troy, New York, 12180, United States
[2] Current address: Department of Chemistry, University of Leeds, LS2 9JT, United Kingdom
[3] Department of Atmospheric and Environmental Sciences, The University at Albany, Albany, New York, 12222, United States

b; Joshi et al., 2009); however, not all montmorillonites are catalytic. The mechanism of the montmorillonite catalysis, used as a model for similar prebiotic chemistry, is still not well understood. It has been observed that the extent of catalysis depends not only upon the magnitude of the negative charge on the montmorillonite lattice and the number of cations associated with it, but also on the pH at which the reaction is promoted and the nature of the clay being investigated. Ongoing research by the Rensselaer Polytechnic Institute (RPI), based in Troy, New York, is providing a basis for further understanding of the physical processes in the mechanism of this catalysis; this work indicates that a link can be made between the geochemistry of the clays and their catalytic activity.

Methodology

Joshi et al. (2009) and Aldersley et al. (2009a) described the catalytic studies carried out on 22 selected Cretaceous and Ordovician bentonite samples from the United States and Japan. Five of the samples (all from the Cretaceous and United States) were rated as having excellent catalytic activity, seven samples had good activity and 10 samples were poor. The catalytic properties of each bentonite sample towards RNA synthesis were assessed from their ability to form oligomers from a suitable activated starting material. Thus, the better the catalyst, the longer the oligomers. Excellent catalysts generally form oligomers in the order of the 9- to 10-mer, good catalysts in the 4-mer (tetramer) region whereas poor or noncatalysts produce only traces of the dimers. Analysis of these very complex RNA mixtures (prepared as described by Ferris and Ertem [1992], Joshi et al. [2009] and under Lab Procedures in Data Repository Item DRI2011006[4]) was facilitated by high-performance liquid chromatography (HPLC) using an anion-exchange column and a reverse phase column. In this technique, the larger the charge on the nucleotide, the longer the retention time (over 25 minutes) and thus, the excellent resolution that is shown in Figure GS-14-2 (from Aldersley et al., 2009a; Joshi et al., 2009). The figure depicts selected high-performance liquid chromatography (HPLC) traces for excellent to poor catalysts from these studies. It should be noted that due to the dilute nature of the solution required to enhance the sensitivity of the

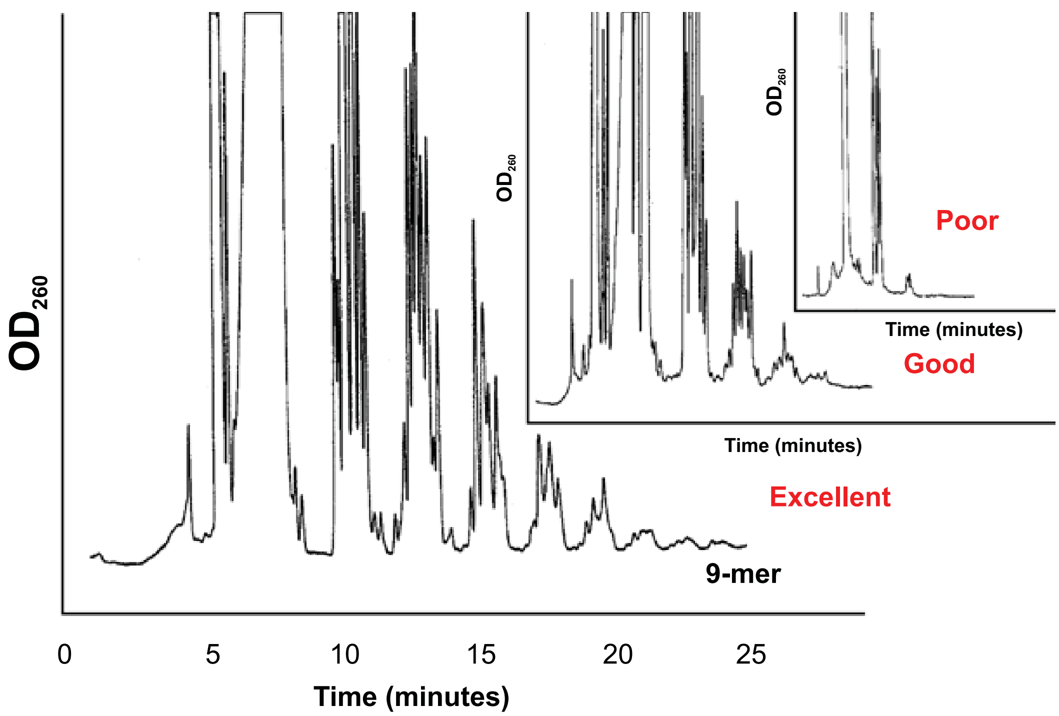

Figure GS-14-2: *Ion exchange high-performance liquid chromatography (HPLC) traces obtained for three representative types of montmorillonite from Joshi et al. (2009) and Aldersley et al. (2009a). The figure depicts the longest oligomer detected and the catalysts' nature (excellent, good, poor) for each sample tested. They are (from bottom to top) Volclay-Supercol, Wyoming (an excellent catalyst), H-28, Little Rock, Arkansas (a good catalyst) and H-23 Chambers, Arizona (a poor catalyst). The magnitude of the time scale on the x-axis (shown as 0 to 25 minutes) for the excellent sample is the same relative time scale for the reduced inset diagrams shown for good and poor samples. Optical density was recorded at 260 nm (OD_{260}).*

[4] MGS Data Repository Item DRI2011006, 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 Innovation, Energy and Mines, 360–1395 Ellice Avenue, Winnipeg, Manitoba R3G 3P2, Canada.

process, that the vertical axis of the HPLC traces are in the order of 0.000 to 0.002. An excellent catalyst from Volclay-Supercol, Wyoming, can be seen having a 9-mer long oligomer (nine distinctive peaks). Also shown in the figure is a good catalyst from Little Rock, Arkansas, with five peaks; and a poor catalyst from Chambers, Arizona, with three peaks. Therefore, the greater number of HPLC peaks; the more catalytic is the bentonite sample.

As a result of finding 12 excellent and good catalysts in these studies, located mainly in the northern United States, it was decided to extend the study area into southern Manitoba (Aldersley et al., 2009b), where bentonite beds were known to be present.

Manitoba bentonite evaluation

Regional setting

Cretaceous bentonite occurrences in Manitoba range upwards from the Ashville Formation to the Odanah Member of the Pierre Shale (Figure GS-14-3). Details of each of these stratigraphic units are described in Bamburak and Nicolas (2009). The bentonite seams range in thickness from <1 to 50 cm in thickness. The highest concentration of seams is found in the lower portion of the Pembina Member of the Pierre Shale, where upwards of 20 distinct seams, ranging in thickness from 2 to 30 cm, occupy roughly two-thirds of a 5 m black shale and whitish bentonite interval. Bertog et al. (2007) referred to this succession of bentonite beds as the 'Ardmore bentonite succession'. In addition, Bertog et al. (2007) also recommended elevating the Pierre Shale to group status and renaming the Pembina Member of North Dakota, as the Sharon Springs Formation. The MGS will retain the previous terminology, as suggested by Gill and Cobban (1965).

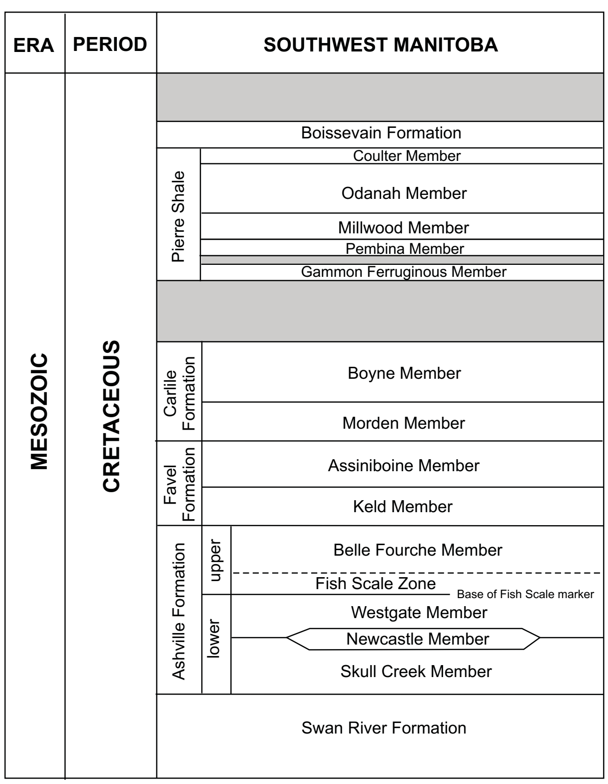

***Figure GS-14-3:** Cretaceous stratigraphy of southwestern Manitoba (Nicolas and Bamburak, 2009).*

Canadian Fossil Discovery Centre samples

Enbridge pipeline site

In November 2009, the Canadian Fossil Discovery Centre (CFDC) provided eight Ardmore bentonite samples (Table GS-14-1) from the Pembina Member of the Pierre Shale (Figure GS-14-3) for catalytic evaluation, at the request of RPI. The samples had been collected by the CFDC along the newly excavated route of the Enbridge pipeline, west of Morden, in L.S. 13, Sec. 17, Twp. 3, Rge. 6, W 1st Mer. (abbreviated 13-17-3-6W1; UTM Zone 14U, 554911E, 5452012N [NAD83]; NTS 62G1NE). The samples were labelled as Pembina Mountain horizon 1 to 8 (PM-H1 to PM-H8, as shown in Figure GS-14-4), in accordance with the format described by Hatcher and Bamburak (2010). It should be noted that the site was subsequently rehabilitated and this section is no longer visible.

The whole-rock and trace-element chemistry and the results of subsequent catalytic studies of the Enbridge pipeline samples are tabulated in Data Repository Item DRI2011006. All eight samples from the pipeline site were determined to be noncatalytic (Table GS-14-1).

Rensselaer Polytechnic Institute samples

In 2009, the RPI collected a total of 24 samples from four sites in southern Manitoba (Table GS-14-1). The samples ranged from the Morden Member of the Carlile Formation to the Odanah Member of Pierre Shale.

All of the samples below were processed by the RPI to determine their catalytic properties and they were all shown to be noncatalytic, as summarized in Table GS-14-1 and described in detail in DRI2011006.

Morden southeast outcrop

One sample (MS1) was taken from a bentonite bed within the Morden Member of the Carlile Formation on the west side of a roadcut, 16 km south-southeast of Morden. The site is situated in 16-10-1-5W1 (UTM Zone 14U, 569940E, 5430982N; NTS 62G1SE).

Holo Crossing outcrops

Three samples (HC 101, 201, 202) were collected along PR 201 near Holo Crossing in the Pembina Valley, southwest of Morden. Sample HC 101 was obtained from

Table GS-14-1: Summary of bentonite samples and catalytic activity, Manitoba.

Sample number	Locality	Catalyst rating
Canadian Fossil Discovery Centre		
PM-H1	Enbridge	poor
PM-H2	Enbridge	poor
PM-H3	Enbridge	poor
PM-H4	Enbridge	poor
PM-H5	Enbridge	poor
PM-H6	Enbridge	poor
PM-H7	Enbridge	poor
PM-H8	Enbridge	poor
Rensselaer Polytechnic Institute		
MS 1	Morden southeast	poor
HC 101	Holo Crossing	poor
HC 201	Holo Crossing	poor
HC 202	Holo Crossing	poor
SB1	Stonehenge	poor
SB2	Stonehenge	poor
SB3	Stonehenge	poor
SB4	Stonehenge	poor
SB5	Stonehenge	poor
SB6	Stonehenge	poor
SB7	Stonehenge	poor
SB8	Stonehenge	poor
SB9	Stonehenge	poor
SB10	Stonehenge	poor
SB11	Stonehenge	poor
SB12	Stonehenge	poor
SB13	Stonehenge	poor
SDO 1	Spencer’s ditch	poor
SDO 101	Spencer’s ditch	poor
SDO 2	Spencer’s ditch	poor
SDO UNK 1	Spencer’s ditch	poor
SDO UNK 2	Spencer’s ditch	poor
SDO UNK 3	Spencer’s ditch	poor
SDO UNK 4	Spencer’s ditch	poor
Manitoba Geological Survey		
99-09-AS-001	Ashville	poor
99-95-MI-1-1	Mount Nebo	poor
99-96-BR-4-4-2	Treherne	excellent
99-08-MT-001	Miniota	good

a bentonite bed within the Odanah Member of the Pierre Shale in a quarry located on the east side of PR 201, near the top of the north wall of the valley. Samples HC 201 and 202 were extracted from two bentonite beds from the upper part of the Boyne Member of the Carlile Formation in 1-13-1-7W1 (UTM Zone 14U, 553407E, 5431337N; NTS 62G1SW).

Stonehenge bentonite outcrops

Thirteen bentonite beds were sampled (SB1 to SB13) from the Pembina Member of the Pierre Shale. The site is located on the north side of the road allowance along 12-21-1-5W1 (UTM Zone 14U, 566979E, 5433657N; NTS 62G1SE).

Spencer’s ditch outcrops

Seven bentonite samples (SDO 1, 101, 2, SDO UNK 1 to 4) were taken from the east wall of Spencer’s ditch, south of the section line in 15-31-3-6W1 (UTM Zone 14U, 553843E, 5457258N; NTS 62G8SW). The bentonite beds are present within the Boyne Member of Carlile Formation.

Manitoba Geological Survey samples

In December 2009, MGS sent four archived bentonite samples for catalytic testing. The samples ranged from the Ashville Formation to the Odanah Member of Pierre Shale.

Ashville Formation outcrop

A sample of yellow bentonite (99-09-AS-001) was collected in 2009 from a conspicuous 0.5 m thick seam within the shale of the Belle Fourche Member of the Ashville Formation in a stream cut on the north bank of the Wilson River (Figure GS-14-5a). The sample site is situated 1 km southwest of Ashville in 14-14-25-21W1 (UTM Zone 14U, 408242E, 5669335N; 62N1NW). The bentonite is interpreted to be the X-bentonite, described by McNeil and Caldwell (1981) as being equivalent to a widespread marker bentonite found in the Western Interior of the United States. Catalytic tests indicated that the Ashville Formation bentonite (or X-bentonite) is a poor catalyst (dimers) as shown in Figure GS-14-6 and listed in Table GS-14-1.

Mount Nebo quarry

Pinkish Ardmore bentonite (99-95-MI-1-1) was collected north of the road allowance in 4-18-4-6W1 (UTM Zone 14U, 552995E, 5460834N; NTS 62G8SW) from the Pembina Member of the Pierre Shale (Figure GS-14-3) within a former bentonite quarry (Figure GS-14-5b) on the eastern flank of Mount Nebo. Catalytic tests indicated that the Mount Nebo bentonite is a poor catalyst (dimers) as shown in Figure GS-14-6 and Table GS-14-1. This is consistent with the results obtained on other Pembina Member bentonite samples collected by the CFDC and RPI.

Treherne quarry

In 1996, greenish swelling bentonite (99-96-BR-4-4-2) was collected from the Odanah Member of the Pierre Shale in an active shale aggregate quarry, 2 km

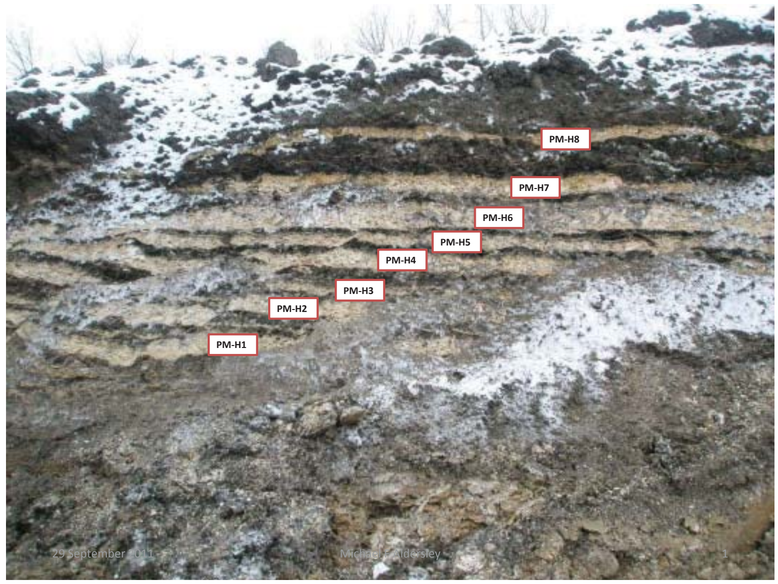

Figure GS-14-4: *Sampled bentonite horizons at the Enbridge pipeline site in L.S. 13, Sec. 17, Twp. 3, Rge. 6, W 1st Mer., southern Manitoba.*

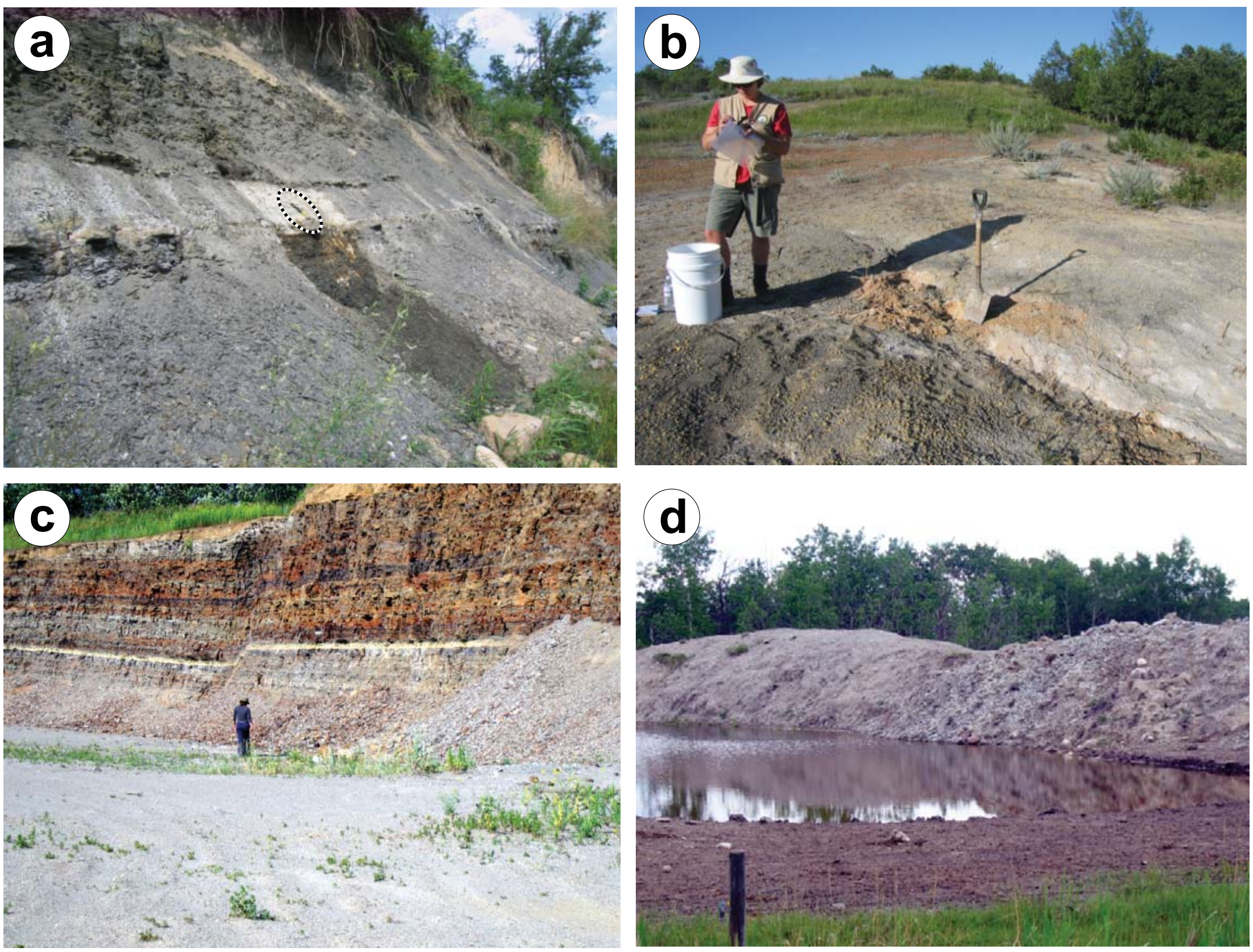

Figure GS-14-5: *Manitoba Geological Survey (MGS) bentonite sample sites in southern Manitoba:* ***a)*** *Ashville Formation outcrop (2009-08-22), hammer marks position of whitish bentonite seam;* ***b)*** *Mount Nebo quarry (2008-08-25), M. Nicolas of MGS sampling the yellowish bentonite seam, marked by the shovel;* ***c)*** *Treherne quarry (2007-07-04), A-M. Janzic of the Canadian Fossil Discovery Centre, in Morden, stands below the distinctive greenish yellow bentonite seam;* ***d)*** *Hawley farm water-filled dugout, Miniota (2008-06-26), weathered bluish bentonite clasts from pit bottom lie on surface of excavated material.*

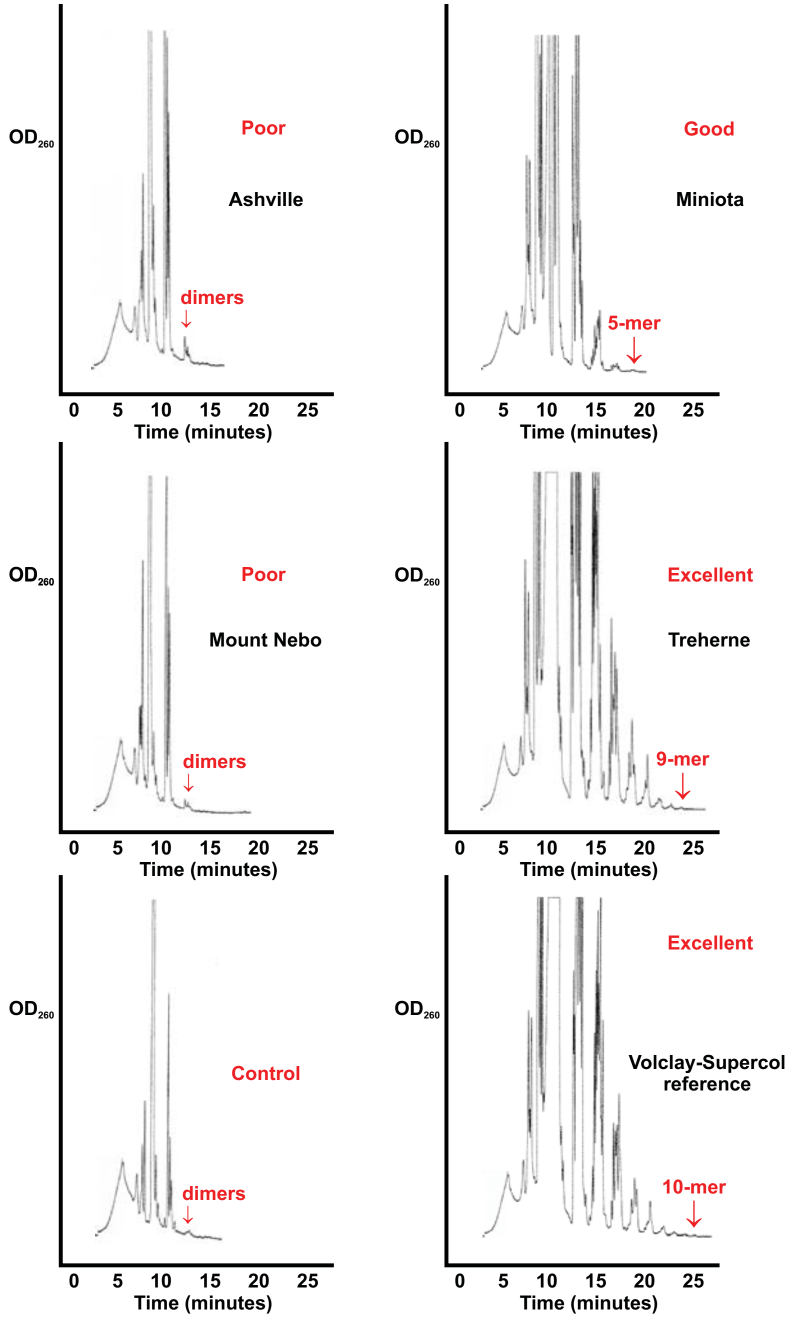

Figure GS-14-6: *Ion exchange high-performance liquid chromatography (HPLC) traces of the RNA products from the catalysis of ImpA oligomerization: Ashville Formation sample, Miniota sample, Mount Nebo sample, Treherne sample, a control sample (dimers) and a Volclay-Supercol reference sample (10-mer). The figure shows the longest oligomer detected and the catalysts' nature (excellent, good, poor) for each sample tested. Optical density was recorded at 260 nm (OD_{260}). Details of the catalytic evaluation of these bentonite samples are described in Data Repository Item DRI2011006.*

south of Treherne. The quarry (Figure GS-14-5c) is located in 12-36-7-10W1 (UTM Zone 14U, 520969E, 5495817N; NTS 62G10SE). Catalytic tests indicated that the Treherne bentonite is an excellent catalyst (9-mer) as shown in Figure GS-14-6 and Table GS-14-1. In addition, the bentonite is different from previous samples and is part of a new class of bentonite, as determined by the magma class from which it was formed.

Hawley farm dugout, Miniota

In 2006, greenish swelling bentonite (99-08-MT-001) was sampled from the Odanah Member of the Pierre Shale. A local resident extracted it from the bottom of the Hawley farm dugout (now water filled; Figure GS-14-5d). The Hawley farm dugout is located 7.5 km southwest of Miniota, north of the road allowance in 2-16-13-27W1 (UTM Zone 14U, 349068E, 5551161N; NTS 62K3SE).

This site was briefly described by Bamburak (2007). Catalytic tests indicated that the Miniota bentonite is a good catalyst (5-mer; Figure GS-14-6, Table GS-14-1).

Discussion

The mechanism by which montmorillonite catalyzes the formation of RNA is the current focus of these investigations. The investigation of the clays found in Manitoba is adding to the knowledge base. To date a total of 36 Manitoba bentonite samples have been evaluated, but only two of these are rated as catalysts: 1) the Treherne Odanah Member bentonite, which is an excellent catalyst, and 2) the Miniota Odanah Member bentonite, which is a good catalyst.

In 2011, three more bentonite samples from the Odanah Member of the Pierre Shale were forwarded to RPI for comparison with the catalytic properties of the Treherne and Miniota bentonite samples. Two of the samples were collected in shale aggregate quarries in Manitoba, one from along the Manitoba Escarpment (west of Miami), and one from the top of the Pembina Valley (southwest of Morden). The third sample was collected from a roadcut (west of Walhalla, North Dakota). Results on these new samples are pending.

The catalytic behaviour of the bentonite beds within Cretaceous stratigraphy of Manitoba may have been affected by the nature of the underlying Paleozoic rock formations. The bentonite beds located southwest of Morden along the Manitoba Escarpment are poor catalysts and are underlain by the Paleozoic Interlake Group, which is composed of theoretically pure dolomite (Bamburak and Gale, 1993). The magnesium contained in these bentonite beds may have been part of the alteration process, when the volcanic glass was converted into clay by magnesium-laden groundwater flowing upwards through fractures in the underlying strata. This can be contrasted with the excellent catalytic properties of the Treherne bentonite, which is underlain by the Paleozoic Souris River Formation, which consists of a complex facies of limestone and less pure dolomite. However, this approach may be too simplistic because of the presence of intervening Jurassic redbeds and evaporates, which may have acted as aquitards between the bentonite beds and the Paleozoic strata and that may have contributed to the chemical changes. As a first approach, testing of the overlying bentonite beds and underlying Paleozoic rock units will be carried out on samples to be supplied by MGS to RPI to determine if the earlier hypothesis is valid.

Economic considerations

Although this study is unlikely to directly influence the economic development of bentonite mineral deposits or occurrences in Manitoba, it will definitely draw public attention to the diversity of the mineral resource base of the province. Further investigation of montmorillonite clays in Manitoba will have only limited impact dependant on the nature of follow-up investigations to be carried out by RPI. However, if the modelling carried out by RPI is successful in using Manitoba bentonite to demonstrate that life on Earth, and possibly Mars, evolved from this parent material, then Manitoba will receive the attention from a worldwide audience through publication and dissemination of this work. This interest could result in increased tourism to the province's unique geological features (Bamburak, oral presentation, 2010), and possibly to investment in other Manitoba mineral commodities.

Acknowledgments

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