

AMORPHOUS COATINGS ON PARTICLES OF SENSITIVE CLAY SOILS

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Abstract—Post-glacial Champlain Sea sediments in Quebec and Ontario are often extremely sensitive. Suggestions of considerable amorphous material in these soils come from X-ray diffraction results, as well as electron micrographs. A method for selective dissolution and analysis of amorphous material is used to study two Champlain Sea deposits. The amorphous material removed amounts to 11–12 per cent of the soils and consists mainly of silica and iron oxide. The treated samples have enhanced X-ray diffraction peaks and much cleaner particles as seen by electron microscopy.

INTRODUCTION

A common engineering problem in large areas of Quebec and Ontario is the very high mechanical sensitivity of clay soils. These soils were deposited in the geologically recent and highly saline Champlain Sea. Their source material is the Canadian Shield rocks of northern Quebec, Ontario and Labrador, which are high in iron content. Post-glacial uplift of these soils has allowed drainage and salt leaching from the profiles, a condition which has led to comparisons of these clay soils with sensitive Scandinavian clays with similar histories. Recently, however, it has become apparent that the mechanisms involved in producing extreme sensitivity in the Champlain Sea clays have strongly bonded, perhaps cemented, particles which can result in sensitivity values of fifty to many hundreds (Soderman and Quigley, 1965; Sangrey, 1972). They are very stiff in the undisturbed state, becoming virtually liquid when extensively sheared (Crawford, 1963). A closer examination of the nature of possible bonding or cementing agents is required for a satisfactory explanation of the behavior of these clays.

MINERALOGY AND FABRIC

The suite of minerals contained in clays over the entire Champlain Sea area is quite uniform. The main clay minerals are chlorite and illite, accompanied by large amounts of feldspar, quartz, amphibole and mica. Carbonates and crystobalite are often found as well, but smectites have not been detected in any appreciable quantity. An example of approximate mineralogical distributions in clay soils from two locations in Quebec are listed in Table 1. These quantities have been determined by comparing the highest X-ray dif-

Table 1. X-ray diffraction analysis of untreated "Champlain Sea clay" minerals

Mineral	St. Vallier clay	St. Louis clay
Quartz	7%	6%
Feldspar	7.5	6.5
Illite and Mica	23	18
Hornblende	9	9
Chlorite	3	4
Total:	49.5%	43.5%

fraction peak heights to the corresponding peak heights of standard pure minerals. This method is only approximate and does not account for small changes in crystal orientation. The apparent totals of crystalline materials in the examples of Table 1 do not equal more than half of the solid mass, which either indicates the presence of non-crystalline material in the soils or illustrates the approximate nature of the technique.

In order to examine the nature and disposition of mineral particles and other substances in these clays, transmission electron microscopy was used because of its high resolving power. First, undisturbed Champlain Sea clay samples were vacuum desiccated and cleaved to provide a fresh surface. The surfaces were then replicated by metal shadowed carbon films, which were subsequently stripped and cleaned in alternating baths of concentrated hydrofluoric acid and 0.2 N NaOH for about 6 hr. Despite some shrinkage during desiccation, the particles of an undisturbed sample of Champlain Sea clay shown in Fig. 1 are fairly open and discrete, reflecting the high natural water content (64 per cent) of this soil. Most particle surfaces, however, are not as smooth as those usually observed on well crystallized mineral particles. They are lumpy and amorphous in appearance, even though the overall particle shapes

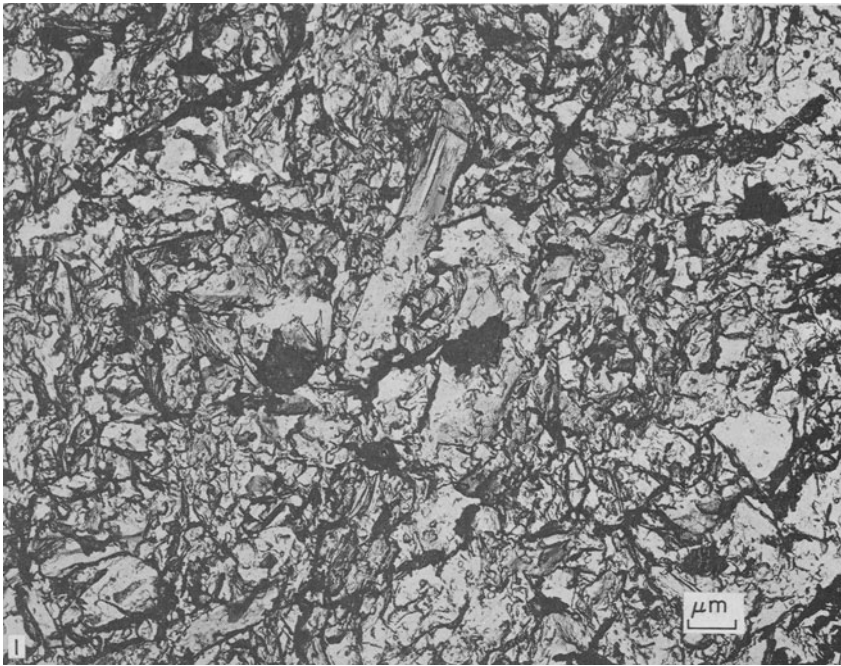


Fig. 1. Replica transmission electron micrograph of a vertical cleavage surface in undisturbed, desiccated St. Vallier clay.

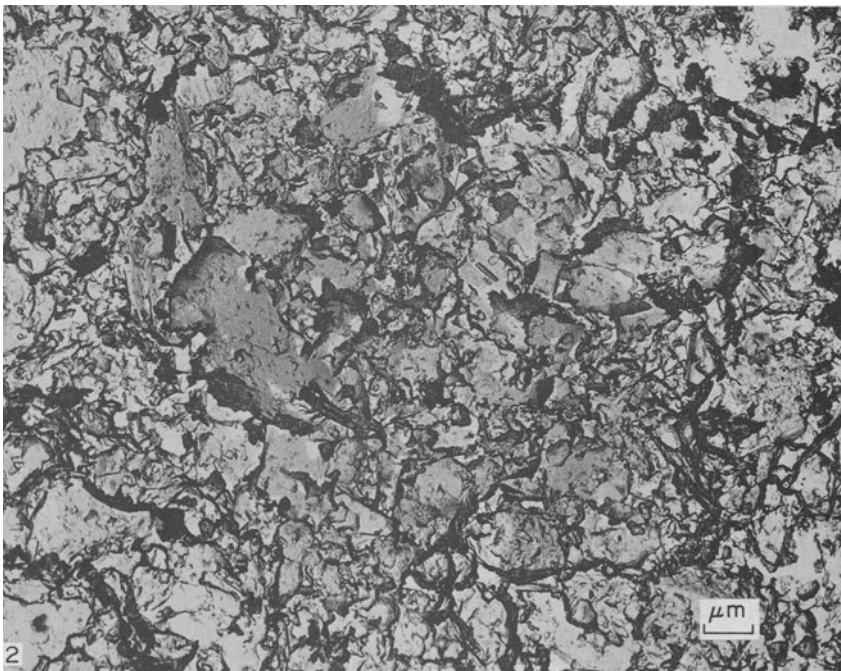


Fig. 2. Replica transmission electron micrograph of a horizontal cleavage surface in undisturbed, desiccated St. Vallier clay.

are typical of microscopic crystals. In Fig. 2 a horizontal section of the same soils is shown in which there are more flat clay particle surfaces visible and less edges. This indicates a somewhat anisotropic soil fabric with a preference for flat particles to lie in the horizontal plane. The surfaces of larger particles in Fig. 2 are lumpy and amorphous as in Fig. 1, and submicron clay particles can be seen adhering to these surfaces. Figure 3 shows a disturbed clay sample which was extensively sheared before cleavage and preparation for viewing. It can be seen that the soil particles are well oriented parallel to the surface, but that they are nearly lost to view in an overall coating of amorphous appearing material. It appears that this amorphous material is somewhat mobile under mechanical action, and it remains to determine the composition and amount of this coating substance.

SELECTIVE DISSOLUTION OF AMORPHOUS MATERIAL

Work has been done on the selective dissolution of, for example, iron and aluminum in some smectites (Osthaus, 1954) and of allophanes in hot caustic soda (Hashimoto and Jackson, 1960). However, a technique has been described by Segalen (1968) by which the quantity and composition of amorphous materials in a soil may be estimated, and both the silica and alu-

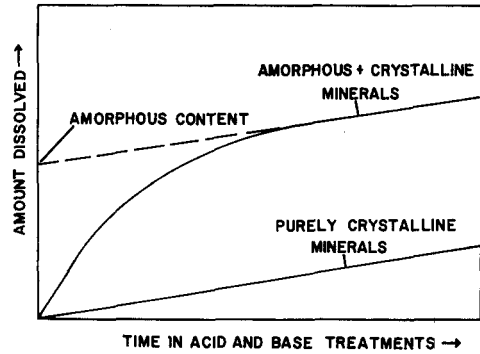


Fig. 4. Dissolution rates of crystalline and amorphous soil materials in HCl and NaOH.

mina components may be removed. It is based on the fact that amorphous soil minerals dissolve faster than crystalline particles in strong acid and alkali solutions. Thus the rate of dissolution of a mixed crystalline and amorphous soil is faster at first than a crystalline sample, as shown in Fig. 4, but after some time it asymptotically slows to the same rate as the latter. It is then assumed that virtually all the amorphous fraction of the soil has been removed, and that the difference in the amount dissolved after this time is the amorphous fraction of the original sample. Because of the faster dissolution of amorphous material and the limited time of laboratory treatment, minimal damage

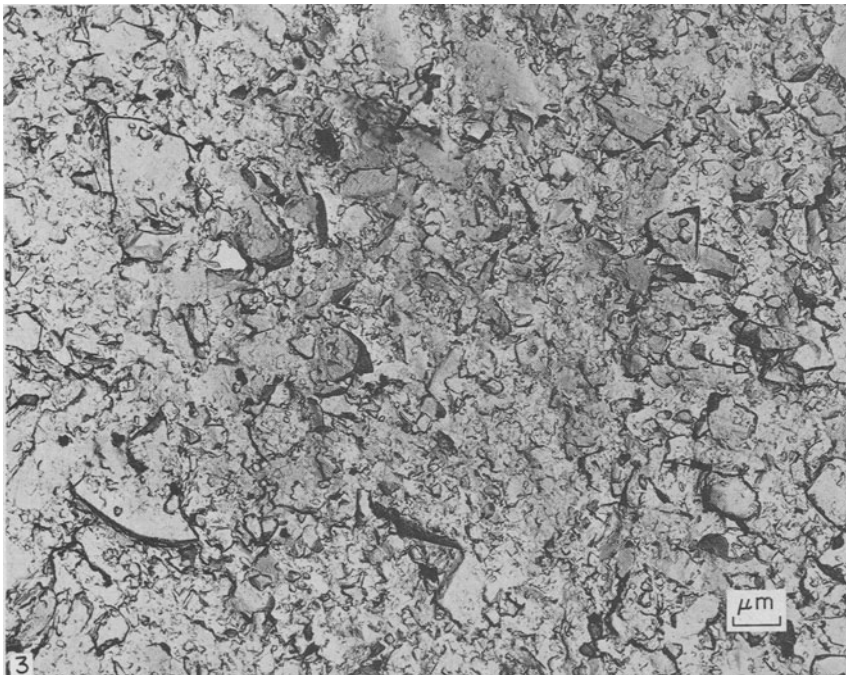


Fig. 3. Replica transmission electron micrograph of a cleavage section in highly sheared St. Vallier clay.

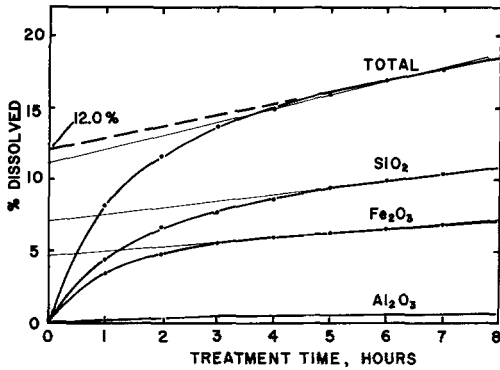


Fig. 5. Dissolution rates of minerals in St. Vallier clay.

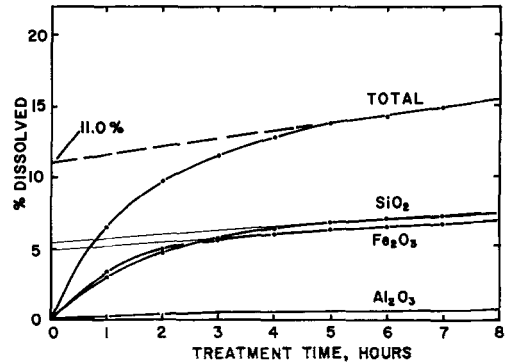


Fig. 6. Dissolution rates of minerals in St. Louis clay.

is expected to the crystalline rock and clay particles. It is possible that amorphous coatings on crystalline particles might hinder the dissolution of the crystalline particles, in which case a slight underestimate of the quantity of amorphous material in a soil could result.

To apply this technique to the clays under study, samples of Champlain Sea soil from St. Vallier and St. Louis, Quebec, were dried, pulverized lightly and then shaken continuously in closed polypropylene tubes containing alternate solutions of 8.0 N HCl and 0.5 N NaOH at room temperature. After each pair of solution treatments, which lasted 30 min per solution, the solids were centrifuged to the bottom of the tubes and the supernatant fluid filtered into polypropylene 50 ml volumetric flasks. The flasks were filled to the mark and their contents analyzed by colorimetric spectrophotometry by a Beckman DU spectrophotometer. This procedure was repeated with the alternating acid and alkali solutions a sufficient number of times on each soil sample to allow the amorphous material to be dissolved completely and analyzed.

Figure 5 and 6 show the results of these selective dissolution tests on the two clays, as well as the analysis of the major components of the dissolved material. The points plotted on the curves are the measured quantities after each pair of HCl and NaOH treatments. In both clays the amorphous material amounted to eleven to twelve percent of the total dry soil weight, with silica and iron oxide being the principal components extracted. The amounts of alumina found in the amorphous extracts were small, probably owing to the high iron content of the soils. The soil materials treated in this way were retained for subsequent observation by X-ray diffraction and electron microscopy.

OBSERVATION OF CLEANED SOILS

X-ray diffraction results from the oriented clay specimens treated by the selective dissolution technique are shown in Figs. 7 and 8, together with results from the untreated soils. Considerable increases are seen in the peak heights for quartz, feldspar and horn-

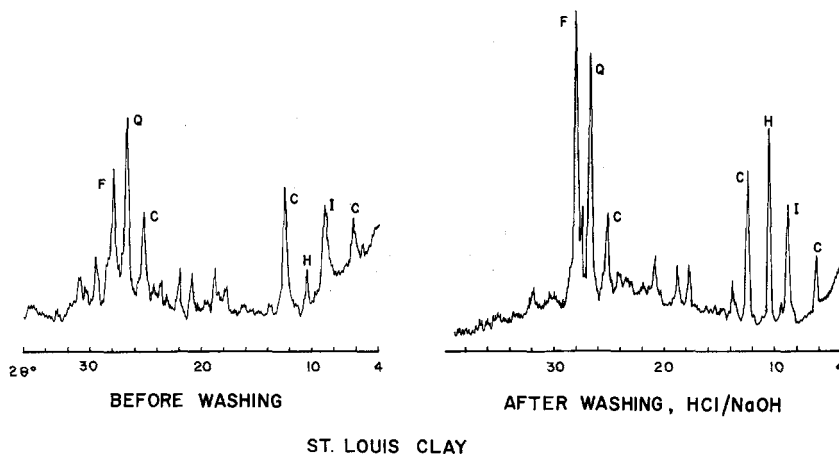


Fig. 7. X-ray diffractogram of oriented slides of St. Louis clay before and after selective dissolution. Q—quartz, F—feldspar, I—illite and mica, H—hornblende, C—chlorite.

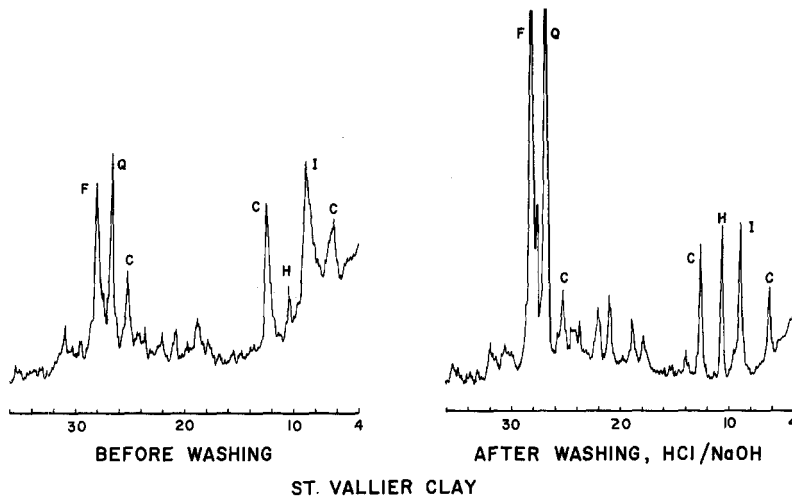


Fig. 8. X-ray diffractogram of oriented slides of St. Vallier clay before and after selective dissolution.

blende following the selective dissolution treatments. This suggests that these minerals were coated with amorphous material prior to the solution treatments, thereby reducing the coherent X-ray diffraction from them. The clay mineral peaks have not changed considerably in size, but they appear much sharper than before. Upon summing the quantities of minerals, as measured by X-ray diffraction, the new totals are 92.5 and 95.5 per cent, as shown in Table 2. The removal of amorphous material has allowed approximate quantification of the crystalline soil minerals.

Figure 9 shows the difference in soil particles deposited on a glass slide before and after the removal of amorphous material. In the latter view (Fig. 9b), virtually all mineral surfaces are clean and flat and the submicron clay particles aggregate together rather than adhering to the surfaces of larger particles. The

Table 2. X-ray diffraction analysis of "Champlain Sea clay" minerals after selective dissolution

Mineral	St. Vallier clay	St. Louis clay
Quartz	13%	8%
Feldspar	15	14
Illite and Mica	29	30
Hornblende	32	39
Chlorite	3.5	4.5
Total:	92.5%	95.5%

evidence strongly suggests that the non-crystalline texture of large particle surfaces in the untreated Champlain Sea clays is caused by coatings of amorphous material consisting mainly of silica and iron oxide. These coatings appear to attract clay particles and to be somewhat mobile under mechanical action.

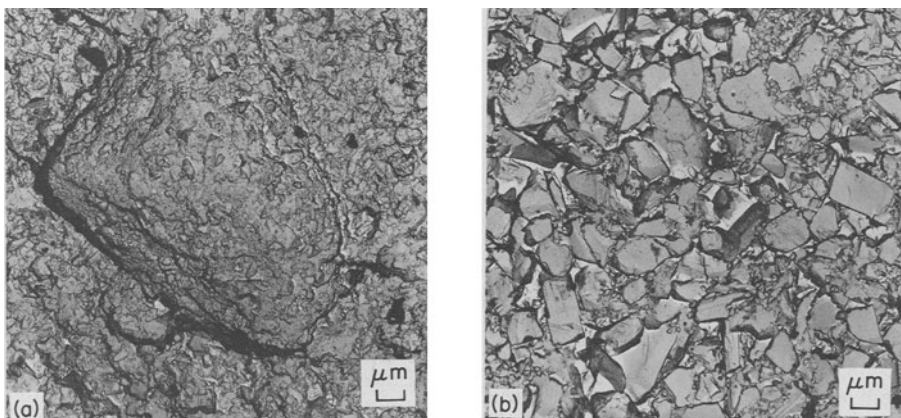
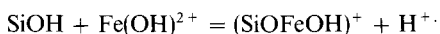


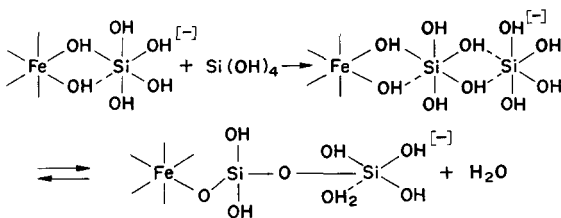
Fig. 9. Replica transmission electron micrograph of oriented slides of St. Vallier clay, (a) before and (b) after selective dissolution.

POSSIBLE STRUCTURE OF AMORPHOUS COATINGS

The chemical analysis of extracted amorphous material from the Champlain Sea clays indicates that SiO_2 and Fe_2O_3 are the main components, with small amounts of Al_2O_3 . In recent work the structure of amorphous mixed silicon-iron hydroxides has been examined but is still not precisely known. It has been found that the solubility of silica is reduced in the presence of iron oxide in the pH range of 2–12 (Jones and Handreck, 1963). Suggestions have been made that silica and iron oxide react chemically in solution (Bastisse, 1964), whereas others explain the formation of a silicon-iron hydroxide complex by the reaction of silanol groups of polysilicic acid with basic metal groups as follows (Jones and Handreck, 1963):



However, this mechanism would produce a positively charged product, while negatively charged silica-iron hydroxide have been observed to have cation exchange capacities of 0.6–90.0 m-equiv/100 g (Herbillon and Tran Vinh, 1969). These latter workers have proposed that silica can be chemisorbed on ferric hydroxide. They suggest the following reaction for $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratios greater than 0.1:



The ratios of amorphous SiO_2 to Fe_2O_3 in the St. Louis and St. Vallier clays are approximately 1.9 and 2.5, respectively, which may be uncommonly high (Herbillon, 1973). Because of the high ratio, the structural organization shown above appears most likely.

SUMMARY AND CONCLUSIONS

The samples of very sensitive clay from the Champlain Sea deposits in Quebec, examined in this study, consist of large particles with bumpy looking surfaces covered with submicron sized particles. X-ray diffraction indirectly indicates the presence of considerable amorphous material. By selective dissolution in acid and alkali baths, it was estimated that eleven to twelve percent of the soil solids consist mainly of amorphous silica and iron oxide. The removal of this material greatly enhanced the X-ray diffraction peak intensities

of the quartz, feldspar and hornblende minerals, and produced a soil of discrete and clean mineral particles. Submicron particles no longer adhere to the larger particles.

From other studies, it could be speculated that the amorphous silica is chemisorbed on ferric oxide, which in turn may have resulted from mineral weathering. Whether this material has formed completely *in situ*, or whether it may have been partly present at the time of transport and deposition is not yet clear. The answer to this question could be of use for a further understanding of the nature of amorphous material in sensitive clays.

It is very likely that the presence of amorphous material as particle coatings has a large effect on the mechanics of these clays. The coatings may well be a major factor in the extreme sensitivity of the soils. It remains to be shown by further work that the removal of amorphous material from Champlain Sea clays has an effect on their sensitivity, or that the introduction of amorphous matter can increase the sensitivity of other clays. If the causes of very high sensitivity can be fully understood, the behavior of these clays can be better predicted, and their properties might be altered by chemical means, in some cases, to the benefit of safety and economy.

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Résumé—Les sédiments post-glaciaires du lac Champlain dans le Québec et l'Ontario sont souvent très instables au point de vue mécanique. Les résultats de la diffraction X et de la microscopie électronique suggèrent la présence dans les sols d'une quantité considérable de matériaux amorphes. Une méthode de dissolution sélective et d'analyse du matériau amorphe a été mise en oeuvre pour étudier deux sédiments du lac Champlain. Le matériau amorphe éliminé atteint 11–12 pour cent des sols et consiste essentiellement en silice et oxyde de fer. Les échantillons traités ont des pics de diffraction X renforcés et de nombreuses particules décapées peuvent être observées au microscope électronique.

Kurzreferat—Postglaziale Sedimente des Champlain-Sees in Quebec und Ontario sind oft außerordentlich empfindlich gegen mechanische Beanspruchung. Die Annahme, daß erhebliche Mengen amorpher Materials in diesen Böden enthalten sind, wird sowohl aus Ergebnissen der Röntgenbeugung als auch aus elektronenmikroskopischen Aufnahmen hergeleitet. Eine Methode zur selektiven Auflösung und Analyse des amorphen Materials wird benutzt, um zwei Champlain-See-Ablagerungen zu untersuchen. Das entfernte amorphe Material betrug 11–12 Prozent der Böden und bestand vorwiegend aus Kieselsäure und Eisenoxiden. Die behandelten Proben weisen verstärkte Röntgenbeugungsreflexe und viel reinere Teilchen auf, wie elektronen-mikroskopisch festgestellt werden kann.

Резюме — Последледниковые осадки Чамплэнского моря в Квебеке и Онтарио часто бывают очень чувствительными. По результатам дифракции рентгеновских лучей и по электронным микроснимкам заключили, что в этой земле имеется значительное количество аморфного материала. Для изучения двух образцов осадков Чамплэнского моря используются методы селективного растворения и анализа. Извлеченный аморфный материал составлял от 11–12 процентов земли и состоял главным образом из кварца и окиси железа. Переработанные образцы показали на рентгенограммах усиленные дифракционные пики, а на электронных микроснимках более чистые частицы.