

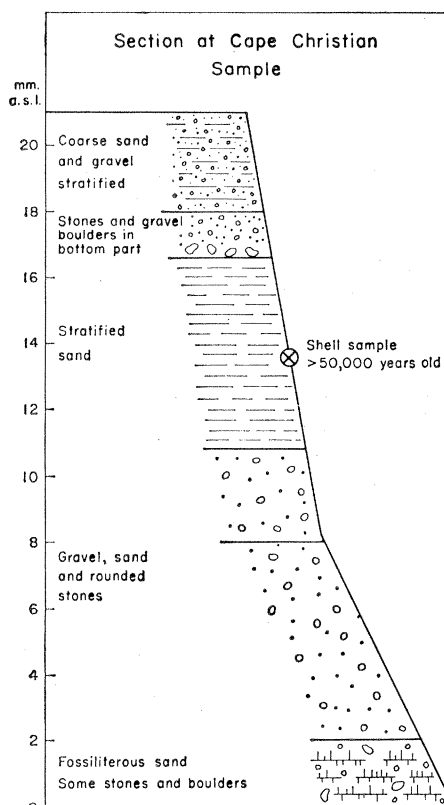


Fig. 2. Stratigraphy of cliffs near Cape Christian.

L., and *H. arctica* L. were identified (3). Many paired bivalves were found in upright positions and the shells were undoubtedly *in situ*.

The sand is overlain by a 1-m-thick gravel bed similar to the one below the sand. The stones and boulders in this stratum decrease in size and increase in roundness upward. The layer is again overlain by a layer of coarse sand and fine gravel.

The bottom stratum, with shell fragments and high clay content, is interpreted as a marine deposit that has been plowed up and redeposited by an advancing glacier. That the dominating sand layer is a marine deposit is shown by the molluscs, and the low sorting coefficient (S_o , 1.33) and the low skewness (S_k , 0.22) indicate that the sand is a littoral deposit. The sand also contains more rounded and subrounded grains than any other part of the section. The coarse strata above and below the sand are both interpreted as glacial deposits, and may be either till or glaciofluvial in origin. The lower parts of both strata, with less sorted material, resemble till, while the upper parts, which are better rounded and sorted, appear to be glaciofluvial. The upper gravel stratum may be a lag deposit that was left after

a more extensive deposit had been washed away; if it is of glaciofluvial origin, its coarse texture indicates that it was deposited near base level. The highest sand and gravel is interpreted as a littoral deposit formed partly by deposition of ice-rafted material as the sea regressed over the area for the last time.

Thus there is evidence of two glacial advances, one of which occurred more than 50,000 years ago, as shown by the age of the overlying sand. The lateral deposits along Patricia Bay and Clyde Inlet show that ice flowed north from the mouth of the inlet, and the decreasing complexity of the stratigraphy of the cliffs immediately northwest of the locality described reflects the extent of this northward flow.

A most intriguing implication of the very great age of the Cape Aston sample is the possible existence of ice-free areas along the east coast during glacial maxima. The Cape Christian sample confirms the great age of the other sample and shows that these very old sediments occur in more than one isolated locality. Especially in Scandinavia (9), but also in North America (10), attention has been given to distribution of plants, insects, and animals, and the evidence strongly suggests that the present distribution pattern is explained by migration from refugia where the organisms survived glaciation.

The Aston delta shows no evidence of having been overrun by ice after its formation, and the same thus applies to the higher hills nearby, which are above the marine limit and would therefore have provided refugia for plants and animals. The evidence suggests the presence of ice-free areas for longer than 54,000 years, but by analogy one may assume that similar conditions existed earlier in the Pleistocene. In the discussion of refugia, attention has been focused on (i) nunatak refugia (on the high coastal mountains) and (ii) on foreland refugia (on the low coastal areas and possibly coastal banks). The refugia near Cape Aston would be of the second type.

In spite of the long period of subaerial weathering, a low knob at the apex of the Aston delta was not covered by mountain-top detritus (11). Although extensively weathered, the structure of the underlying bedrock was clearly visible and the surface resembled that of the "middle zone" in the Torngat Mountains of northern Labra-

dor, thus indicating that the "upper trimline" in that area is older than 50,000 years (12).

The two samples gave the oldest radiocarbon ages obtained in arctic Canada, although a number of samples have proved older than 40,000 years; one cannot yet correlate the described deposits with any other features in the area or in southern Canada. The cliff sequence north of Cape Christian should yield a chronology reaching far back into the late Pleistocene.

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13. I thank M. Stuiver for the radiocarbon dates, F. J. E. Wagner for identifying the molluscs, and M. Stuiver, A. L. Washburn, and colleagues at the Geographical Branch for valuable comments on the manuscript. The radiocarbon determinations were financed by NSF grant GP 4879.

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Nickel Orthouronate: High-Pressure Synthesis

Abstract. The compound NiUO_4 has been synthesized at high pressure and temperature. No material of this composition is known to be synthesized at ambient pressure. The NiUO_4 structure is of the orthorhombic body-centered MgUO_4 type; cell dimensions: a_1 , 6.415 Å; a_2 , 6.435 Å; and a_3 , 6.835 Å.

When mixtures in proper proportions of MgO and U_3O_8 were fired in air at 1000° to 1200°C , the orthouronate MgUO_4 was formed. In mixtures of NiO and U_3O_8 fired at temperatures

Table 1. Indexing of NiUO₄ and MgUO₄ x-ray powder patterns on an orthorhombic cell.

MgUO ₄			NiUO ₄	
<i>d</i> (Å)	<i>I</i> : <i>I</i> ₀	<i>hkl</i>	<i>I</i> : <i>I</i> ₀	<i>d</i> (Å)
4.67	100	110	80	4.54
3.45	10	002	15	3.41
3.28	80	200	90	3.22
2.77	80	112 121,211	100 10	2.73 2.659
2.389	60	022	30	2.334
2.316	10	220	30	2.282
2.075	50	130,310	40	2.042
1.924	40	222 123,213	20 10	1.896 1.789
1.782	70	132,312 004	70 15	1.754 1.709
1.651	10	040		
1.627	40	400	30	1.605
1.560	10	141	20	1.527

from 700° to 1200°C, there was no apparent reaction; x-ray diffraction analysis disclosed only NiO and U₃O₈. These findings were consistent with the Brisi (1) work on uranates: by decomposing MU₃O₁₀-type compounds at 900°C, he obtained CoUO₄, MnUO₄, and CuUO₄, while NiU₃O₁₀ decomposed to NiO and U₃O₈.

The Brisi MUO₄ compounds had the orthorhombic MgUO₄ crystal structure; the unit cells were larger than the MgUO₄ cells. Because of the smaller Ni-ion radius, the unit cell of NiUO₄, if it did exist, might be smaller than the MgUO₄ cell. It seemed possible therefore that high pressure might favor the formation of NiUO₄.

For the high-pressure experiment, a 1 : 1 mixture of NiO and UO₃ was fired in a sealed platinum tube, at 1100°C and 60 kb pressure, in a belt-type apparatus (2). The x-ray powder pattern of the resulting compound was nearly identical with that of MgUO₄.

The crystal structure of MgUO₄ was determined by Zachariasen (3) to be orthorhombic body-centered, with space group Iman; the powder data have not been published. In Table 1, powder data for both NiUO₄ and MgUO₄ are indexed on the Iman orthorhombic cell. The cell dimensions for NiUO₄ are: *a*₁, 6.415 Å; *a*₂, 6.435 Å; and *a*₃, 6.835 Å. For MgUO₄ they are: *a*₁, 6.520 Å; *a*₂, 6.595 Å; and *a*₃, 6.924 Å.

Slater (4) has tabulated the interatomic distances in about 1000 crystalline materials; regardless of whether compounds are ionic or covalent, the

observed distances between any pair of unlike atoms are generally close to the sum of the atomic radii. For the interatomic bonds to be stable, there must be some overlap between orbitals of neighboring atoms. The spacing between pairs of atoms in a crystal depends on the balance of repulsive and attractive forces between all the atoms in the crystal. If the spacing between an atom pair is close to the greatest possible distance at which orbital overlap can occur, compound formation by substitution of a slightly smaller atom for one of the pair may not be possible. However, if pressure is applied, the other bonds in the potential compound may be shortened enough to reduce the critical interatomic spacing and provide sufficient orbital overlap for crystal formation.

The Slater tabulation indicates that in the MUO₄-type compounds, MgUO₄ and NiUO₄, the M-O distances are critical in determining the stability of these compounds. In MgUO₄ there are two Mg-O bonds with distance 1.98 Å and four bonds with distance 2.19 Å; the latter is the greatest Mg-O distance in the Slater tabulation. Apparently, in equilibrium

with the other interatomic forces, the Mg and O atoms are held apart in the MgUO₄ structure. If Ni and O atoms were held apart the same distance, there might not be enough orbital overlap for Ni-O bonding. The largest Ni-O spacing in the Slater tables is 2.17 Å in NaNiO₂. It seems likely that in crystal formation of NiUO₄ at high pressure the O-O and U-O bonds are shortened enough to allow sufficient overlap of Ni and O orbitals for Ni-O bonding. Once the NiUO₄ is formed, it is metastable at ambient pressure and room temperature. In NiUO₄ at ambient pressure there are two Ni-O bonds with distances 1.93 Å and four with distance 2.16 Å—close to the upper limit for Ni-O bonding.

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Electrochromatography with Reversing Electrophoretic Field

Abstract. *A protein mixture can be separated in a flow column by application of a transverse electrophoretic field to carry faster-migrating components of the mixture into a fixed gel bed at one side of the column, so that slower components move along in a buffer stream. The field is then reversed to return the faster-moving components to the buffer stream. The cycle is repeated many times to complete the separation.*

We present here a process which combines the rapid migration and the resolving power of electrophoresis with the multiplier effect of a column chromatographic process to achieve improved protein separations. This technique has two unique features: (i) components are eluted in the inverse order of their electrophoretic mobilities (that is, slowest first) and (ii) a simple adjustment of electrophoretic field strength produces an effect analogous to gradient elution.

The separating column (Fig. 1) consists of a tube of rectangular cross section with a dialysis membrane and a block of gel matrix on opposing faces. We used polyacrylamide gel (1) to minimize endosmosis. The column was

supported by Plexiglas cooling plates and was immersed in a suitable (one in which all components of interest migrate electrophoretically in the same direction) buffer solution between two electrodes which were parallel to the column. The buffer stream flowed through and completely filled the space between membrane and gel. The effluent was collected in a fraction collector or was passed directly to an analyzer cell.

The electric field from the external electrodes was passed across the column through the dialysis membrane and the gel. In one direction of the field electrophoretically faster components migrated into the gel, leaving the buffer stream enriched in slower compo-