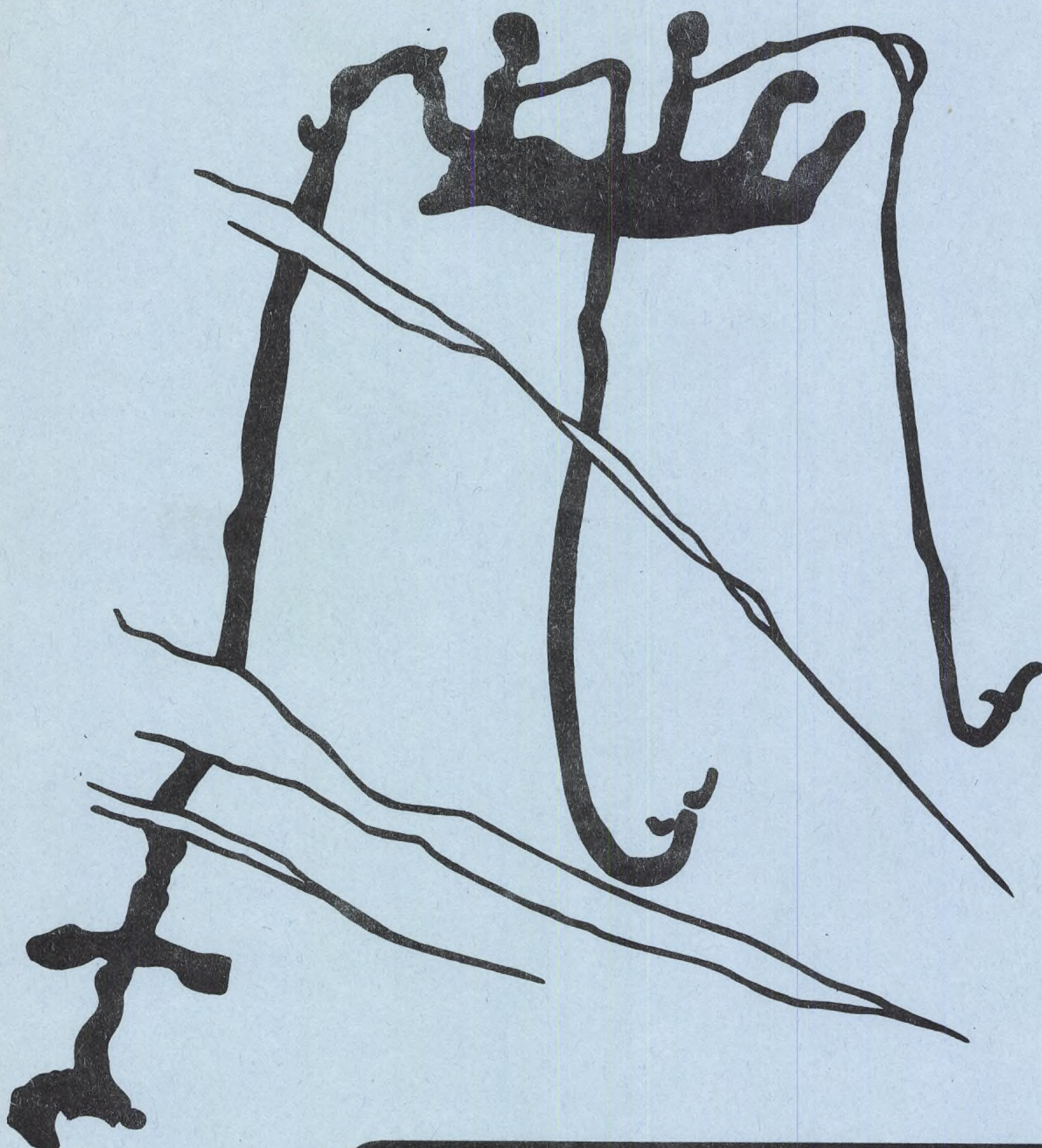
Ödsmål, Kville sn, Bohuslän

Hällristning
Fiskare från
bronsåldern

Rock carving
Bronze age
fishermen



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BROFJORDEN II

A FORMULA SYSTEN FOR PRIMARY PRODUCTION

by

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When computing large numbers of primary production data it is desirable to replace the older methods of reading tables and nomograms with formulas suitable for a computer. In this paper formulas are given which from temperature, salinity and pH values compute the total carbon dioxide content of the water. A formula using this carbon dioxide value and the number of geiger-müller-counts from the filter analysis then compute the final primary production value obtained by the C^{14}-technique.

Symbols used in the text

p	as a prefix denote the negative 10-logarithm of the following variable
K_1	first thermodynamic constant of carbon dioxide
K_2	second " " " " "
K_1'	first dissociation " " carbonic acid
K_2'	second " " " " "
a H_2O	molecular activity of water
a_H	hydrogen ion activity
C_o	solubility of carbon dioxide in pure water
C_s	" " " " " sea water
K_B'	dissociation constant of boric acid
Alk.	alkalinity
total CO_2	total content of carbon dioxide
C	primary production
S	salinity
Cl	chlorinity

Hydrographical measurements performed by the Fishery Board of Sweden in investigating the Brofjorden and primary production measurements by The Marine Botanical Institute, University of Gothenburg, have taken place in close cooperation. A formula system has been developed in order to integrate the primary production data into the data processing.

The formula system is used to calculate values of primary production using the carbon -14 method.

The analyses are performed by the International Agency for ^{14}C determination in Denmark, which gives the number of counts for the samples and values of the strength of the ampoules. The temperature and salinity values are obtained from the hydrographical measurements, and the pH values are measured from the production samples.

According to Sverdrup et. al. 1946 the first dissociation constant of carbonic acid is given by

$$PK_1' = PK_1 - f \times \sqrt[3]{Cl}$$

Where PK_1 is given by Buch (1951) as

$$PK_1 = 17052/T_{abs} + 215.21 \times {}^{10}\log T_{abs} - 0.12675 \times T_{abs} - 545.560$$

and f is derived from the same source as $f = 0.145 - 0.00025 \times T$

K_1' is then obtained by $K_1' = 10^{-PK_1'}$

The term A_H is conventionally obtained as $A_H = 10^{-PH}$

and A_{H_2O} is given by Harvey (1966) as

$$A_{H_2O} = 1 - 0.000969 \times Cl$$

The proper relations for the temperature and chlorinity dependance of the factors C_o and C_s were at this stage too laborious to work out, and they are here given in intervals according to Buch (1945) for

T (°C)	$C_o \times 10^4$	C_s
-2	894	$C_o - 7.22 \times 10^{-4} \times Cl$
±0	770	$C_o - 6.51 \times 10^{-4} \times Cl$
5	640	$C_o - 5.37 \times 10^{-4} \times Cl$
10	536	$C_o - 4.28 \times 10^{-4} \times Cl$
15	458	$C_o - 3.54 \times 10^{-4} \times Cl$
20	394	$C_o - 2.80 \times 10^{-4} \times Cl$
25	341	$C_o - 2.33 \times 10^{-4} \times Cl$
30	299	$C_o - 1.96 \times 10^{-4} \times Cl$

The second dissociation constant for carbonic acid is with some modification taken from Buch (1951)

$$\log K_2 = -2902.39/T_{abs} + 6.4980 - 0.02379 \times T_{abs}$$

$$PK_2' = - \log K_2 - 0.510 \times {}^3 Cl$$

$$K_2' = 10^{-PK_2'}$$

For the principal case, when computing primary production in the open ocean, the boric acid dissociation constant must be established. The following formula $PK_B' = 9.22 - 1.023 \times \sqrt[3]{Cl} - 0.0086 \times Cl + 0.17 - 0.0093333 \times T$ is based on Buch's formula from 1932 for the chlorinity dependance and is modified to account also for the temperature variation, a modification which is based on Buch's figures.

Then K_B' is obtained from $K_B' = 10^{-PK_B'}$

Then according to Harvey (1966) the titration alkalinity is $0.123 \times Cl \times 10^{-3}$ and the carbonate alkalinity is calculated as carbonate alkalinity = titration alkalinity -

$$\frac{K_B' \times 2.2 \times Cl \times 10^{-5}}{A_H + K_B'}.$$

However, for the actual case, the Brofjorden, the so obtained alkalinity is found to be considerably too low because of the Baltic water influence in the upper layer.

Another relation is therefore chosen which is deduced from Buch (1945) and originally established by Hanna Wittig.

This is $Alk = (1.26 + 0.056 \times Cl) \times 10^{-3}$

This relation is closely similar to $Alk = 1.26 + 0.031 \times S$ which is used by the International Agency for ^{14}C - determination in Denmark. It must be clearly pointed out that this formula holds only for this specific area.

The S - Cl relation is given by Knudsen (1901) as $S = 0.030 + 1.8050 \times Cl$

For other areas, e.g. the Baltic, other relations for Alk must be established.

All these expressions now give the total carbon dioxide value for Brofjorden

$$\text{Total } CO_2 = \frac{Alk\left(1 + \frac{K_2'}{a_H} + \frac{C_s \times a_H}{K_1' \times C_o \times a_{H_2O}}\right) \times 12010}{1 + \frac{2\,K_2'}{a_H}} \quad mg/l$$

For the general case of the open ocean Alk is replaced by titration alkalinity.

The primary production is then given by

$$C_{prod} = \frac{\text{counts} \times \text{total } CO_2 \times 10^{+3}}{\text{ampstr.} \times \text{duration}} \left[mg\ C/m^3 \times h\right]$$

Where counts is counts/minute from the Danish carbon isotope analyses and ampstr. is the strength of the C^{14} - ampoule

In ALGOL the formula system looks like follows.

```
PROD: GETREAL(PH(I),1);
      GETREAL(COUNTS(I),1);
      GETREAL(DARKCOUNTS(I),1) ;
      'IF' ?NIX             'THEN'  'BEGIN'
      FACT:= 0.145- 0.00025*T ; 'COMMENT' FACT IS CALC FROM BUCH 1951 ;
      PK1 := 17052/TABS + 215.21*LN(TABS)/LN10 - 0.12675*TABS - 545.560
      PK1PRIM:= PK1 - FACT*CL**(1/3); K1PRIM:= 10**(-PK1PRIM) ;
      'COMMENT' SVERDRUP 1946 PAGE 200 WITH FACT AND PK1 REAL CONSTANTS
      'IF' T 'GQ'-3 'AND' T<-1 'THEN' 'BEGIN'
       CNULL:= 849 ; CS:= CNULL - 7.22*CL
                     'END''ELSE''IF' T 'GQ'-1 'AND' T<2.5 'THEN''BEGIN'
       CNULL:= 770; CS:= CNULL -6.51*CL
                     'END''ELSE''IF' T'GQ'2.5 'AND' T<7.5 'THEN''BEGIN'
       CNULL:= 640 ; CS:= CNULL - 5.37*CL
                     'END''ELSE''IF' T'GQ'7.5 'AND'T<12.5 'THEN''BEGIN'
       CNULL:= 536 ; CS:= CNULL - 4.28*CL
                     'END''ELSE''IF'T'GQ'12.5 'AND'T<17.5 'THEN''BEGIN'
       CNULL:= 458 ; CS:= CNULL - 3.54*CL
                     'END''ELSE''IF'T'GQ'17.5 'AND'T<22.5 'THEN''BEGIN'
       CNULL:= 394 ; CS:= CNULL - 2.80*CL
                     'END''ELSE''IF'T'GQ'22.5 'AND'T<27.5 'THEN''BEGIN'
       CNULL:= 341 ; CS:= CNULL - 2.33*CL
                     'END''ELSE''IF'T'GQ'27.5               'THEN''BEGIN'
       CNULL:= 299 ; CS:= CNULL - 1.96*CL 'END''ELSE''GOTO'SEC;
      'COMMENT' ACC TO BUCH 1945 FENNIA 68 NO 5 PAGE 14 ;
AHA:  AH:= 10**(-PH(I));
      AH20:= 1-0.000969*CL ; 'COMMENT' HARVEY 1966 PAGE 169 ;
      LOGK2:= -2902.39/TABS + 6.4980 - 0.02379*TABS;
      PK2PRIM:= -LOGK2 - 0.510*CL**(1/3) ; K2PRIM:= 10**(-PK2PRIM);
      'COMMENT' BUCH 1951 HELSINKI HAVSFORSKNINGST SKRIFTNO 151 PAGE7;
      PKBPRIM:= 9.22 -0.123*CL**(1/3) - 0.0086*CL + 0.17 - 0.00933333*T
      KBPRIM:= 10**(-PKBPRIM);  'COMMENT' REF RAPP. ET PROC.VERB. DES
      REUNIONS VOLUME LXXXV 1932 PAGE 73 KURT BUCH MODIF BY ÖSTRÖM 1973
      TITRALK:= 0.123*CL*10**(-3) ; 'COMMENT' HARVEY 1966PP161 AND177;
      CARBALK:= TITRALK - KBPRIM*2.2*CL*10**(-5) /(AH+KBPRIM);
      'COMMENT' HARVEY 1966 PAGE 166;
      ALK :=(1.26 + 0.055789 * CL) *1E-3     ;
      'COMMENT'  ALTERNATIVE ALK = (1.26 + 0.030907 * S) *1E-3     ;
      CARB(I):=     ALK*(1 +K2PRIM/AH +CS*AH/(K1PRIM*CNULL*AH20))*12010/
                 (1 +2*K2PRIM/AH) ; 'COMMENT' HARVEY 1966 PAGE 172 MODIF
      DURAT:= DURHO + DURMIN/60 ;
      CPROD(I):= COUNTS(I) * CARB(I)*  1E3 /(AMPSTR      * DURAT) ;
      DARKPROD(I):= DARKCOUNTS(I) *CARB(I)* 1E3/(AMPSTR*DURAT);
      'IF' DARKPROD(I)>0'AND'DARKPROD(I)<CPROD(I)'THEN'NETPROD(I):=
      CPROD(I) - DARKPROD(I)
      'ELSE'NETPROD(I):=-1;
      CORPRO(I):= CPROD(I)*1.1;
      NETCOR(I):= NETPROD(I)*1.1;
```

Certain information in this paper is taken from

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