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DETERMINATION OF OPAL IN MARINE SEDIMENTS

By

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ABSTRACT

The opal contents of recent marine sediments are ascertained by conversion of the opal to crystobalite by heating and by a subsequent quantitative x-ray diffraction analysis of the crystobalite. An opal stratigraphy is evident in Bering Sea deposits. Further, the opal concentrations appear to be covariant with barium, an element previously suggested as indicative of biological productivity in overlying water masses.

INTRODUCTION

One of the principal constituents in some marine sediments is opal, a highly disordered form of silicon dioxide, which generally contains less than 12% water. This opal originates in the plant and animal life of the sea as frustules of diatoms or as skeletal remains of such organisms as radiolarians and sponges. There is no evidence for the inorganic deposition of opal in the marine environment. Although siliceous ooze and siliceous muds are defined in terms of the amount of opal present, there have been no direct methods of assay other than that of visual estimation. This situation prompted a survey of possible analytical techniques. Professor William D. Johns of Washington University, St. Louis, suggested converting the opal to crystobalite by heating and carrying through a quantitative x-ray diffraction analysis of the crystobalite. This paper covers preliminary results of experiments that consider such a method.

EXPERIMENTAL

General Method. A calcium carbonate-free marine sediment sample of 0.5–1.5 g, ground to a fine powder (100–200 mesh), was placed in a platinum crucible and heated at 900°C for four hours. The height of the resultant 4.04 Å diffraction peak of crystobalite was determined on a Norelco X-Ray Diffraction Spectrometer at 35 KV.
and 20 mA, using copper $K\alpha$ radiation. In order to secure the most reproducible results, known amounts of opal (10 and 20% by weight) were added to a second and third sample respectively, and these samples were then heated simultaneously; peak height determinations were subsequently made. The opal content of the sample was found from the best fit to the following equations, where $x$ is the original percentage of opal in the sediment, $k$ a proportionality factor, and $P_n$ the intensity of the 4.04 Å line obtained in samples with an added percentage $n$ of cristobalite:

(a) \[ x = k P_0 \],
(b) \[ x + 10 = k P_{10} \],
(c) \[ x + 20 = k P_{20} \].

Note 1. Opal standards. Sponge spicules, obtained from live animals taken from Mission Bay, San Diego, California, constituted the primary opal standard. The sponges, treated with a mixture of one part nitric and one part perchloric acid, were heated to a temperature approaching the boiling point of the mixture to destroy the organic phases and subsequently cooled. The residue of spicules was washed repeatedly with distilled water, dried and ground to a 100–200 mesh powder.

Note 2. The temperature of 900°C and the heating time of four hours were arrived at empirically. Typical conversion data are given in Table I for diatomaceous earth from the Monterey formation at Palos Verdes, California.

<table>
<thead>
<tr>
<th>Heating Time (hrs)</th>
<th>Heating Temperature (°C)</th>
<th>Peak Height of Cristobalite (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>800</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>800</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
<td>13</td>
</tr>
<tr>
<td>1</td>
<td>900</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>900</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>900</td>
<td>31</td>
</tr>
<tr>
<td>8</td>
<td>900</td>
<td>30</td>
</tr>
<tr>
<td>Untreated Control</td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

Note 3. Inasmuch as calcium carbonate and silicon dioxide interact at the heating temperature to form the calcium silicate woll-


astonite, samples containing calcium carbonate were initially washed with 0.01 N hydrochloric acid, rinsed with distilled water, and dried before heating.

Note 4. Heating to or above 1000° produced glassy materials, and the resultant diffraction intensity of cristobalite was not as high as at 900° C and was not in general reproducible.

TABLE II. TYPICAL OPAL RUNS ON A SEDIMENT SAMPLE. SAMPLE FROM BERING SEA, CHINOOK 9 CORE SCRAPINGS

<table>
<thead>
<tr>
<th></th>
<th>x = k 23</th>
<th>(a-b) k = 10/23 = 0.43</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>x + 10 = k 46</td>
<td>(a-c) k = 20/43.5 = 0.46</td>
</tr>
<tr>
<td>(b)</td>
<td>x + 20 = k 66.5</td>
<td>(b-c) k = 10/20.5 = 0.49</td>
</tr>
</tbody>
</table>

Average k = 0.46

Percent opal in sample is 11 %.

Note 5. In the initial work, uric acid was added to the samples (following heating) as an internal standard. However, this technique was abandoned in favor of the "use of incremental amounts of opal as internal standards" because it was found that the amount of...
conversion was a function of any previous chemical treatments the samples had received. Washing with HCl, NH₄Cl or distilled water reduced the intensity of the resultant crystobalite peak and/or broadened the peak. These disturbances, introduced by such washings, were eliminated by introduction of the "incremental opal" to the samples before washing.

Note 6. The reproducibility of the results appears to be of the order of ±10%₀. Table II gives illustrative data on a typical set of replicate runs. The lower limit of detection was 2%₀ opal.

![Figure 2. Opal and barium oxide concentrations in Chinook 9, from Lat. 52°25.2' N, Long. 176°24.5' W at a depth of 3440 m.](image-url)
RESULTS

The depth distribution of opal in a pair of diatomaceous sediment cores from the Bering Sea, Chinook 8 and Chinook 9, is shown in Figs. 1 and 2. In both cores, obtained not far from one another, an opal stratigraphy appears. There is a marked decrease of opal with depth, with values of 20% by weight at the surface and of 10–15% at about 30 cm. In Chinook 9 there is a clear increase again at about 48 cm. The significance of such concentration changes is not as yet understood.

Of interest, however, is the possibility of a relationship between the opal, presumed to represent in these cores a measure of the biogenous contribution to the sediment, and barium, an element believed to be related to the productivity of an area (Goldberg and Arrhenius, 1958). Figs. 1 and 2 clearly demonstrate the covariance between barium and opal. The barium values were determined by emission spectroscopy (Goldberg and Arrhenius, 1958).

Since concentrations of barium are markedly higher in pelagic sediments below productive oceanic areas than in either the calcareous or siliceous parts or in the dried organic phases of the marine biosphere, barium is probably accumulated in deep sea deposits through chemical reactions involving organic debris. High barium contents are associated with both siliceous and calcareous deposits. One possibility may be the release of high concentrations of sulphate ion, resulting from oxidation of organically bound sulphur, in such deposits with a consequential precipitation of barium sulphate (Arrhenius, 1959).

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