Reports

High Cristobalite and High Tridymite in a Middle Eocene Deep-Sea Chert

Abstract. *The high-temperature forms of cristobalite and tridymite have been found occurring in a Middle Eocene, radiolarian-rich claystone. Evidence indicates that these crystals formed at low temperature and were chemical precipitates. Scanning electron microscopy, energy-dispersive x-ray analysis (microprobe), and x-ray diffraction provided the data upon which the determinative mineralogy was based.*

X-ray diffraction studies have indicated that disordered low cristobalite–low tridymite (opal-CT) is an abundant constituent of Tertiary deep-sea cherts (*1*). Earlier studies by Wise and others (*2*), using a scanning electron microscope (SEM), have revealed that this cristobalite-tridymite occurs in the form of spherical bodies 3 to 10 μm in diameter that are chemically precipitated in void spaces such as intergranular pores and chambers of microfossils. Furthermore, Weaver and Wise (*3*) revealed the ultramorphology of the cristobalite spherules as a complex intergrowth of blades 300 to 500 Å in thickness.

In a SEM study of Middle Eocene cherts from the Atlantic Ocean, JOIDES (Joint Oceanographic Institutions for Deep Earth Sampling) deep-sea drilling project sample 8A-2-1 (20-22), a silicified, radiolarian-rich claystone, was found to contain several vugs partially filled with octahedral crystals (Fig. 1). In some instances these were seen in association with hexagonal plate-like crystals (Fig. 2). The crystals occur on the interior walls of radiolarian tests (Fig. 3). The octahedral and hexagonal plates extend from a substrate of smaller void-lining crystals of similar octahedral nature.

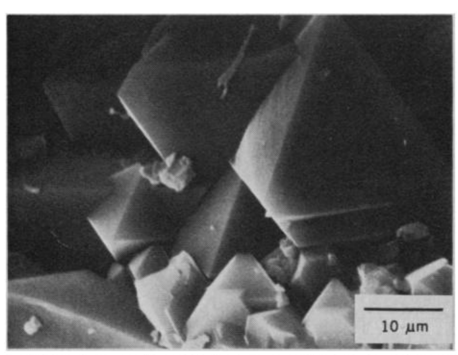
An energy-dispersive x-ray analysis (EDA) of the crystals yielded the characteristic x-ray energy indicative of K-radiation from silicon (1.72 kev). A slight asymmetry occurred in a few EDA spectra on the low-energy side of these peaks, suggesting the possible presence of minor amounts of aluminum (1.48 kev). When the EDA system was switched to a line profile mode of operation, increased silicon K-radiation was obtained from the crystals above that of the silicon background, an indication that the x-rays were emanating from the crystals and do not represent stray radiation from the surrounding chert. This indicates that the crystals are composed of silica.

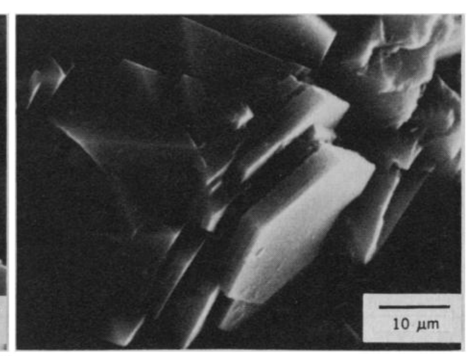
Bulk x-ray diffraction analysis indicates that the sample is mineralogically quite simple, consisting of montmorillonite, opal-CT, quartz, and clinoptilolite. In thin section the montmorillonite is the matrix, the opal-CT is in the spherulitic habit, the quartz is present in the form of granular microcrystalline quartz and chalcedony, and no clinoptilolite is visible (nor is it visible via SEM). Stereo SEM photomicrographs of the octahedra confirm that they are isometric but somewhat malformed. This finding suggests unequal growth rates in different crystallographic directions.

Most minerals that are isometric or hexagonal are not silicates (*4*). Cristobalite may belong to either the isometric (high cristobalite) or the tetragonal (low cristobalite) crystal systems (*5*). It may occur as spherical aggregates of blade-like crystals or as octahedral crystals, generally less than 1 mm in size (*4–6*). High tridymite is hexagonal; low tridymite is orthorhombic (*5*). Tridymite occurs as thin, fragile, or thick, tabular hexagonal plates, flattened on (0001) (*4–6*).

A comparison of the photomicrographs of Grieg *et al.* (*7*) and Dutton (*8*) with these SEM micrographs indicates that the octahedral crystals do resemble crystals grown earlier, identified as cristobalite. Oehler (*9*) synthesized tridymite-like crystals that are similar to the hexagonal plates in question except that his were of the thin, fragile variety. Frondel (*10*) points out that the tridymite plates shown in Fig. 2 are oriented parallel to the (111) face of cristobalite, which is the expected epitaxial orientation.

The morphological data coupled with the chemical data strongly suggest that these crystals in this deep-sea chert are high cristobalite and high tridymite. Unlike previously reported occurrences of cristobalite-tridymite in deep-sea cherts, these are discrete crystal growths of the high-temperature silica phases. However, because of the small amount of these minerals present in this sample, it is not possible to definitively ascertain whether these crystals are the high-temperature silica polymorphs by x-ray diffraction. A SEM examination indicates that other chert samples within the same core section





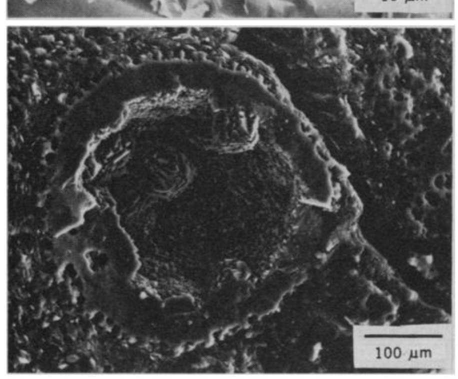


Fig. 1 (top left). Octahedral crystals of cristobalite found lining the interior of a radiolarian test. Fig. 2 (top right). Hexagonal tridymite crystals seen in conjunction with octahedra of cristobalite. Fig. 3 (bottom left). Cristobalite and tridymite crystals constituting a void filling on the interior wall of a radiolarian test in a silicified, radiolarian claystone.

do not exhibit these crystal forms; only spherules of opal-CT are found. This suggests that this particular core segment did not experience any pervasive thermal anomalies which could account for these minerals. The sample was recovered from a depth of 295 m below the sea floor. Under a normal geothermal gradient, it could not have formed at temperatures significantly above 20°C; however, high cristobalite and high tridymite are thermodynamically stable above 1470° and 870°C, respectively. Furthermore, the assemblage opal-CT consisting of two varieties of quartz, cristobalite, and tridymite is highly unusual. It further illustrates the disequilibrium conditions under which this sample was formed.

The existence of discrete crystalline growths of cristobalite and tridymite in void fillings undoubtedly represents a higher degree of ordering of silica phases than the disordered cristobalite-tridymite spherules that are so common in Tertiary deep-sea cherts. Euhedral crystals found in vugs are normally assumed to represent direct precipitates. This is observed here, an indication that these crystals are direct precipitates from interstitial solutions rather than a recrystallization of former opal or cristobalite spherules. It is likely that these crystals reflect slower rates of nucleation rather than a step in the inversion from cherts rich in opal-CT to quartzose cherts.

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Internal Waves: Measurements of the Two-Dimensional Spectrum in Vertical-Horizontal Wave Number Space

Abstract. *Thermistor chain measurements of internal wave motions below the thermocline in the western North Atlantic have been spectrally decomposed in vertical-horizontal wave number space. The measured two-dimensional spectrum exhibits a systematic deviation from the corresponding Garrett and Munk model for internal wave spectra.*

Internal gravity waves are local oscillations about the equilibrium stable density stratification of the earth's oceans and atmosphere. In the ocean, the statistical properties of motions with horizontal scales ranging from tens of meters to tens of kilometers and temporal scales ranging from tens of minutes to tens of hours appear to scale consistently with the predictions of linear internal gravity wave propagation theory (*1, 2*). The primary internal wave scaling relationship is that energy densities vary in direct proportion to the local Brunt-Väisälä frequency N, which is defined in the upper ocean in terms of the local vertical gradient, $d\rho/dz$, by

$$N^2 = -\frac{g}{\rho}\frac{d\rho}{dz}$$

where g is the acceleration of gravity. Furthermore, such motions are generally found to be statistically isotropic in horizontal planes (*3, 4*). If such motions are in fact manifestations of random internal wave fields, then by virtue of the frequency–wave number dispersion relation for internal waves, a complete spectral decomposition of the wave field requires information in only two of the remaining three independent coordinate dimensions (time and vertical and horizontal space). Although it is unlikely that the field of internal wave motions constitutes a normal random process, there is evidence to the effect that it is very nearly normal (*5*), and it is well known that the spectrum of a normal random process provides a complete statistical description of the process (*6*).

Invoking elements of internal wave theory and drawing on available empirical data, Garrett and Munk (*2*) constructed a model (designated GM75) for the two-dimensional spectral decomposition of the internal wave field in the ocean, $F_\zeta(\alpha, \beta; \omega(\alpha, \beta))$. Unfortunately, the data base available to them was intrinsically one-dimensional, being composed of frequency spectra from moored current meters and wave number spectra from towed or dropped instruments, together with some limited coherences between pairs of instruments separated in space or time. Here, we present data on the two-dimensional spectral decomposition of the internal wave field in vertical-horizontal wave number space. Although one-dimensional spectra in the vertical and horizontal derived from our two-dimensional spectrum agree with published spectra that represent a portion of the data base for the GM75 model, systematic deviations from the complete (two-dimensional) model are observed in the vertical-horizontal wave number plane.

During the period 22 August to 12 September 1974, the U.S.N.S. *Lynch* was deployed in the western North Atlantic between Cape Hatteras and Bermuda. During this time measurements were made of the two-dimensional (vertical-horizontal) structure of the oceanic internal wave field. The basic measurement system consisted of a towed thermistor chain. The chain has connections for mounting 70 sensors at an average vertical spacing of 1.4 m at normal towing speeds. Here, we analyze the data from 32 thermistors located in the lower portion of the chain, where curvature effects associated with the chain profile are minimized during towing. For this portion of the chain, the average vertical spacing between thermistors was 1.27 m (*7*). Supporting environmental data were provided by salinity-temperature-depth (STD) recorder and profiling current meter casts and by parachute drogues deployed at various depths. The STD data provided estimates of the average temperature and Brunt-Väisälä frequency profiles, which are required for proper data scaling. The nominal center line tow depth was 100 m, which placed the thermistor array below the seasonal thermocline in a region where the average temperature gradient and Brunt-Väisälä frequency varied only slightly over the sampling region, so that special processing techniques (*8*) were not required for spectral decomposition in the vertical. Our analysis of the parachute drogue and current meter data indicates an absence of significant background current shear over the range of depths of interest here.

The thermistor chain measurements were made during four basic exercises (see Table 1), each consisting of a box pattern of four 8-km tow legs at a nominal speed of 3 m sec^{-1} (*9*). Data were sampled every