

Characteristics of Fluorescent Inclusions in Quartz Crystals Hosted by Organic-Rich Black Limestone in Sakawa Town, Kochi Prefecture, Southern Shikoku, Japan

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Abstract

The Torinosu Limestone in Sakawa Town, Kochi Prefecture, Japan, is rich in organic matter and has long been recognized as a black limestone with a high concentration of organic material. Quartz containing petroleum-like substances occurs in veins within this black limestone. The quartz hosting these petroleum-like fluid inclusions typically exhibits a bipyramidal to tabular habit. Under ultraviolet light, the fluid inclusions display intense fluorescence. The polycyclic aromatic hydrocarbon (PAH) fraction extracted from the fluorescent quartz contains significant amounts of methylnaphthalene and methylphenanthrene, which are responsible for the observed fluorescence. In addition to these compounds, unsubstituted pyrene, chrysene, and perylene were detected in the black limestone. Methylnaphthalene, methylphenanthrene, and squalene—the primary fluorescent components—were likely derived from the organic-rich black limestone during the formation of the quartz veins and subsequently incorporated into the quartz.

Keywords

Alkyl Naphthalene, Alkyl Phenanthrene, Double-Terminated Quartz, Fluorescent Inclusion, Torinosu Limestone

1. Introduction

In the area around Sakawa Town, Kochi Prefecture (**Figure 1**), the Torinosu Limestone, which dates from the Late Jurassic to Early Cretaceous, is widely distributed [1]. This limestone contains veins filled with well-developed quartz crystals.

tals that host fluorescent fluid inclusions. In this study, we conducted organic geochemical analyses of the fluorescent fluid inclusions and the surrounding black limestone matrix to characterize the fluorescent compounds and to infer their origin.

The Torinosu Limestone contains a fossil assemblage known as the Torinosu fauna, including scleractinian corals, stromatoporoids, calcareous algae, and bryozoans, indicating deposition in a pelagic, warm-water, reef-like environment extending from nearshore to offshore settings [2]. The limestone is characterized by its dark gray color and emits a petroleum-like odor when struck with a hammer [3]. The area near Torinosu in Sakawa Town also contains small nodules of bituminous material that release a similar petroleum odor upon impact [4]. The occurrence of limestone rich in organic matter led to petroleum exploration in the area. In 1926, a 300-m-deep borehole was drilled along the axis of the limestone anticline to explore for oil, but no evidence of petroleum was found. The samples used in this study were collected from the Torinosu Limestone approximately 1 km northwest of JR Sakawa Station. In the sampling area, the limestone occurs in scattered, lenticular bodies that are frequently segmented by faults. Sample collection was carried out by staff of the Sakawa Geology Museum and Institute, and subsequent analyses were performed at the Department of Earth and Planetary Science, Graduate School of Science, The University of Tokyo.



Figure 1. Map showing the study area.

2. Samples

The samples used in this study consist of black limestone and quartz crystals occurring within quartz veins that cut through the black limestone. Organic matter is locally accumulated in drusy cavities within the limestone. This organic matter is a light brown, petroleum-like substance that is highly volatile and contains a small amount of asphaltic material. Chemical analyses revealed that the total or-

ganic carbon (TOC) content of the Torinosu Limestone reaches up to 0.81% [3]. Quartz containing petroleum-like substances occurs as quartz veins within the black limestone. The thickness of these veins ranges from a few millimeters to approximately 1 cm and varies laterally. Larger quartz crystals are developed in the thicker portions of the veins. The crystals range in size from a few millimeters to about 2 cm, and most exhibit a bipyramidal habit. A photograph of the separated quartz crystals is shown in **Figure 2**. Fluid Inclusions and Crystal Textures. Fluid inclusions in the quartz exhibit fluorescence under ultraviolet (black) light. No apparent pattern was observed in the distribution of inclusions within individual quartz crystals. **Figure 3** shows the fluorescence emitted under 365 nm ultraviolet light. The quartz crystals were crushed, and the fluorescent inclusions were subsequently analyzed.



Figure 2. Quartz samples were collected from black limestone. The double-terminated platy morphology is characteristic of these quartz crystals.

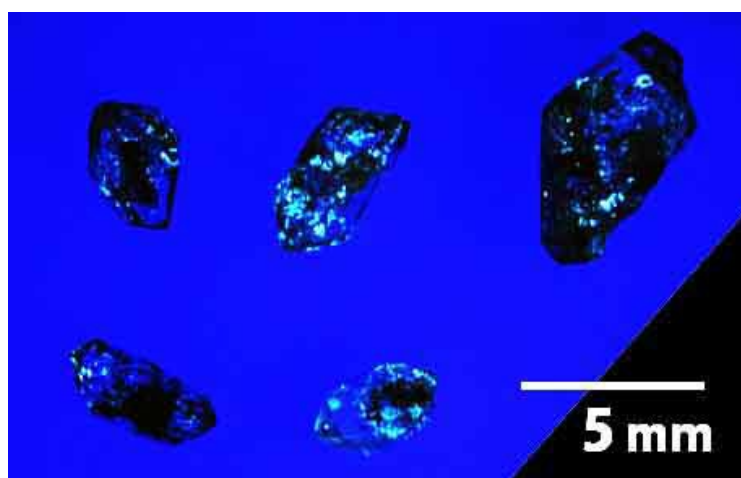


Figure 3. Fluorescence of quartz under 365 nm ultraviolet light.

The quartz in the veins consists mainly of tabular crystals whose plates are aligned parallel to the vein surfaces. At first glance, the crystals appear to have been compressed within the veins. The quartz is greenish in color owing to the presence of small green inclusions and is therefore referred to as green quartz. A thin section was prepared parallel to the vein surface. Under the microscope, double-terminated quartz crystals are aligned parallel to the thin-section surface (*i.e.*, the vein plane). Chlorite inclusions occur in a banded pattern, forming distinct zoning (**Figure 4**). **Figure 5** shows a quartz vein that was opened along the vein surface.

To observe the inclusions, the analyzer was rotated approximately 30° from the extinction position. The growth direction (*c*-axis) of the platy quartz crystals is parallel to the vein plane, and crystals growing perpendicular to the vein base—typical of ordinary quartz veins—are absent. Although the origin of the platy quartz crystals was not investigated in this study, it represents an important topic for future mineralogical research.

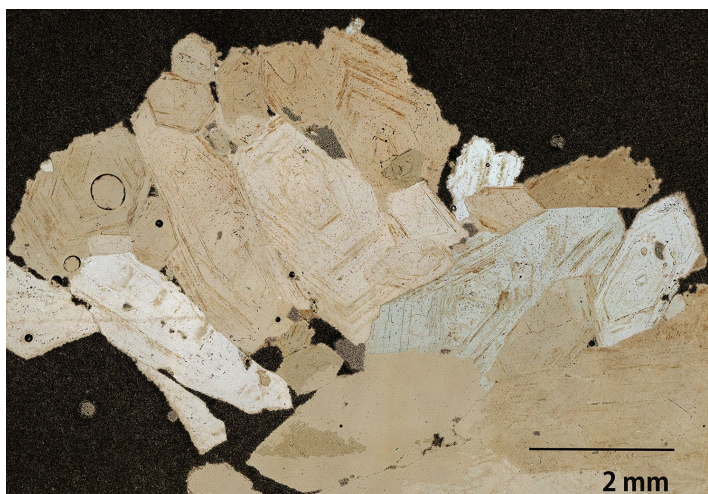


Figure 4. Photomicrograph of platy quartz, viewed parallel to the platy crystal plane.



Figure 5. Occurrence of double-terminated platy quartz in a vein.

3. Compound Identification

The quartz crystals containing fluorescent substances were ground in a mortar. After grinding, dichloromethane was added to the mortar to wash the quartz. The washing solution was picked up, then concentrated, fractionated, and analyzed. Regarding the black limestone, approximately 3 g of the powdered sample obtained after crushing was used to extract bitumen using the conventional Soxhlet method. Soxhlet extraction using dichloromethane/methanol (93/7, v/v) was performed for 70 h to extract biomarkers. The solvent extract was concentrated using a rotary evaporator, and the isolated lipid fraction was separated into four components by silica-gel column chromatography.

A hydrocarbon fraction was obtained using two column volumes of n-hexane; a polycyclic aromatic hydrocarbon (PAH) fraction was obtained with two volumes of n-hexane/dichloromethane (2/1, v/v); an aliphatic ketone/ester fraction was obtained with seven volumes of n-hexane/dichloromethane (1/1, v/v); and a polar fraction was obtained with an excess of dichloromethane/methanol (1/1, v/v). Two of these fractions—the hydrocarbon and PAH fractions—were analyzed by GC-MS.

GC-MS analyses were performed using a Shimadzu QP-2010 Plus system equipped with a 30 m fused-silica capillary column (Thermo Scientific TG-5MS; 0.25 mm i.d., 0.25 μ m film thickness) and a splitless injector. The temperature program was as follows: isothermal at 60°C for 1 min; 60°C to 175°C at 10°C min⁻¹; 175°C to 225°C at 6°C min⁻¹; 225°C to 300°C at 4°C min⁻¹; and isothermal at 300°C for 20 min. Mass spectra were recorded in electron-impact (EI) mode at 70 eV, scanning from m/z 50 to m/z 520. This procedure corresponds to a standard analytical method for biomarker identification. The structures of the organic compounds were determined based on their mass spectra and the retention indices of unsubstituted polycyclic aromatic hydrocarbons (PAHs). Unsubstituted PAHs, ranging from naphthalene to perylene, were identified by comparing their MS spectra and retention indices with those of standard reference materials. PAHs with molecular weights greater than that of coronene were identified by reference to previous studies [5] [6]. Other compounds were identified by comparison with the NIST05 mass-spectral database. This analytical procedure follows the method described by [7].

4. Results

This study focuses on the PAH fraction among the four fractions, as it exhibited strong fluorescence under ultraviolet irradiation. **Figure 6** shows the total ion chromatograms (TICs) of the PAH fractions from the black limestone (bottom) and from the fluorescent inclusions in quartz (top). Both samples contain the bicyclic compound naphthalene and the tricyclic compound phenanthrene, as well as their alkylated homologues (C₁-C₄ for naphthalenes and C₁-C₃ for phenanthrenes). Compared with the unsubstituted parent compounds, the alkylated derivatives generally occur in higher abundances. C₁-fluorene was also commonly

detected. In addition to PAHs, squalene was identified in the fluorescent inclusions of the quartz. Squalene is of fungal origin [8] and exhibits fluorescence at around 730 nm when exposed to long-wave ultraviolet light [9]. These compounds represent the major components of the PAH fraction in the quartz samples. In the silica-gel column chromatography, to ensure the quantitative collection of naphthalene—which elutes near the boundary between the hydrocarbon fraction and the early part of the PAH fraction—the fractionation boundary was set slightly toward the hydrocarbon side. Consequently, a small amount of n-alkanes appears in this chromatogram. The n-alkanes shown in **Figure 6** (top) correspond to this overlap. In contrast, the black limestone sample contained tetracyclic compounds such as pyrene and chrysene, as well as the pentacyclic compound perylene. A small amount of methylchrysene was also detected, although alkylated derivatives were present only in trace quantities. The methylphenanthrene index (MPI-1) was calculated to be 0.72 for the black limestone and 1.11 for the fluorescent inclusions in quartz. Using the equation $Ro = 0.38 + 0.61 \times MPI-1$ [7], the equivalent vitrinite reflectance (Ro) values were estimated to be 0.82 and 1.06, respectively. Both values fall within the oil-generation window [10].

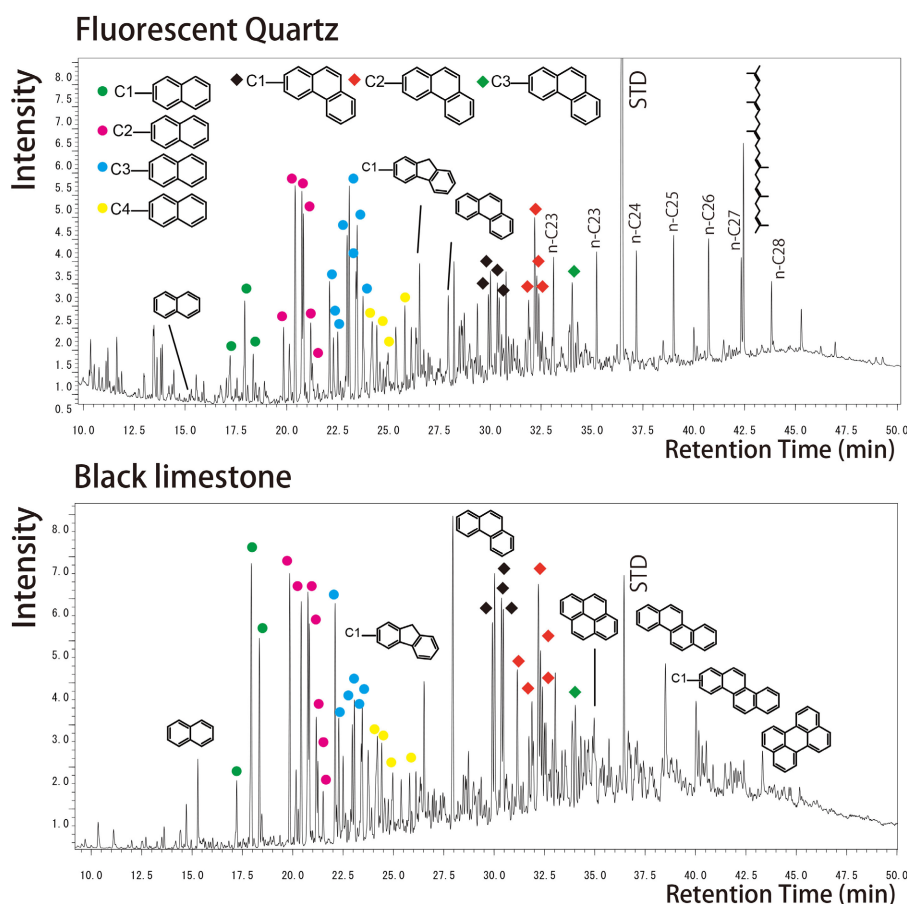


Figure 6. Total ion chromatograms (TICs) of the PAH fractions extracted from fluorescent quartz (top) and black limestone (bottom). The peak labels correspond between the two chromatograms.

5. The Origin of Quartz Fluorescence

The fluorescence observed in the fluid inclusions within quartz originates from alkylnaphthalenes and alkylphenanthrenes. Unsubstituted PAHs and squalene are generally present in low concentrations and therefore contribute little to the overall fluorescence signal. These compounds are consistent with the organic components characteristic of the black limestone. However, pyrene, chrysene, and perylene, which occur in the black limestone, were not detected in the quartz. This compositional difference suggests that relatively low-molecular-weight alkylnaphthalenes and alkylphenanthrenes were selectively extracted from the black limestone during the formation of the quartz veins and subsequently incorporated into the quartz. The difference in the methylphenanthrene index (MPI-1) between the limestone and the quartz inclusions is interpreted to reflect variations in extraction efficiency between unsubstituted and methylated phenanthrenes.

6. Summary

Fluorescent inclusions occurring in the organic-rich Torinosu Limestone of southern Shikoku, Japan, originate from alkylnaphthalenes and alkylphenanthrenes. These compounds were extracted from the organic-rich black limestone during the formation of quartz veins and were incorporated into the quartz, where they produce the characteristic fluorescence observed under ultraviolet light.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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