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Chemical compositions and precipitation timing of basement calcium carbonate veins from the South China Sea

Weiwei Ding[a,b], Yifeng Chen[c,*], Zhen Sun[d], Zihua Cheng[b]

[a] Second Institute of Oceanography, State Oceanic Administration, Hangzhou 310012, China
[b] School of Earth Science, Zhejiang University, Hangzhou 310027, China
[c] CAS Key Laboratory of Ocean and Marginal Sea Geology, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (CAS), Guangzhou 510640, China
[d] CAS Key Laboratory of Ocean and Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences (CAS), Guangzhou 510301, China

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ABSTRACT

Sixteen calcium carbonate veins (CCVs) within the igneous basement recovered from both East and Southwest Sub-basin, close to the fossil spreading ridge of the South China Sea during the Integrated Ocean Drilling Program (IODP) Expedition 349 were investigated. The CCVs are composed primarily of either calcite or aragonite, and some of mixed aragonite and calcite. The $\delta^{18}O$ values of CCVs range from 25.5 to 31.8‰ VSMOW, indicating these are typical low temperature basement carbonates precipitated at temperatures of 12–40 °C. The $^{87}Sr/^{86}Sr$ ratios of CCVs from Site U1431 show a strong negative correlation with $\delta^{18}O$-calculated temperatures, regardless of carbonate phases – calcite or aragonite, indicating CCVs with lower $^{87}Sr/^{86}Sr$ ratios have precipitated from moderately warmer and more geochemically evolved hydrothermal fluids, and reflecting that precipitation of CCVs might have occurred any time between 14.5 and 0 Ma at Site U1431. The formation timing of CCVs at Site U1431 is consistent with the ongoing hydrothermal flow and circulation led by recharging seawater into the volcanic basement through the nearby outcropped seamount. The oldest ages of CCVs from Site U1433 at the Southwestern sub-basin of SCS were determined to be ~18–11 Ma, based on basement age of 18.5 Ma and the well-established seawater $^{87}Sr/^{86}Sr$ ratio curve. It indicates that the hydrothermal circulation at Site U1433 which is more distal to a recharging/discharging site was only active until ~11 Ma. In consequence, the CCVs within basalts from Sites U1431 and U1433 provide more insights into the past hydrologic conditions and hydrothermal circulation along the fossil ridge flank in the SCS.

1. Introduction

Circulation of seawater through the ocean crust along the flanks of mid-ocean ridges has profound effects on the composition of both seawater and crust, and is also a principal mechanism of heat loss from the Earth's interior (e.g. Staudigel et al., 1981; Brady and Gíslason, 1997; Coggon et al., 2004, 2010). It causes approximately one third of convective heat loss with the crustal ages > 1 Ma (e.g. Sclater et al., 1980; Stein and Stein, 1994; Elderfield et al., 1999). Seawater-derived hydrothermal fluid circulation within the basement will lead to hydrothermal fluid-rock interaction, which causes the dissolution of primary igneous minerals and formation of secondary minerals. The secondary minerals replace the primary minerals and fill veins/fractures, vesicles and pore spaces within the basalts. Calcium carbonate veins (CCVs), composed of either calcite or aragonite, are typical low-temperature (< 100 °C) hydrothermal by-products and are common in the upper oceanic crust. The weathering of igneous minerals especially Ca^{2+}-rich plagioclase and clinopyroxene etc. in oceanic crust driven by the circulation of hydrothermal fluids, releasing Ca^{2+} to the fluid and generating alkalinity, likely promotes authigenic calcium carbonate precipitation in veins and vesicles within basalt (Coogan and Gillis, 2013). The CCVs within basalt in upper oceanic crust provide an archive to understand the chemistry and evolution of hydrothermal fluids and alteration of upper oceanic crust, the temperatures and the duration of hydrothermal activities (e.g. Elderfield et al., 1999; Coggon et al., 2004, 2010; Rausch et al., 2013; Li et al., 2014).

No oceanic basement drilling work has been carried out in the South China Sea (SCS) until 2014. International Ocean Discovery Program Expedition 349 (IODP 349) — South China Sea Tectonics drilled five sites in the SCS, three of which cored into oceanic basement near the fossil spreading ridge, i.e. Sites U 1431, U1433 and U1434 (Fig. 1). Fractures and veins occur throughout the basalt in all these three sites. Most of the veins are composed of secondary calcium carbonates, which provide an archive to explore the effects of hydrothermal circulation on

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[*] Corresponding author.
E-mail address: yfchen@gig.ac.cn (Y. Chen).

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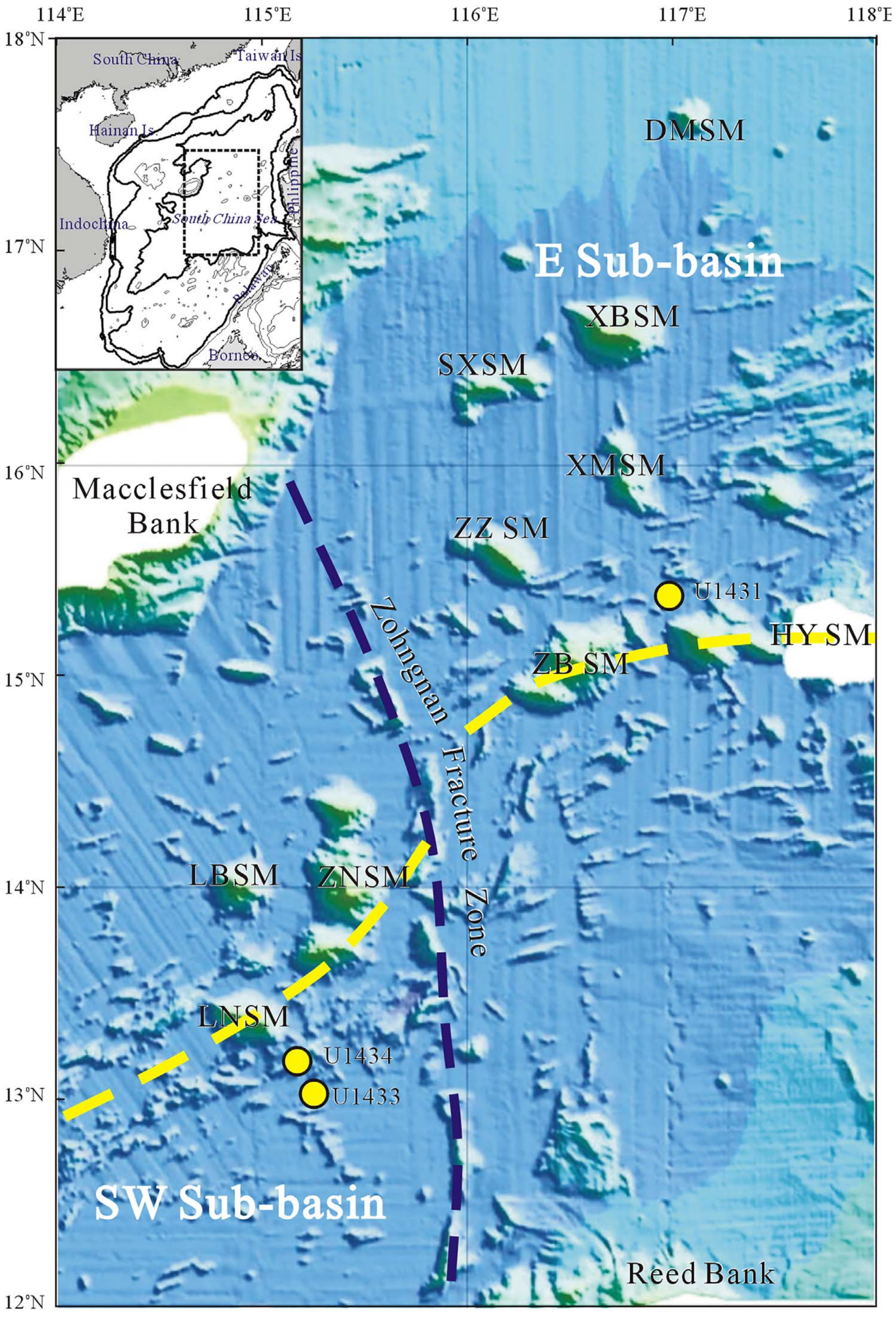

Fig. 1. Morphological map showing the locations of drilling sites near the fossil spreading ridge from which calcium carbonate veins (CCVs) were recovered during the IODP 349. Blue broken line shows the boundary between the East Sub-basin and the Southwest Sub-basin (referred from Franke et al., 2014). Yellow dashed line is the fossil spreading ridge (referred from Sibuet et al., 2016). The seamount closest to the Site U1431 has no name yet, though most seamounts around the fossil ridge have been named, such as ZBSM: Zhenbei Seamout; HYSM: Huangyan Seamount; DMSM: Daimao Seamount; XBSM: Xianbei Seamount; SXSM: Shixing Seamount; ZZSM: Zhangzhong Seamount; XNSM: Xiannan Seamount; LBSM: Longbei Seamount; LNSM: Longnan Seamount; ZNSM: Zhongnan Seamount.

the upper oceanic crust. Only two CCVs were collected from Site U1434, thus CCVs from this site will not be included here. Carbonate mineralogy, the Mg/Ca and Sr/Ca ratios, trace element contents, stable carbon and oxygen isotopic compositions and ^{87}Sr/^{86}Sr ratios of CCVs within the basalt from Sites U1431 and U1433 were investigated to address the hydrothermal fluid chemistry and evolution in the upper oceanic crust, during the ending of the seafloor spreading of SCS. In addition, the global seawater Sr-isotope stratigraphy was used to determine the possible timing of carbonate vein precipitation, which in turn provides some constraint to the duration of hydrothermal circulation within the ocean crust at the flank of the fossil ridge in SCS.

2. Regional setting and geology

The SCS is a western Pacific marginal sea situated at the junction of the Eurasian, Pacific, and Indo-Australian plates. It is composed of three main sub-basins – East Sub-basin, Southwest Sub-basin and Northwest Sub-basin (Fig. 1). It has been developed by latest Cretaceous to Paleogene magma-poor rifting, seafloor spreading in the Oligocene–-middle Miocene, followed by southward subduction beneath Borneo during the Paleocene and middle Miocene, and eastward subduction under the Philippine Sea plate starting at early middle Miocene (i.e. Taylor and Hayes, 1983; Briais et al., 1993; Cullen et al., 2010; Franke et al., 2014; Li et al., 2015b; Ding and Li, 2016; Sibuet et al., 2016; Hayes and Nissen, 2005; McIntosh et al., 2013). The opening scenario of the SCS was first proposed by Taylor and Hayes (1983) and Briais