BIOMARKERS, INCLUDING BOTRYOCOCCENES, IN MAAR LAKE SEDIMENTS FROM VIETNAM RECORD FLUCTUATIONS IN PHYTOPLANKTON DYNAMICS

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Introduction

The Pleiku volcanic field of the Central Highlands of Vietnam features numerous maar lakes ranging in age from 2.4-0.2 Ma (Hoàng *et al.*, 2013). Sediment archives from these lakes provide opportunities to elucidate environmental and climatic change affecting this region linked to variations in the strength of the monsoon and the impact of human activities in more recent times. This investigation focuses on the sedimentary record of Lake Biển Hồ seeking evidence for recent temporal variations in phytoplankton assemblages and inputs from terrestrial vegetation based on the composition of specific algal and plant biomarkers (Brassell *et al.*, 1983; Eglinton and Eglinton, 2008; Castañeda and Schouten, 2011).

Biomarkers Compositions of Biển Hồ Sediments

Preliminary biogeochemical investigations have been performed on a short core collected from Biển Hồ, a maar lake near Pleiku (14° 03' N, 108° 00' E). Six sediment samples were taken from the core, extracted, fractionated, and analyzed by GC-QTOF-MS, including low eV to reduce fragmentation where beneficial. The prominent hydrocarbons of all samples (Table 1) comprise: (i) C_{21}-C_{35} *n*-alkanes and *n*-alk-1-enes (Yongong *et al.*, 2015), with a pronounced odd/even predominance, (ii) a series of C_{34}-C_{37} mono- and bicyclic botyrococcenes (Gao *et al.*, 2007; de Mesmay *et al.*, 2008), (ii) C_{27}, and C_{29}-C_{30} ββ-hopanes, C_{30} αβ-hopane, C_{31} 2-methylhopane (Summons *et al.*, 1999), and hop-22(29)-ene, and (iv) degraded triterpanes, notably des-A-lupane (Corbet *et al.*, 1980; van Bree *et al.*, 2016), and an unknown C_{30} alkene. Polar fractions contained suites of sterols, notably C_{27} and C_{28} Δ^5-stenols and 5α(H)-stanols, C_{28} and C_{29} $\Delta^{5,22}$-stenols and several 4-methylsterols derived from dinoflagellates (Brassell and Eglinton, 1983; Robinson *et al.*, 1984; Volkman, 1986). The dysoxic nature of the sediments may be reflected by the gradual increase with sediment depth (Table 1) in the 5α(H)-stanol to Δ^5-stenol ratio, which attests to sedimentary hydrogenation of stenols (Nakakuni *et al.*, 2018). Perylene is also a prominent component of the 20 cm horizon (Venkatesan, 1988).

Environmental Changes Recorded by Temporal Variations in Biomarker Compositions

There are marked differences in the biomarker composition of individual horizons within the sediment core reflecting changes in the lake environment and its phytoplankton (Table 1). The dominance of plant wax *n*-alkanes in the two lower intervals, complemented by prominent degraded triterpenoids, attest to inputs from terrestrial land plants. *n*-Alk-1-enes, maximizing at C_{25}, suggest contributions from chlorophytes that increase upward to the 11 cm horizon. The 2-methylhopanoids in the 20 cm interval indicate cyanobacteria, and perhaps changing nutrient conditions in the lake. However, the most pronounced change in composition is the dominance of mono- and bicyclic botyrococcenes in the 6, 11 and 16 cm intervals, in contrast to the minor amounts observed in the other samples. The occurrence of these botyrococcenes echoes their prevalence in maar lakes elsewhere (Huang *et al.*, 1996; Fuhrmann *et al.*, 2003; de Mesmay *et al.*, 2008). The downcore biomarker profiles likely reflect signatures of deforestation and subsequent fluctuations in phytoplankton populations linked to variations in nutrient supply.

Table 1: *Summary of biomarker compositions in Biển Hồ sediment samples*

Core depth (cm)*	*n*-Alkanes & *n*-Alkenes (C_{no} max)	Botryococcenes (C_{34}-C_{37} mono- & bicyclic)	ββ-Hopanes, αβ-Hopane & Hopenes	Triterpenoids (pentacyclic & degraded)	Sterols (5α-stanol/Δ^5-stenol ratio)
1	C_{25}; minor *n*-alkenes	Minor, with C_{37} max.	C_{27}, C_{29}-C_{31}; major C_{30} $\Delta^{22(29)}$	Minor	0.35
6	C_{25}; minor *n*-alkenes	Dominant, with C_{37} max.	C_{27}, C_{29}-C_{31}; minor C_{30} $\Delta^{22(29)}$	Dominant C_{30} alkene	n.d.
11	C_{31}; minor *n*-alkenes	Dominant, with C_{37} max.	C_{27}, C_{29}-C_{31}; major C_{30} $\Delta^{22(29)}$	Minor	0.40
16	C_{31}; major *n*-alkenes	Dominant, with C_{37} max.	C_{27}, C_{29}-C_{31}; minor C_{30} $\Delta^{22(29)}$	Dominant C_{30} alkene	n.d.
20	C_{27}; major *n*-alkenes	Traces of C_{34} C_{36}	2-methyl C_{31} Major C_{30} $\Delta^{22(29)}$	Major Des-A-lupane	0.76
23	C_{31}; major *n*-alkenes	Traces of C_{34}, C_{36}	C_{27}, C_{29}-C_{31}; Major C_{30} $\Delta^{22(29)}$	Major Des-A-lupane	n.d.

*The sediment/water interface was not captured.

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