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Short communication

Note on the isotopic geochemistry of fossil-lacustrine tufas in carbonate plateau—A study from Dungul region (SW Egypt)

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ABSTRACT

Lithological, chemical, and stable isotope data are used to characterize lacustrine tufas dating back to pre-late Miocene and later unknown times, capping different surfaces of a Tertiary carbonate (Sinn el-Kedab) plateau in Dungul region in the currently hyperarid south-western Egypt. These deposits are composed mostly of calcium carbonate, some magnesium carbonate and clastic particles plus minor amounts of organic matter. They have a wide range of $(Mg/Ca)_{molar}$ ratios, from 0.03 to 0.3. The bulk-tufa carbonate has characteristic isotope compositions: ($\delta^{13}C_{mean} = -2.49 \pm 0.99‰$; $\delta^{18}O_{mean} = -9.43 \pm 1.40‰$). The $\delta^{13}C$ values are consistent with a small input from C4 vegetation or thinner soils in the recharge area of the tufa-depositing systems. The $\delta^{18}O$ values are typical of fresh water carbonates. Covariation between $\delta^{13}C$ and $\delta^{18}O$ values probably is a reflection of climatic conditions such as aridity. The tufas studied are isotopically similar to the underlying diagenetic marine chalks, marls and limestones ($\delta^{13}C_{mean} = -2.06 \pm 0.84‰$; $\delta^{18}O_{mean} = -10.06 \pm 1.39‰$). The similarity has been attributed to common meteoric water signatures. This raises large uncertainties in using tufas $(Mg/Ca)_{molar}$, $\delta^{13}C$ and $\delta^{18}O$ records as proxies of paleoclimatic change and suggests that intrinsic compositional differences in material sources within the plateau may mask climatic changes in the records.

1. Introduction

Tufas are ambient temperature carbonates formed either in fluvial channels or in lacustrine settings (e.g. Ford and Pedley, 1996). They are precipitated as a result of the physico-chemical and biological elimination of CO_2 from carbonate enriched waters. The presence of prokaryote–macrophyte biofilms is equally important for tufa growth in slow and near static systems (Pedley et al., 2009). The tufaceous carbonate usually precipitates on the leaves and stems of growing plants and so often preserves some of their structures. Tufa deposition has been severely limited at low temperature as this condition severely restricts limestone dissolution and soil zone activity (Pentecost, 1995). Most of the World's tufa deposits are of Quaternary (especially Holocene) age, with fewer Tertiary and even less late Mesozoic examples (Ford and Pedley, 1996). This trend must, in part, reflect the preservation potential of terrestrial carbonates within the geological record.

Carbon-13 to carbon-12 ($\delta^{13}C$) and oxygen-18 to oxygen-12 ($\delta^{18}O$) analysis on tufa carbonate is a common tool to produce paleorecords of climate change in Holocene environments (e.g. Andrews et al., 2000; see Andrews, 2006 for a thorough review). Climatic change is also recorded by magnesium (Mg) to calcium (Ca) ratios in modern (Ihlenfeld et al., 2003) and Holocene tufas (Garnett et al., 2004). However, interpretation of $\delta^{13}C$, $\delta^{18}O$, and Mg/Ca data from tufa paleorecords, particularly in limestone bedrock settings, is complicated by large uncertainties in the magnitudes of many factors influencing tufa basins (i.e. bedrock–water interaction, dissolution and precipitation). Thus, the stable isotope and chemical components in the tufa paleorecord are not unique indicators of the conditions of tufa formation but be carefully reviewed in conjunction with other evidence.

This study presents the results of lithological, chemical, and stable isotope analyses of tufas from the Sinn el-Kedab plateau, located in the Dungul region, SW Egypt (Fig. 1). These analyses were conducted both to characterize these lacustrine deposits and to investigate whether their record can provide information reliable for paleoenvironmental reconstruction.

1.1. Site description

Historically, the Sinn el-Kedab plateau was a refuge for many Stone Age people until ~5000 years ago when the current state of hyperaridy ensued (Haynes, 2001). This plateau is partially capped with inactive deposits of tufa. These deposits were formed in spring-fed lacustrine basins, such that in a single basin the higher tufa would be the oldest and the lowest would be the youngest

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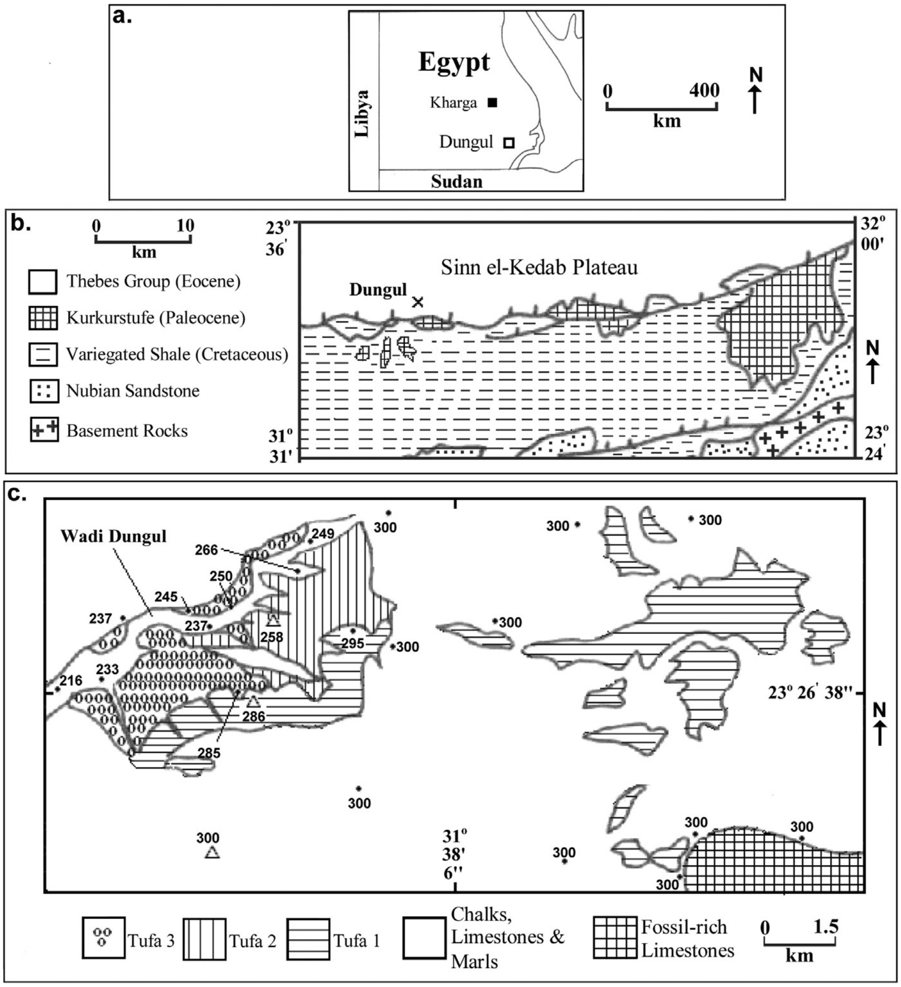

Fig. 1. (a) Location map of Dungul region, (b) the distribution of major rock units in the south-western Egypt and (c) geologic map of the Dungul vicinity; revised from Said (1969). Triangular (Δ) and elevation (·) points are in meters above sea level.

(Said, 1969, 1991). The data analysis suggests that there were at least three different generations of tufa in plateau. The deposits of each of these generations (Fig. 1) are associated with a particular plateau altitude. The oldest of these deposits is a massive tufa (Tufa 1) which lies on marls and chalks at an elevation of 295 m above sea level. Tufa 1 is represented by 8–16 m high hillocks made up of dark-gray solid crystalline carbonate stones without bedding, and pockets, up to 1 m in diameter, that contain boulders of local origin. The tufa mass is a hard carbonate rock that was precipitated around various plant species, of which the stems and internal structures are still preserved. The age of these massive tufas is difficult to ascertain, but it is surely formed prior to the excavation of the Dungul oasis depressions and is, therefore, of pre-late Miocene age (Said, 1991).

The next younger tufa deposit (Tufa 2) is lying on a fossil-rich ochrous limestone at an elevation of 260 m. This tufa is represented by up to 8 m of vesicular crystalline carbonate that is high in plant molds and casts and has reddish and yellow colors. These colors, which are most likely due Fe(III) minerals, might be attributed to the migration of iron-bearing waters through vegetation mats.

The youngest tufa deposits include ~1 m thick dark gray to faint blue carbonate (Tufa 3). These deposits are resting on a brown limestone at 250 m altitude and have abundant plant prints (mainly leave structures). The ages of Tufa 3 and Tufa 2 are unknown.

2. Methods

Samples of Tufas 1–3, as well as representative samples of the marine carbonates – chalks, marls, brown and ochrous limestones – underlying these deposits were collected in the field. The samples were taken from beds showing minimal weathering. All samples were hand ground for analysis. Mineralogy of powder samples was made at the Central Metallurgical Research and Development Institute, Egypt, using a Phillips diffractometer PW 1399 with Fe-filtered Cu K_α radiation. Percentages of organic matter were determined as the loss in mass after dry tufa samples were heated for 1 h at 525 °C in a muffle furnace (Williams, 1974) at the Department of Inorganic Chemistry, National Research Center, Egypt. Three samples of Tufa 1, two samples of Tufa 2, and one sample of Tufa 3 were analyzed at a chemical laboratory facility, Nuclear Materials Authority, Egypt with wet chemical methods (Shapiro and Bannock, 1962).

Carbon and oxygen isotopic measurements were conducted on the carbonate of the tufas (19 samples) and marine carbonate (6 samples). Aliquot samples were placed in stainless steel boats and heated at 380 °C in vacuum for 1 h to remove volatile contaminants. Then, they were placed in individual borosilicate reaction vessels and reacted at 76 ± 2 °C with a few drops of 100% anhydrous H_3PO_4 acid in a Finnigan Kiel preparation device coupled directly to the inlet of a Finnigan MAT 251 triple collector isotope ratio mass spectrometer at the Stable Isotope Laboratory of the University of Michigan, Ann Arbor, USA. Isotopic raw data were corrected for acid fractionation and ^{17}O contribution. Samples were calibrated to a best-fit regression line defined by three NBS standards, NBS-18, NBS-19, and NBS-20. The results are expressed in delta (δ) notation in units per mil (‰) relative to the Vienna Pee Dee Belemnite (V-PDB) international standard. The expression is as follows:

$$\delta^{13}\mathrm{C}\ \text{or}\ \delta^{18}\mathrm{O}\,(‰) = \frac{R_{\text{sample}}}{R_{\text{V-PDB}} - 1} \times 1000$$

where R is the ratio $^{18}O/^{16}O$ or $^{13}C/^{12}C$. A positive value means that the sample is enriched relative to the V-PDB in the heavy isotope. On the other hand, a negative