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Influence of bottom water anoxia on nitrogen isotopic ratios and amino acid contributions of recent sediments from small eutrophic Lonar Lake, central India

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Abstract

Lonar Lake is a eutrophic, saline soda lake with permanently anoxic deep water. The high pH and deoxygenation result in very elevated $\delta^{15}N$ of suspended particulate matter (SPM) and sediments due to denitrification and pH-related loss of gaseous ammonium. SPM and sinking particles are predominantly aquatic in origin, whereas surface sediments are of mixed terrestrial plant and planktonic source. An indicator of degradation intensity was derived from a principal component analysis of the spectral distribution of amino acids and named Lonar degradation index (LI). A ratio of individual amino acids (Ox : Anox ratio) was additionally used to determine the relative degree of aerobic vs. anaerobic degradation. These two biogeochemical indicators can be used to detect changes in degradation intensity and redox conditions in the geological history, and thus the paleoclimatic interpretation of Lonar sediments. Surface sediments can be divided into three zones: (1) a nearshore, oxic zone of predominantly aquatic organic matter, in which oxidation leads to a strong diagenetic increase of $\delta^{15}N$; (2) an alluvial zone with a predominance of isotopically depleted land plant and soil organic matter degraded under oxic conditions; and (3) an anoxic, deep zone, which receives aquatic organic matter and land plant–derived material transported near the bottom and in which organic matter is well preserved due to anoxic diagenetic conditions.

Lonar Lake is a crater lake with small streams and surface runoff as major water sources and no outflow. It is saline, alkaline, eutrophic, and below ~ 4 m water depth permanently sub- to anoxic, which is typical for closed-basin saline lakes (Eugster and Hardie 1978). The laminated sediments in the deep, permanently anoxic part of the lake provide one of the very scarce climate records in Central India (S. Prasad unpubl.). Due to their high resolution, these sediments provide an excellent archive of recent climate change. We tested common productivity and degradation proxies that are based on nitrogen isotopic ratios and amino acid assemblages for their applicability in Lonar Lake. For the current investigation terrestrial plants and soils from the inner Lonar crater as well as suspended particulate matter (SPM) were sampled. Sediment traps were installed to sample sinking particles in seasonal resolution and to study the effect of early degradation on sinking organic matter (OM). Surface sediments were analyzed to determine the state of degradation and to understand the differences in effect of early degradation under oxic and sub- to anoxic conditions. Furthermore, the ratio of the two stable carbon isotopes was used to determine the percentage of terrestrial and aquatic OM in the surface sediments and the pathways of CO_2 uptake of different plants.

The nitrogen cycle in aquatic systems is often investigated using the ratio of nitrogen isotopes $^{15}N : {}^{14}N$ of OM. This ratio, expressed as $\delta^{15}N$, can serve as an indicator of the inorganic nitrogen source of aquatic plankton, and it reflects isotopic fractionation of the different transformation processes within the nitrogen cycle (Brandes and Devol 2002). In small, isolated waterbodies short-term changes in the water chemistry, catchment ecology, or nitrogen source or cycle can alter the $\delta^{15}N$ of the sediment quickly (Hodell and Schelske 1998). Trend and magnitude of OM nitrogen isotopic ratio alteration during early degradation depend on the availability of oxygen (Macko and Estep 1984; Freudenthal et al. 2001; Lehmann et al. 2002). In this study the differences of aerobic and anaerobic degradation of similar source sediments in a natural environment were discovered.

Amino acids are important components in biochemical research as they are ubiquitous in OM and are the major constituent of nitrogen in fresh OM (Lee 1988). Frequently they are used to determine the state of degradation in marine OM since the distribution of individual amino acids shows characteristic changes during degradation. Hence, degradation indices based on the amino acid assemblages in OM were developed, such as the degradation index (DI) introduced by Dauwe and Middelburg (1998) and Dauwe et al. (1999) as well as the reactivity index (RI) established by Jennerjahn and Ittekkot (1997). These proxies were also applied to terrestrial aquatic systems (Verma and Subramanian 2002; Meckler et al. 2004; Unger et al. 2005). However, due to differences in amino acid spectra between terrestrial and marine OM, common degradation indices have to be tested and possibly modified in terrestrial-dominated environments (Gaye et al. 2007). Differences in

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amino acid assemblages of OM degraded under aerobic and OM degraded under anaerobic conditions as observed by Cowie et al. (1995) could also be detected in Lonar Lake sediments. Therefore, we used the ratio of the amino acids that become relatively enriched during aerobic decomposition to the amino acids relatively enriched during anaerobic decomposition. This results in high ratios if sediments are degraded under aerated conditions and low ratios if degraded in permanently anoxic sediments; this ratio might also be applicable to paleorecords.

Study site

Geology—Lonar Lake, located at 19°58′N and 76°30′E, occupies the floor of a Middle to Late Pleistocene meteorite impact crater on the Deccan Plateau in Buldhana District, Maharashtra, Central India (Fig. 1A). Origin and formation age of the crater were subject to various investigations (Misra et al. 2010). The crater is almost circular and its rim-to-rim diameter averages 1880 m (Fig. 1B). The modern crater floor is located at ~ 470 m above sea level, which is around 140 m below the rim crest elevation. The inner rim wall is fairly steep with slopes of 15–18° in the east and up to ~ 30° in the west and southwest. The shape of the crater floor is almost planar, dipping only very slightly to the west due to the impact direction of the meteorite, which struck the target rock from the east with an angle of 30–45° (Misra et al. 2010). The inner crater wall is characterized by erosion features such as rills and gullies. In the northeast, an incised channel developed as a consequence of two small streams flowing into the lake. Erosion by these streams has led to an incision on the scale of 30–40 m depth and some 300 m distance.

Climate and hydrology—Lonar Lake is located in India's core monsoon zone. The annual climate can be divided into three periods: (1) hot (average temperature = 31°C) and dry weather during the pre-monsoon from March to beginning of June, (2) hot (average temperature = 27°C) and wet weather from June to end of September (southwest monsoon) with strong winds and rainfall averaging 680 mm, and (3) relatively cool (average temperature = 23°C) and dry weather during post-monsoon from October to February (N. Basavaiah unpubl.).

The lake itself covers an area of nearly 1 km^2 and is fed by three perennial streams (Fig. 1B). Two of them, the Dhara spring and the Sitanahani spring, are entering the crater from the northeast. They formed the Dhar Canyon, an erosive incision, and built up an alluvial fan into the lake. On this fan, crops such as banana (*Musa* × *paradisiaca*), millet (*Setaria italica*), corn (*Zea mays*), custard-apple (*Annona reticulata*), and papaya (*Carica papaya*) are cultivated. The third stream feeding the lake springs from the inner crater wall and enters the lake from the eastern shore. Today the three streams are diverted toward the Dhara fan to irrigate the agricultural fields. Apart from these streams, ephemeral runoff during the monsoon rainfalls and seepage of water from the country rocks are contributing to the water supply. Water discharge is only conducted by evapotranspiration. No outflowing stream is present and no seepage loss occurs since the lake level is below the local groundwater level (Nandy and Deo 1961).

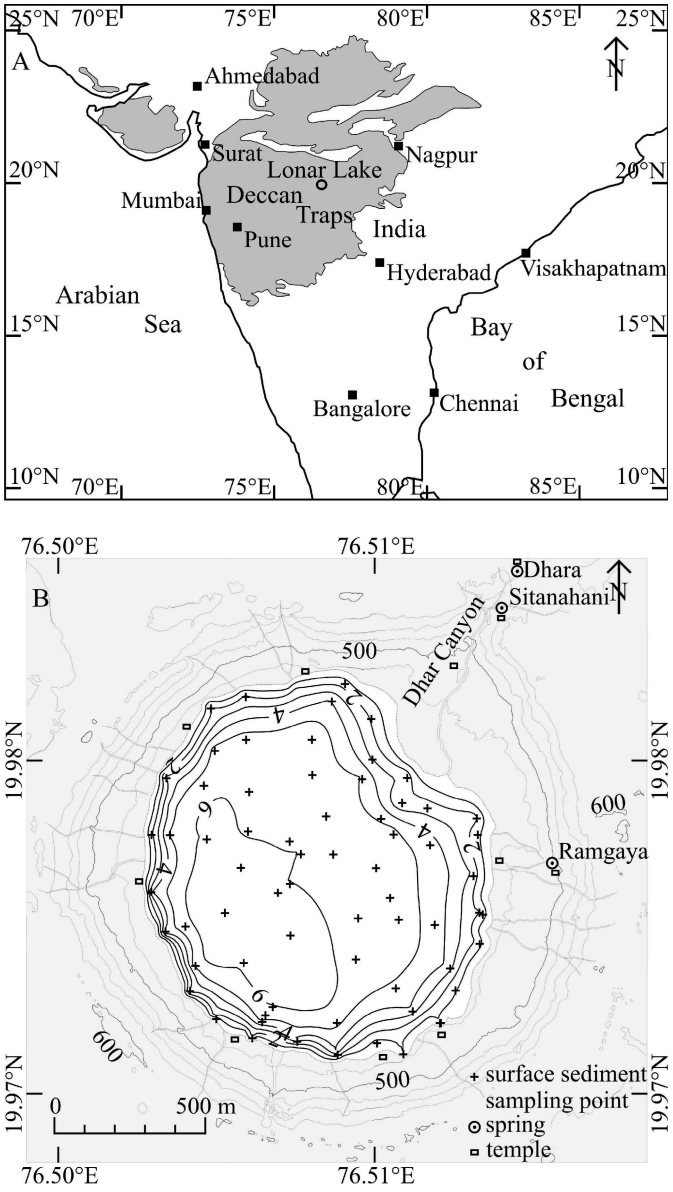

Fig. 1. (A) Location map showing the position of Lonar Lake on the Deccan Traps in Central India. (B) Map of Lonar Lake showing the bathymetry (m) and surface sediment sampling points.

During our investigations, the lake water was brackish (salinity: 8.0–12.3‰) and alkaline with pH values between 8.7 and 10.7 (N. Basavaiah unpubl.). The lake groups into the Na-Cl-CO_3 subtype of saline lakes (Eugster and Hardie 1978). Since no outflow is present, the lake level fluctuates seasonally with highest level after and lowest level before the southwest monsoon. However, since 1985 the lake level has increased significantly (Badve et al. 1993), which is obvious from dead trees drowned in the shallow water of the modern lake. Given that precipitation has been relatively reduced during the first half of the 1980s (Badve et al. 1993), the main cause of the lake level increase is likely

to be seepage of water along fractures into the lake from the Kalapani Dam, a large rainwater reservoir that was constructed near the southwestern rim of the crater in 1970–1973 (Surakasi et al. 2007). This seepage may also explain the gradual reduction of the lake's salinity as noticed by Badve et al. (1993) and Surakasi et al. (2007). Enhanced lake level fluctuation in the recent past is not only indicated by the drowned trees but also by trona ($Na_3(HCO_3)(CO_3)\cdot 2H_2O$) precipitates covering the walls of shore temples, which were built in medieval times during the rule of the Yadavas (Malu et al. 2005).

Biology—The algal assemblage is dominated by Cyanophyceae (> 98%); minor species are largely pennate diatoms, such as *Cymbella*, *Cocconeis*, *Nitzschia*, and *Navicula*, as well as Euglenophyceae and Chlorophyceae (Badve et al. 1993). The non-nitrogen-fixing, filamentous *Arthrothrix fusilini* (formerly *Spirulina platensis*) was reported to be the major Cyanophyceae species in Lonar Lake; also *Planktothrix agardhii* (formerly *Oscillatoria agardhii*) and *Dactylococcopsis* sp. were found to be abundant (Badve et al. 1993; Mahajan 2005). Dense and locally surface-floating blooms were observed particularly after the monsoon (Badve et al. 1993). Mahajan (2005) reported that zooplankton in Lonar Lake are restricted to a few species and are generally low in number. Beside some protozoans, mainly ciliates, identified zooplankton species are the rotifers *Brachionus* sp., *Philodina* sp., and *Testudinella* sp., culicid larvae, and very few exemplars of the ostracod *Cypris subglobosa* (Badve et al. 1993; Mahajan 2005). Branchiopoda have not been observed (Mahajan 2005). The lake is fishless, and only one gastropod species (*Lymnea acuminate*) was found (Badve et al. 1993). The non-Cyanophyceae microbial community consists of thermophilic, halophilic, and alkalophilic bacteria (10^2 to 10^4 viable cells mL^{-1}; Joshi et al. 2008). Also, methanogenic archaea were reported (Surakasi et al. 2007).

The vicinity of Lonar crater is characterized by semiarid vegetation, but at the present time most of the area is under agricultural land use. Within the crater, the vegetation is more diverse. The rim is overgrown by grass, shrub, and dry deciduous forest. A plain of alluvial material surrounding the lake has formed at the crater floor. This plain predominantly hosts semievergreen forest and is ~ 5–100 m broad except at the Dhara fan in the northeast, where it reaches a breadth of > 300 m. The Dhara fan is mostly under land use with crop plantations and meadows for grazing cattle. Also, swamp vegetation is common on the Dhara fan. Most trees growing in the Lonar crater were afforested during 1986 to 1992 by the Forest Department (Malu et al. 2005). In addition to native species, such as *Acacia nilotica*, *Azadirachta indica*, *Dendrocalamus strictus*, and *Tectona grandis*, nonindigenous species were planted, such as *Eucalyptus* sp., *Delonix regia*, and *Prosopis juliflora*.

Methods

Sampling—Surface sediment samples were collected in January 2007 and May 2008 at 68 locations using a Wildco Ponar-type grab sampler with a maximum penetration depth of 5–7 cm. Additionally, 28 samples were taken along the shoreline consisting of soil, terrestrial plants, and plankton.

Water samples were taken in May 2008 and February 2011 with a Niskin 1011 water sampler activated by a General Oceanics Devil messenger (model 1000MG) attached to a hydrocable that was marked in 10 cm intervals. The samples were filtered immediately after retrieval onto pre-combusted and pre-weighed Whatman GF/F filters (0.45 μm) and air-dried. Water samples were stored frozen until further analysis in the laboratory.

Sediment traps were deployed at two stations from February 2011 to May 2011 and from May 2011 to October 2011 ~ 70 cm above the lake floor. The trap bottles were not poisoned because the study location is a natural heritage site, and the use of toxic chemicals is prohibited.

Data on air temperature, rainfall, evapotranspiration, wind speed, and wind direction were acquired from the India Meteorological Department, Pune, and from the India Water Portal (http://indiawaterportal.org/met_data/).

Surface samples from the Himalayan lakes Rewalsar, Renuka, and Mansar were taken with grabs or short corers by one of the authors (B.K.D.) over the last decades, and sampling details as well as further information on the lakes are available in Das et al. (2008).

Analytical methods—Prior to analyses, the surface sediment, soil, and plankton samples were rinsed with distilled water and centrifuged at 4000 revolutions min^{-1} until the supernatant water was clear and attained an electrical conductance coefficient of < 1000 μS. This treatment was done to remove any salts dissolved in the pore water. Subsequently, the samples were freeze-dried for 72 h and aliquots were ground manually in an agate mortar.

Total carbon and nitrogen (C_{tot}, N_{tot}) were measured on a Carlo Erba Nitrogen Analyzer (NA) 1500 elemental analyzer; the standard deviation of the duplicate analyses was 0.15% for carbon and 0.005% for nitrogen. Organic carbon (C_{org}) analyses were performed on the same instrument after pretreating the samples with 2 mol L^{-1} HCl to eliminate inorganic carbon. The relative error of this method was ± 5%. Carbonate carbon (C_{carb}) was defined as the difference between total and organic carbon; the values were converted to calcite as this was the only carbonate phase detected in the sediments.

$^{13}C:{}^{12}C$ isotope ratios were determined using a Finnigan MAT 252 gas isotope mass spectrometer after high-temperature flash combustion in a Carlo Erba NA-2500 elemental analyzer at 1100°C. Values are expressed as $\delta^{13}C$ (‰) = $[(R_{sam}:R_{std}) - 1] \times 10^3$, where R_{sam} = $^{13}C:{}^{12}C$ ratio of the sample and R_{std} = $^{13}C:{}^{12}C$ ratio of the reference standard PDB (PeeDee Formation Belemnite Limestone). Analytical precision was better than 0.1‰ based on replicate measurements of a reference standard; duplicate measurements of samples resulted in a mean deviation of 0.2‰.

The ratio of the two stable nitrogen isotopes ($^{15}N:{}^{14}N$) is expressed as $\delta^{15}N$ after determining the abundance of the two isotopes in samples (after combustion and reduction of NO_x to N_2) by mass spectrometry: $\delta^{15}N$ (‰) = $[(R_{sam}:R_{std}) - 1] \times 10^3$, where R_{sam} = $^{15}N:{}^{14}N$ ratio of

the sample and R_{std} = $^{15}N:^{14}N$ ratio of the reference standard, atmospheric N_2 ($\delta^{15}N$ = 0‰). $\delta^{15}N$ values were determined using a Finnigan MAT 252 gas isotope mass spectrometer after high-temperature flash combustion in a Carlo Erba NA-2500 elemental analyzer at 1100°C. Pure tank N_2 calibrated against two reference standards of the International Atomic Energy Agency (IAEA), IAEA-N-1 and IAEA-N-2, as well as a sediment standard was used as a working standard. Analytical precision was better than 0.1‰ based on replicate measurements of a reference standard. Duplicate measurements of samples resulted in a mean standard deviation of 0.11‰.

Nitrate and nitrite concentrations of filtered water samples were measured with standard colorimetric techniques (Grasshoff et al. 1999) on an AutoAnalyzer 3 by Bran and Luebbe. Detection limit of nitrate and nitrite concentration was 0.15 and 0.02 μmol L^{-1}, respectively.

Amino acid analyses were carried out on a Biochrom 30 Amino Acid Analyzer according to the method described in Lahajnar et al. (2007).

Results

C_{org}, N_{tot}, C_{carb}, C : N—The C_{org}, N_{tot}, C_{carb}, and atomic $C_{org}:N_{tot}$ (C : N) ratio values of the analyzed samples are shown in Table 1. The surface sediment data were reported by N. Basavaiah (unpubl.). C_{org} and N_{tot} of the surface sediments show values of 0.25% to 6.28%, and 0.02% to 0.88%, respectively. C_{carb} values of the sediments vary between 0.23% and 2.48%, and the atomic C : N ratios range from 7.8 to 17.6.

$\delta^{13}C$—The $\delta^{13}C$ values of surface sediments were investigated by N. Basavaiah (unpubl.). $\delta^{13}C$ of surface sediments range between −23.1‰ and −15.2‰ with lowest values off the Dhara river mouth and along the westernmost lakeshore and highest values in the deep central part of the lake. SPM filtered from shallow (0.5 m) as well as from deep (4 m) water has $\delta^{13}C$ values of −9.4‰ to −8.2‰. Sediment trap material shows $\delta^{13}C$ values of −8.5‰ to −5.0‰. Terrestrial C_3 and C_4 plants have mean $\delta^{13}C$ values of −29.1‰ and −12.1‰, respectively. Depending on the percentage of C_3 and C_4 plant material in the soils, their $\delta^{13}C$ values vary between −26.7‰ and −18.1‰.

$\delta^{15}N$—The $\delta^{15}N$ values of the surface sediments show a clear correlation with water depth (Fig. 2A). Samples from depths > 4 m have values of 7.8‰ to 13.6‰ (mean = 10.8‰). $\delta^{15}N$ of samples from stations shallower than 4 m range between 10.5‰ and 18.2‰ (mean = 15.3‰; Fig. 2B). $\delta^{15}N$ of SPM group in a narrow range of 10.1–10.8‰. Sediment trap material has $\delta^{15}N$ values of 16.1‰ to 18.6‰ and does not show a systematic difference between the two stations or the two sampling intervals. The analyzed vegetation samples have a wide range of $\delta^{15}N$ values from −2.8‰ to 12.1‰ with a mean of 4.4‰, which is well in the range of terrestrial plants (Maksymowska et al. 2000). Five of the 12 vegetation samples show relatively ^{15}N-depleted values between −2.8‰ and 0.9‰, indicating N_2-fixation. In fact, these vegetation samples were taken from genera of the family Fabaceae, which is known to form root nodules associated with symbiotic nitrogen-fixing bacteria (Soltis et al. 1995), including the species *Acacia nilotica*, *Prosopis juliflora*, and *Tamarindus indica*. The remaining seven vegetation samples have $\delta^{15}N$ values of 2.7‰ to 12.1‰ (mean = 7.4‰). The sampled soils show diverse $\delta^{15}N$ values of −0.4‰ to 16.1‰ (mean = 6.2‰), mostly depending on the vegetation close to the sampling points.

Amino acids—The amounts of total hydrolyzable amino acids and hexosamines of the different samples are shown in Table 1. Amino acid contents in the surface sediments range between 1.1 and 31.4 mg g^{-1} and are significantly correlated with organic carbon content. The amount of organic carbon and total nitrogen incorporated into amino acids (AA-C; AA-N) is 10.3% to 33.5% (mean = 18.2%) and 36.8% to 73.4% (mean = 50.0%), respectively. Sediment trap samples and SPM are relatively enriched in total amino acid content and also show elevated AA-C and AA-N values compared to surface sediments. The analyzed soils are the most depleted samples in terms of amino acid content and AA-C and AA-N percentages. The average distribution of the individual amino acids in surface sediments, sediment traps, SPM, terrestrial plants, and soils are given in Table 2.

Discussion

C_{org}, N_{tot}, C_{carb}, C : N—Despite eutrophic conditions, C_{org} and N_{tot} values in the modern Lonar Lake sediments are low compared to most reported values for eutrophic lakes (Dean and Gorham 1998). The low C_{org} and N_{tot} concentrations of the sediments are due to the high input of lithogenic material, which is eroded from the steep slopes of the crater and transported into the lake during monsoonal rainfall events. The C_{carb} sources are carbonate crystals formed during lake level decline in dry years and during maximum photosynthesis. Similar to C_{org} and N_{tot} concentrations, C_{carb} concentrations are related to lithogenic matter input and are therefore higher in the central and lower in the nearshore area.

The C : N ratio is often used in lake studies to estimate the terrestrial and aquatic fraction of OM in the sediments (Meyers 1994). C : N ratios of aquatic OM vary between 4 and 10, whereas C : N ratios of terrestrial vascular plant material show values of 20 and greater (Meyers 1994). The surface sediments of Lonar Lake have C : N ratios of 7.8 to 17.6 with a mean value of 10.7, indicating a dominance of aquatic OM. C : N ratios may increase during early diagenesis as N-bearing components (proteins, peptides, and free amino acids), particularly in protein-rich OM derived from aquatic source, are preferentially decomposed (Meyers 1997). On the other hand, C : N ratios of OM of terrestrial origin may decrease during degradation as a consequence of preferential removal of C-rich lipids and sugars (Meyers 1997). In organic-poor sediments, ammonium sorbed by clay minerals can be a significant N-contributor, reducing C : N ratios (Müller 1977). Since these diagenetic effects usually are of minor magnitude, the C : N ratio still serves as a good indicator of the OM source.

Table 1. Bulk biogeochemical parameters, and amino acid and amino sugar concentrations of different Lonar samples. C_{carb} values of surface sediment samples as well as C_{org}, N_{tot}, C : N, and $\delta^{13}C$ values of all samples except for those of sediment traps were taken from N. Basavaiah (unpubl.).

Sample type	C_{org} (%)	N_{tot} (%)	C_{org} : N_{tot} atomic	C_{carb} (%)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	THAA (mg g^{-1})	AA-C (%)	AA-N (%)	THHA (mg g^{-1})	HA-C (%)	HA-N (%)
Surface sediments (n=66; 26*)	2.65±1.47	0.30±0.19	10.71±1.66	1.23±0.42	−18.32±1.81	12.62±2.64	11.33±7.35	18.23±5.02	49.98±8.32	0.82±0.63	1.17±0.39	2.02±0.59
Soil samples (n=17; 6*)	0.52±0.62	0.08±0.07	15.77±24.03	0.33±0.54	−22.56±2.95	5.84±1.53	3.02±3.77	13.39±9.90	38.01±24.31	0.59±0.83	2.39±1.81	3.84±2.66
Suspended particulate matter (SPM)												
Shallow-water SPM (0.5 m; n=2)	28.72±2.48	4.54±0.24	7.41±1.02	nd	−8.79±0.83	10.18±0.15	250.18±15.95	38.90±5.82	73.55±1.23	2.40±0.23	0.34±0.00	0.41±0.06
Deep-water SPM (4 m; n=2)	35.17±5.39	5.23±0.69	7.99±2.26	nd	−8.97±0.61	10.59±0.35	317.55±38.45	41.02±10.88	81.67±0.66	2.24±0.29	0.26±0.07	0.33±0.00
Sediment trap samples												
Western trap Feb–May 2011	17.24	3.21	6.26	0.24	−4.96	16.09	135.15	34.48	56.42	2.04	0.47	0.50
Eastern trap Feb–May 2011	26.82	5.68	5.90	0.04	−6.99	18.57	157.01	35.65	53.97	2.87	0.58	0.57
Western trap Jun–Oct 2011	20.98	3.56	6.88	0.08	−8.49	18.17	170.30	36.07	64.33	2.80	0.54	0.62
Eastern trap Jun–Oct 2011	30.16	4.39	8.59	0.11	−8.45	16.49	323.34	37.52	83.25	4.62	0.48	0.69
Vascular plant samples												
Prosopis juliflora leaves	45.09	4.58	11.49	nd	−30.52	−1.64	176.74	17.55	52.61	0.62	0.06	0.11
Tectona grandis leaves	38.99	1.04	43.74	nd	−28.65	2.66	39.31	4.58	50.83	0.50	0.05	0.37
Azadirachta indica leaves	44.94	3.13	16.74	nd	−28.52	5.17	138.64	13.81	60.39	0.66	0.06	0.16
Acacia nilotica leaves	43.89	1.24	41.45	nd	−28.71	−2.75	49.09	5.09	54.52	0.37	0.03	0.23
Heteropogon sp.	42.49	0.59	84.59	nd	−12.13	10.03	24.29	2.60	37.79	3.67	0.36	3.31

Abbreviations: THAA, total hydrolyzable amino acids in mg g^{-1} dry sample; THHA, total hydrolyzable hexosamines in mg g^{-1} dry sample; HA-C, percentage of organic carbon present as hexosamines; HA-N, percentage of total nitrogen present as hexosamines; nd, not detected.

* Number of samples analyzed for amino acids.

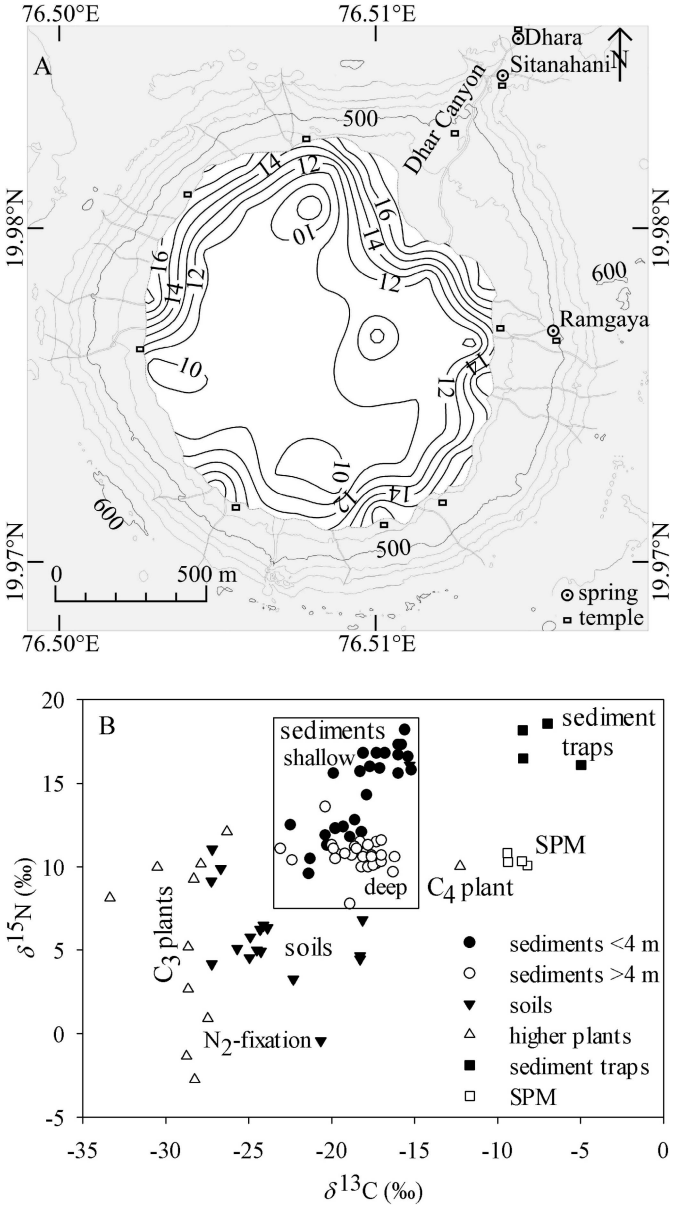

Fig. 2. (A) Spatial distribution of δ^{15}N (‰) in Lonar surface sediment organic matter. (B) Stable carbon vs. nitrogen isotopic ratios of the different Lonar samples.

However, as δ^{13}C of aquatic and terrestrial OM in the Lonar Lake and its catchment are fairly different and in a narrower range than C : N, δ^{13}C of organic carbon seems to be a better proxy to identify the source of surface sediment OM in Lonar Lake (Table 1).

δ^{13}C and δ^{15}N—Compared to the majority of lakes from the literature, both δ^{13}C and δ^{15}N are considerably enriched in Lonar surface sediments (Meyers and Teranes 2002). Figure 3 shows a comparison of the Lonar data to those from Himalayan lakes of similar altitude but of different trophic status. The δ^{13}C of the oligotrophic lake Rewalsar and the mesotrophic lakes Renuka and Mansar are in the range of C_3 plants with admixture of C_4 plants (−28‰ to −22‰), and δ^{15}N values vary around 4‰, generally considered as the average of land plants (Maksymowska et al. 2000). Lonar SPM is highly enriched in ^{13}C, with δ^{13}C values of −9.4‰ to −8.2‰. These values are consistent with reported δ^{13}C values of Lonar dissolved inorganic carbon (DIC), being in the high range of 11‰ to 14.8‰ (Anoop et al. in press), as plankton are usually depleted in ^{13}C by 20‰ compared to their DIC source (O'Leary 1988). As discussed by N. Basavaiah (unpubl.), the high δ^{13}C values of Lonar DIC are due to the high pH of the lake water. In this case, lake water is depleted in CO_2(aq), and plankton utilize HCO_3^- for photosynthesis, which is enriched in ^{13}C by ~ 8.7‰ (at 25°C) compared to CO_2(aq) (Zhang et al. 1995). With an aquatic δ^{13}C end-member of −9‰ and a terrestrial end-member of −28‰, N. Basavaiah (unpubl.) calculated the percentages of terrestrial OM in Lonar surface sediments (32.5–74.0%; mean = 49.1%) by a δ^{13}C two end-member mixing equation.

δ^{13}C in combination with C : N ratio and AA-C is used to identify the source of the sediment trap material. These parameters indicate that the contribution of resuspended surface sediment, soil OM, and terrestrial plants to the sediment trap samples is low (Table 1). Thus, the dominant source of sediment trap samples is SPM and microorganisms decomposing it, as discussed in the amino acid section. Degradation processes may affect δ^{13}C during early diagenesis as, for example, the hydrolysis of proteins is accompanied by an enrichment of ^{13}C in the residual material (Silfer et al. 1992). This effect might be responsible for the slight increase in δ^{13}C values between SPM and sediment trap material. The sediment trap material is enriched in ^{13}C by 2.5‰ before the onset of the monsoon compared to the monsoon despite the higher productivity during the monsoon season. As the lower summer δ^{13}C values are accompanied by C : N ratios elevated by 1.7 (Table 1), we believe that the relative amount of terrestrial OM is slightly higher, which is related to ephemeral runoff causing enhanced erosion and transport of terrestrial OM into the lake.

The elevated δ^{15}N values in Lonar SPM and surface sediments can be attributed to the sub- to anoxic conditions in the hypolimnion in conjunction with the high pH (Heaton 1986). Nitrate in the hypolimnion becomes denitrified associated with a fractionation factor of ε = −30‰ to −22‰ (Brandes et al. 1998), leaving the remaining nitrate pool enriched in ^{15}N. Elevated δ^{15}N values are also related to high salinity and the associated high pH of Lonar Lake (Heaton 1986). At high pH values, the equilibrium of NH_4^+ and NH_3 shifts towards NH_3 (pKa of NH_4^+ = 9.3), leading to ^{15}N enrichment of NH_4^+ relative to NH_3 by 20‰ to 35‰ (Casciotti et al. 2011). The pH values of ~ 9.3 below 4 m water depth and ~ 10.5 at shallower depth result in ~ 50% to 90% NH_3, respectively, which can escape. Concentrations of nitrate and nitrite were very low in the epi- and hypolimnion in February 2011, with values between < 0.15 to 0.94 μmol L^{-1} and 0.24 to 0.52 μmol L^{-1}, respectively. This property may be related to uptake in surface waters and to anoxia below 4 m water depth. The high δ^{15}N values of plankton (mean = 10.4‰) sampled in February 2011 when nitrate and nitrite were almost depleted in the epilimnion do not suggest that

N_2-fixation is a dominant nitrogen source in Lonar Lake. Whereas the intense plankton blooms during the monsoon are related to the in-wash of nutrients from the ephemeral runoff, the nutrient source during post-monsoon may be small streams and recycling of nutrients in the water column and the surface sediments.

The spatial variability of $\delta^{15}N$ of surface sediment is depth dependent (Fig. 2A) and is most likely linked to the stratification of the lake, with oxic surface water up to about 4 m depth and sub- to anoxic water in > 4 m depth (N. Basavaiah unpubl.). Lehmann et al. (2002) found a $\delta^{15}N$ decrease by 3‰ during anoxic incubation and an increase of $\delta^{15}N$ by > 3‰ within the first months of oxic incubation before $\delta^{15}N$ slowly dropped to the initial source values. Since the traps at Lonar Lake were not poisoned, microbial growth and related OM degradation could occur during the time of deployment (3–4 months). While installing the traps, oxic surface water filled the sampling bottles so that, at least to some extent, degradation under oxic conditions could play a role in OM respiration in the traps and explain the elevated $\delta^{15}N$ values compared to SPM and surface sediments from anoxic sampling points. Macko and Estep (1984) analyzed the effect of aerobic microbial degradation on different nitrogen-containing substrates. Their findings show that deamination and transamination of different amino acids can result in both elevated and reduced $\delta^{15}N$ values of the residual OM. Comparison with the results of the amino acid analysis of the Lonar Lake samples shows that the elevated $\delta^{15}N$ values in shallow surface sediments and sediment trap material can be attributed to aerobic microbial degradation. Further indications of degradation processes derived from the analysis of amino acids are given in the following section.

Amino acid concentrations—Since most amino acids in fresh OM are more labile than other carbon compounds present in particulate matter (Lee 1988), they are preferentially lost during degradation. The mean amino acid content in sediment trap samples is 87.4 mg g^{-1} lower compared to that of SPM (Table 1), which is a reduction by 30%. C_{org} and N_{tot} content in the trap samples are reduced by 25% and 20% compared to SPM, respectively. C : N ratio, $\delta^{13}C$ values, and AA-C are in the same range in sediment trap and SPM samples, corroborating the assumption that the sediment trap material is dominated by SPM-derived OM with only very minor contribution of land-derived OM sources. Thus, the loss of amino acids must be due to the preferential removal of amino acids during early decomposition. In surface sediments only about 8% of the C_{org}, 6% of the N_{tot}, and 4% of the amino acid content found in SPM are present, which is partly due to degradation but also to enhanced contribution of amino acid–poor terrestrial OM as indicated by enhanced C : N ratios, depleted $\delta^{13}C$ values, and decreased AA-C (Table 1). In environments with varying amounts of terrestrial OM, such as the Lonar Lake, AA-C values are strongly influenced by the distribution of aquatic- and terrestrial-derived OM in the sediments (Haake et al. 1992; Verma and Subramanian 2002), whereas AA-N is more sensitive to degradation (Henrichs et al. 1984; Cowie and Hedges 1992). Terrestrial OM, particularly woody fragments, has lower AA-C values than plankton due to the lower percentage of proteins, peptides, and free amino acids in terrestrial plants and the higher percentage of nitrogen-deficient organic compounds (Rashid 1985).

Individual amino acid assemblages—Sources of the OM of the sediments are terrestrial plant tissue of differing reactivity, moderately to intensely degraded soils, dead plankton degraded during sinking, bacterial OM, and resuspended lake sediment. The most important processes, modulating the amino acid assemblage of source material, are aerobic microbial degradation at the water–sediment interface in the shallow oxic part of Lonar Lake, anaerobic microbial degradation within the sediments and at the water–sediment interface in the deeper sub- to anoxic part of the lake, and lysis of cells and cell compounds. Generally, the amino acid spectra indicate that Lonar sediments are less degraded than sediments in other shallow freshwater environments (Verma and Subramanian 2002; Unger et al. 2005; Das et al. 2010) and resemble those of suspended matter or plankton (Lee 1988; Cowie and Hedges 1992). This difference is most likely attributable to the high productivity in combination with high sedimentation rates due to slope erosion during the southwest monsoon, leading to fast burial of the OM in the sediment where anoxic conditions prevent enhanced degradation (Hulthe et al. 1998; Lehmann et al. 2002; Moodley et al. 2005). The lack of higher organisms that feed on the suspended and surface sediment OM may additionally diminish the state of degradation.

The amino acid assemblages of Lonar SPM differ from those reported for marine SPM (Lee 1988). Lonar SPM is comparatively enriched in glutamic acid (Glu), alanine (Ala), valine (Val), leucine (Leu), and isoleucine (Ile), and depleted in lysine (Lys), serine (Ser), aspartic acid (Asp), and glycine (Gly). These differences can be attributed to dominance of cyanobacteria in the plankton community of Lonar Lake. In diatom-dominated marine sediments, Asp : Gly ratios are 0.6–0.8 (Ittekkot et al. 1984), whereas Lonar sediments have Asp : Gly ratios of 0.86–1.16. The most abundant cyanobacterium in Lonar Lake is *Arthrothrix fusilini*, which is enriched in Ile, Ala, Val, and Leu and depleted in Gly, Glu, Lys, Asp, and Ser (Becker 2007) compared to marine plankton (Lee 1988). Glu is highly enriched in many microbes, especially in gram-positive bacteria (Tempest et al. 1970). In summary, the difference between amino acids spectra of Lonar SPM, trap material, and surface sediments compared to other lacustrine and marine samples results from the high amounts of bacterial biomass.

The amino acid assemblages of the analyzed vascular plant samples are quite different from those of the SPM samples as they show significantly lower values of Glu and markedly higher values of histidine (His), Lys, and the nonprotein amino acids β-alanine (β-Ala) and γ-aminobutyric acid (γ-Aba) (Table 2). The elevated Glu values in Lonar SPM are related to high microbial OM contribution in the lake. His is usually more abundant in plants than in phytoplankton and

Table 2. Amino acid composition (mol%) of the different Lonar samples.

Sample type	Asp	Thr	Ser	Glu	Gly	Ala	Val	Met	Ile
Surface sediments (n=26)	12.99±0.73	5.62±0.45	6.06±0.58	11.90±0.45	12.60±1.12	10.97±0.51	6.72±1.09	0.38±0.17	4.30±0.92
Soil samples (n=6)	16.57±0.69	5.71±0.19	6.80±0.47	12.17±0.77	15.07±0.69	10.51±0.26	5.02±0.16	0.43±0.25	2.78±0.13
Suspended particulate matter									
Shallow-water SPM (0.5 m; n=2)	10.75±0.27	5.59±0.02	6.15±0.22	18.01±0.16	9.12±0.02	11.18±0.19	7.83±0.20	0.53±0.06	5.64±0.01
Deep-water SPM (4 m; n=2)	10.77±0.45	5.51±0.15	6.17±0.26	17.28±1.76	9.05±0.22	11.38±0.66	7.79±0.38	0.46±0.07	5.65±0.31
Sediment trap samples									
Western trap Feb–May 2011	12.42	6.80	5.53	12.49	10.82	10.95	8.36	0.28	5.74
Eastern trap Feb–May 2011	12.38	6.65	5.74	12.79	10.96	10.79	8.04	1.12	5.51
Western trap Jun–Oct 2011	12.14	6.74	5.76	12.38	10.94	10.80	8.39	0.16	5.66
Eastern trap Jun–Oct 2011	12.05	6.68	5.67	12.90	10.74	10.74	8.39	0.25	5.65
Vascular plant samples									
Prosopis juliflora leaves	17.66	5.23	6.17	10.93	9.43	8.33	6.44	0.18	4.46
Tectona grandis leaves	10.63	5.78	6.94	11.80	10.62	9.30	7.50	1.04	5.70
Azadirachta indica leaves	11.39	4.82	6.07	17.14	9.28	9.42	6.21	0.43	4.69
Acacia nilotica leaves	10.38	5.41	7.31	11.29	10.32	9.49	7.36	0.44	5.29
Heteropogon sp.	10.08	7.13	7.82	13.06	10.58	10.29	7.41	1.50	5.12

even more in fungi (Cowie and Hedges 1992). Lys, being an essential amino acid to most animals, is synthesized in higher plants from Asp by the enzyme aspartate kinase (Azevedo and Lea 2001). Elevated β-Ala and γ-Aba values in vascular plant tissue compared to plankton were reported by Cowie and Hedges (1992). In addition, γ-Aba is known to be produced by plants as a response to environmental stress

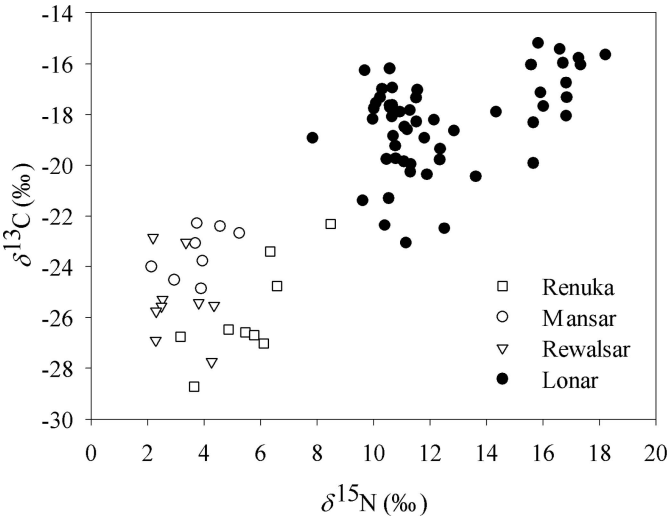

Fig. 3. Comparison of the stable carbon vs. nitrogen isotopic ratios of Lonar Lake and Renuka, Mansar, and Rewalsar Lakes.

linked to heat, salt, and flooded soil (Kinnersley and Turano 2000), which regularly occur in the Lonar crater.

Characteristic changes in amino acid spectra, such as relative increases in Asp, Gly, and non-protein amino acids as well as decreases of the essential amino acids Val, Ile, Leu, and arginine (Arg), indicate that degradation is progressing from SPM to sediment trap samples to surface sediments and that soils are even more degraded than lake sediments (Fig. 4). Higher plants are an additional amino acid source for the sediments with a wide range of amino acid spectra (*see* above). However, although terrestrial plants contribute about 50% of organic carbon to lake sediments (*see* above), their contribution to total amino acids is lower due to the low amino acid content of most higher plants (Rashid 1985).

One of the prominent changes from SPM to trap material is the drop of Glu by 5 mol%. When attributing this difference to the preferential microbial removal of Glu from the aquatic OM, the elevated δ^{15}N values in the sediment trap samples and in the oxic shallow-water sediments could be explained as follows. Macko and Estep (1984) showed that amino acid degradation by aerobic heterotrophic bacteria occurs via different pathways, depending on the substrate amino acids. Whereas bacteria that utilize Glu and Asp can incorporate these amino acids into the metabolic pathways without preceding deamination, Ala, Ser, and threonine (Thr) have to be deaminated and transformed to glutamate or aspartate. Both pathways

Table 2. Extended.

Leu	Tyr	Phe	β-Ala	γ-Aba	His	Trp	Orn	Lys	Arg
7.30±0.71	2.49±0.34	4.29±0.47	0.54±0.19	0.48±0.13	2.57±0.69	0.22±0.09	0.58±0.17	3.81±0.35	4.24±0.54
5.33±0.36	1.44±0.23	2.80±0.13	1.60±0.62	0.71±0.18	4.80±0.98	0.48±0.27	0.71±0.33	3.73±0.23	3.33±0.35
8.80±0.16	2.69±0.06	3.76±0.03	0.10±0.00	0.06±0.00	1.58±0.02	0.10±0.00	0.09±0.00	2.81±0.10	5.20±0.23
8.95±0.35	2.87±0.10	3.71±0.07	0.07±0.01	0.04±0.01	1.48±0.01	0.10±0.02	0.09±0.07	3.18±0.30	5.43±0.55
8.06	3.10	4.64	0.11	0.11	1.99	0.09	0.10	4.01	4.39
7.88	3.28	4.57	0.10	0.23	1.86	0.07	0.13	3.55	4.36
8.26	3.10	4.77	0.09	0.10	1.82	0.08	0.20	3.96	4.66
8.15	3.22	4.63	0.09	0.11	1.85	0.08	0.10	3.89	4.78
8.74	3.27	4.94	0.15	0.65	2.31	0.25	0.00	5.97	4.90
9.97	3.49	5.02	0.38	0.44	2.21	0.17	0.00	4.73	4.28
8.34	3.24	4.44	0.31	0.90	2.32	0.13	0.07	5.57	5.23
9.35	3.57	5.19	0.30	0.57	2.50	0.15	0.00	6.61	4.48
8.08	2.85	3.39	0.43	0.59	2.87	0.25	0.74	4.63	3.20

are associated with a release of ^{13}C-depleted CO_2, which is reflected in the Lonar sediment trap samples as these show $\delta^{13}C$ elevated by 1.7‰ relative to SPM (Table 1). The Glu- and Asp-based aerobic metabolism is accompanied by the excretion of ^{15}N-depleted ammonia, whereas during aerobic Ala, Ser, and Thr decomposition ^{15}N-enriched ammonia is excreted (Macko and Estep 1984). Thus, microbial OM predominantly growing on Glu and Asp shows elevated $\delta^{15}N$ values compared to its substrate, which seems to be the case for the Lonar sediment trap and shallow-water surface sediments. Enhanced microbial contribution to the sediment trap material is also evident by diminished C : N ratios as bacterial OM is characterized by low C : N ratios of about 5 (Goldman et al. 1987) and by a 33% increase in hexosamines from SPM to trap material (Table 1), especially in galactosamine, which is mostly associated with bacterial cell walls (Kandler 1979; Haake et al. 1992). Thus, the ratio of glucosamines and galactosamines (Gluam : Galam) can be used to identify the sources of hexosamines to sediments and trap samples; bacterial OM is associated with Gluam : Galam ratios of 1 to 3, whereas higher ratios are present in chitinaceous OM, which is usually most abundant in zooplankton. Gluam : Galam ratios of Lonar sediment trap and surface sediment samples range between 1.4 and 2.0, indicating bacterial origin of the hexosamines (Haake et al. 1992). This corroborates the finding of Mahajan (2005), who reported only sparse zooplankton abundances in Lonar Lake.

To integrate the degradation trends and attribute a degradation state to each sample, we carried out a principal component analysis (PCA) of the amino acid assemblage of the different Lonar samples. The Lonar degradation index (LI) follows the approach of the DI calculation by Dauwe et al. (1999) with the additional amino acids Lys, tryptophan (Trp), β-Ala, γ-Aba, and ornithine (Orn). The LI of a sample is defined as:

$$\mathrm{LI} = \sum_i \left[\frac{\mathrm{var}_i - \mathrm{AVGvar}_i}{\mathrm{STDvar}_i}\right] \times \mathrm{fac.coef.}_i \qquad (1)$$

where var_i is the mole percentage of amino acid i, AVGvar_i and STDvar_i are its mean and standard deviation in all samples, and $\mathrm{fac.coef.}_i$ is the factor coefficient of the first axis of the PCA (values shown in Table 3).

The first axis explains 46% of the total variance, and most negative LI values are representative for the freshest (SPM) samples. Trap samples and terrestrial plant samples also have negative values. The most degraded samples, thus represented by the highest LI values, are soil samples from the lake's vicinity. The surface sediments show values varying between −0.8 and 0.8, with one exceptional high value of 1.28 off the perennial streams in the east. Most elevated values, thus the most degraded sediments, occur in the northeast and east off the Dhara fan and the perennial streams (Fig. 5), indicating the supply of degraded terrestrial OM (e.g., soils) to the eastern part of the lake. Lowest

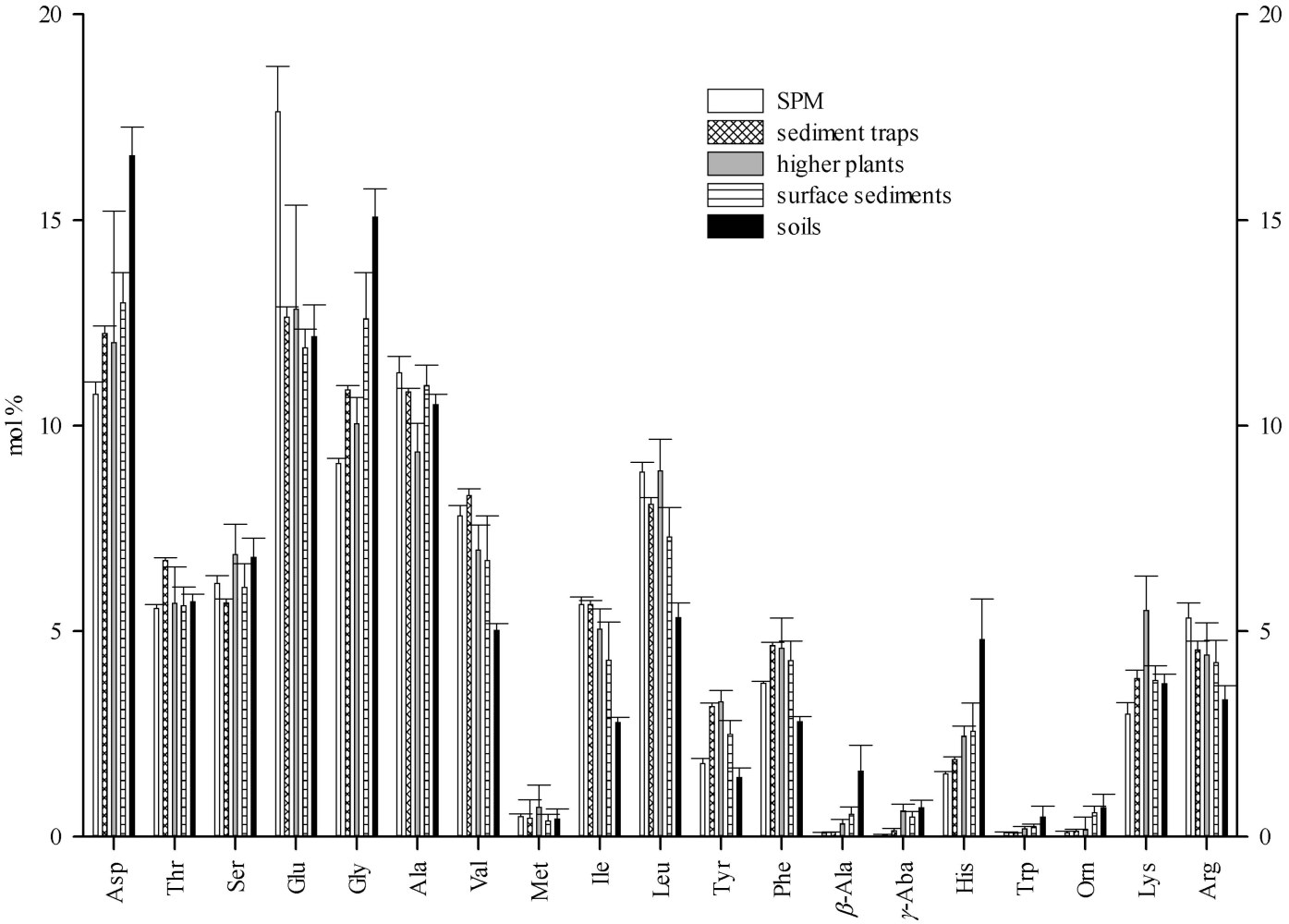

Fig. 4. Mean contributions (mol%) of the individual amino acids to the total hydrolysable amino acid pool of the different Lonar samples. Error bars denote the standard deviation.

LI values are present in the center of the lake, where input of terrestrial sediment is less and sub- to anoxic water reduces the effects of early degradation.

The influence of aerobic and anaerobic degradation on the amino acid assemblage seems to play a significant role in Lonar Lake. Therefore, we decided to use the differences in the amino acid assemblage most probably related to the degree of oxygenation to calculate an indicator of degradation under oxic vs. anoxic conditions. Our calculation is based on the observations made by Cowie et al. (1995), who investigated the differences of anaerobic and aerobic degradation on the amino acid assemblage of identical turbiditic sediments. The Ox : Anox ratio uses the sum of amino acids (mol%) relatively enriched during aerobic degradation and those relatively depleted during anaerobic degradation (Asp, Glu, β-Ala, γ-Aba, Lys) divided by the sum of amino acids relatively depleted during aerobic and relatively enriched during anaerobic degradation (Ser, Ile, Leu, methionine [Met], tyrosine [Tyr], phenylalanine [Phe]). The Ox : Anox ratio of the predominantly undegraded SPM, sediment trap, and higher plant samples are in the range of 0.87 to 1.30 (mean = 1.09). The soil samples, degraded mostly under oxic conditions, have Ox : Anox values of 1.66 to 2.05. The values of surface sediment Ox : Anox ratios vary between 0.98 and 1.44, with highest values in the shallowest parts of the lake and especially off the Dhara fan, where input of aerobically degraded terrestrial OM is highest and the permanent supply of stream freshwater prevents the development of anoxic lake water (Fig. 6). Samples from deeper water stations in the center of the lake show lowest Ox : Anox ratios due to almost permanently anoxic conditions as observed by N. Basavaiah (unpubl.). The Ox : Anox ratio of surface sediments correlates with the LI, thus suggesting that aerobic amino acid degradation is stronger and leads to an overall enhanced state of OM degradation compared to anaerobic degradation.

Depositional environments—According to the spatial differences in Lonar Lake's sedimentation and degradation processes, the lake can roughly be divided into three zones (Fig. 7). These zones do not have distinct boundaries but merge seamlessly. The three zones are (1) the shallow ($<$ 4 m water depth), nearshore parts of the lake; (2) the eastern part of the lake influenced by the inflow of the perennial streams entering the lake from the east and northeast; and (3) the deep ($\geq$ 5 m water depth) part in the central and southwestern lake. The characteristics of the

Table 3. Parameters of the PCA of the Lonar sample set.

Amino acids	First axis factor coefficient	AVG	SD
Asp	0.091	13.089	1.907
Thr	−0.016	5.686	0.550
Ser	0.053	6.205	0.641
Glu	−0.049	12.690	1.840
Gly	0.099	12.100	1.879
Ala	0.002	10.781	0.715
Val	−0.096	6.856	1.203
Met	−0.011	0.438	0.276
Ile	−0.103	4.486	1.093
Leu	−0.105	7.465	1.201
Tyr	−0.088	2.491	0.596
Phe	−0.082	4.144	0.716
β-Ala	0.104	0.573	0.511
γ-Aba	0.077	0.456	0.229
His	0.104	2.653	1.098
Trp	0.073	0.225	0.157
Orn	0.080	0.458	0.293
Lys	−0.001	3.867	0.733
Arg	−0.076	4.232	0.691

Abbreviations: AVG, mean contribution of individual amino acids to the amino acid assemblage in mol%; SD, standard deviation.

different zones are discussed below, and the corresponding values are shown in Table 4.

Zone I: shallow, nearshore lake—The most striking features of this zone are the exceptionally high $\delta^{15}N$ values, elevated $\delta^{13}C$, C_{org}, N_{tot}, and amino acid content values, and relatively low C : N ratios, indicating the deposition of predominantly aquatic organic matter, mostly floating cyanobacterial mats drifting to the shores by wind and by inflow-driven surficial currents. These algal mats are heavily microbially reworked as indicated by slightly elevated LI values and especially by the highest contribution of hexosamines with lowest Gluam : Galam ratios. Due to the oxic water conditions in zone I, the Ox : Anox ratios are elevated.

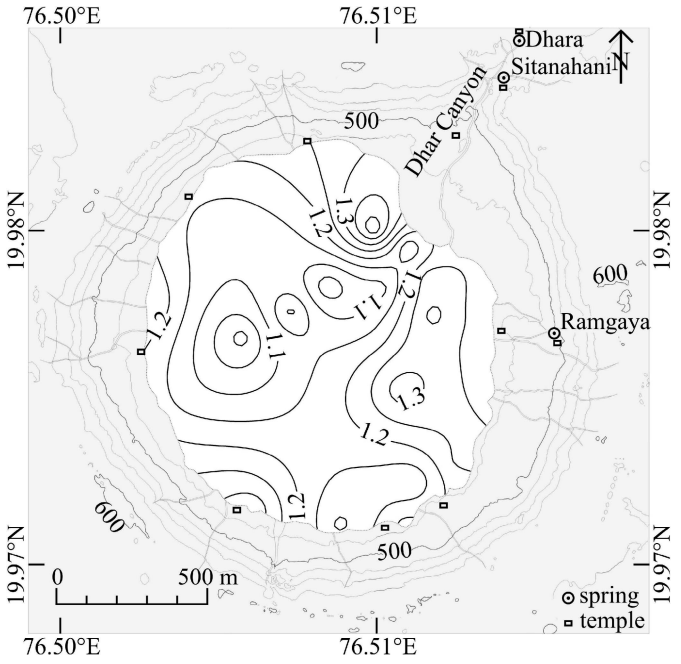

Fig. 6. Spatial distribution of the Ox : Anox ratio in Lonar surface sediment organic matter.

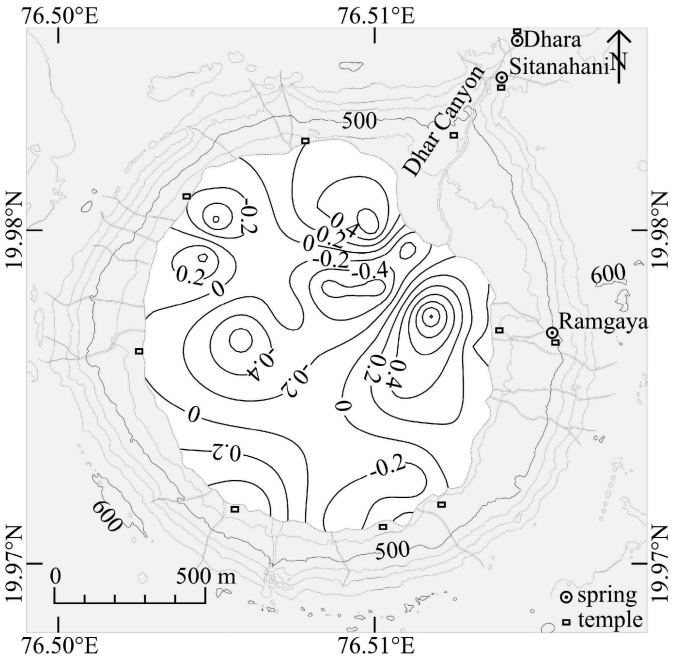

Fig. 5. Spatial distribution of the Lonar degradation index (LI) in Lonar surface sediment organic matter.

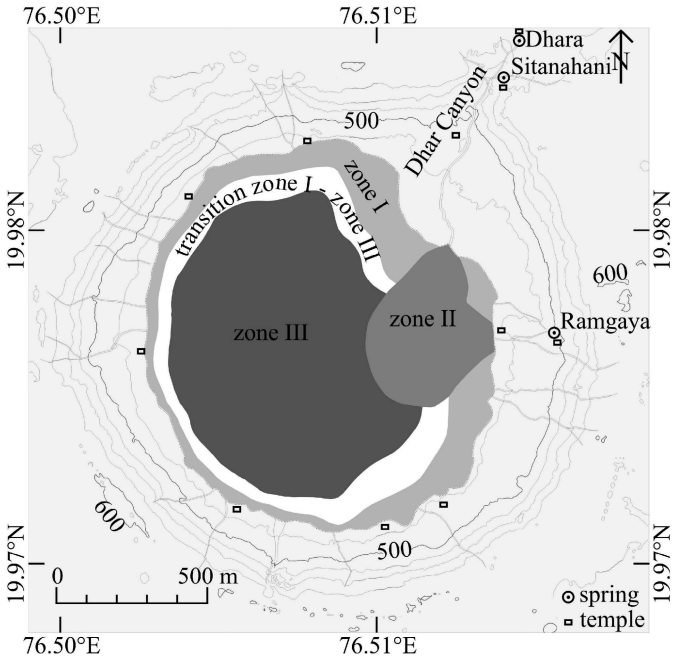

Fig. 7. Map showing the different depositional zones of Lonar Lake.

Table 4. Bulk biogeochemical parameters, amino acid and amino sugar concentrations, and degradation indices of the different depositional environments of Lonar Lake. C_{org}, N_{tot}, C : N, C_{carb}, $\delta^{13}C$, and Ter. C_{org} values were calculated from data reported by N. Basavaiah (unpubl.).

Surface sediments	C_{org} (%)	N_{tot} (%)	C_{org} : N_{tot} atomic	C_{carb} (%)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
Whole lake (n=66; 26*)	2.65±1.47	0.30±0.19	10.71±1.66	1.23±0.42	−18.32±1.81	12.62±2.64
Zone I (n=24; 10*)	3.14±1.81	0.40±0.24	9.63±1.22	1.23±0.50	−17.48±1.94	15.67±1.59
Zone II (n=8; 5*)	1.24±0.43	0.12±0.05	12.35±2.51	0.90±0.19	−20.40±1.58	11.51±0.93
Zone III (n=26; 8*)	2.47±0.98	0.26±0.11	11.31±1.19	1.25±0.32	−17.97±0.95	10.48±0.72

Abbreviations: THAA, total hydrolyzable amino acids in mg g^{-1} dry sample; THHA, total hydrolyzable hexosamines in mg g^{-1} dry sample; Ter. C_{org}, calculated percentage of organic carbon derived from terrestrial source.
* Number of samples analyzed for amino acids.

Zone II: the eastern part of the lake at the stream mouths—The sediments of this zone are characterized by high C : N ratios and low $\delta^{13}C$ values, indicating relatively high contributions of terrestrial OM from the streams. Additionally, dilution with lithogenic material input is obvious from the low C_{org}, N_{tot}, and C_{carb} values in the surface sediments. Although aerobic degradation is suggested to occur, the $\delta^{15}N$ values of zone II sediments are much more depleted compared to the values from shallow zone I. This feature can be attributed to the higher contribution of relatively ^{15}N-depleted terrestrial OM and the faster burial of the OM into the anoxic sediments according to stream-controlled elevated sedimentation rates. Recently, the streams have been diverted to the alluvial fan at the northeastern shore for irrigation purposes. However, their influence on the distribution of the OM can still be seen in zone II. Delineating the C_{org} and N_{tot} values, the amino acid content in zone II sediments is lowest. The input of more degraded soil and terrestrial plant remains results in highest LI values and lowest AA-C and AA-N percentages. The calculated Ox : Anox ratios are elevated due to the influence of oxic stream water and the incorporation of high amounts of terrestrial OM that was exposed to subaerial degradation.

Zone III: deep, sub- to anoxic part of the lake—The deepest part of the lake is characterized by sub- to anoxic waters, which is reflected by high sulfur contents and low Mn : Fe ratios in the surface sediments (N. Basavaiah unpubl.). C_{org}, N_{tot}, C : N, and $\delta^{13}C$ values of zone III sediments are in the range of the whole-lake mean values and lie between those of zone I and zone II. $\delta^{15}N$ values are lowest in this zone, which is consistent with the findings that ^{15}N enrichment is restricted to degradation under oxic conditions, whereas under anoxic conditions no changes or even decreasing trends were observed (Freudenthal et al. 2001; Lehmann et al. 2002). The mean amino acid concentrations in the sediments in zone III are lower than the lake mean. This may be due to dilution with fine clays, which accumulate in the deep lake in addition to some coarse material bypassing the lake slopes (N. Basavaiah unpubl.). Lowest LI values confirm that reduced degradation of organic matter in sediments is related to the anoxic conditions in zone III with its lowest Ox : Anox ratios.

Implications of our results—High pH, brackish water, constantly elevated temperatures, eutrophic conditions, and water column stratification with oxic waters in ~ 0–4 m depth and sub- to anoxic waters in ~ 4–6 m depth result in unusually high $\delta^{15}N$ values and amino acid assemblages of Lonar Lake OM that differ from most marine and lacustrine environments. The high $\delta^{15}N$ values are due to denitrification in the anoxic deep water, resulting in strongly elevated $\delta^{15}N$ of the residual NO_3^-. Furthermore, at the high pH, the NH_4^+-NH_3 equilibrium shifts towards NH_3, which is depleted in ^{15}N and can escape from the lake water. As these two mechanisms are associated with high fractionation factors, they mainly control the ^{15}N enrichment of the inorganic nitrogen pool of Lonar Lake, and thus the ^{15}N enrichment of the phytoplankton.

Differences in amino acid assemblage between SPM of Lonar Lake and other aquatic environments can be attributed to the unique ecosystem. The exceptional conditions have yielded an aquatic ecosystem sparse in species but rich in individuals of adapted organisms. Hence, the absence or underrepresentation of common species, such as diatoms and most zooplankton, and the dominance of adapted species, such as cyanobacteria, as well as the contribution of terrestrial OM have led to the development of a unique amino acid assemblage of the Lonar Lake OM. Comparison with amino acid assemblages of other aquatic environments is therefore problematic. This is also indicated by the poor correlation of the two commonly used degradation indices, DI and RI. Thus, we calculated a specific Lonar degradation index (LI) on the basis of the DI calculation (Dauwe et al. 1999).

The comparison of $\delta^{15}N$ values of potential sources of OM to the lake sediments, i.e., terrestrial plants, soils, SPM, and sediment trap material, to $\delta^{15}N$ values of the sediments from different regions of the lake showed that $\delta^{15}N$ of OM changes during early degradation as a function of local redox conditions. During anaerobic degradation, apparently no change or only a slight increase occurs whereas aerobic degradation yields $\delta^{15}N$ increases of 5‰ to 9‰. A previous study of Macko and Estep (1984) examined the effect of aerobic microbial degradation on $\delta^{15}N$ of individual amino acids. According to their findings, we can relate the $\delta^{15}N$ increase during aerobic degradation mostly to the preferential microbial remineralization of ^{15}N-depleted Glu.

To understand the redox-related changes during early degradation, we calculated a ratio based on the study by Cowie et al. (1995), who identified amino acids that become relatively enriched during aerobic decomposition and amino acids relatively enriched during anaerobic decomposition.

Table 4. Extended.

Ter. C_{org} (%)	THAA (mg g^{-1})	AA-C (%)	AA-N (%)	THHA (mg g^{-1})	Gluam : Galam	LI	Ox : Anox
49.06±9.50	11.33±7.35	18.23±5.02	49.98±8.32	0.82±0.63	1.66±0.12	0.03±0.49	1.20±0.11
44.64±10.22	16.97±8.13	21.30±4.88	53.30±8.88	1.34±0.62	1.62±0.10	0.15±0.36	1.25±0.09
59.99±8.31	4.27±1.88	14.66±3.14	47.81±5.99	0.28±0.12	1.69±0.13	0.39±0.54	1.27±0.07
47.24±4.99	8.93±4.88	16.96±4.99	48.52±8.91	0.60±0.48	1.67±0.15	−0.13±0.50	1.12±0.09

This ratio (Ox : Anox) successfully distinguished samples from the oxic shallow water from samples from the anoxic deep water. For future consideration, the calculation of this ratio might be improved by the incorporation of additional data sets from other sites with varying redox conditions and the weighting of the individual amino acids on basis of a PCA calculation.

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