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Origin and evolution of the Lago Maggiore gas seeps revealed by geochemical techniques

with 12 figures, 3 tables and 3 appendices

by EMIL GREBER[1] and ROLAND WYSS[1]

Abstract

The gas seeps from the upper Lago Maggiore were investigated using modern geochemical methods sponsored by the National Energy Research Fund (NEFF). Two different gas types occur: (1) Gas seeps within the Lago Maggiore and the Verzasca River with high CH_4 and low N_2 contents and (2) gas seeps in rock fissures at Rivapiana with rather low CH_4 but high N_2 contents. Based on measured Ar/N_2 ratios, $\delta^{13}CH_4/CO_2$ data, carbon-14 measurements and noble gas data, the gases in the rock fissures are interpreted as being bacterially transformed gases of the first gas type. Clear evidence for a biogenic origin of all gases is provided by $\delta^{13}CH_4$, δD_{CH4} and $\delta^{13}CO_2$ data. Thermogenic or even Earth's mantle gas components as postulated by other authors can be precluded based on isotopic data. Total gas flux in the upper Lago Maggiore area is estimated to be in the range of 100,000 m^3/year. The geochemical characteristics of the upper Lago Maggiore gas seeps differ distinctly from the Po basin gases (Northern Italy) and also from the thermogenic gas of the Stabio spa (southernmost part of Switzerland).

Riassunto

Nell'ambito di un progetto del Fondo Nazionale per la Ricerca sull' Energia (NEFF) sono state studiate fuoriuscite di gas nella regione settentrionale del Lago Maggiore per mezzo di moderni metodi geochimici di analisi. E stata rilevata la presenza di due tipi differenti di gas: (1) fuoriuscite di gas ricche di CH_4 e povere di N_2 nella zona settentrionale del Lago Maggiore e nel fiume Verzasca e (2) fuoriuscite povere di CH_4 ma abbondanti in N_2 da fessure nelle rocce di Rivapiana. I gas nelle fessure sono stati interpretati come modificazioni, per azione batterica, del primo tipo di gas, come imostrato dal rapporto Ar/N_2, dal rapporto isotopico $\delta^{13}CH_4/CO_2$, da misurazioni del C-14 e dai dati dei gas nobili. I dati di $\delta^{13}CH_4$, δD_{CH4} e $\delta^{13}CO_2$ testimoniano chiaramente l'origine batterica della totalità dei gas. Gas primordiali o di origine termocatalitica, di cui la presenza è stata postulata da altri autori, sono da escludere sulla base dei dati degli isotopi. Il flusso totale di gas nella regione settentrionale del Lago Maggiore è stimato a 100'000 m^3/anno. La caratteristiche geochimiche dei gas del Lago Maggiore si differenziano fortemente da quelle dei gas della Pianura Padana (Italia Settentrionale) come pure da quelle dei gas termogenici delle sorgenti minerali di Stabio (Mendrisiotto).

Zusammenfassung

Die Gasaustritte im Gebiet des oberen Lago Maggiore wurden im Rahmen eines NEFF-Projekts mittels moderner geochemischer Methoden untersucht. Zwei verschiedene Gastypen treten auf: (1) Gasaustritte im oberen Lago Maggiore und in der Verzasca mit hohen CH_4- und geringen N_2-Anteilen und (2) Gasaustritte in Klüften des Felsens bei Rivapiana mit relativ kleinen CH_4-, aber bedeutenden

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N_2-Anteilen. Basierend auf gemessenen Ar/N_2-Verhältnissen, $\delta^{13}CH_4/CO_2$-Daten, Kohlenstoff-14-Messungen und Edelgasdaten werden die Gase in den Klüften als bakteriell umgewandelte Gase des ersten Gastyps interpretiert. Die $\delta^{13}CH_4$-, dD_{CH4}- und $\delta^{13}CO_2$-Daten zeigen klar, dass sämtliche Gase bakteriellen Ursprungs sind. Thermokatalytische oder gar primordiale Gase, wie sie von anderen Autoren postuliert wurden, können aufgrund der Isotopen-Daten ausgeschlossen werden. Der totale Gasfluss im Gebiet des oberen Lago Maggiore wird auf etwa 100'000 m^3/Jahr geschätzt. Der geochemische Charakter der Lago Maggiore Gase unterscheidet sich stark von denjenigen der Poebene (Norditalien) und auch vom thermogenen Gas der Stabio-Mineralquellen (Mendrisiotto).

1. Introduction

Many gas seeps are observed in the upper Lago Maggiore, most of them close to the Ticino/Verzasca alluvial fan, others not far from the minor deltas of Alabardia, Vira and Magadino along the southern shore line (Fig. 1). Gas seeps are also known from the Verzasca River, about 70 m away from the lake. The only known gas seeps on land occur in rock fissures at Rivapiana.

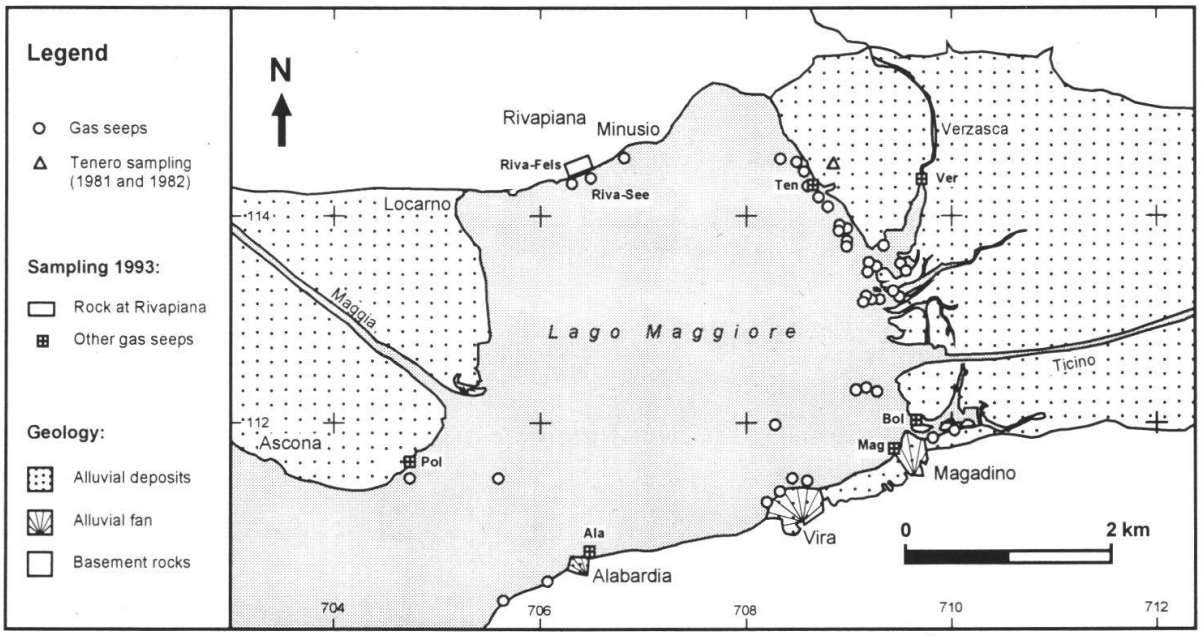

Fig. 1: Gas seeps in the upper Lago Maggiore area. Also indicated are sample locations from the 1993 campaign (map modified from BÜCHI & WILD 1986).

The gas seeps in the upper Lago Maggiore have been known for several centuries. Discussions about their origin, however, have been controversial up to now. ALTHAUS (1943) and RICKENBACH (1947) assumed a biogenic origin to the gases because of the thick alluvial deposits in the Ticino/Verzasca delta. The gas seeps from the northern and the southern lake shore were interpreted as thermogenic by WERENFELS (1939) and WEBER (1943) because in these areas the basement rocks are shallow and the alluvial thickness is only minor. Bituminous Triassic dolomites occurring as tectonic lenses along the Insubric Line were assumed to be their source rocks.

First extensive investigations of the gases started in the early eighties, initiated by W. Wild (Contra). Gas analyses and C-14 measurements were financed by SWISSGAS, Zurich (BÜCHI 1982) and further research was supported by NEFF, the Swiss Energy Research Fund. In the NEFF project No. 261 (BÜCHI & WILD 1986, WILD 1990), - besides biogenic gases - gas components originating from the Earth's mantle were postulated in accordance with the theory of Th. Gold (GOLD 1979, GOLD & SOTER 1980a and 1980b).

In order to elucidate the origin of the Lago Maggiore gases, a new NEFF project was initiated by Geoform (Winterthur) in 1992. Based on complete gas and isotope analyses, clear statements about the origin, evolution and - if possible - gas quantities were expected. In addition to new gas analyses, a reinterpretation of the older gas data from BÜCHI & WILD (1986) and WILD (1990) was proposed. The results of these investigations are presented in this paper (see also GEOFORM 1994, GREBER 1994 and GREBER in press).

2. Geologic/tectonic setting and potential gas sources

Gas occurrences are generally closely related to their geological setting. This allows an early evaluation of the gas origin. The area of the upper Lago Maggiore, however, is geologically of such a complexity that at first glance no gas origin may be ruled out.

In the study area the Insubric Line separates the Central Alps (European plate) from the Southern Alps (Adriatic plate; HEITZMANN 1987 and 1991, SCHMID et al. 1987 and 1989, ZINGG 1983). Both structural elements are dominated by crystalline rocks like gneisses, micaschists, amphibolites or marbles (Fig. 2). The complex structure of this major tectonic contact has recently been elucidated by new results from the National Research Programme NFP 20 (FREI et al. 1992). Reflection seismic studies show that a wedge of the Adriatic lower crust is indented into the European crust (e.g. BERNOULLI & BERTOTTI 1991; Fig. 3). Thus, the former Central Alpine "root zone" is now interpreted as the frontal fold of a major backthrust of the Central Alps that were displaced over the Southern Alps (HEITZMANN 1987).
The tectonics of the Southern Alps are dominated by south-vergent, northward dipping upper crustal thrust faults (SCHUMACHER 1990), involving crystalline basement rocks and Upper Paleozoic to Miocene sediments and volcanic rocks.
East of Locarno the mylonites of the generally ductile Insubric Line are overprinted by brittle faults along the Tonale Line (SCHMID et al. 1987). West of Locarno brittle deformation is only subordinate along the some 1 km broad mylonite belt of the Canavese Line. This lineament is the NE-SW striking part of the Insubric Line, separating the Sesia from the Ivrea Zone originating as a response to the rise of the Sesia Zone (SCHMID et al. 1987, ZINGG & HUNZIKER 1990). The brittle Centovalli Line (MANCKTELOW 1985) is interpreted as the western continuation of the Tonale Line (SCHMID et al. 1987, HEITZMANN 1987).

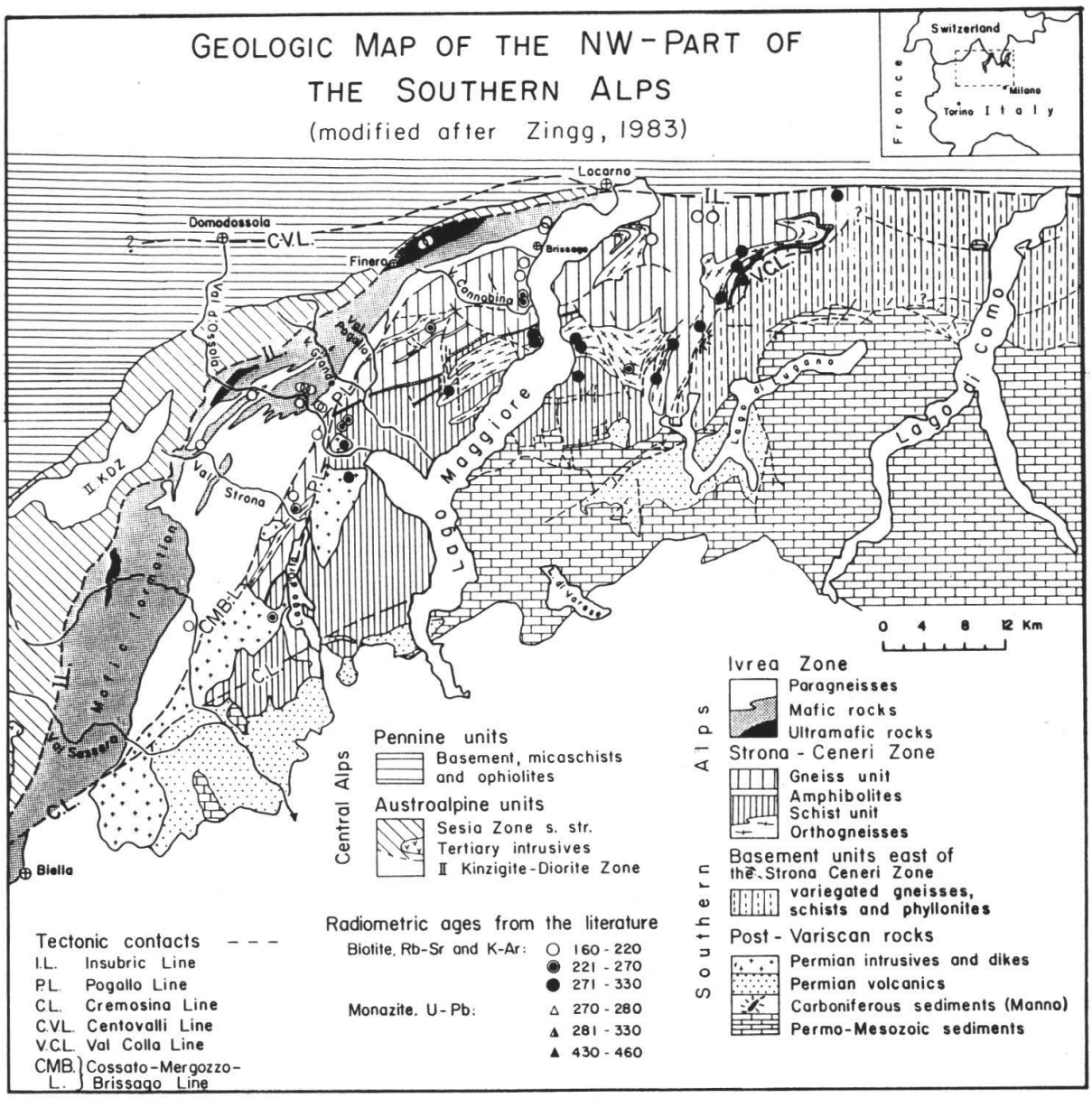

Fig. 2: Geological map of the Southern Alps (from HANDY 1987, modified from ZINGG 1983).

Another important fault is the Pogallo Line, a variably thick band of ductile and subordinate brittle tectonites, separating the Ivrea Zone (lower crust) from the Strona-Ceneri Zone (Southern Alpine basement) (SCHMID et al. 1987, HANDY 1987).This same contact becomes gradual towards the Lago Maggiore (SCHMID et al. 1987).

Source rocks which could produce thermogenic gases are rare in the study area. Partially bituminous Triassic sediments that occur in tectonic lenses along the Insubric/Canavese Line can also be expected at greater depths, where high temperatures could generate thermogenic gases. Another favourable possibility for source rock positioning may be related to the complex indenting of the Adriatic into the European plate. In the Southern Alps north of Lugano, basement slivers are involved in ramp-flat systems, with Raibl beds as main décollement horizons

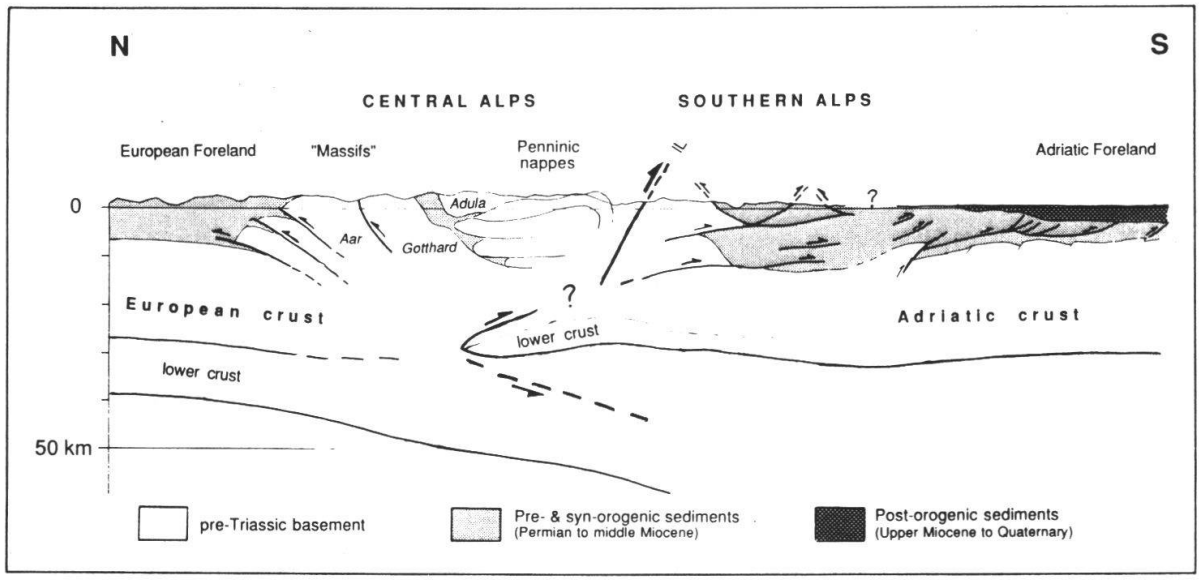

Fig. 3: Interpreted cross section through the Central and Southern Alps, based on the results of the NFP 20 and reflexion seismic profiles across the Po Plain (IL = Insubric Line, taken from BERNOULLI & BERTOTTI 1991).

(LAUBSCHER 1985). However, it is not clear how far north along these thrust faults that the sediments were transported.
As a consequence, the generation of thermogenic gases in the subsurface of the Lago Maggiore area cannot be excluded. Either sediments in tectonic lenses or sediments involved in the Adriatic wedge formation come into question as potential source rocks. Such thermogenic gases could ascend along brittle elements of the Tonale and Canavese Lines.

The morphology of the upper Lago Maggiore area is strongly influenced by the Magadino Plain. From the new seismic reflection profile 92-NF-01 (carried out in the framework of the NFP 20 project), the incision depth is estimated to be about 750 m below ground level (GREBER & LEU in GEOFORM 1994). According to some authors (FINCKH 1978, FINCKH et al. 1984, FREI 1993) this deep incision can be attributed to fluvial erosion at a time of lower erosional level during the Messinian Mediterranean salinity crisis (HSÜ et al. 1973). This fluviatile origin, however, is still controversial and remains unproven despite modern seismic data. Little is known about the sedimentary infill of this deep structure, as the deepest drillings reach depths of only 120 m. Marine Pliocene sediments are proposed at the base by FELBER (1993). The parallel seismic facies with continuous high amplitude reflections indicate that the majority of the infill probably consists of Pleistocene lacustrine sediments. Fluviatile organic-rich sediments dominate in the uppermost 100 m. Today, enormous quantities of detrital sediments including wood are deposited during storm events in the Ticino/Verzasca and Maggia deltas. An annual input of some 325,000 m^3 is reported in the Maggia delta and about 300,000 m^3 in the Ticino/Verzasca delta (LAMBERT 1988).
From the above geological considerations of the Quaternary, there is good reason to believe that biogenic gas could easily be produced in these mainly unconsolidated,

partially organic-rich strata. It is conspicuous that all the gas seeps - except for those along the northern shore - are observed above alluvial fan deposits.

In comparison to thermogenic or biogenic gases, however, gases from the Earth´s mantle - as postulated by WILD (1990) - are from a geological point of view less probable. At present it is unclear if there is a connection between the surface and the African Moho that lies at a depth of about 30 km beneath the study area (HEITZMANN 1991) by the ductile Insubric Line or if this line is of solely intracrustal nature (Fig. 3).

3. Geochemical results

3.1 Methodology

Twenty new gas samples were taken in the summer of 1993 (Fig. 1, Appendix 1), using four different sample vessels: regular 250 ml two-tapped glass vessels, highly evacuated one-tapped 100 ml vessels, large 2.5 l bags coated with aluminium in order to sample large gas volumes and 1 m copper tubes for noble gas analyses.
The sample technique applied had to be adapted for each gas seep situation. All gases in the lake and the Verzasca River were taken on the lake, or river bed respectively, by means of up to four lead-loaded funnels. From these funnels, plastic tubes led to the sampling site (either on land or in a boat). The water in the funnels and tubes was driven out by closing a tap at the end of the tubes. The samples were then taken, but only after careful flushing.
As the gas flux through the rock fissures at Rivapiana is rather small compared to the fluxes in the lake (Table 1), a more sophisticated sampling technique had to be applied at this site: A fissure was connected by means of clay to a tube which in turn was joined to a 5.5 l bottle filled with water. As the exact gas flux was unknown, the water in the bottle was poured out at a very low discharge rate of about 16 ml/min. The volume of water drained off was then replaced by gas. The sampling methods are described in more detail in GEOFORM (1994).

Location (sample denomination)	Gas flux (m^3/year)
Maggia-Polenhafen (Pol)	~ 500
Rock fissures at Rivapiana (Riva-Fels)	~50
Rivapiana-See (Riva-See)	~ 200
Tenero (Ten)	48,000[1)]
Verzasca (Ver)	~200
Bolette (Bol)	~ 800
Magadino (Mag)	~ 1,000
Alabardia (Ala)	~ 800
Other locations (inclusive Vira)	~ 1,000
TOTAL	~ 52,500

Table 1: Estimated gas flux at each gas seep location (for locations see Fig. 1). [1)] measurements during the industrial exploitation of the gases in the Tenero area by SWISS JEWEL in the years 1943 to 1945 (RICKENBACH 1947).

N_2, O_2,, CO_2,, H_2, CH_4, ethane, propane, i- and n-butane, i- and n-pentane were measured by GEMAG (Alberswil) in 6 of the samples. The same components and additionally Ar, i- and n-hexane, $\delta^{13}CH_4$, δD_{CH4}, $\delta^{13}C_{ethane}$, $\delta^{13}C_{propane}$, $\delta^{13}CO_2$, and $\delta^{18}CO_2$, were analysed by GCA (Lehrte) in the other 14 samples. Because of lack of measurable amounts of ethane and propane, no isotope analyses could be carried out on these compounds.
In addition to the gas analyses described above, a soil-gas campaign was carried out on the Magadino Plain together with GEMAG.

In the following interpretations all available data since 1981 (data from BÜCHI 1982, BÜCHI & WILD 1986, WILD 1990) were taken into consideration (Appendix 1).

3.2 Gas fluxes

Based on observations and measurements during sampling, gas fluxes of each gas seep location were estimated (Table 1):

These values have to be considered as minimum gas fluxes as (1) only the visible gas seeps close to the shore lines are included, (2) gases ascending through high water columns may be dissolved, (3) in the centre of the lake more gas can be held back in the pore space due to higher hydrostatic pressures (RICE & CLAYPOOL 1981) and (4) considerable amounts of CH_4 may be oxidized at the bottom of the lake (e.g. BOSSARD 1981). Nevertheless, it does not seem to be reasonable to assume a total gas flux (including visible and invisible gas seeps) of more than about 100,000 m^3/year for the upper Lago Maggiore area.

3.3 Gas composition

Assuming that all the O_2 content in the samples is due to air contamination during sampling, the measured N_2, Ar and CO_2 portions were corrected in accordance to their atmospheric ratio to O_2. Only 3 samples of the 1993 campaign show elevated O_2 content levels (> 7 vol%). See Appendix 2 for the corrected data.

Samples that were taken over a long time span of several years, at the same location and using the same sampling method, show a rather constant gas composition. This can be demonstrated by the samples taken at the gas seep location Magadino (Fig. 4). These gases are characterized by CH_4 portions between 85 and 90 vol%, CO_2 portions between 8 and 14 vol% and low N_2 contents of less than 2 vol%. Four exceptions exist: CO_2 is almost missing in the two samples dated 26/4/86. This can be explained by the fact that, because of high water, these samples were not taken from the lake bed but from the surface of the lake. Obviously, the CO_2 was dissolved during the ascent of the gas through the water column. The sample dated 23/9/81 was also taken at the surface. In addition to the dissolution process in the 1986 samples, a contamination with N_2, either gaseous or dissolved in water, occurred. The sample dated 4/5/82 is also contaminated by N_2, however,

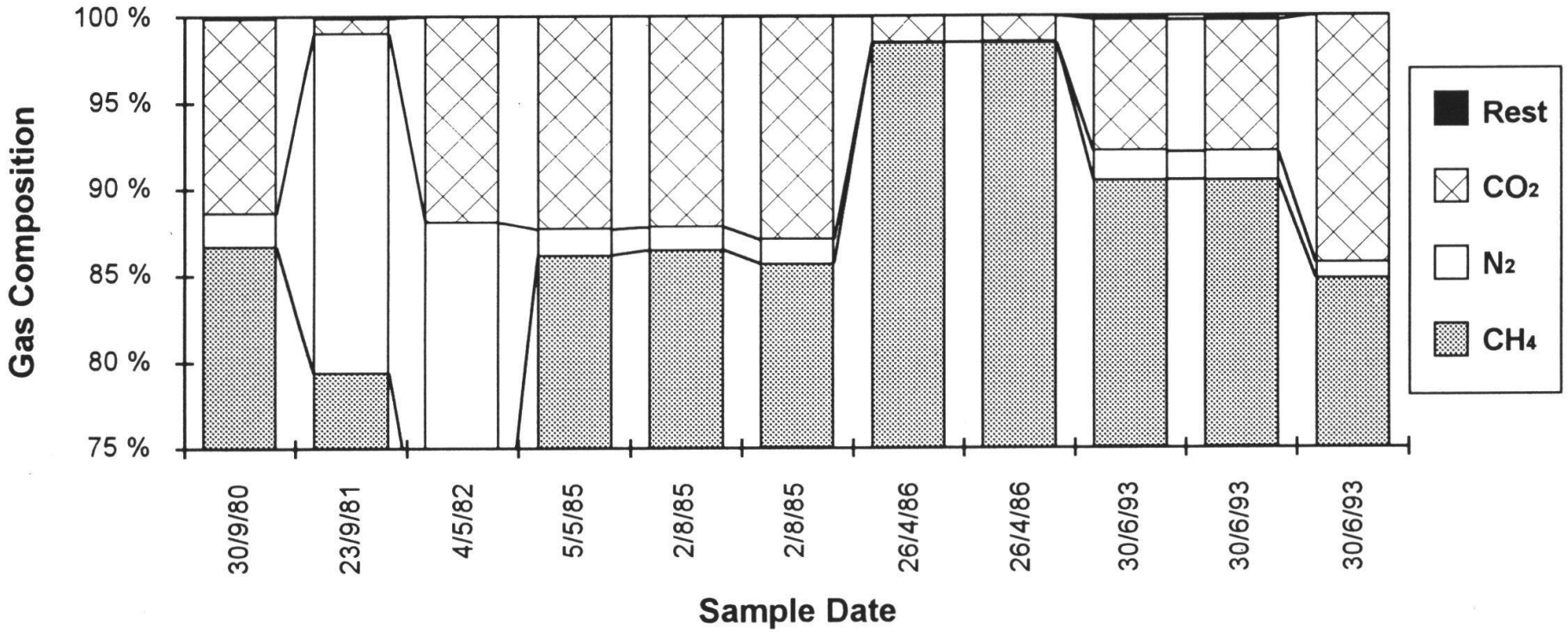

Fig. 4: Gas composition at the Magadino site. Only 25 % of the gas composition is presented in the diagram, the other 75 % is methane. The gas composition is not subject to large variations. The exceptions can be explained by different sampling techniques applied (see text for further explanation).

it is not reported if this sample was taken on the lake bed or not. Such high N_2 contaminations do not necessarily combine with elevated O_2 contents, because O_2 is rapidly consumed in the slightly reduced hydro- and geosphere.
At first sight, the gas composition of the location Tenero seems to be subject to large variations (Appendix 2). The large N_2 portions of the 1981/1982 samples, however, become comprehensible, if it is taken into consideration that at that time the samples were not taken at the bottom of the lake but on land via a tube used by SWISS JEWEL to capture the gas. It must be assumed that this tube, which was dug into the ground, was leaking and that some reduced O_2-free soil gas could have invaded the tube and mixed with the CH_4-rich gas.
All gases are dominated by CH_4, N_2 and CO_2. All other components are smaller than 1 vol%. Roughly two gas types can be distinguished: (1) The gas seeps in the Lago Maggiore and the Verzasca River are characterized by high CH_4 portions (>85 vol%) and low N_2 portions (generally at about 5 vol%) whereas (2) the seeps in the Rivapiana rock fissures show distinctly higher N_2 portions (60 to 80 vol%) but lower CH_4 portions (10 to 35 vol%).
At first no relation seems to exist between these two gas types. But from atmospheric Ar/N_2 ratios of the 1993 Riva-Fels samples (Fig. 5) it must be assumed that their high N_2 and Ar portions originate from the O_2-depleted air. If the Riva-Fels samples are corrected to account for air contamination not only by O_2 but also by N_2 (or Ar), the resulting gas can hardly be distinguished from the gas seeps in the lake or the Verzasca River (Table 2).

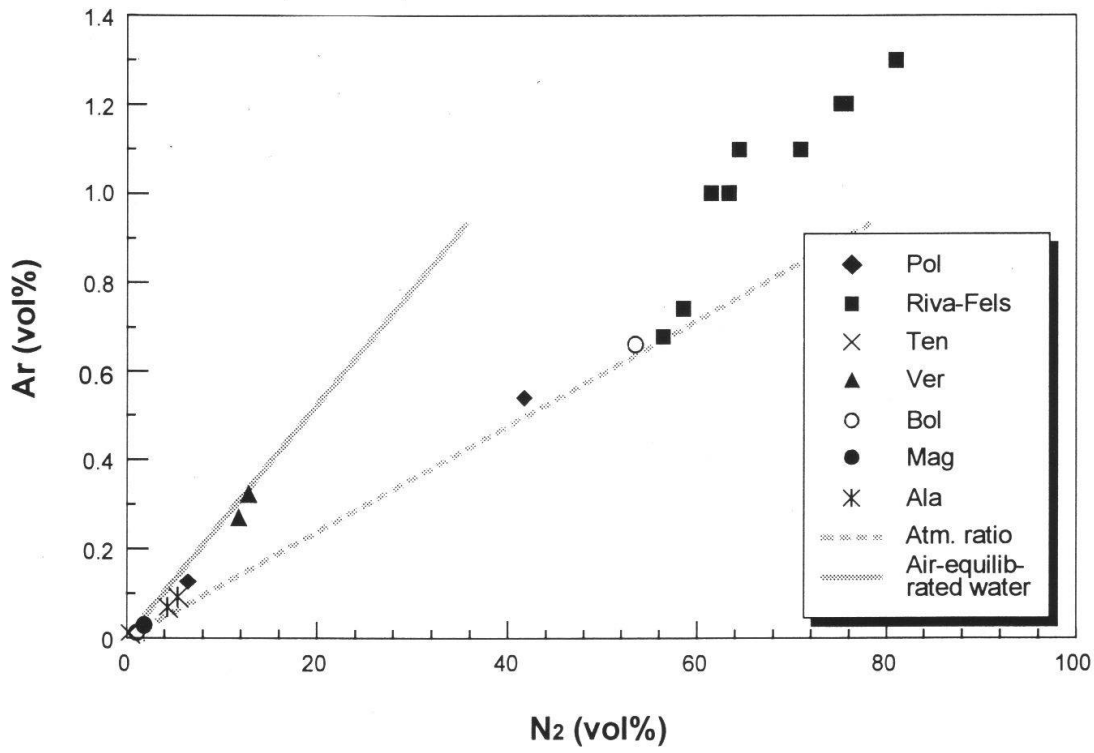

Fig. 5: The two Riva-Fels samples of the 1993 campaign are characterized by an atmospheric argon/nitrogen ratio. Both gases probably originate from soil air. The argon and nitrogen in the samples taken in the lake also originate from air, but in this case the gases must have been dissolved in the interstitial waters and stripped off into the gas phase by the ascending methane-rich gases, as they show a ratio of air-equilibrated water. The older argon data from the Riva-Fels samples may be due to analysis errors.

Gas	Riva-Fels 1 (29/6/93)			Riva-See (27/11/84)
	Before any correction	After O_2 correction	After N_2 correction	After O_2 correction
N_2 (vol%)	56.40	56.16	0.00	1.58
CH_4 (vol%)	34.30	34.69	80.40	97.93
CO_2 (vol%)	8.32	8.41	19.44	0.49
Ar (vol%)	0.68	0.68	0.02	not measured
H_2 (vol%)	0.06	0.06	0.14	not measured
O_2 (vol%)	0.23	0.00	0.00	0.00

Table 2: Correction of the Riva-Fels samples for contamination with reduced air.

The N_2 corrected Riva-Fels 29/6/93 sample is richer in CO_2 than the Riva-See 27/11/84 sample, which was taken by W. Wild in the lake just some 20 m away from the rock fissures at Rivapiana.
These observations lead to the hypothesis that the gases in the Rivapiana rock fissures are transformed gases of the same type that occur in the Lago Maggiore and the Verzasca River. This transformation can be summarized as follows: Small amounts of CH_4-rich and N_2-poor gases reach the rock fissures at Rivapiana from the lake sediments through fissures striking more or less perpendicular to the shore line. In the unsaturated zone of the fissures, they mix with reduced O_2-depleted or even O_2-free soil air. Most of the CO_2 probably originates from the soil air. A minor part of the CO_2 may be due to the oxidation of CH_4, as the CH_4-rich gases reach a relatively more oxidizing zone, which in turn of course is more reducing than atmospheric air.

Such a N_2 correction would also be applicable to two other air-contaminated samples: Pol and Bol (Fig. 5). But because in this case the mixing with air occured during sampling, the high N_2 contents are also combined with elevated O_2 contents (10.5 and 14.1 vol% resp.).

In contrast to the Riva-Fels gases, those in the lake and the Verzasca River show Ar/N_2 ratios equivalent to the ratio of these gases dissolved in water in contact with air (Fig. 5). From this it can be concluded that Ar and N_2, which are dissolved in the interstitial formation water, are brought into the gas phase and are stripped-off by the uprising CH_4-rich gases.

It is conspicuous that the measured Ar contents of older Riva-Fels analyses are rather high, e.g. higher than the Ar portion in the atmosphere (0.93 vol%; Fig. 5). Of course, Ar contents produced in the subsurface can exceed the atmospheric concentration by as much as 16 times (LOOSLI & LEHMANN 1991). But this cannot explain the large differences in Ar content between the 1993 and the older samples. Analysis errors have to be taken into consideration.

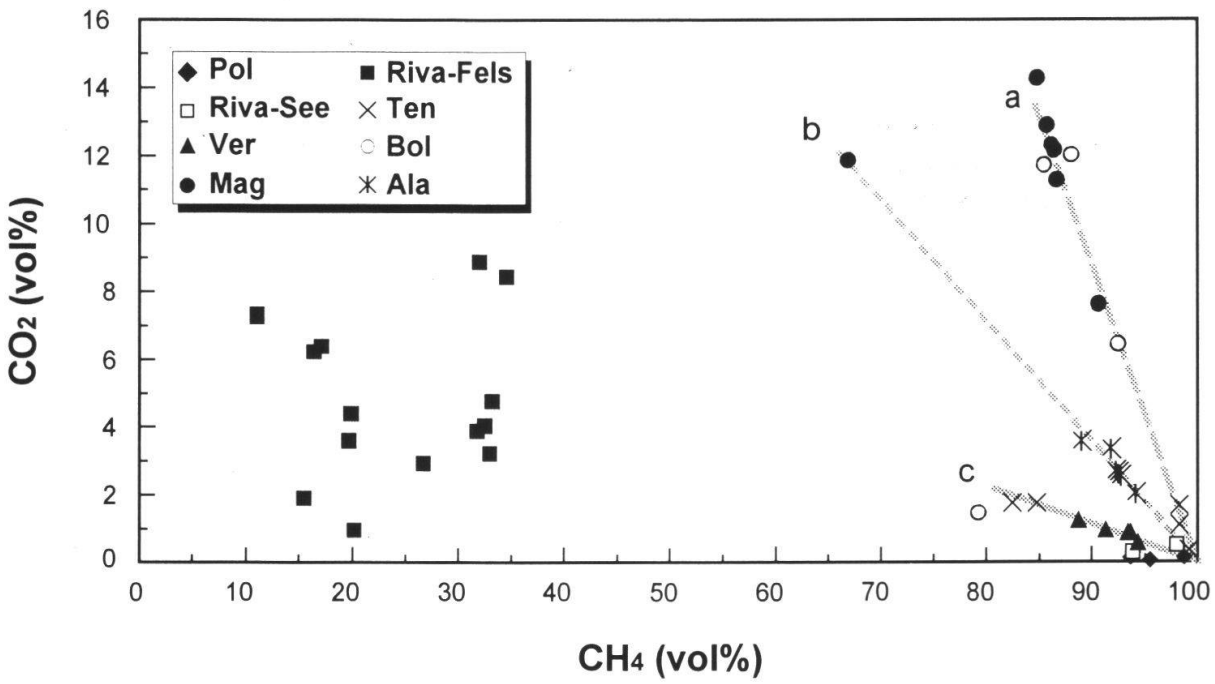

Fig. 6: Three different carbon dioxide/methane correlations are observed (a, b and c). This might be attributed to secondary processes like e.g. contact with different redox zones or dissolution phenomena. The low methane content of the Riva-Fels samples is due to mixing with reduced air.

Certain regularities exist between the three main gas components CH_4, CO_2 and N_2 (Fig. 6). The gas seeps in the lake and the Verzasca River show three different CO_2/CH_4 and CO_2/N_2 ratios resp.. Secondary processes, such as contact with different redox zones or dissolution phenomena, may be responsible for these well-defined relations. Primary processes, e.g. release of these gases in defined ratios during the either bacterial or thermogenic decomposition of organic matter, are less probable as there is no indication of a non-atmospheric origin to the N_2 (see above).

There is a lack of higher hydrocarbons in all gases. All C_2 to C_6 contents are below 0.0001 vol%. This implies that the gas seeps of the upper Lago Maggiore are either biogenic or high-mature metagenic dry gases (TISSOT & WELTE 1984). There is no indication for the presence of a catagenic wet gas component. Mantle gas components, on the other hand, cannot be excluded solely based on the gas composition.

3.4 Stable isotopes

In geochemical studies, stable isotope data of CH_4, CO_2 and - if present - of higher hydrocarbons are a powerful tool in the determination of the gas origin.

Using the classical δD-$\delta^{13}CH_4$ diagram of WHITICAR et al. (1986), a clear biogenic origin can be postulated for the Lago Maggiore gas seeps (Fig. 7). There are no

indications at all for the presence of either a thermogenic (wet or dry) or a mantle component. The relatively positive $\delta^{13}CH_4$ values (mean value: -62.5 ‰$_{PDB}$) may be explained by (1) a late diagenesis stage (RICE AND CLAYPOOL 1981), (2) bacterial oxidation of CH_4 (COLEMAN et al. 1981), (3) high metabolic rates supported by high organic substrate concentrations (BARKER & FRITZ 1981) and/or (4) organic substrates enriched with carbon-13.

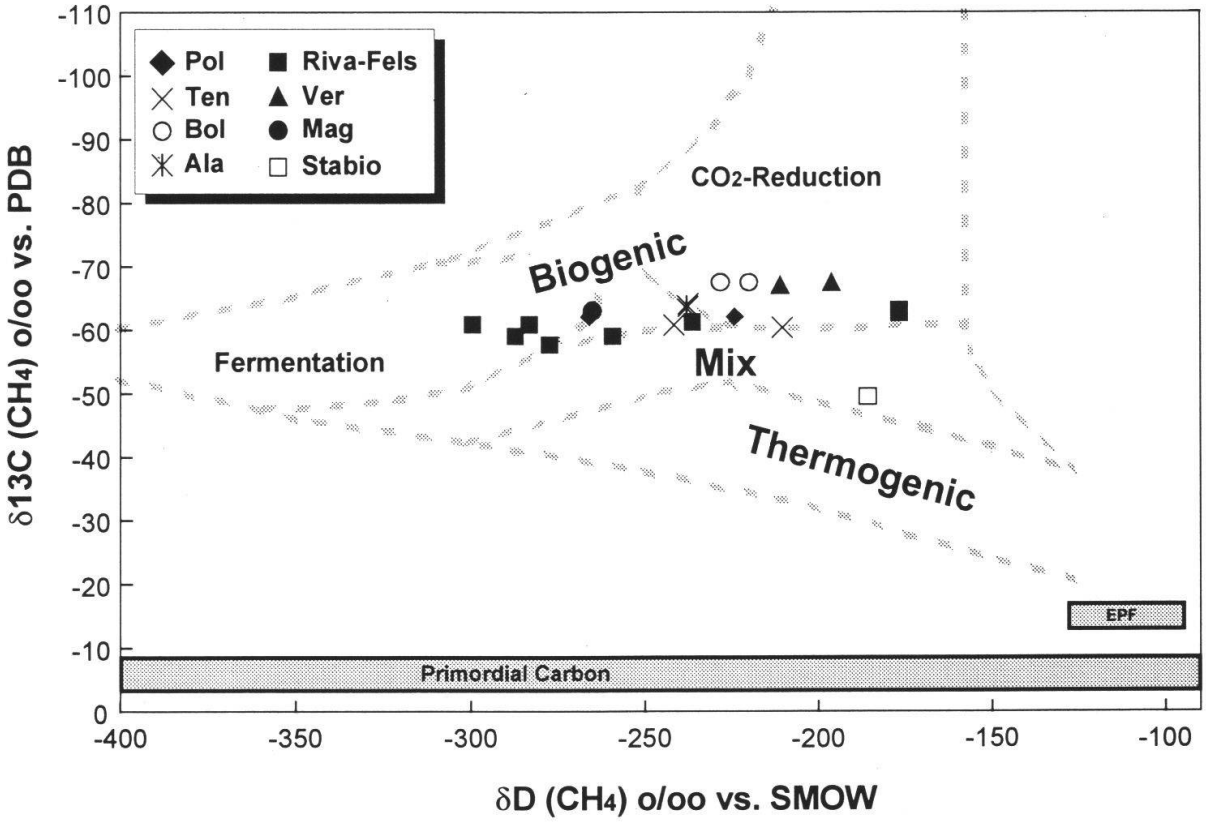

Fig. 7: All samples lie in the field of biogenic gases. There is no indication for either a thermogenic or a primordial gas component. Diagram modified from WHITICAR et al. 1986; EPF = East Pacific Rise, the isotopic range for primordial carbon taken from WELHAN 1988).

Very large variations in the δD values (-177 to -299 ‰$_{SMOW}$), even in samples taken at short time intervals, are observed. δD data of biogenic gases generally determine a biogenic generation in either freshwater (mainly by acetate fermentation) or in marine environments (mainly by CO_2 reduction, WHITICAR et al. 1986). However, this is not possible in the case of the Lago Maggiore gases. Changing substrates and H_2 sources, sulphur-reducing bacteria or even isotope fractionation during sampling may be responsible for the large δD variations.

The $\delta^{13}CO_2$ data also gives no further information about the process of CH_4 formation (Fig. 8). Most of the data is close to the intersection of the CO_2 reduction and fermentation fields of biogenic gases. Only the data from the two locations Pol and Ver fall more or less inside the fermentation field. But as the CO_2 portion of these gas seeps is small (0.17 to 1.22 vol%), their $\delta^{13}CO_2$ values may be submit-

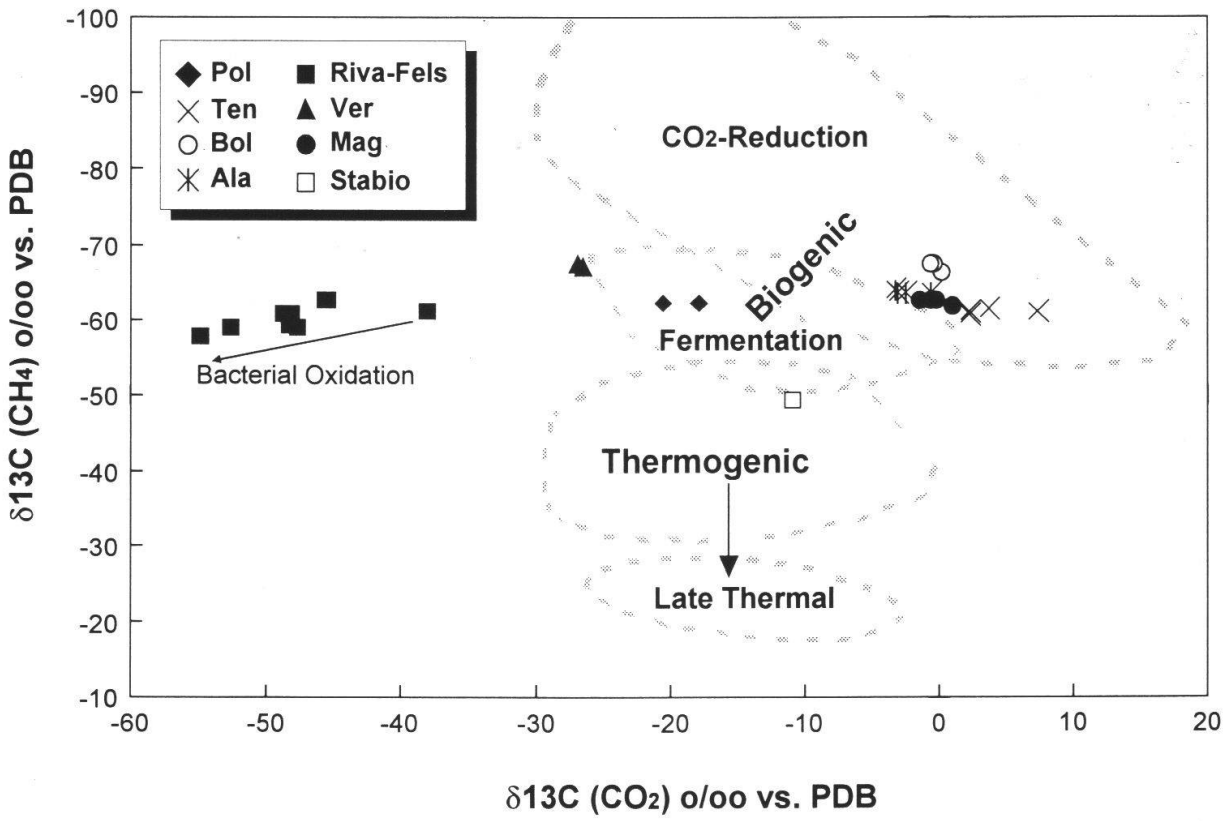

Fig. 8: A clear indication for a bacterial origin of the Lago Maggiore gases is also inferred by the carbon isotopes from methane and carbon dioxide. The extremely negative $\delta^{13}C$ values of the Riva-Fels samples are attributed to bacterial oxidation processes.

ted to bacterial changes. At least, the $\delta^{13}CO_2$ data from the same locations do not show such large variations as the δD data.

Consequently, an indirect indication for the presence of marine Pliocene sediments beneath the Magadino Plain, as postulated by FELBER (1993), cannot be concluded from the isotopic data from the biogenic gases.

The $\delta^{13}CO_2$ values of the Riva-Fels samples are extremely negative (Fig. 8), even when compared to reported values (e.g. STUIVER & POLACH 1977, FUEX 1977, DEINES 1980). Obviously, the Riva-Fels gases are the subject of severe bacterial oxidation processes (COLEMAN et al. 1981) which are responsible for a ^{13}C-enrichment in CH_4 and a ^{13}C-depletion in CO_2. This can be supported by diagrams in which CH_4 is plotted against $\delta^{13}CO_2$ and $\delta^{13}CH_4$ (Fig. 9). Such diagrams are drawn based on the plausible assumption that the samples with the highest CH_4 portions are the least changed and therefore the most original gases. A corresponding D-enrichment in CH_4, often observed in bacterial oxidation processes (COLEMAN et al. 1981), however, is not observed.
This isotopic evidence adds weight to the argument that the Riva-Fels gases are overprinted by mixing with soil air, as already postulated from the considerations concerning gas composition. As a steady-state with a roughly constant CH_4 supply can be assumed, not all CH_4 can be oxidized to CO_2.

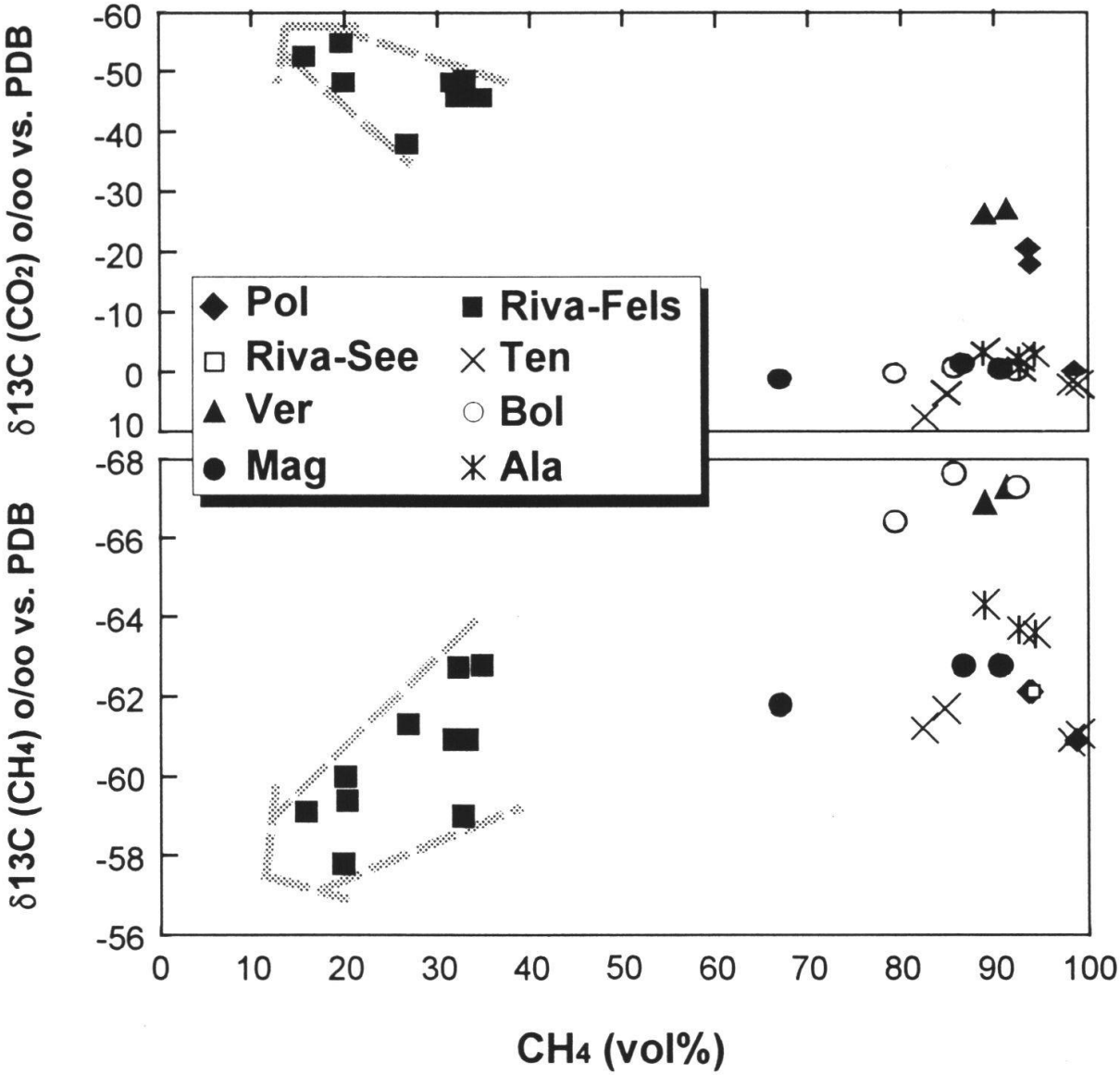

Fig. 9: Bacterial oxidation of the Riva-Fels gases is indicated by a carbon-13 enrichment in the methane and a carbon-13 depletion in the carbon dioxide.

3.5 Carbon-14

The carbon-14 data from gases should be interpreted very carefully. No "ages" can be expected because carbon is present in countless compounds, many showing a rather reactive behaviour (for these problems see e.g. BALDERER 1983 and 1985). C-14 measurements are nevertheless helpful in recognizing "young" C-14-rich gas components.

Measured C-14 concentrations in CH_4 are between 42.9 and 76.9 % MOD (Fig. 10 and Appendix 1). From this, considerable amounts of post-Pleistocene gas components are to be expected. It is conspicuous that all the samples with C-14

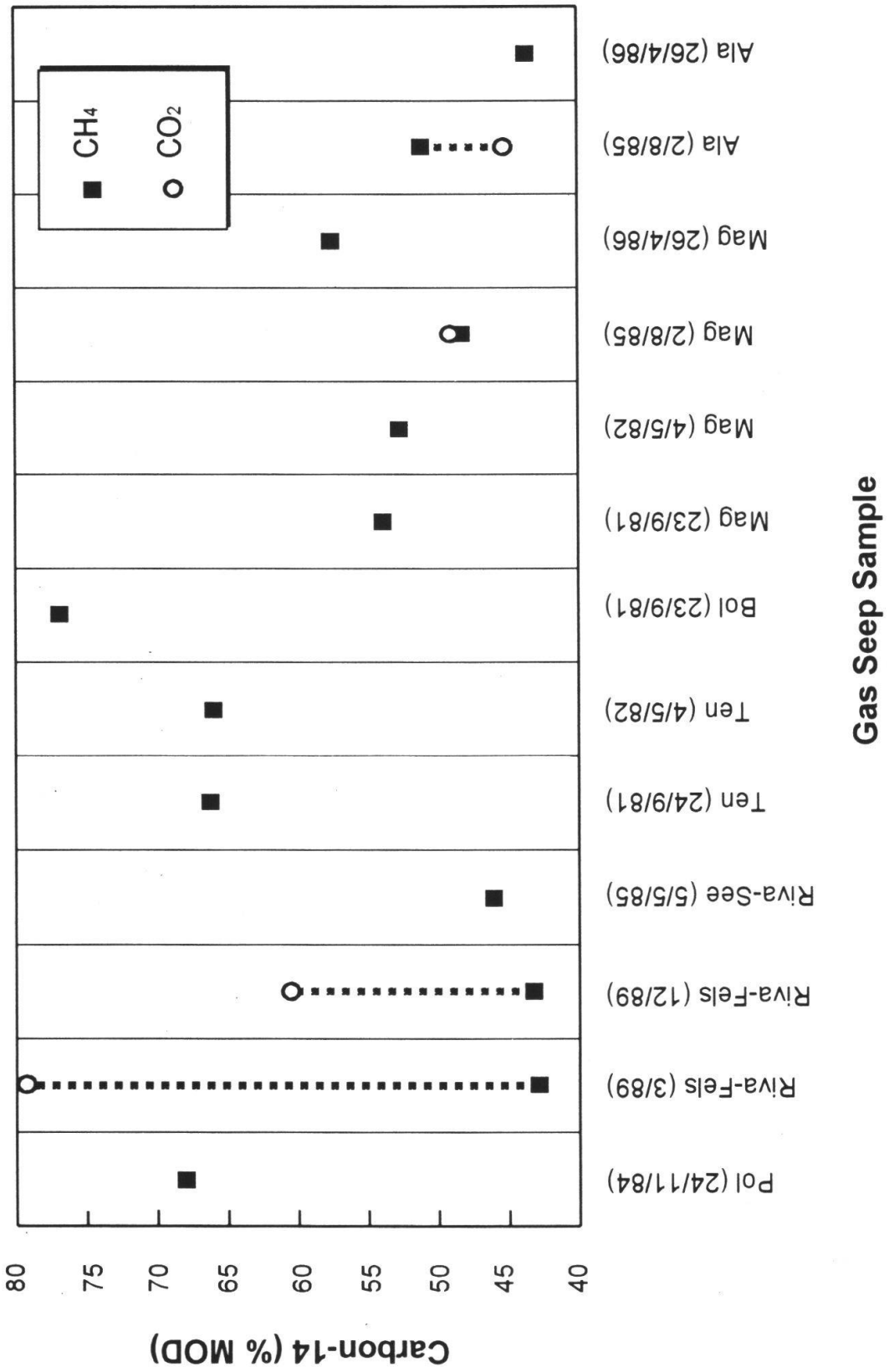

Fig. 10: The carbon-14 content in the methane seems to be correlated with the alluvial thicknesses at the sample locations. The higher C-14 content in the carbon dioxide than in the methane of the Riva-Fels samples further supports the hypothesis that these gases are overprinted by a mixing with soil air.

concentrations in CH_4 higher than 60 %MOD are from areas with very thick alluvial layers (samples Bol and Ten: Verzasca/Ticino delta, sample Pol: Maggia delta). On the other hand, the gas seeps of the northern and southern shore lines (samples Mag, Ala, Riva-Fels, Riva-See), where the basement is rather shallow, show distinctly lower concentrations. These observations are not unusual as the production of biogenic gases is - besides other factors - dependent on a sufficient supply of organic material.

The above hypothesis that the CH_4 of the Riva-Fels samples has the same origin as the Riva-See gas seeps is further supported by very similar C-14 contents. However, there is a striking discrepancy between the C-14 concentrations in the CH_4 and the CO_2 of the Riva-Fels samples. The distinctly higher concentrations of carbon-14 in CO_2 (79.2 and 60.5 vs. 42.9 and 43.2 % MOD) can be explained by a CO_2 generation postdating that of CH_4. This is compatible with the hypothesis that the Riva-Fels gas seeps are strongly influenced by the mixing with "young" reduced CO_2-rich soil air.

3.6 Noble gases

In radioactive decay reactions in the Earth´s crust, large amounts of helium-4, but only minor amounts of helium-3, are produced. The He-3/He-4 ratio in the Earth´s mantle is thus with 3±2•10E-05 considerably higher than in the crust with 2•10E-08. Consequently, He-3 can be used as a tracer for fluids from the Earth´s mantle (MAMYRIN & TOLSTIKHIN 1984, for applications see e.g. MATTHEWS et al. 1987).
As the concentrations of He-3 and He-4 are generally extremely low, carrier gases like CO_2 or CH_4 are postulated (KIPFER 1991). If mantle gas components are present in the Lago Maggiore gases, this should be recognized by elevated He-3/He-4 ratios. Primordial components were postulated by WILD (1990).

Based on He-4 and Ne-20 measurements and the determination of the He-3/He-4 ratio, total helium can be assigned to the reservoirs atmosphere, crust and mantle (for calculation formula see GEOFORM 1994). As there is no significant subsurface neon production, neon can be used for atmospheric corrections. However, these calculations have to be treated cautiously because He-3 can also originate from the radioactive decay of tritium. Tritium was discharged into atmosphere in large quantities due to worldwide nuclear tests from 1952 onwards.
Calculated He_{mantle} portions vary between 0 and 3.0 vol% (Appendix 3). Only minor differences between the "real" and "apparent" (calculated) mantle portions, however, can be expected from samples with low Ne-20 contents (little atmospheric influence) and high He-4 concentrations (long circulation paths in crystalline rocks rich in uranium and thorium). The apparent He_{mantle} portions in samples with low Ne-20/He-4 ratios are very low (< 0.3 vol%, Fig. 11). Almost all helium in these samples can be assigned to atmospheric and crustal provenance.

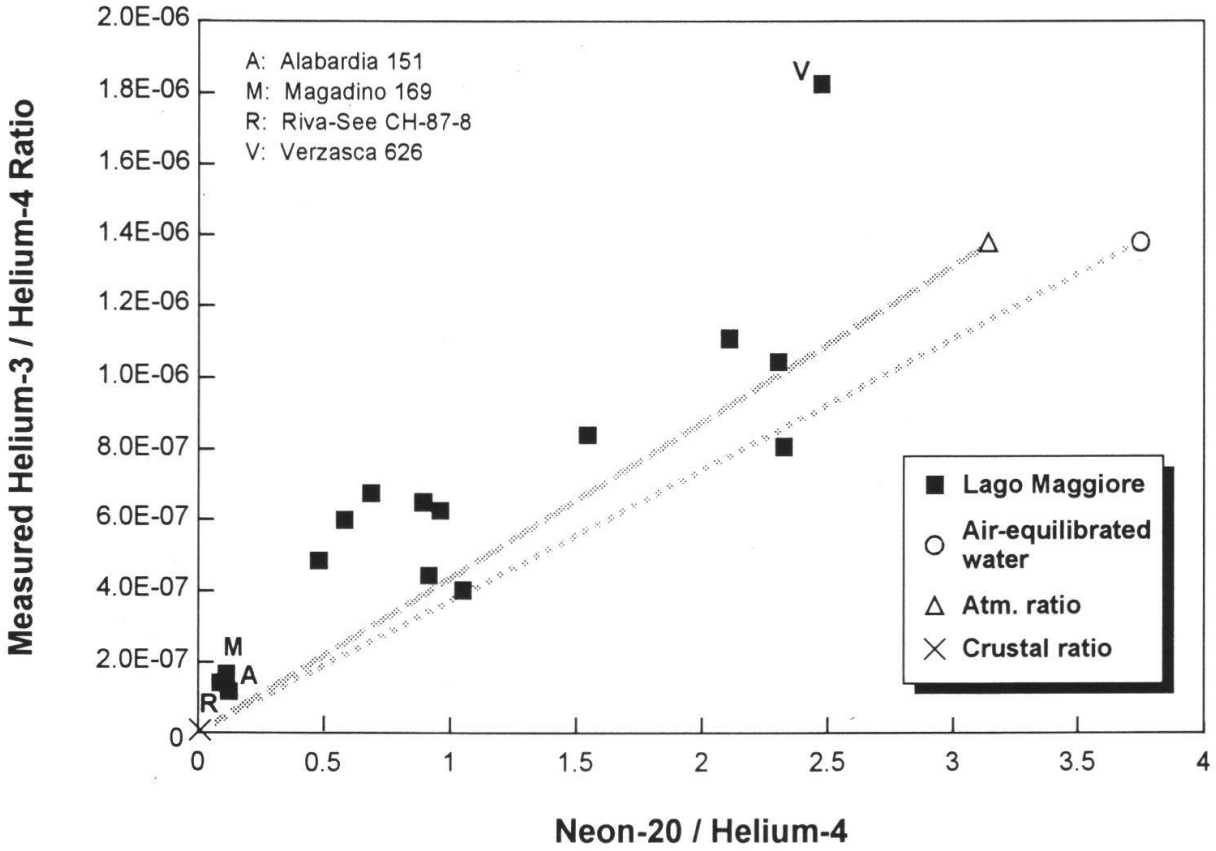

Fig. 11: The measured helium-3/helium-4 and neon-20/helium-4 ratios can be explained by a mixing of atmospheric and crustal helium. The helium-3 excess which is observed especially in the Verzasca 626 sample (V) is most probably due to tritiogenic helium-3 from the groundwater. The most reliable data (samples A, M and R) shows a distinct crustal helium-3/helium-4 ratio.

Most conspicuous is the data from the Verzasca 626 sample (Fig. 11). As unique sample its measured He-3/He-4 ratio lies between the primordial and atmospheric ratio and the apparent He_{mantle} portion is by far the largest of all the samples (3.0 vol%). This high "mantle" portion is obviously inconsistent with its very hig Ne-20/He-4 ratio. For this reason a non-mantle helium-3 origin has to be taken into consideration. There are some good arguments for assigning the observed He-3 excess to tritiogenic He-3 production (radioactive decay of the tritium in the water).

The question arises why such significant amounts of tritiogenic He-3 are only observed at the Verzasca site. This gas seep is unique in that it occurs in a running water environment. It is plausible that the groundwater is constantly supplied with new tritium by the infiltration of river water. He-3 that is produced by the decay of this tritium could easily be stripped off by the ascending CH_4 rich gases (Dr R. Kipfer, personal communication).

The hydrogeological situation at the other gas seep locations in the lake is different, in that stagnant conditions prevail as far as the interstitial waters are concerned and the waters are probably older and thus depleted in tritium.

The production of tritiogenic He-3 can be calculated using the formula from TORGERSEN et al. (1977). The boundary conditions, however, are very difficult to assess and the above hypothesis cannot be proved until further hydrogeological and tritium data from the two environments is available.

At the Riva-Fels site mixing processes with soil air (see above) can also be recognized by Ne contents (ø 2.27•10E-05 cc Ne-20/cc gas) that are considerably higher than those of the gas seeps in the lake (ø 6.12•10E-07 cc Ne-20/cc gas).

3.7 Soil gas campaign

Gas seeps are much more difficult to discover on land than in open waters, where they are easily detected by rising gas bubbles. In order to provide evidence of bacterial gas production beneath the Magadino Plain, a soil gas campaign was carried out together with GEMAG, in which soil gas samples were taken at 12 sites by means of shallow (up to 1.3 m deep) drillings into the unsaturated soil zone (Table 3).

Location point	x-coord.	y-coord.	Laboratory	CH4 ppm	n-butane ppm	i-pentane ppm	N2 vol%	O2 vol%	CO2 vol%	H2 ppm	Ar vol%	d13C(CH4) o/ooPDB
MG 1	710.325	114.575	GEMAG	1.6	< 0.1	< 0.1	78.3	17.69	3.13	< 2	n.m.	n.m.
MG 2	710.690	113.525	GEMAG	9.5	< 0.1	< 0.1	83.66	9.91	6.16	< 2	n.m.	n.m.
MG 3	710.710	111.850	GEMAG	10.5	< 0.1	< 0.1	78.26	20.04	0.67	< 2	n.m.	n.m.
MG 4	713.190	112.275	GEMAG	0.3	< 0.1	< 0.1	78.41	7.49	13.1	< 2	n.m.	n.m.
MG 5	713.175	112.960	GEMAG	10.1	< 0.1	< 0.1	80.11	9.71	9.89	< 2	n.m.	n.m.
MG 6	713.200	114.150	GEMAG	2.2	0.4	0.4	80.86	7.29	11.34	10	n.m.	n.m.
MG 6A	"	"	GCA	12	< 1	< 1	82.0	4.32	12.76	50	0.95	-44.2
MG 7	714.960	114.675	GEMAG	0.4	< 0.1	< 0.1	83.48	9.73	5.61	< 2	n.m.	n.m.
MG 8	715.840	113.175	GEMAG	0.5	< 0.1	< 0.1	81.81	6.79	11.16	< 2	n.m.	n.m.
MG 9	716.000	111.900	GEMAG	0.6	< 0.1	< 0.1	82.69	14.92	1.73	< 2	n.m.	n.m.
MG 10	719.510	112.925	GEMAG	0.6	< 0.1	< 0.1	80.27	8.72	10.48	< 2	n.m.	n.m.
MG 11	719.250	113.640	GEMAG	0.5	< 0.1	< 0.1	83.29	7.63	8.84	< 2	n.m.	n.m.
MG 12	718.660	114.775	GEMAG	0.4	< 0.1	< 0.1	82.00	11.44	6.5	< 2	n.m.	n.m.

Table 3: Gas data from the free soil gas campaign carried out by GEMAG on 20 July 1993 in the Magadino Plain area.

Based on the rather high O_2 and N_2 portions, all samples are interpreted as reduced atmospheric air mixed with CO_2 produced in the aerial respiration zone (e.g. STUMM & MORGAN 1981). The measured CH_4 portions are very low (< 12 ppm).
One rather positive $\delta^{13}CH_4$ value of -44.2 ‰$_{PDB}$ was measured in the sample MG 6A by GCA (Lehrte). This value, in the range of thermogenic CH_4, is most probably due to bacterial oxidation (COLEMAN et al. 1981) as the CH_4 content of 12 ppm is very low and the O_2 content at 4.32 vol% is rather high.

Thus, although a significant production of bacterial gases beneath the Magadino Plain can be expected, no positive evidence resulted from our soil gas campaign.

4. Conclusions

Although from a geological point of view, dry or wet thermogenic components would not be surprising in the Lago Maggiore gas seeps, no geochemical evidence exists for such gas components. Based on $\delta^{13}CO_2$, $\delta^{13}CH_4$ and δD_{CH4} data, a biogenic origin of the Lago Maggiore gases must be inferred.
Gas components originating from the Earth's mantle are very improbable as the $\delta^{13}CH_4$ values of the gases studied are too negative in comparison to primordial carbon and as helium can be assigned to atmospheric, crustal and probably minor tritiogenic provenace.

The gas seeps in the Lago Maggiore and the Verzasca River are geochemically rather inconspicuous. During the bacterial decay of organic matter, almost pure CH_4 gases are produced. As they ascend through the interstitial waters of the lacustrine sediments, they are mixed with small amounts of atmospheric N_2 and Ar that were previously dissolved in the interstitial waters. The small percent of CO_2 may be produced together with the CH_4 or may have been added at a later stage from a shallower redox zone.

The only gas seeps on land, the Riva-Fels gases, emerging from rock fissures at Rivapiana, must be considered as transformed gases of the above described gas type. A severe overprinting by mixing with reduced soil air is supported by (1) an atmospheric air Ar/N_2 ratio, (2) an isotopic shift towards more positive $\delta^{13}CH_4$ values and more negative $\delta^{13}CO_2$ values, (3) considerably higher carbon-14 contents in CH_4 than in CO_2 and (4) rather high neon-20 concentrations. Small amounts of CH_4-rich gases reach the rock fissures from the lacustrine sediments, possibly because their vertical ascent is hindered by layers of low permeability. The gases encounter soil air in the unsaturated zone which results in the onset of bacterial oxidation processes.

The total amount of emerging gas in the upper Lago Maggiore region is estimated to be in the order of 100,000 m^3/year. This is compatible with the calculated potential biogenic gas production in the area (GEOFORM 1994).

The Lago Maggiore gases show no affinities to either the Po basin gases or to the relatively wet gas of the Stabio spa (Fig. 12).

Although many aspects of the origin and evolution of the Lago Maggiore gas seeps could be elucidated in our study, some unsolved problems are still open for discussion: (1) Which process is responsible for the three different CO_2/CH_4 resp. CO_2/N_2 ratios observed? (2) How can the large variations in δD_{CH4} values from identical gas seep locations be explained? (3) Why is the CH_4 oxidation in the rock fissures at Rivapiana only combined with a carbon-13 enrichment in CH_4, but not also with a deuterium enrichment? (4) Is the elevated He-3/He-4 ratio in the Verzasca sample indeed due to tritiogenic helium-3?

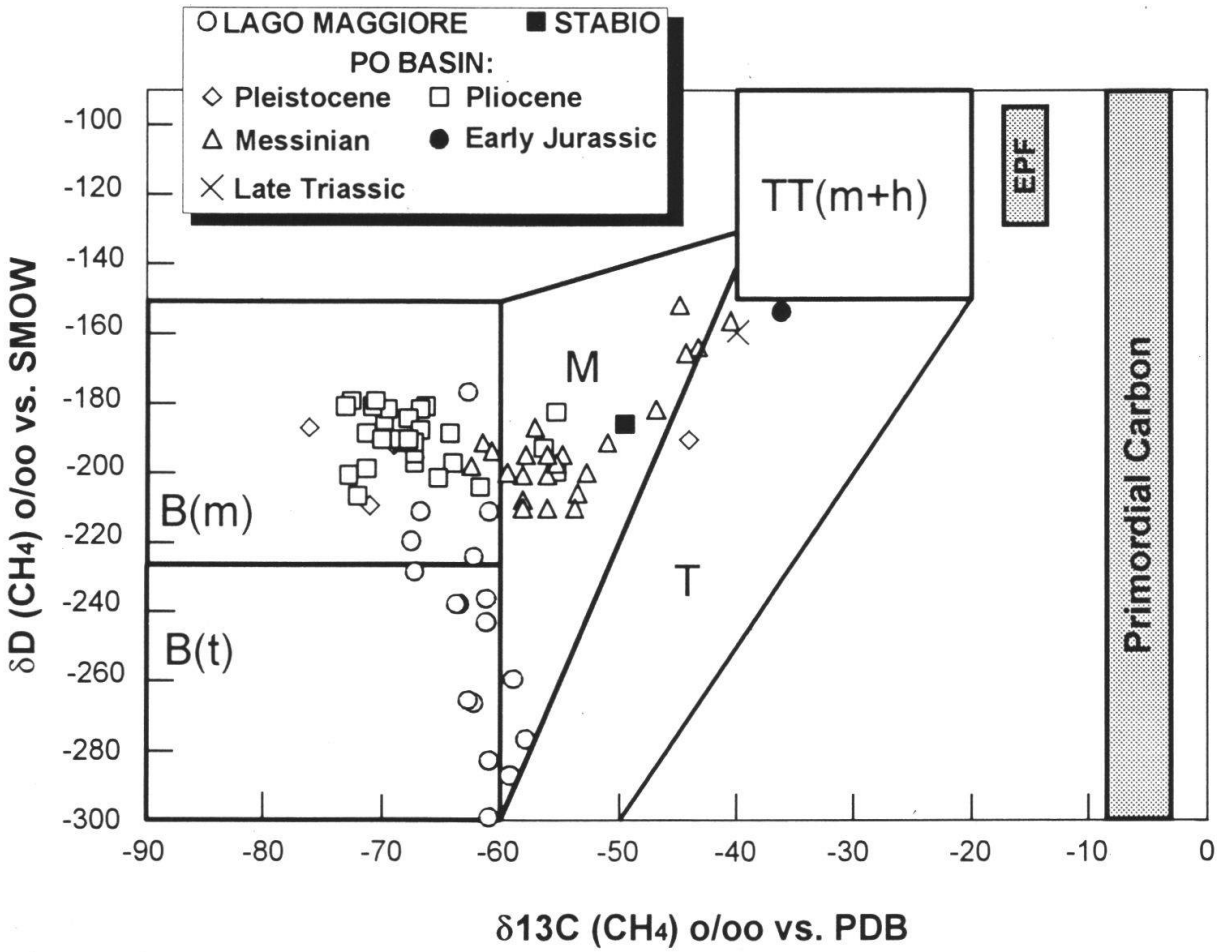

Fig. 12: The Lago Maggiore gases show different geochemical characteristics than those from the Po Plain (Northern Italy) and that of the Stabio spa (southernmost part of Switzerland). Gas fields: B = Biogenic gas (m = marine and t = terrestrial environment), T = Thermogenic associated gas, M = Mixture gas, TT(m+h) = non-associated, highly mature dry gases (m+h = humic and liptinitic sapropelic organic matter) and EPF = East Pacific Rise (primordial carbon data from WELHAN 1988; diagram modified from SCHOELL 1983). For the Po basin gases (data from MATTAVELLI et al. 1983) reservoir ages are indicated.

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Appendix 1: Raw gas data from the Lago Maggiore and the Stabio spa gases (undet. = undetectable, n.m. = not measured, - = no data available). Data older than 1993 is taken from BÜCHI (1982), BÜCHI & WILD (1986) and WILD (1990).

Sample	Sampling date	O2 vol%	CH4 vol%	N2 vol%	CO2 vol%	H2 vol%	Ar vol%	d13C(CH4) o/ooPDB	dD(CH4) o/ooSMOW	d13C(CO2) o/ooPDB	d18O(CO2) o/ooPDB	C-14 (CH4) % MOD	C-14 (CO2) % MOD
Pol													
Pol	24/11/84	0.71	95.39	3.76	0.13	n.m.	n.m.	-60.9	n.m.	n.m.	n.m.	68.1 +/- 1.2	n.m.
Pol 1	7/7/93	0.2	92.7	6.51	0.17	0.26	0.13	-62.1	-266	-20.6	-13.3	n.m.	n.m.
Pol 2	7/7/93	10.45	47.0	41.71	0.15	0.12	0.54	-62.1	-224	-17.9	-16.4	n.m.	n.m.
Pol 3	7/7/93	0.53	90.64	6.19	0.07	undet.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Riva-Fels													
Riva-Fels	11/2/85	0.60	31.94	64.32	3.14	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Riva-Fels	4/5/85	4.60	8.71	80.94	5.75	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Riva-Fels	4/5/85	4.60	8.73	80.98	5.69	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Riva-Fels	25/8/87	-	-	-	-	-	-	-59.4	n.m.	-48.2	n.m.	n.m.	n.m.
Riva-Fels	27/8/87	-	-	-	-	-	-	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Riva-Fels	27/8/87	-	-	-	-	-	-	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Riva-Fels 1	3/89	0.07	27.0	70.9	2.9	0.03	1.1	-61.3	-236	-38	n.m.	42.9 +/- 0.9	79.2 +/- 0.7
Riva-Fels 2	3/89	0.00	31.7	64.5	3.9	n.m.	1.1	-60.9	-299	-48	n.m.	n.m.	n.m.
Riva-Fels 3	3/89	0.00	32.5	63.4	4	n.m.	1	-59	-259	-47.7	n.m.	n.m.	n.m.
Riva-Fels 4	3/89	0.08	33.1	61.5	4.8	n.m.	1	-60.9	-283	-48.6	n.m.	n.m.	n.m.
Riva-Fels 5	12/89	2.70	13.6	80.9	1.7	n.m.	1.3	-59.1	-287	-52.5	n.m.	43.2 +/- 1.0	60.5 +/- 0.8
Riva-Fels 6	12/89	0.90	18.7	75.7	3.4	n.m.	1.2	-57.8	-277	-54.8	n.m.	n.m.	n.m.
Riva-Fels 7	12/89	0.10	20.0	75.0	4.4	n.m.	1.2	-60	n.m.	-48.2	n.m.	n.m.	n.m.
Riva-Fels 1	29/6/93	0.23	34.3	56.4	8.32	0.06	0.68	-62.8	-177	-45.7	-3.9	n.m.	n.m.
Riva-Fels 2	29/6/93	0.45	31.3	58.6	8.69	0.24	0.74	-62.7	-177	-45.5	-8.9	n.m.	n.m.
Riva-See													
Riva-See	27/11/84	1.55	90.75	7.25	0.45	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Riva-See	5/5/85	1.28	88.26	10.16	0.3	n.m.	n.m.	-62.1	n.m.	n.m.	n.m.	46.1 +/- 0.8	n.m.
Ten													
Ten	24/9/81	1.2	79.8	17.3	1.7	0.01	n.m.	-61.7	n.m.	3.6	n.m.	66.3 +/- 0.5	n.m.
Ten	4/5/82	0.85	79.00	18.37	1.75	0.03	n.m.	-61.2	n.m.	7.4	n.m.	66 +/- 0.4	n.m.
Ten 1	1/7/93	0.07	97.7	0.84	1.17	0.18	0.02	-60.9	-211	2.2	-10.5	n.m.	n.m.
Ten 2	1/7/93	0.03	98.9	0.34	0.47	0.27	0.01	-61.1	-243	2.3	-10.6	n.m.	n.m.
Ten 3	1/7/93	0.44	93.49	1.93	1.68	undet.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Ver													
Ver	15/4/91	0.14	93.03	5.94	0.88	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Ver 5	15/4/91	0.08	92.99	6.05	0.88	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Ver 1	2/7/93	1.04	84.4	12.85	1.16	0.2	0.32	-66.9	-211	-26.5	-9.2	n.m.	n.m.
Ver 2	2/7/93	1.29	85.6	11.8	0.88	0.19	0.27	-67.3	-196	-27	-9.3	n.m.	n.m.
Ver 3	2/7/93	0.76	90.63	7.73	0.57	undet.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Bol													
Bol	23/9/81	2.7	69.2	26.8	1.3	0.02	n.m.	-66.4	n.m.	0.1	n.m.	76.9 +/- 0.5	n.m.
Bol 1	1/7/93	0.06	92.1	1.18	6.46	0.17	0.01	-67.3	-228	-0.4	-8.7	n.m.	n.m.
Bol 2	1/7/93	14.13	27.9	53.48	3.82	0.03	0.66	-67.6	-220	-0.7	-9.0	n.m.	n.m.
Bol 3	1/7/93	7.35	56.21	26.97	7.66	undet.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Mag													
Mag	30/9/80	0.4	85.1	3.4	11.1	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Mag	23/9/81	0.8	76.4	21.9	0.9	0.03	n.m.	n.m.	n.m.	n.m.	n.m.	53.9 +/- 0.5	n.m.
Mag	4/5/82	0.2	66.1	21.88	11.8	0.02	n.m.	-61.8	n.m.	1.1	n.m.	52.8 +/- 0.4	n.m.
Mag	5/5/85	0.23	85.24	2.33	12.21	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Mag 1	2/8/85	0.25	85.47	2.25	12.03	n.m.	n.m.	-62.8	n.m.	-1.4	n.m.	48.3 +/- 0.4	49.0 +/- 0.6
Mag 2	2/8/85	0.22	84.81	2.2	12.77	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Mag 1	26/4/86	1.59	92.65	4.34	1.42	n.m.	n.m.	-63.7	n.m.	-2.2	n.m.	57.5	n.m.
Mag 2	26/4/86	1.64	92.58	4.36	1.42	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Mag 1	30/6/93	0.07	90.2	1.91	7.57	0.19	0.03	-62.8	-265	-0.7	-8.8	n.m.	n.m.
Mag 2	30/6/93	0.06	90.2	1.86	7.6	0.23	0.03	-62.8	-265	-0.3	-8.5	n.m.	n.m.
Mag 3	30/6/93	0.84	80.82	3.99	13.65	undet.	n.m.	n.m.		n.m.	n.m.	n.m.	n.m.
Ala													
Ala 1	2/8/85	0.63	89.81	7.03	2.53	n.m.	n.m.	-63.7	n.m.	-0.7	n.m.	51.2 +/- 0.4	45.2 +/- 0.6
Ala 2	2/8/85	0.57	89.82	6.97	2.64	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Ala 2	26/4/86	0.46	86.95	9.09	3.5	n.m.	n.m.	-64.3	n.m.	-3.2	n.m.	43.6	n.m.
Ala 1	30/6/93	0.18	93.4	4.21	2.02	n.m.	0.07	-63.6	-238	-3	-8.3	n.m.	n.m.
Ala 2	30/6/93	0.23	91.6	5.32	2.53	n.m.	0.09	-63.7	-238	-2.4	-8.8	n.m.	n.m.
Ala 3	30/6/93	1.41	84.75	9.71	3.09	undet.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Stabio													
Stabio 2	14/6/93	13.2	20	65.1	0.9	0.054	0.7	-49.4	-186	-11	-10.2	n.m.	n.m.

Sample	Sampling date	CH4 vol%	N2 vol%	CO2 vol%	H2 vol%	Ar vol%
Pol						
Pol	24/11/84	98.72	1.15	0.13	n.m.	n.m.
Pol 1	7/7/93	93.63	5.82	0.17	0.26	0.12
Pol 2	7/7/93	93.81	5.51	0.28	0.24	0.16
Pol 3	7/7/93	95.49	4.44	0.07	undet.	n.m.
Riva-Fels						
Riva-Fels	11/2/85	32.88	63.89	3.23	n.m.	n.m.
Riva-Fels	4/5/85	11.13	81.52	7.35	n.m.	n.m.
Riva-Fels	4/5/85	11.16	81.57	7.27	n.m.	n.m.
Riva-Fels	25/8/87	20.24	78.78	0.98	n.m.	n.m.
Riva-Fels	25/8/87	16.42	77.32	6.26	n.m.	n.m.
Riva-Fels	25/8/87	17.1	76.53	6.37	n.m.	n.m.
Riva-Fels 1	3/89	26.6	69.5	2.9	0.03	1.1
Riva-Fels 2	3/89	31.7	64.4	3.9	n.m.	1.1
Riva-Fels 3	3/89	32.5	63.4	4.0	n.m.	1.0
Riva-Fels 4	3/89	33.1	61.1	4.8	n.m.	1.0
Riva-Fels 5	12/89	15.6	81.1	1.9	n.m.	1.4
Riva-Fels 6	12.89	19.6	75.6	3.6	n.m.	1.3
Riva-Fels 7	12.89	20.0	74.5	4.4	n.m.	1.2
Riva-Fels 1	29/6/93	34.69	56.16	8.41	0.06	0.68
Riva-Fels 2	29/6/93	31.98	58.16	8.88	0.24	0.74
Riva-See						
Riva-See	27/11/84	97.93	1.58	0.49	n.m.	n.m.
Riva-See	5/5/85	93.95	5.73	0.32	n.m.	n.m.
Ten						
Ten	24/9/81	84.6	13.6	1.8	0.01	n.m.
Ten	4/5/82	82.31	15.84	1.82	0.03	n.m.
Ten 1	1/7/93	98.05	0.58	1.17	0.18	0.02
Ten 2	1/7/93	99.02	0.23	0.47	0.27	0.01
Ten 3	1/7/93	97.94	0.29	1.76	undet.	n.m.
Ver						
Ver	15/4/91	93.67	5.44	0.89	n.m.	n.m.
Ver 5	15/4/91	93.33	5.78	0.88	n.m.	n.m.
Ver 1	2/7/93	88.84	9.44	1.22	0.21	0.28
Ver 2	2/7/93	91.19	7.45	0.94	0.2	0.22
Ver 3	2/7/93	94.31	5.10	0.57	undet.	n.m.
Bol						
Bol	23/9/81	79.31	19.18	1.49	0.02	n.m.
Bol 1	1/7/93	92.38	0.96	6.48	0.17	0.01
Bol 2	1/7/93	85.58	2.52	11.69	0.09	0.12
Bol 3	1/7/93	88.02	0	11.98	undet.	n.m.
Mag						
Mag	30/9/80	86.7	1.9	11.3	n.m.	n.m.
Mag 1	23/9/81	79.4	19.6	0.9	n.m.	n.m.
Mag	4/5/82	66.8	21.3	11.9	0.02	n.m.
Mag	5/5/85	86.18	1.49	12.33	n.m.	n.m.
Mag 1	2/8/85	86.47	1.36	12.17	n.m.	n.m.
Mag 2	2/8/85	85.69	1.40	12.90	n.m.	n.m.
Mag 1	26/4/86	98.49	0.00	1.51	n.m.	n.m.
Mag 2	26/4/86	98.49	0.00	1.51	n.g	n.m.
Mag 1	30/6/93	90.53	1.65	7.6	0.19	0.03
Mag 2	30/6/93	90.48	1.64	7.62	0.23	0.03
Mag 3	30/6/93	84.78	0.90	14.32	undet.	n.m.
Ala						
Ala 1	2/8/85	92.57	4.82	2.61	n.m.	n.m.
Ala 2	2/8/85	92.32	4.96	2.71	n.m.	n.m.
Ala 2	26/4./86	88.88	7.54	3.58	n.m.	n.m.
Ala 1	30/6/93	94.19	3.57	2.04	0.14	0.06
Ala 2	30/6/93	92.65	4.51	2.56	0.2	0.08
Ala 3	30/6/93	91.83	4.82	3.35	undet.	n.m.

Appendix 2: Gas data corrected for air contamination during sampling (in accordance with the atmospheric ratio of the gases to O_2.

Sample	Sampling date	Laboratory	Helium-4 cc 4He/cc gas	Neon-20 cc 20Ne/cc gas	(3He/4He)meas	Apparent atmospheric helium (vol%)	Apparent mantle helium (vol%)	Apparent crustal helium (vol%)	(R/Ra)c
Pol									
178	7/7/93	EAWAG-IKP	7.28587E-07	6.50474E-07	6.4913E-07	23.9	1.0	75.1	0.3
			+/- 1.45002E-08	+/- 1.33077E-08	+/- 1.0201E-08				
Riva-Fels									
CH-87-3	1/8/87	O'Nions	3.25E-05	7.57E-05	8.03E-07	(62.2)	(-0.2)	(38.0)	(-0.1)
CH-1	1/3/89	O'Nions	1.82E-05	8.79E-06	4.84E-07	12.9	1.0	86.1	0.3
CH-2	1/3/89	O'Nions	1.67E-05	1.61E-05	6.22E-07	25.8	0.8	73.4	0.3
5	1/12/89	Hydroisotop	9.00E-06	1.39E-05	8.40E-07	41.3	0.9	57.9	0.3
6	1/12/89	Hydroisotop	1.32E-05	2.78E-05	1.11E-06	56.3	1.1	42.7	0.5
7	1/12/89	Hydroisotop	2.39E-06	5.50E-06	1.04E-06	61.5	0.6	37.9	0.4
98	29/6/93	EAWAG-IKP	1.18922E-05	1.09332E-05	4.4301E-07	24.6	0.3	75.1	0.1
			+/- 2.54551E-07	+/- 2.3953E-07	+/- 4.5846E-09				
Riva-See									
CH-87-8	1/8/87	O'Nions	7.478E-06	6.53E-07	1.40E-07	2.3	0.3	97.4	0.1
Ten									
137	1/7/93	EAWAG-IKP	1.51183E-07	1.0342E-07	6.7395E-07	18.3	1.3	80.4	0.4
			+/- 3.03002E-09	+/- 2.67815E-09	+/- 5.535E-08				
Ver									
Ver	2/7/93	EAWAG-IKP	4.73001E-07	1.16954E-06	1.821E-06	66.1	3.0	30.9	1.9
			+/- 9.45012E-09	+/- 2.38772E-08	+/- 2.3E-08				
Bol									
184	1/7/93	EAWAG-IKP	1.25041E-07	7.28469E-08	5.9796E-07	15.6	1.2	83.2	0.3
			+/- 2.52699E-09	+/- 1.76344E-09	+/- 5.4317E-08				
Mag									
CH-87-5	1/8/87	O'Nions	3.871E-07	4.079E-07	4.07E-07	28.2	0.0	71.8	0.0
169	30/6/93	EAWAG-IKP	1.39497E-06	1.61798E-07	1.624E-07	3.1	0.3	96.6	0.1
			+/- 2.79314E-08	+/- 3.72795E-09	+/- 9.0727E-09				
Ala									
151	30/6/93	EAWAG-IKP	9.71669E-06	1.22412E-06	1.1362E-07	3.4	0.2	96.5	0.1
			+/- 1.9431E-07	+/- 2.80072E-08	+/- 2.8043E-09				

Appendix 3: Noble gas data from the Lago Maggiore samples with calculated "apparent" atmospheric, mantle and crustal helium portions. The calculations do not take possible contributions of tritiogenic helium into account. Data older than 1993 is taken from WILD (1990).