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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

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Geologia — *Karstification, glaciation and atmospheric CO_2* (*). Nota di ARTURO DEBENEDETTI, presentata (**) dal Socio R. MALARODA.

ABSTRACT. - A general relationship is proposed between glaciation, CO_2 content in atmosphere and oceanic water and velocity of karstification phenomena. True "acid rain" and acid melting water are assumed to have acted more efficiently on limestones during the ice age than in present times.

KEY WORDS: Carbon dioxide; Karst; Climatology; Glaciation.

RIASSUNTO. - *Carsificazione, glaciazioni e CO_2 atmosferica.* La notevole velocità con cui si sono esplicati i fenomeni carsici nel corso del Quaternario viene posta in relazione con la maggior abbondanza di CO_2 nell'atmosfera, nelle masse glaciali e nelle acque continentali. Ciò è attribuito alla minor quantità di questo gas immobilizzata nelle acque oceaniche nel corso delle glaciazioni in conseguenza del loro minor volume.

Karst morphology is generally considered to be an inevitable feature of the surface and subsurface of limestone formation on the grounds that these are invariably affected by the continuous dissolution of carbonates produced by the presence of CO_2 in meteoric and runoff water. Now many karst phenomena are closely linked in both distribution and development to Pleistocene glaciation. I suggest here, more generally, that the origin of karstification may lie in the increased capacity for carbonate solution that characterized glacial environments as in the case of the karst in NW Europe (Corbel, 1957).

In addition to decalcification processes such as the origin of the *ferretto* in Piedmont and Lombardy in Northern Italy as well as the *terra rossa* elsewhere, many true karst phenomena arose during the Ice Age. According to some radiometric measurements (Bögli, 1978; Fornaca Rinaldi e Radmilli, 1968; Schwarcz *et alii*, 1976),

(*) Dipartimento di Scienze della Terra dell'Università di Torino. La Nota esce postuma, ma con stesura completamente di mano dell'autore, benché scomparso il 24 Luglio 1984 (vedi necrologio e bibliografia di R. Compagnoni in Rend. It. Min. Petr., *41*, 1986, 413-416). Viva gratitudine viene espressa al dott. C. Vita-Finzi per i commenti critici ed al prof. G.C. Bortolami per i dati relativi alla regione veneta.

(**) Nella seduta del 20 Novembre 1987.

the age of speleothems of different karstic caves (Tuscany, North America) in the majority of the cases exceeds 10 kyr b.p., in a few cases about 6 kyr and in one 300 kyr. It is obvious that the caves must be still older, having been excavated in periods distinct from those of the formation of the speleothems. Furthermore, the velocity of formation of both caves and speleothems seems to have been relatively great and to correspond respectively to dissolution actions stronger than those to be expected from present-day theory and experiments (Bögli, 1978; Dreybrodt, 1981), and to particularly high $CaCO_3$ content in the water from which the speleothems were laid down. Other calcareous deposits thought to date from glacial time include *Kalktuffe* and *Kalksinter* (Bögli, 1978), *Quelletuffe, Seekreide* and travertines in Switzerland (Heim, 1919), the *ceppo* (a name now extensively used for breccias and conglomerates with either compact or vacuolar carbonate matrix) which is found both in the bedrock of many Alpine valleys (Gortani, 1912) and at their outlet in the alluvial plain (Heim, 1919; Serv. Geol. It., 1969), the *caranto* and similar calcareous formations in the Venice and Ferrara regions (Northern Italy) (Bortolami *et alii*, 1977), many conglomerates and travertine formations in the Apennines and Southern Italy (Demangeot, 1973), Belgium (Geurts, 1976), Near East (Magaritz *et alii*, 1979), etc. The fact that deposits laid down before and after the Ice Age are often not cemented by secondary calcite reflects less favourable conditions for $CaCO_3$ dissolution and deposition.

In addition to those in NW Europe (Corbel, 1957), more indications of karstification in the Ice Age are the submarine springs off the Mediterranean coasts of Italy (Liguria, Apulia, Sardinia) (Stefanon e Cotecchia, 1969), France, Greek Islands, Yugoslavia (Bögli, 1978), Turkey, Near East, and also outside the Mediterranean (Kohout, 1966). Like the submarine karst morphology in the bay of Villefranche (France) (Bourcart, 1960), these features must have developed subaerially and their presence and depth in widely separated areas beneath the sea suggests that they originated during some periods of glacio-eustatic lowering of the sea level. More or less contemporary limestone dissolution phenomena include the buried gorges now filled with thick alluvial material that were discovered during dam construction in the Alps (Heim, 1919; Lugeon, 1933).

During the Ice Age the Karst region of Yugoslavia and many other regions which now have a similar morphology were covered with, or close to, ice caps and sheets (Messerli, 1967). The coincidence in time and space of karst manifestations and glaciations hints at a cause and effect relationship. The particular CO_2 content and the pressure conditions which must have prevailed in the ice masses and in the water when they melted appear to justify the hypothesis.

It can be assumed that in the glacial masses, as in the present-day glaciers, CO_2 was present in *autogènes* and *xénogènes* bubbles and possibly also in the ice lattice (Lliboutry, 1964). In the ice of the glaciers the content of CO_2 must be relatively high: a specially strong dissolving power of the water flowing out from their snouts has been repeatedly assumed (Corbel, 1957; Lliboutry, 1964; Martin, 1903) and is confirmed by some calcite deposits (Ford *et alii*, 1970; Magaritz, 1973).

In the Ice Age the content of CO_2 in the ice must have been still higher. A high content of CO_2 has been found in ice samples from deep levels of the Arctic and Antarctic sheets (Raynaud e Delmas, 1977), although in some cases the partial pressure of CO_2 in the enclosed air bubbles was lower than in the present-day atmosphere (Delmas *et alii*, 1980).

At the peak of the Pleistocene glaciations sea level is generally thought to have dropped by about 140 m, the volume of evaporated water being about 50×10^6 km^3 (55×10^6 km^3 of ice). The content of CO_2 in present-day oceanic waters between the surface and the -150 level is assumed to be about 300 ppm (Schwarcz, 1967): if it was the same at the corresponding depths when the glaciation started, the CO_2 of the evaporated water would have been about 1.5×10^{13} tonnes, that is 6.4 times the amount (2.33×10^{12} tonnes) assumed to exist at present in the atmosphere (Rösler e Lange, 1972). The partial pressure of CO_2 in the atmosphere - which determined the content of CO_2 in the meteoric precipitation "congealed" in the ice - could have increased from 3×10^{-4} to 2.3×10^{-3}. At the same time, as the ice was growing, CO_2 gradually decreased in the atmosphere and in the air bubbles trapped in the ice.

The ice masses themselves played an important part in developing karst features. At its greatest extent the ice covered about one third of the continental area (Holmes, 1965) or 50×10^6 km^2. The average thickness of the ice was about 1.000 m, but thicknesses of over 2.000 m occurred in the Alps and elsewhere. At the bottom of an ice layer 2.000 m thick the pressure melting temperature could have been reached. The high pressure and low temperature greatly favoured the dissolution of CO_2 in the water (Stephen, 1933), which thus became highly aggressive.

Limestone or other carbonate rocks present in the bedrock beneath the ice would have been easily dissolved. As dissolution progressed, the more or less saturated water gradually disappeared into the cavities which it was creating, but was promptly replaced by the melting of more ice and in this water CO_2 was dissolved in new equilibrium conditions. More and more limestone could have been dissolved, in conditions different from the theoretical model (Garrels, 1960) by these mixed waters, thus giving rise to a continuous process by which far-reaching corrosion features were produced. The greater the amount of dissolved matter, the lower the freezing point and the easier the melting of the ice: the volume of subglacial water thus progressively increased under special - neither vadose nor phreatic - hydrological conditions. Deep vertical and/or long horizontal caves of different size, shape and extent could develop within the subglacial bedrock below its surface. True subglacial lakes could be formed, like those discovered beneath the Antarctic ice sheet (Drewry, 1982), a process which would explain the over-deepening of the basins of the subalpine lakes more satisfactorily than the classical erosion hypothesis.

In the interglacial and postglacial periods the atmospheric partial pressure of the CO_2 which went back into the atmosphere as ice melted must again have been high. A corresponding high amount of CO_2 must then have been dissolved in the rain of pluvial times, true "acid rain" which gave origin both to karst corrosion and to $CaCO_3$ in runoff water in large surface areas even far from those which had been covered with ice, as well as to land and sea calcareous deposits at a greater distance (Berger, 1982). Fairly great amounts of calcite of this origin make up the cement of beachrocks at different levels of many coasts, such as, in the Mediterranean area, the cement of the *panchina* in Italy, of the *kurkar* and *nari* in the Levant, and similar formations. Quaternary calcareous crusts, calcrete, travertine are also known in the continental area around the Mediterranean in Spain (Blumenthal, 1949), Italy, Greece, North Africa (Vita Finzi, 1969) and the Nile basin (Said, 1981). The regular position of these horizons in the stratigraphical sequence shows that the deposits originated in particular periods of the Pleistocene alternating with periods in which the calcite deposition ceased or was greatly reduced. It is interesting to note that in Israel the δO^{18} values of the calcite cementing Pleistocene rocks of the coastal region, ranging in age from 500 to 50 kyr b.p. resemble those found in caves and veins (Geurts, 1976). The values of the oxygen isotopic ratio of some travertines in the Apennines are similar and suggest also that these rocks were laid down at low temperature (Manfra *et alii*, 1976), thus supporting the hypothesis of the connection with glaciation.

The subsurface circulation and emergence of karst water would also explain a variety of anomalous secondary, postorogenetic, deposits of compact calcite or of breccias and conglomerates with calcitic matrix, found in, or in contact with, various geological formations to which they are in general extraneous. Examples of deposits of this type are some calcareous veins in silico-clastic Carboniferous (Fabre, 1961) and in non-calcareous crystalline formations of the Alps (Liborio e Mottana, 1964), in limestone formations of the Apennines (Scarsella, 1959), as well as, especially, in the Alps, in the Apennines and in Spain, thick breccias in which there are elements certainly younger than the stratigraphical position apparently pertinent to the breccias. The latter is the case of at least some Rauhwacke (*carniole, cargneules, cornieules*) in the Alps (Debenedetti e Turi, 1975), of the *brecce sedimentarie poligeniche* in the Apennines (Cerrina Ferroni *et alii*, 1976) and of the *konglomeratischer Mergel* in the Betic Cordillera (Rutten, 1969). Many more deposits of a similar origin can certainly be found in all the regions where direct and indirect effects of the glaciations can have developed: the abundant geological literature concerning travertines, calcretes and similar secondary calcareous deposits in these regions deserves to be critically analysed in this light. The occurrences may have escaped notice because of their less frequent or less evident anomalous features or of a more conventional interpretation of their origin. Identification can be helped by obtaining oxygen and carbon isotopic ratios, in concurrence with a closer consideration of the geological data. In particular, a probably equivocal interpretation is that of some presumed carbonatites, whose oxygen and carbon isotopic ratios (Deines e Gold, 1973; Pineau *et alii*, 1973) are similar to those of deposits which can be assumed to be of glacial karst origin. The geography and geology of the outcrops of these rocks are additional indications that the alternative hypothesis of their origin deserves attention.

In conclusion, a general close relationship appears thus to exist between glaciation, variation of the atmospheric CO_2 and karstification. In particular, the hypothesis of the connection with the glaciations seems to explain the origin of the karst features more adequately than the conventional actualistic one; at the same time, it suggests a further explanation of the variations of the content of CO_2 in the atmosphere in the Ice Age (Broecker, 1984).

OPERE CITATE

BERGER W.H. (1982) – *Increase of carbon dioxide in the atmosphere during deglaciation: the coral reef hypothesis.* "Naturwiss", *69*, 87-88.

BLUMENTHAL M.M. (1949) – *Estudio geológico de las cadenas costeras al Oeste de Malaga, entre el Rio Guadalharce y el Rio Verde.* "Bol. Inst. Geol. Min. España", *62*, 164-165.

BÖGLI A. (1978) – *Karsthydrographie und physische Speläologie.* Springer, Berlin.

BOURCART J. (1960) – *Les divers modes de sédimentation observés en Méditerranée Occidentale.* "Report 21st Int. Geol. Congr." *23*, 1-18.

BORTOLAMI G.C., FONTES J. Ch., MARKGRAF V. e SALIEGE J.F. (1977) – *Land, sea and climate in the northern Adriatic region during late Pleistocene and Holocene.* Palaeogeogr., Palaeoclim., Palaeoecol., *21*, 139-156.

BROECKER W.S. (1984) – *Carbon dioxide circulation through ocean and atmosphere.* "Nature", *308*, 602.

CERRINA FERRONI A., NUTI S., PERTUSATI P.C. e PLESI G. (1976) – *Sulla probabile origine carsica delle brecce sedimentarie associate al calcare cavernoso dell'Appennino Settentrionale.* Boll. Soc. Geol. It., *95*, 1161-1174.

CORBEL J. (1957) – *Les karsts du Nord-ouest de l'Europe.* "Inst. Étud. Rhodan. Univ. Lyon, Mém. Docum.", *12*.

DEBENEDETTI A. e TURI B. (1975) – *Carniole della Valle d'Aosta. Studio isotopico ed ipotesi genetica.*, "Boll. Soc. Geol. It.", *94*, 1883-1894.

DEINES P. e GOLD D.P. (1973) – *The isotopic composition of carbonatite and kimberlite carbonates and their bearing on the isotopic composition of deep-seated carbon.* "Geochim. Cosmochim. Acta", *37*, 1709-1733.

DELMAS R.J., ASCENZIO I.M. e LEGRAND M. (1980) – *Polar ice evidence that atmospheric CO_2 at 20.000 yr BP was 50% of present.* "Nature", *284*, 155-157.

DEMANGEOT J. (1973) – *Néotectonique et dépôts quaternaires dans l'Apennin.* In: "Moderne vedute sulla Geologia dell'Appennino". "Acc. Naz. Lincei, Quaderni", *183*, 215-233.

DREWRY D.J. (1982) – *Antarctica unveiled.* "New Scientist", *95*, 247-251.

DREYBRODT W. (1981) – *Kinetics of the dissolution of calcite and its application to karstification.* "Chem. Geol.", *31*, 245-269.

FABRE J. (1961) – *Contribution à l'étude de la Zone Houillère en Maurienne et en Tarantaise.* "Mém. Bur. Rech. Géol. Min.", 2, 83-84.

FORD D.C., FULLER P.G. e DRAKE J.J. (1970) – *Calcite precipitation at the soles of temperate glaciers*'. "Nature", *226*, 441-442.

FORNACA RINALDI G. e RADMILLI A.M. (1968) – *Datazione con il metodo Th^{230}/U^{238} di stalagmiti contenute in depositi mousteriani.* "Atti Soc. Tosc. Sc. Nat.", ser. A, *75*, 639-646.

GARRELS R.M. (1960) – *Mineral equilibria.* Harper, New York, 43-59.

GEURTS M.A. (1976) – *Genèse et âge des travertins de fond de vallée sous climat tempéré océanique.* "Compt. Rend. Ac. Sc. Paris", *282 D*, 275-276.

GORTANI M. (1912) – *Sull'età delle antiche alluvioni cementate nella Valle del Tagliamento.* "Boll. Soc. Geol. It.", *31*, 388-394.

HEIM A. (1919) – *Geologie der Schweiz.* Tauchnitz, Leipzig, vol. I, 286-292.

HOLMES A. (1965) – *Principles of Physical Geology.* Nelson, London, p. 677.

KOHOUT F.A. (1966) - *Submarine springs*. In: "Encyclopedy of Oceanography, Fairbridge R.W. ed., Reinhold, New York", 878-883.

LIBORIO G. e MOTTANA A. (1964) - *Segnalazione di lembi calcarei nel basamento cristallino subalpino della zona di Pizzo di Rodes*. "Boll. Serv. Geol. It.", *85*, 41-44.

LLIBOUTRY L. (1964) - *Traité de Glaciologie*, Masson, Paris.

LUGEON (1933) - *Barrages et Géologie*, Rouge, Lausanne, 28-29.

MAGARITZ (1973) - *Precipitation of secondary calcite in glacier areas: carbon and oxygen isotopic composition of calcites from Mt. Hermon, Israel and the European Alps*. "Earth Planet. Sc. Lett.", *17*, 385-390.

MAGARITZ M., GAVISH E., BAKLER N. e KAFRI U. (1979) - *Carbon and oxygen isotope composition, indicators of cementation environment in Recent, Holocene and Pleistocene sediments along the coast of Israel*. "Journ. Sed. Petrol.", *49*, 401-412.

MANFRA L., MASI U. e TURI B. (1976) - *La composizione isotopica dei travertini del Lazio*. "Geol. Rom.", *15*, 127-174.

MARTIN D. (1903) - *Faits nouveaux ou peu connus rélatifs à la période glaciaire*. "Mém. Ac. Sc. Belles Lettres Arts Lyon", *8*, 1-37.

MESSERLI B. (1967) - *Die eiszeitliche und die gegenwärtige Vergletscherung im Mittelmeerraum*. "Geogr. Helv.", *3*, 105-228.

PINEAU F., JAVOY M. e ALLÈGRE C.J. (1973) - *Étude systématique des isotopes de l'oxygène, du carbone et du strontium dans les carbonatites*. "Geochim. Cosmochim. Acta", *37*, 2363-2377.

RAYNAUD D. e DELMAS R. (1977) - *Composition des gaz contenus dans la glace polaire*. In: "Isotopes and impurities in snow and ice - Grenoble 1975 IUGG Meeting (IAHS publ.)", *118*, 377-381.

RÖSLER H.J. e LANGE H. (1972) - *Geochemical tables*. Elsevier, Amsterdam, 243.

RUTTEN M.G. (1969) - *The Geology of western Europe*. Elsevier, Amsterdam, 403.

SAID R. (1981) - *The geological evolution of the River Nile*. Springer, New York.

SCARSELLA F. (1959) - *"Filoni sedimentari" nel Calcare Massiccio hettangiano del Corno Grande (Gran Sasso d'Italia)*. "Boll. Soc. Geol. It.", *77*, 15-27.

SCHWARCZ H.P. (1967) - In: "Handbook of Geochemistry, Wedepohl H.H. ed., Springer, Berlin", vol. II-1.

SCHWARCZ H.P., HARMON R.S., THOMSON P. e FORD D.C. (1976) - *Stable isotopes studies of fluid inclusions in speleothems and their palaeoclimatic significance*. "Geochim. Cosmochim. Acta", *40*, 657-665.

SERVIZIO GEOLOGICO D'ITALIA (1969) - *Note Illustrative alla Carta Geologica d'Italia alla scala 1:100.000, fogli 56-57 (Torino-Vercelli)*.

STEFANON A. e COTECCHIA F. (1969) - *Prime notizie sulle caratteristiche di efflusso e sulle modalità di investigazione delle sorgenti subacquee ai fini di una loro captazione*. "La Ricerca Scientifica (C.N.R.), Quaderni", *58*, 165-195.

STEPHEN H. e T. (1933) - *Solubilities of inorganic and organic compounds*. Pergamon, Oxford, 365-367.

VITA FINZI C. (1969) - *The Mediterranean valleys. Geological changes in historical times*. Cambridge Un. Press.