QUATERNARY DEDOLOMITIZATION ALONG FRACTURE SYSTEMS IN A LATE TRIASSIC DOLOMITIZED PLATFORM (WESTERN SOUTHERN ALPS, ITALY)

¹P. Ronchi, ²F. Jadoul, and ¹R. Savino

¹ENI-Exploration & Production Division, Via Emilia 1, S.Donato Milanese. Italy ²Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Mangiagalli 34, Milano. Italy

ABSTRACT: The studied area belongs to a south vergent thrust and fold belt of the Southern Alps of central Lombardy where the norian Dolomia Principale crops out. This up to 2 km thick carbonate platform succession has been massively dolomitized from early to shallow burial diagenesis.

Dark grey, bedded dolostones (basal Dolomia Principale), outcropping along the both lower slopes of Iseo Lake (lower Camonica Valley), show a complex network of dedolomitized white-grey areas. The calcareous lenses show an irregular, elongated (up to few meters large) shape; they are usually located along fault-fracture systems and extending along the strata bedding. Two main fabrics have been recognized: the fabric A is formed by a reticulate of small fractures filled by calcite and surrounded by fine grained calcitized halos, the fabric B is associated to more intense fracturation process that locally gave rise to breccia fabric; moreover a ochre-reddish internal sediment is locally present in small cavities or as a breccia matrix, a huge speleothem-like cementation is associated to these dedolomitized fabric.

This study was aimed to reconstruct the dedolomitization process and to propose a relevant genetic model. The petrographic analyses, integrated using cathodoluminescence and electron scanning microscope allowed to find out that dedolomitization process is composed of a first phase of dolomite dissolution along permeable path ways, both at the macro and at the micro scale, followed by calcite precipitation in the pore spaces.

The negative δ^{18} O and δ^{13} C values of the calcite cements and the calcitic fraction of the dedolomitized fabrics suggest precipitation in presence of meteoric water derived fluids.

Radiometric absolute age determination $(^{230}\text{U}/^{234}\text{Th})$ indicates that calcite cements precipitated in the last 100000 years: age during which the area was subject to several advances and retreats of glacial tongues.

The field mapping, analytical data and the geomorphology of the areas where the dedolomitized patches are more frequent, in correspondence of a narrow passage of the lower Camonica valley, allowed us to infer that the dedolomitization developed during glacial-interglacial phases particularly active in the region during the Pleistocene. In particular we propose that the fracturation and the first phase of dedolomitization (fabric A) occurred during the glacial period, while extensive calcite precipitation and brecciation (fabric B) formed during the interglacial periods, dominated by a warm climate during which extensive soil cover and karst processes developed.

INTRODUCTION

The dedolomitization process has been described as replacement of dolomite by calcite at first by Lucia (1961). Subsequently it has been studied through staining technique (Evamy 1963) and it was recognised as the result of dolomite dissolution, followed by calcite precipitation (Mattavelli 1966). Since then, many dedolomitization case histories have been described, in a wide range of geologic setting and diagenetic environment. The process may occur in the deep burial environment (Budai et al. 1984; Woronik and Land 1985; Woo and Moore 1996), but the most common setting is related to near surface conditions: associated to ground water of meteoric origin just after deposition (Goldberg 1967; Jones et al. 1989; Canaveras et al. 1996), in schizohaline environment (Magaritz and Kafri 1981; Arenas et al. 1999) and as a result of fresh water weathering during post burial surface exposure (Al-Hashimi and Hamingway 1971; Chafetz 1972; James 1981; Wallace et al. 1991).

Geochemical studies proved that the dedolomitization process can occur at low temperature in presence of

Carbonates and Evaporites, v. 19, no. 1, 2004, p. 51-66.

understurated fresh waters (De Groot 1967), while other works pointed out that the presence of calcium-sulphaterich solution derived from evaporites dissolution helps the process providing Ca source (Al-Hashimi and Hamingway 1973). Nevertheless the dolomitization is also related to flushing of undersaturated fresh waters without evaporite dissolution being involved (Theriault and Hutcheon 1987). In carbonate aquifers dedolomitzation has been encountered both in presence or not of sulphate dissolution (Longmann and Mench 1978; Back et al. 1983). According to other studies (Frank 1981) a selective dedolomitization is confined in more soluble, Fe rich zones, of dolomite rombohedrons which are dissolved and replaced by calcite. The dedolomitization process has been described as the result of several processes of dolomite dissolution followed by calcite precipitation by Jones et al. 1989. Finally, in some cases, dedolomitization is regarded as a porosity enhancement process in the subsurface setting (Evamy 1967; Purser 1996).

This work presents the reconstruction of the dedolomitization process occurred in an Alpine valley (lower Camonica Valley, Iseo Lake) in exhumed dolomitic

formation, during the Quaternary. The proposed model points out that dedolomitization process is a surface process occurred in presence of meteoric derived waters and strictly associated to the presence of glacier: the alternated phases of advancing and retreat of the glacier on the slopes of the valley strait is proved to be a key factor for the fracture formation that allowed the undersaturated waters to flux and dissolve the dolomite. The following processes of extensive calcite precipitation are supposed to be associated to humid climate that alternated to the glacial phases.

METHODS

The distribution of the dedolomitized fabrics and the relationships between the fractures, cavities, cements and diagenetic calcite have been studied at first through field observations along both sides of Iseo Lake. A mesostructural survey, carried out at four sites, was focused on determining the geometric relationships between fractures, with or without dedolomitization, and bedding.

About 40 samples, representative of the unaltered dolomite rock, various dedolomitized fabrics, internal sediments and calcite cements have been studied through laboratories techniques.

Petrographic analyses have been carried out on polished thin sections, few of which stained with Alizarina-S, under optical normal polarised light and cathodoluminescence. The instrument used for the C.L. is a TECHNOSYN construction (model 8200 MK 2), voltage employed is generally 12 kV with 300-400 μ A Gun Current. Few thin sections and bulk samples have been examined using a Scanning Electron Microscope (SEM), model Leika



Figure 1. Location and geologic map of the studied area. The outcropping monocline Triassic series shows southward dipping beds. 1) Anisian to Carnian Formations, including S. Giovanni Bianco Formation, mixed siliciclastic and carbonate marginal marine deposits with gypsum lenses; 2) Castro Formation, lagoon limestone with intraformation carbonate breccias (Carnian); 3a) Dolomia Principale Lower Member, well bedded dark dolostones of a restricted basin (Norian); 3b) Dolomia Principale, massive dolostones of platform margin to peritidal carbonates(Norian); 4) Zorzino Limestone, thin bedded dark grey limestones of intraplatform basin (Norian); 5) Riva di Solto Shale, black shales with embedded limestone layers of anoxic basin (Norian); 6) Quaternary deposits; 7) Ceppo Unit, cemented carbonate breccia slope; 8) Thrust; 9) Fault; 10) Deep seated slope gravitational deformation; 11) Dedolomitization areas; Open fratures with dedolomitization. Note that dedolomitization is developed in correspondence of the strait.

Cambridge Stereoscan 360° with backscattered detector (bse).

The analysis of stable isotopes of carbon and oxygen has been made on all the fabrics and calcite cement sampled with an ultrasound micro core barrel. Few mg of carbonate (4-6 mg) are allowed to react with concentrated orthophosphoric acid at 25 °C for calcite and at 60 °C for dolomite. The CO₂ content is measured at the mass spectrometer and results are expressed in parts per thousand (delta units) compared to the PDB international standard (Pee Dee Belemnite formation).

Absolute age determination was done on a few samples of calcite cements using the ²³⁰Th/²³⁴U radiometric method (IFE, Norway). The samples were ground in an agate mortar, than they have been dissolved in 6 M HCl and electrolysed on a polished steel *planchette*. The samples deposited on the steel *planchettes* were, after been subjected to a-spectrometry, transferred with 6M HCl

to an ion-exchange column in order to get rid of Th and subsequent measurement of the ${}^{234}U/{}^{238}U$.

GEOLOGICAL SETTING

The studied area belongs to a south vergent thrust and fold belt ("Parautoctono" unit, Gaetani and Jadoul 1979; Jadoul and Rossi 1982) of the Southern Alps of central Lombardy, which is mainly composed of Triassic formations. The dedolomitization is observed in the Norian Dolomia Principale (Fig. 1), that is a thick carbonate platform succession (thickness up to 2 km), that has been massively dolomitized during an early to shallow burial diagenesis (Frisia and Wenk 1993; Frisia 1994). This formation is characterized by a Lower Member composed of subtidal dolostones which grades upward into massive, recrystallized dolostones rich in platform margin and slope facies (serpulid-microbial mounds)associate with amalgamated breccia wedges (Jadoul et a. 1992; Jadoul et al. 1994; Berra and Jadoul 1996; Cirilli et al. 1999).



Figure 2. A) Iseo lake eastern side, Dolomia Principale of Corna Trentapassi; B) The Iseo lake view from the south.

The Dolomia Principale overlays recrystallized and calcitised intraformational carbonate breccia unit (Castro Formation, Jadoul et al. 1991) and the late Carnian evaporites of the upper S. Giovanni Bianco Formation. At its top intraplatform basin limestone and shales are present (Zorzino Limestone and Riva di Solto Shales, Norian).

The dedolomitization only involves the Dolomia Principale Lower Member along both the slopes of Iseo Lake in correspondence of the lake narrowing of the Camonica Valley (between the Corna Trentapassi and the Monte Clemo, Figs. 1, 2). This mainly subtidal unit is characterized by thin bedded dark grey dolostones, up to 250 m thick, made of an association of laminated dolomitized calcsilities, calcarenites, locally with intraformational breccias, slumpings and scatterred microbialitic laminae, domal mounds. Strata dip south-west with high angle.

In the valley, during Quaternary, the Camuno Glacier tongue advanced and retreated several times. The lowermost Camonica valley is now occupied by the Iseo Lake. Between the last glacial phases in some areas of the western slope of the Iseo Lake thick continental fan breccia were deposited forming the Ceppo Unit (Nangeroni 1964). At the both sides of the Iseo Lake, in the area we observed deep seated gravitational slides and fractures that can be interpreted as related to the multiphase glaciar advances and retreats. Similar structures have been observed in alpine region and attributed to the glacial retreat (Panizza 1973; Forcella 1983).

DEDOLOMITE DISTRIBUTION

Areal Distribution

The dedolomitized areas are present in the outcrops of the Dolomia Principale facing northward, in correspondence to the lake narrowing present between the steep slopes of Monte Clemo (Fig. 1) and the Corna Trentapassi (Fig. 2); they are more widespread in the lower part of the outcrops from the lake level upward to three hundred meters; dedolomitized fabrics have never been detected at altitudes higher than 650-700 m (Iseo lake is at about 185 m s.l.). That altitude corresponds to the Pleistocene glacial terrace in the area (Corbari and Bini 2001).

Macroscale Facies Observation

The calcitized patches, characteried by a white-grey colour, are strictly related to fracture networks and their width ranges from few centimetres up to few meters on both sides of the fracture walls (Fig. 3); in these areas the calcitization can reach the 60% of the bulk volume. The fractures associated to dedolomitization may still be open or sealed by a thick (up to 5 cm) calcite cement characterised by a withish and honey/orange colour and a speleothem-like texture (Fig. 3 and 4E).

In Fig. 4 a schematic drawing and photographs gather the different features present in the dedolomitized area. The calcitization is stronger in the areas close to the fracture and vanishes away in both directions; the transition between dedolomitized and unaltered rock in the thin fractures is usually sharper than around the larger ones (Fig. 4A and B). Locally, in some large fractures, "pseudobreccia" bodies are present (Fig. 4 C): the angular clasts are made of dedolomitized micrite and are cemented by calcite. Ochre-reddish sediment, infiltrated between the clasts, is sometimes observed; locally, the same internal sediment has been found in small cavities associated to the larger dedolomitized fractures (Fig. 4 D). The sediment is made of thin plane horizontal laminae of fine grained calcsiltiteslutites, which sometimes contain small ostracods, suggesting a phreatic environment.

Some of the dedolomitized areas are overlain by a dolomitic breccia which forms large, lenticular and clinostratified fan debris on the lower slopes of the Monte Clemo and the Corna Trentapassi (Fig. 5). This breccia, called Ceppo Unit has been interpreted as an interglacial slope deposit ("Iseo Lake Ceppo" of Nangeroni 1964); the centimetric-decimetric angular dolomite clasts (deriving



Figure 3. Iseo lake western side, fractures with dedolomitized area (white-grey).

RONCHI, JADOUL, AND SAVINO



Figure 4. The drawing shows the main features associated to the dedolomitization, the photographs were taken on different outcrops at both lake sides. A) Dedolomitized fractures (whitish) on grey laminated Dolomia Principale; B) Fracture network with sharp dedolomitization boundaries (light grey); C) Dedolomitized breccia cemented by calcite, the clasts are made of calcitized micrite; D) Reddish laminated matrix filling a large dissolution pocket along dedolomitized fracture; E) Thick crusts of calcite cement in an open fracture with dedolomitized side walls. [below]

from the Dolomia Principale overlying outcrops) are often dedolomitized. The breccia is cemented by thick bladed isopacous speleothem-like calcite cements; locally the intergranular porosity is filled with yellowish silty clay internal sediments (Fig. 5A). The calcite cements shows typical alternation of several thin rims of withish and honey/ orange colour. The breccia associated to dedolomitization and the Ceppo Unit breccia exhibit similar fabrics; nevertheless the dedolomitized breccias locally show stress features, such as stylolites and small faults (fig. 5B and C); while any compressional evidence has never been found in the Ceppo Unit.

STRUCTURAL ANALYSIS

Data

The mesostructural analyses, performed on four sites (about 200 measures), considered the bedding planes, the dedolomitized and non dolomitized fractures (Fig. 6). The strata bedding has a dominant $110-120^{\circ}$ strike with 75-

 90° dip. Three main fracture sets are present: the most dominant set has a $110-120^{\circ}$ strike with subvertical dip; the second group has a 45° dip, and the third group as a 45° 50° strike and 40° dip. Both the dedolomitizaed and non dedolomitized fractures belong to these three groups.

Interpretation

Most part of the fractures associated to dedolomitization belongs to the 110-120° strike set which has a reconstructed NE oriented σ 3, a similar stress orientation is reported for the Messinian/Pliocene Alpine tectonic extension phase (Castellarin et al. 1992); nevertheless not all the these fractures and faults are dedolomitized, great part of them are sealed while dedolomitization is present only along open fractures. It is likely that these fractures, opened during the tectonic phase hve been re-opened afterwards, allowing the dedolomitizing fluids flow in. One of the most probable cause of this new opening event may be the tensional release due to the glacial retreat associated to gravitational deformation, as it is suggested by the



Figure 5. The drawing shows the relationships between the dedolomitized areas, associated to deep gravitational faults, and the Ceppo Unit breccia (quaternary continental slope fan); A) polished slab of Ceppo Unit Breccia: the Dolomia Principale clasts are cemented by calcite and the interparticle porosity is partially filled with reddish laminated internal sediment; B) polished slab of dedolomitized breccia (fabric B2) cemented by calcite; C) the same sample of B shows a fault plane cutting the latest calcite cements.



Figure 6. Rose diagrams of the bedding planes and fractures. Note that the fractures with dedolomitization show the same orientation of the not dedolomitized ones; this suggests that a the dedolomitization process acted only along the fractures that underwent an extension which allowed water flux.

orientation of the fractures in the area parallel to the lake slope (Fig. 1).

PETROGRAPHY

Dedolomitized Fabrics

Petrographic observations on several "dedolomite" samples, collected at different distance from the calcite fractures and with various macroscopic features, allowed to group few main fabrics characterised by similar macro and microfacies (Fig. 7 and 8). Along the fracture planes the simpler fabric is always observed and only locally it is accompanied by a more complex fabric that represents the evolution of the first one. Here below, the petrographic description of each fabric, defined through optical microscopy observation is provided (Fig. 8).

Fabric A.-- It is the simplest fabric corresponding to the

first stage of the process not involved by the next steps. The original texture, made of dolomite mudstones and wackestones, shows a network of thin (mm wide) fractures filled with calcite cement. Under cathodoluminescence (CL) the different colours of the calcite cements allow to distinguish at least two precipitation events: the first is orange-yellow while the second one is not luminescent (Fig. 7A). The dolomite bulk rock is partially dedolomitized in the areas close to the fracture planes: the texture is detectable under C.L. or SEM observation, being formed by small calcite crystals precipitated in intercrystalline porosity of the fine grained dolomite. In C.L. this calcite cement may be yellow or not luminescent, depending on which phase it belongs to (Fig. 7A, B).

Fabric B.-- The fabric A, in areas close to the main fractures can have been subjected to another fracturation event followed by calcite cementation; locally a breccia is formed, being completely cemented by several calcite



Figure 7. Photomicrographs of dedolomitized fabrics. A) Fabric A, dedolomitized micrite showing two sets of microfractures, the first set is cemented by calcite with orange colour under CL (A'), and it is cut by a second fracture filled of not luminescent calcite; B) Fabric A, deeply dedolomitized matrix with multiphase dissolution and calcite cementatation; note in B' (CL image) the dolomite rhomboedron mold that is filled at first by first stage yellow calcite and then by the second black one; C) Fabric B, microbreccia made of clasts of calcite cements belonging to the second fracturation event (not luminescent, in C') in a dedolomitized fine grained orange matrix; D) close up of a calcite cement formed by several layers of calcite cement separated by micrite internal sediment; E) Fabric B breccia showing clasts compacted along stylolites. Scale bar is about 1 mm.

DEDOLOMITIZATION, SUBAERIAL DIAGENESIS



Figure 8. Dedolomitization process main phases at the microscale. Fabric A underwent two fracturation phases with infilling of different calcite cements (first luminescent and the second not luminescent in CL); fabric B represents the brecciation of fabric A and calcite cementation; fabric B1 is made of reworking of fabric B with internal sediment infilling; fabric B2 shows compaction and presso-solution between the clasts.

rims (Fig. 5B). This thick calcite rim is made of several layers of orange/beige bladed calcite, separated by thin laminae of micritic sediment (Fig. 7D); the calcite is not luminescent under CL. The thickness of the calcite cement is about a few millimeters in the breccia and reaches few centimeters when it grows along large fractures (Fig. 4E). These calcite rims have a spelothem aspect similar to that found cementing the Ceppo Unit breccia. The mono-phase fluid inclusions observed in the lare calcites and the low T° ice suggest that these cements precipitated at relatively low temperature (minor than about 50° C) from fresh water derived fluids (E. Imperial, Pavia University, pers. comm.).

Fabric B1.-- Movements along the fractures or collapses may have caused a brecciation of the fabric B, locally accompanied by infiltration of internal sediment: the size ranges from few millimeters up to few tens of centimetres. In the largest pockets the sediments consist of thin laminae made of fine debris of calcite and dolomite micro-fragments containing variable amount of organic matter, shale and Fe oxides which give the typical ochre-reddish colour. Under CL these sediments are not luminescent. The lamination and the presence of few ostracods suggest a phreatic environment. The badly preserved ostracods do not give any stratigraphic or precise environmental indication; the organic fraction is oxidised and no determinable pollen specimens have been observed (Biffi-ENI pers. comm.). It is inferred that the reddish clay may had come from reworked palaeosoils.

Fabric B2.-- This facies is the result of compaction and/or fracture of the fabric B: locally stylolitization of the clasts boundary (Fig. 7E) proves a compressive overprint on some sample. In other cases the calcite breccia can be cut by small faults (Fig. 5C).

SEM Observation

*Data.--*The Scanning Electron Microprobe (SEM) observations on polished thin sections and rough samples allowed to reconstruct the dedolomitization process at the

microscale. The calcitized areas close to the fractures and the clasts of breccia usually show a micritic texture and only the whitish colour and the HCl or Alizarina staining allow to distinguish the dedolomitized zones in outcrop. Even under microscope the detection of the dedolomitized structure, is not simple: an aid is provided by the SEM analyses on thin sections. In the SEM images of Fig. 9, where the grey is dolomite, white is calcite and black is pore space, the mineralogic composition of the areas is well detectable. The calcitization comprises the calcite precipitation in the solution enlarged intercrystalline pores and in the crystal boundaries; the process is more pervasive in the fine grained micrite than in the coarse crystalline calcite cement (Fig 9B and C).

In order to better understand the dedolomitization process, a thin section of fabric A has been examined under SEM: the area is about 1 cm wide (Fig. 10) and three images were taken at progressive distance from a calcitized microfracture (A,B,C). An image analysis software allowed to measure the percentage areas (%) of the three components: 1) residual porosity, 2) calcite, 3) dolomite; while the sum of calcite and residual porosity represents the porosity developed during dissolution of the dolomite, here called "dissolution porosity".

In the fracture nearest area (A) the highest "dissolution porosity" has been measured (22,3%) but it is almost filled with calcite (20,4%); in the next area (B) the "dissolution porosity" decreases (15,4%) but it is less cemented (12%)and in the farthest area (C) the "dissolution porosity" is low (5,4%) and it is hardly reached by calcite cementation (0,5%).

Interpretation.-- This SEM analysis shows that the dedolomitization process acted in the same way both at the large and the micro scale: the dedolomitizing fluids percolated and permeated the rock along permeable ways represented by large fractures, small fractures, microfractures and crystal boundaries. The process proves to be represented by two steps: the dolomite dissolution phase and the calcite precipitation phase. The SEM observations demonstrated that the dissolution proceeded from the main fracture into the rock, along minor discontinuities as the microfractures and the crystal boundaries, the maximum dissolution was reached in the



Figure 9. A) Thin section photomicrograph showing a mudstone with cemented vug and fracture, from the polarized light image it is difficult to detect calcite and dolomite; B) Close up of A under SEM evidences the deeply dedolomitized micrite (mottled grey: white is calcite, grey is dolomite) and the different filling of the pore spaces: the vug was cemented by dolomite (grey), the fracture filling is calcite (white). The dedolomitization is more pervasve in the fine grained dolomite than in the coarse one (cement). C) A SEM closer view of image B shows the calcite cement which filled the intercrystalline space. D) A closer view of C under CL: dolomite is orange, calcite cement is not luminescent.

DEDOLOMITIZATION, SUBAERIAL DIAGENESIS



IMAGE ANALYSIS DATA OF THE AREAS

S.E.M. IMAGES OF THE SELECTED AREAS

Figure 10. Polished thin section SEM images of dedolomitized areas at different distances from the calcite filled fracture. Note the decrease of calcite cementation (white) and dissolution (sum of remnant porosity and calcite) from area A to area C. Black is pore space grey is dolomite, white is calcite.

area next to the main fracture vanishing away into the host rock. The calcite precipitation followed the same pathway, filling the dissolution porosity. These two processes needed peculiar fluids capable of dolomite dissolution and calcite precipitation; from the petrographic observation it is still uncertain if dolomite dissolution and calcite precipitation, were caused by an unique fluid or two different ones that fluxed the rock in different phases.

Interpreted Dedolomitization Phases

The field and petrographic observations allowed us to reconstruct the main phases which caused the dedolomitization. Two main different processes seem to have acted in the dedolomitized areas: the first one caused the pervasive dedolomitization along the fractures and the second one is responsible of the strong calcite cementation in the breccias and in the main open fractures.

PHASE 1 .-- At first the dolomite host rock was fractured and the fractures at different scale acted as permeable ways to the flux of undersaturated water. At the microscale these fluids enhanced intercrystalline porosity of the dolomite matrix on the both sides of the microfracture plane, extending for few millimeters from it. The influx of different fluids or the reached saturation condition with respect to calcite, caused calcite precipitation in the intercrystalline porosity and along the fractures. The result of the process in a volume of rock intensively fracturated, was a almost completely calcitized microspar. This process may have repeated a few times as it is shown by the different sets of micro and macrofractures that intersect each other and are filled with calcite of different luminescence (bright orange and not luminescent). The product of this stage of dedolomitization is the fabric A.

PHASE 2.-- Locally the process proceeded, and a new fracturation event enlarged the previous fractures and

gave rise to breccias. This phase was accompanied by speleothem-like calcite cements and infiltration of reddish sediment. Various brecciation events insisted on the same areas giving rise to complex breccia features containing clasts made of calcite cements. Locally compaction produced pressure-solution structures (stylolites) between the clasts of the breccia and few small faults that cut the calcite crusts. This process produced the fabric B, B1 and B2. The last calcite precipitation phase is that responsible of the cementation of the Ceppo Unit brecia, which consists of a few centimetres thick speleothem-like crusts never followed by compressional stress: it is likely that one of the speleothem-like rim cements present along the open fractures belonged to this last precipitation phase.

GEOCHEMISTRY

Stable Isotopes Analyses

Data.-- Oxygen and carbon stable isotopes analyses have been done on representative samples of the different dedolomitized fabrics, on few bulk samples of unaltered Dolomia Principale and on few calcite cements belonging to the underlying Castro Fm and the overlying pleistocenic Ceppo continental slope breccias (Fig. 11).

The unaltered Dolomia Principale bulk rock shows positive δ^{13} C (+0.5 to 3.5 ‰) values related to the marine derived dolomitizing fluids; only two serpulid bafflestone samples, that underwent a fresh water overprint in the early diagenetic phase, shows slightly negative carbon values. On the whole the Dolomia Principale isotopic values are consistent with those reported by authors in the area (Jadoul et al. 1995; Frisia 1994; Iannace and Frisia 1994); a shift toward more depleted δ^{18} O values may be related to water/rock interaction during burial or in presence of hydrothermal fluids (Frisia and Wenk 1994).



Figure 11. Stable isotopes diagram. The values distribution field of Dolomia Principale shifts towards more depleted values in the dedolomitized sample (more negative $\delta^{13}C$ and $\delta^{18}O$ values). The most depleted values belongs to the late stages of calcitization events and are similar to the Ceppo Unit cements and late calcite cements present in the Castro Formation. These values may indicate the isotopic signature of the quaternary fresh water.

The dedolomitized fabrics show altered isotopic signatures with a shift of the δ^{13} C toward more and more depleted values in relation to the increase of calcitization (from a A to B): the most negative carbon values (δ^{13} C about -5 ‰) belong to the last calcite cement and internal sediment, which represent the last phase of the dedolomitization. The δ^{18} O show a similar decrease trend reaching values between -7 and -8 ‰.

The double values referred to the each dolomitic limestone or calcareous dolomite result from two sample preparations, in order to extract CO₂ from calcite and dolomite.

Interpretation.-- The presented isotopic values suggest that dolomite maintains its original signature, similar to that of the unaltered Dolomia Principale; while calcite records the isotopic signature of the dedolomitizing fluids. Even if some admixture phenomena may have occurred between the dolomite and calcite, the very different field of values allows us to believe that the depletion trend of isotopes values are mainly due to the diagenetic overprint. In the diagram (Fig. 11) the oxygen and carbon values pattern indicates alteration and equilibration along the "meteoric calcite line" (Lohman 1988). On the whole, the stable isotopic diagram shows a pattern typical of a carbonate which underwent a subaerial diagenesis (Allan and Matthews 1982).

In particular it has to be highlighted that the isotopic values of the bladed calcite cements, the internal sediments of the dedolomitized breccia and the calcite cements of the Ceppo Unit have the same distribution field. Being the Ceppo cements undoubtedly precipitated at surface conditions during late Pleistocene, it can be safely stated that the $\delta^{18}O$ negative values (-7 to -8 %) reflect the meteoric water signature. In this context, the depleted oxygen values of calcite cements and calcitized fabrics of the dedolomitized areas can be related to an original fluid signature and not to a "high temperature effect". In conclusion the isotopic values of the examined fabrics indicate a surface diagenetic environment in presence of meteoric derived waters (James and Choquette 1984; Moore 1987). These isotopic data agree with the indication coming from the fluid inclusion analyses that suggest poor salted cool precipitation fluids.

Radiometric Age Determination

On two samples of thin calcite cements of fabric A, the

Table 1.

Sample	A	B	C D		D/A	Age, t
	238U	234Th	²³⁴ Th+ ²³⁴ U	²³⁶ Th calculated	²³⁶ Th/ ²³⁴ U	1000 years
1	207+-14	56+-9	215+-15	64+-22	0.31+-0.11	40+-12
2	150+-12	34+-6	176+-13	60+-19	0.40+-0.13	55+-15

Table 2.

Sample	U ppm	²³⁴ U/ ²³⁴ U	²⁵⁶ Tb/ ²⁵⁴ U	²⁵⁶ Th/ ²³² Th	(²³⁴ U/ ²³⁶ U)t=0
3	0,184+- 0.002	1,029+-0,010	1,798+-0,218	12+-6	

absolute age determination has been done using the ²³⁰Th/ ²³⁴U radiometric method (Faure 1986) which gives good results for a time span of about 350.000 years BP. The data summarised in the following table (Table 1) : the results from the a-spectrometry area are too low, which makes it difficult to get an acceptable error for age determination. We are near to the detection limit and it would have been preferable with about 5-10 times higher U-Th concentrations in order to get more accurate ages.

The following formula (Faure 1986) is used for the age determination:

 $D/A = 1 - e^{-\lambda 230t}$ or t= $-1/\lambda_{230} ln (-D/A)$

Where

D = counts of ²³⁸U (=²³⁴U) B = counts of ²³⁰Th (24%) and trace amounts of ²³⁴U C = counts of ²³⁰Th (76%) and trace amounts of ²³⁴U (100%) D = calculated counts for ²³⁰Th = B+C-A $\lambda_{230} = 9,22 \times 10^{-6}$ year ⁻¹ t = age, year In the samples the ²³⁴U/²³⁸U ratio equals 1.

In spite of the scarce quality, the data even if not indicating a precise time interval, suggest a relative recent time interval for the precipitation of the fabric A calcite, compatible with a Late Pleistocene, glacial period.

The latest calcite thick bladed calcite (fabric B) present in fracture, has been analysed through the same method (Quinif pers. com.) and despite the large amount of rock sample, it has been impossible to obtain an age determination, in fact the 230 Th/ 234 U is greater than 1 as shown in the following table (Table 2).

This could be explained in two different ways: contamination by detritic elements (clays) or colloïds (iron oxydes,...), or the geochemical system has been opened open. Because the isotopic ration ²³⁰Th/²³²Th is a mean values, the second explanation is more likely. On the whole the age determination data suggest that the last phases of dedolomitzation process, corresponding to the last calcite crusts (fabric B), occurred in a period not older than Late Pleistocene and occurred therefore in a time interval when the area was subject to the last advances and retreats of the Camuno Glacier.

DISCUSSION

The genetic interpretation of the dedolomitization process, recognised in the Dolomia Principale of the Iseo Lake takes into account different kinds of considerations, ranging from the petrographic and geochemical to geomorphologic ones.

Previous studies have shown that dedolomitization occurred in very different environments, ranging from subsurfacedeep burial to subaerial weathering. Therefore, we have to detect which was the main environment of the studied dedolomitization before proceeding.

The stable isotopic analyses of the dedolomitized fabrics and calcite cements, compared with those of the Ceppo Unit breccia cements, suggest that the process occurred at surface condition in presence of meteoric derived waters; this is confirmed by the fluid inclusion data whose characteristics allow us to exclude a hydrothermal or burial environment for the process.

The dedolomitized patches, confined on the slopes of the Camonica Valley in correspondence to a narrowing between the dolomitic massifs of Corna Trentapassi to the east and Monte Clemo to the west (Fig. 2), suggest that the morphology of the valley had a key role leading the process. The dedolomization process was observed along a bend comprised between the lake level up to the altitude of the Pleistocene glacial terrace (about 650-700 m s.l.) infer that the glacier presence may have had some influence in triggering the dedolomitization.

The absolute age determination $(^{230}Th/^{234}U)$, even if not precise, suggests a very recent age for the calcite cements

(Late Quaternary, younger than 100.000 ybp) compatible with the last glaciations which involved the Southem Alps region.

All these data support us to interpret this dedolomitization as a surface process occurred when the Camonica Valley glaciers advanced and retreated several times in the last 100.000 years.

As reconstructed through the field and petrographic observations, the dedolomitization process is composed of two phases: the first one was responsible of the fracture opening, dolomite dissolution and minor calcite precipitation, while during the second one large quantities of calcite cements precipitated in the breccia and along the open fractures, and reddish internal sediments percolated in fractures and breccia inteparticle pore spaces.

The first phase (fabric A) required the formation of the fracture network percolated by a large quantity of dolomite undersaturated waters in order to produce the dolomite dissolution and the calcite precipitation; we interpret that these processes occurred during the glacial phase, when the two conditions were present (Fig. 12A). In this period the southward glacier flow, along the Camonica Valley, was obstructed in correspondence to the strait between M.te Clemo and Coma Trentapassi, this determined compression on the valley slopes causing the formation of fractures which allowed a huge amount of glacial melting waters to stream in the side rock. We propose that the dolomite undersaturated melting waters caused the dissolution along fractures, microfractures and crystal boundaries and precipitated the blocky calcite observed in fabric A. The calcite cements of fabric A show low $\delta^{13}C$ and $\delta^{18}O$ values that agree with precipitation from fresh water (Allan and Matthews 1982) and, even if major quantities of calcite are usually coupled with warm climate, subglacial calcite and aragonite cements have been found at the base of glacier sheets ("subglacial calcite" F. Jadoul and M. Mutti, pers. comm.).

The second phase of dedolomitization (fabric B), with its speleothem-like calcite cements and reddish internal sediments shows strong petrographic and geochemical similarities with the calcites and internal sediments found in the Ceppo Unit (Figs. 5 and 11). This fact allows us to suppose that the two phenomena developed during analogue environmental conditions, which, for the Ceppo Unit, are referred to the interglacial phase (Nangeroni 1964). During periods of glacier retreats, characterized by warmer and more humid environmental conditions, with the development of soil covers, the main phase of dedolomitization (calcitization) occurred (Fig. 12 B). The lack of the ice pressure along the slopes of Iseo Lake caused the re-opening of the joints formed during the glacial compression phase and the fractures and faults related to the recent Alpine tectonic phase (Castellarin et al. 1992);

to the same process we refer the activation of deep seated gravitational deformations on the dolomitic Trentapassi-M. Clemo slopes, with formation of landslides (Fig. 12B). Along slopes the accumulation of alluvial dolomitic breccias of the Ceppo Unit occurred. The ground water system, developed in a humid warmer environment, may have caused the precipitation of speleothem-like calcite crusts typical of the fabric B and the Ceppo Unit cements and found in the open, dedolomitization related, fractures. The reddish internal sediment found in both in the Ceppo Unit and in the dissolution pockets and breccia, associated to fabric B, can be explained as due to percolation of mud reworked from palaeosoils that may have formed in warm and humid climatic condition on the Dolomia Principale carbonate massif; the formation of a vegetation cover and pedogenic alteration of carbonate substratum in fact may account for the isotopic values of the speleothemlike fracture calcite cements, red internal sediment and calcite of fabric B (Fig. 11). The occurrence of ostracods in the reddish internal sediment account for the presence in the area of ephemeral ponds or lakes. The presence of fractures and small faults cutting the cements of the fabric B (Fig. 5) indicates that compression phases occurred after this interglacial phase: this suggests that the phenomenon probably repeated various times.

CONCLUSION

The discussed data, collected on the dedolomitized patches of the Dolornia Pincipale along the Iseo Lake, allow us to propose a peculiar genetic model that involves the presence of the multiphase advances and retreats of the Pleistocene Camuno glacier in the area during the Quaternary. The morphology of the valley in the area is one of the main causes that allowed the glacier to be one of the triggering factors of the extensive dedolomitization.

During glacial periods the presence of the straight between Monte Clemo and Corna Trentapassi forced the glacier into a gorge causing strong pressure along the slopes. The glacier pressure generated some of the fractures in the Dolomia Principale and provided the huge quantity of dolomite- undersaturated melting waters. During this phase the fabric A is supposed to be formed with its fine reticulate of dedolomitized fractures.

During the interglacial periods the sudden lack of the glacier strong pressure along the slopes determined reopening of some of the fractures and caused the dccp seated gravitational deformation and some landslides breccia; the Ceppo Unit deposited along the slopes. The humid and warm climate gave rise to the soils coverings and karst processes that were responsible of the extensive calcite precipitation of the second dedolomitization phase (fabric B).

The glacial and interglacial environments alternated few



Glacial phase (Fabric A formation)

Fracturation, due to the glacler pressure in the strait between Corna Trentapassi and Monte Clemo. The glacial melting waters flow into the open fractures causing first phases of dedolomitization (dolomite dissolution and calcite precipitation).



Interglacial phase (Fabric B formation)

Activation of deep seated gravitational deformations and fractures opening in the dolomitic Trenta Passi-M. Clemo slopes with landslides and alluvial dolomitic breccias (Ceppo Unit). The last dedolomitization phase occurs with calcite cementation in the dolomitic breccias and in open fractures. Pedogenic alteration of carbonate substratum and soil is remobilized into fractures and dissolution pockets. Lacustrine deposits may develop in ephemeral lakes.

Figure 12. Dedolomitization process model.

times during the Quaternary: the restoration of the glacier compression in the gorge area (last quaternary glaciation phase) may has been responsible of the compaction features observed on some dedolomitized breccia (fabric Bl and B2).

The fact that compression features have not ever found in the Ceppo breccia suggests that dedolomitization process started before the Ceppo Formation deposition in the Iseo Lake area.

The calcite cementation in the Ceppo Unit represents the most recent calcitization processes, which includes the precipitation of thick bladed calcite cements in veins of the Dolomia Principale (even in areas without dedolomitization) and in the intraformational carbonate breccias of the Castro Formation facing the Iseo Lake.

AKNOWLEDGMENTS

We are grateful to ENI people that helped us in this work: T. Ricchiuto provided the stable isotopes analyses, C. Toscano helped us in collecting and A. Bersani and I.P. Van Dijk in elaborating structural data. We also thank G. Aberg (IFE, Norway) and Quinif (Faculté Polytechnique de Mons, Belgique) who provided the radiometric age determination. Many thanks are due to S. Frisia for helpful discussions.

REFERENCES

- ALLAN, J.R. and MATTHEWS, R.K., 1982, Isotope signatures of meteoric diagenesis: *Sedimentology*, v. 29, p. 709-817.
- AL HASHIMI, W.S. and HEMINGWAY, J.E., 1973, Recent dedolomitization and the origin of the rusty crusts of the Northumberland: *Journal of Sedimentary Petrology*, v. 43, p. 82-91.
- ARENAS, C., ALONSO, A.M., and PARDO, G., 1999, Dedolomitization and other early diagenetic processes in Miocene lacustrine deposits, Ebro Basin (Spain): *Sedimentary Geology*, v. 125, p. 23-45.
- BACK, W., HANSHAW, B.B., PLUMMER L.N., RAHN, P.H. RIGHTMIRE, C.T., and RUBIN, M., 1983, Process and rate of dedolomitization: mass transfer and ¹⁴C dating in a regional carbonate aquifer: *Geological Society of America Bulletin*, v. 94, p. 1415-1429.
- BERRA, F. and JADOUL, F., 1996, Norian Serpulid and Microbial Bioconstructions: Implications for the Platform Evolution in the Lombardy Basin (Southern Alps, Italy): *Facies*, v. 35, p. 143-162.
- BUDAY, J.M., LOMAHN, K.C, and OWEN, R.M., 1984, Burial dedolomite in the Mississippian Madison Limestone, Wyoming and Utah Thrust belt: *Journal Sedimentary Petrology*, v. 54, p. 276-288.
- CANAVERAS, J.C., SANCHEZ-MARAL, S., CALVO, J.P., HOYOS, M., and ORDONEZ, S., 1996. Dedolomites associated with karstification. An example of early dedolomitization in lacustrine sequences from the Tertiary Madrid Basin, Central Spain: *Carbonates and Evaporites*, v. 11, no. 1, p. 85-103.
- CARTA EOLOGICA DI PERGAMO SCALA 1:50000, NOTE

ILLUSTRATIVE, 2000.

- CASTELLARIN, A, CANTELLI, L., FESCE, A.M., MERCIER, J., PICOTTI, V., PINI G.A., PROSSER, G., and SELLI, L., 1992, Alpine compressional lectonics in the Southern Alps. Relationships with the N-Apennines: *Annales Tectonicae*, v. 6, p. 62-94, Firenze.
- CHAFETZ, H.S., 1972, Surface diagenesis of limestone: Journal of Sedimentary Petroolgy, v. 42, p. 325-329.
- CIRILLI, S., IANNACE, A., and ZAMPARELI, V., 1999, Microbial-serpulid build-ups in the Norian-Rhactian of the western Mediterranean area: ecological response of shelf margin communities to stressed environments: *Terra Nova*, v. 11, p. 195-202.
- CORBARI D. and BINI A., 2001, La cartografia dei depositi quaternari nel progetto CARG della Regione Lombardia : il caso dell'Anfiteatro Sebino (Lago d'Iseo, BS). Poster FIST, GEOITALIA.
- DE GROOT, K., 1967, Experimental dedolomitization: Journal of Sedimentary Petrology, v. 37, no. 4, p. 1216-1220.
- EVAMY, B.D.,1963, The application of a chemical staining technique to a study of dedolomitization: *Sedimentology*, v. 2, p. 164-170.
- EVAMY, B.D., 1967, Dedolomitization and the development of rhombohedral pores in limestones (Upper Cambrian), Southeast Missouri: *Journal of Sedimentary Petrology*, v. 5, p. 7-17.
- FAURE, G., 1986, Principles of Isotope Geology, John Wiley & Sons, Inc. New York/Chichester/Toronto/Singapore, 335 p.
- FORCELLA F., 1983, Un eccezionale esempio di tettonica gravitativa di versante: il sakung sviluppato tra il M. Padrioe e il Varadega, Alpi Centralli , Italia: *Rivista Museo Scienze Naturali di Bergamo*, v. 5, p. 11-23.
- FRANK, J.R., 1981, Dedolomitization in the Taum Sauk Limestone (Upper Cambrian), Southeast Missouri: Journal of Sedimentary Petrology, v. 51, no. 1, p. 7-18.
- FRISIA, S., 1994, Mechanisms of complete dolomitization in a carbonate shelf: comparison between the Norian Dolomia Principale (Italy) and the Holocene of Abu Dhabi Sabkha. Special Publication of International Association Sedimentologists, v. 21, p. 55-74.
- FRISIA, S. and WENK, R., 1994, TEM and SEM study of pervasive, multi-stepdolomitization of the Upper Triassic Dolomia Principale northern Italy: *Journal of Sedimentary Petrology*, v. 63, no. 6, p. 1049-1058.
- GAETANI, M. and JADOUL, F., 1979, Controllo ancestrale sui principali linementi strutturali delle Preali Lombarde centrali: *Rendiconti Società Geologica Italiana*, v. 10, p. 21-24, Roma.
- GOLDBERG, M., 1967, Supratidal dolomitization and dedolomitization in Jurassic rocks of Hamakhtesh Haqatan, Israel: Journal of Sedimentary Petrology, v. 37, no. 3, p. 760-773.
- IANNACE, A. and FRISIA, S., 1994, Changing dolomitization styles from Norian to Rhaetian in the Southern Tethys realm. Special Publication of International Association Sedimentologists, v. 21, p. 75-89.
- JADOUL, F., BERRA, F., FRISIA, S., RICCHIUTO, T., and RONCHI, P., 1992, Stratigraphy, paleogeography and genetic model of Late Carnian carboante breccias (Castro Formation, Lombardy, Italy): *Rivista Italiana Paleontologia e Stratigrafia*, v. 97, p. 355-392.
- JADOUL, F., BERRA, F. and FRISIA, S., 1992, Stratigraphic and paleogeographic evolution of a carbonate platform in

an extensional tectonic regime: the example of the Dolomia Principale in Lombardy: *Rivista Italiana Paleontologia e Stratigrafia*, v. 93, p. 29-44.

- JADOUL, F., MASETTI, D., CIRILLI, S., BERRA, F., CLAPS, M. and FRISIA, S., 1994, Norian_Rhaetian Stratigraphy and Paleogeographic evolution of the Lombardy Basin (Bergamasc Alps). *In* G. Carannante and R. Tonielli, eds., IAS 15th Regional meeting, Ischia, Fieldtrip Guidebook, Excursion B1, p. 3-38.
- JADOUL, F. and ROSSI, P.M., 1982, Evoluzione paleogeograficostruturale e vulcanismo triassico nella Lombardia centrooccidentale. *In* A. Castellarin, ed., Guida alla geologia del Sudalpino centro-occidentale. Guide geologiche regionali, Società geologica Italiana, p. 143-155.
- JAMES, R.F., 1981, Dedolomitization in the Taum Sauk limestone (Upper Cambrian), Southeast Missouri: *Journal* of Sedimentary Petrology, v. 51, p. 7-18.
- JAMES, N.P. and CHOQUETTE, P.W., 1984, Diagenesis 9. Limestones – the meteoric diagenetic environment: *Geoscience Canada*, v. 11, p. 161-194.
- JONES, B., PLEYDELL, S.M., KWOK CHOING, and LONGSTAFFE, F.J., 1989. Formation of poikilotopic calcite-dolomite fabric in the Oligocene-Miocene Bluff Fm of Ground Cayman British West Indies: Bulletin of Canadian Petroleum Geology, v. 3, p. 255-265.
- LOHMANN, K.C., 1988, Geochemical patterns of meteoric diagenetic systems and their applications to studies of paleokarst, *in* N.P. James and P.W. Choquette, eds., Paleokarst. Springer-Verlag, New York, p. 58-80.
- LONGMAN, M.W. and MENCH, P.A., 1978, Diagenesis of cretaceous limestones in the Edwards aquifer system of South-central Texas: a scanning electron microscope study: *Sedimentary Geology*, v. 21, p. 241-276.
- LUCIA, F.J., 1961, Dedolomitization in the Tansill (Permian) Formation: *Geological Society of America Bulletin*, v. 72, p. 1107-1110.
- MAGARITZ, M. and KAFRI, U., 1981, Stable Isotope and Sr/Ca evidence of diagenetic dedolomitization in a schizohaline environment: Cenomanian of Northern Israel: *Sedimentary Geology*, v. 28, p. 29-41.

- MATTAVELLI, L., 1966, Ossevazioni petrografiche sulla sostituzione della dolomite con la calcite (dedolomitizzazione) in alcune facies carbonate italiane: *Atti della Società Italiana di Scienze Naturali*, v. CV, Fasc. III., p. 294-316.
- MOORE, C.H., 1989, Carbonate diagenesis and porosity: Development in Sedimentology, no. 46, Elsevier, Amsterdam, 338 p.
- NANGERONI, 1964, La geomorfologia della regione del Sebino. Proceedings of XIX Congresso Geografico Italiano, Como.
- PANIZZA, M., 1973, Glacio-pressure implications in the production of landslides in the dolomitic area: *Geologia Applicata Idrogeologia*, v. 8, p. 289-297.
- PURSER, B.H., 1996, Dedolomite porosity and reservoir propetries of Middle Jurassic Carbonates in the Paris Basin, France: *Carbonates and Evaporites*, v. 11, no. 1, p. 343-355.
- THERIAULT, F. and HUTCHEON, I., 1987, Dolomitization and calcitization of Devonian Grosmont Formation, Northern Alberta: *Journal of Sedimentary Petrology*, v. 57, no. 6, p.955-966.
- WALLACE, M.W., KERANS, C., PLAYFORD, P.E., and MCMANUS, A., 1991, Burial diagenesis in the Upper Devonian Reef Complexes of the Geikie Gorge Region, Canning Basin, Western Australia: American Association of Petroleum Geologists Bulletin. v. 75, no. 6, p.1018-1038.
- WOO, K.S. and MOORE, C.H., 1996, Burial dolomitization and dedolomitization of the Late Cambrian Wagok Formation, Yeongweol, Korea: *Carbonates and Evaporites*, v. 11, no. 2, p. 104-112.
- WORONICK, R.E. and LAND, L.S., 1985, Late Burial Diagenesis, lower Cretaceous Pearsall and lower Glen Rose Fms, South Texas, *in* P.M. Harris and N. Schneiderman, eds., Carbonate Cements. SEPM Special Publication, v. 36, p. 265-276.