Hydrothermal dolomitization of Jurassic-Cretaceous limestones in the Southern Alps (Italy) its relationship with tectonics and volcanism

Author(s):
Spencer-Cervato, Cinzia

Publication Date:
1990

Permanent Link:
https://doi.org/10.3929/ethz-a-000592511

Rights / License:
In Copyright - Non-Commercial Use Permitted
HYDROTHERMAL DOLomitization of JurassIC-Cretaceous LIMESTones in the SOuThern Alps (ItAlY): Its reLationship with Tectonics and Volcanism.

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY, ZURICH
for the degree of
Doctor of Natural Science

Presented by:
Cinzia Spencer-Cervato
Dottore in Scienze Geologiche
University of Padova, Italy

Born: 29 March, 1961
in Padova (Italy)

accepted by recommendation of:

Prof. Dr. Kenneth J. Hsü, Referee
PD Dr. Helmut Weissert, Co-Referee
Dr. Günther Kahr, Co-Referee

1990
To my parents,
whose support never failed.
Thank you

Ai miei genitori,
il cui sostegno non mi è mai venuto a mancare.
Grazie
Abstract

In the Central Southern Alps (Feltre, Verona - Italy), a 750 m thick interval of Jurassic and Cretaceous pelagic limestones shows post-depositional partial brecciation and dolomitization. The overlying 500 m thick Tertiary sedimentary sequence is unaffected. Through the Paleogene, mostly submarine, mafic volcanism has been documented in the area. Small-scale extensional features were observed in the limestone near the contact with the dolomitized breccias. Their orientations measured in the field correspond to the tectonic framework of the area and give evidence for the contemporaneousness of the volcanic activity and the brecciation. The distribution and petrologic characteristics of the basalts, combined with the orientation of the extensional features observed in the field, allow a paleotectonic reconstruction. This tectonic scenario can be viewed as a back-arc extension, an eastward prolongation of the spreading that divided Southern France from the Sardinia-Corsica-Calabria block, generating the Ligurian-balearic basin in the Late Oligocene.

The dolomite is fine-grained to sucrosic, with a microamygdaloidal porosity, partially filled with ankerite and calcite. The matrix shows a homogeneous, orange-red cathodoluminescence, indicating a single phase of iron-poor dolomite. The carbonate fraction consists of more than 90% dolomite. The dolomite is almost stoichiometric (Ca$_{0.98}$Mg$_{0.4}$ to Ca$_{0.93}$Mg$_{0.95}$). The $\delta^{13}$C values of the dolomite are less than 1‰ more negative than the unaffected limestone. The $\delta^{18}$O values are between -5‰ to -13‰, with a depletion of 2 - 11‰ relative to the undolomitized limestone. The depleted oxygen isotope ratios in the dolomitized rock can be derived either from fluids impoverished in the heavy isotopes (e.g. meteoric water) or high temperatures. The unvaried carbon isotopic ratios make the second interpretation the most acceptable. As the $^{87}$Sr/$^{86}$Sr values increase from a mean of 0.7077 in the unaffected limestones to 0.7085 in the dolomitized limestones, a derivation of the dolomitizing fluids from the volcanic rocks can be excluded. Comparing the obtained data with the Phanerozoic seawater isotope curve, however, the radiogenic Sr may be derived from marine waters of Late Oligocene-Early Miocene age. Microthermometric analyses of the fluid inclusions in the dolomite crystals from the bulk rocks and from the veins suggest a trapping temperature ranging from a minimum of 70°C (dolomite rock) to a maximum of 120°C (dolomite in veins). The solution contained in the inclusions is water with NaCl and MgCl$_2$, with salinities of 44‰ (dolomite bulk rock) and 17‰ (dolomite in veins). The pressure correction calculated from the fluid inclusion data is about 250 bars, which roughly correspond to the lithostatic pressure over the Mesozoic limestones in the Early Miocene. The presence of newly formed Mg-chlorite in the clay fraction in some of the dolomitized samples suggests that post-burial temperatures did not exceed 100°C to 150°C. The chert fragments included in the dolomitized rock are recrystallized along microcracks, but are only slightly depleted in the heavy oxygen isotope ratio compared to the undolomitized limestone.
isotope. At the time of the dolomitization, chert was already lithified and, therefore, was only superficially affected by the dolomitizing fluids.

These results point to a hydrothermal origin of the dolomitization during the Late Oligocene-Early Miocene, as ascertained from the strontium isotope and fluid inclusion data. The circulation of hot marine water through the brecciated limestones in convective cells, triggered by the geothermal gradient related to the volcanic activity, is the proposed hydrodynamic model. Hydrologic considerations demonstrate that the proposed model is feasible.
Zusammenfassung

In den zentralen Südalpen (Feltre, Verona - Italien) eine etwa 750 m dicke Abfolge jurassischer und kretazischer pelagischer Kalken nach der Ablagerung zum Teil brekzisiert und dolomitisiert wurde, während die darüberliegenden 500 m mächtigen tertiären Sedimente keine Dolomitisierung zeigen. Im Paläogen ist im Gebiet ein mafischer, vor allem mariner Vulkanismus dokumentiert. Kleinmassstäbliche listrische Brüche in Kalken am Kontakt mit der dolomitisierten Brekzie entsprechen geometrisch einem grossräumigen extensiven Regime im Paläogen. Sie beweisen die Gleichzeitigkeit der vulkanischen Aktivität und der Brekzierung. Die Verteilung und petrographischen Eigenschaften der Basalte, mit der Geometrie der Extensionsstrukturen, erlauben eine paläotektonische Rekonstruktion. Diese tektonische Situation entspricht einem back-arc basin und stellt die östliche Verlängerung des ligurischen-balearischen Beckens dar, das Südfrankreich vom Sardinia-Corsica-Calabria-Block im späten Oligozän getrennt hat.

Der Dolomit ist fein- bis zuckerkornig, mit mikroamygdaloidaler Porosität, die teilweise mit Ankerit und Calcit gefüllt ist. Die dolomitisierten Kalkze zeigen eine homogene orange-rote Kathodenlumineszenz, die auf eine einphasige Bildung eisenarmer Dolomite hinweist. Die Karbonatfraktion setzt sich aus mehr als 90% Dolomit zusammen. Der Dolomit ist beinahe stöchiometrisch (Ca0.6Mg0.4 bis Ca0.5Mg0.5).

Die $\delta^{13}C$-Werte der Dolomite sind weniger als 1‰ negativer als die entsprechender nicht dolomitisierter Kalke. Die $\delta^{18}O$-Werte (relativ zum PDB-Standard) variieren zwischen -5‰ und -13‰, das ist 2 bis 11‰ negativer als die nicht dolomitisierte Kalke. Dies wird auf erhöhte Bildungstemperaturen zurückgeführt.

Ein Anstieg der $^{87}Sr/^{86}Sr$-Signaturen im Mittel von 0.7077 in den nicht dolomitisierten Kalken auf 0.7085 in den dolomitisierten Kalken schliesst eine Herkunft der dolomitisierenden Fluide von den vulkanischen Gesteinen aus. Beim Vergleich der Isotopensignaturen mit der phanerozoischen Meerwasser-Isotopenkurve, könnte aber das radiogene Strontium von spät Oligozänem - früh Miozänem Meerwasser kommen.

Mikrothermometrische Analysen flüssiger Einschlüsse in Dolomitkristallen im Gestein und in Adern deuten auf eine Einschlussstemperatur von 70°C (Dolomitgestein) bzw. 120°C (Dolomit in Adern) hin. Die Lösung in den Einschlüssen ist Wasser mit NaCl und MgCl₂, mit einer Salinität von 44‰ (Dolomitgestein) bzw. 17‰ (Adern). Die aus den Einschlüssen berechnete Druckkorrektur ist etwa 250 bar. Dies entspricht ungefähr der früh Miozänen Gesteinssäule über den mesozoischen Kalken. Neugebildeter Mg-Chlorit in dolomitisierten
Kalken deutet an, dass während der Dolomitisierung Temperaturen von 100°-150°C erreicht wurden.

Riassunto

Nella parte centrale delle Alpi Meridionali (Feltre, Verona - Italia), un intervallo di circa 750 m di potenza di calcari pelagici giurassico-cretacici risulta parzialmente brecciato e dolomitizzato in fase post-deposizionale. I sedimenti terziari sovrastanti, dello spessore di circa 500 m, non sono interessati dal fenomeno. Durante il Paleogene nell’area è documentato un vulcanesimo a carattere basico, prevalentemente sottomarino. Nel calcare a contatto con la breccia dolomitizzata sono state osservate strutture estensive a piccola scala. Le loro orientazioni, misurate in campagna, mostrano una certa concordanza con le linee di faglia che attraversano l’area, e permettono di ipotizzare un’origine tettonica. La dolomite è formata a temperature di circa 70-120°C, che possono essere calcolate sperimentalmente utilizzando i dati microtermometrici delle inclusioni fluide presenti nelle dolomiti. La soluzione contenuta nelle inclusioni è acqua marina con sale di NaCl e MgCl₂, con salinità rispettivamente di 44% (roccia dolomitica) e 17% (dolomite in vene). La pressione calcolata dai dati delle inclusioni flan-che, che corrisponde all’incirca alla pressione litostatica escrescita sui calcoli mesozoici nel Miocene inferiore. La presenza di clorite di neoformazione nella frazione argillosa di alcuni dei campioni dolomitizzati, suggerisce che le temperature di
seppellimento non superarono i 100° - 150°C. I frammenti di selce contenuta nella roccia dolomitizzata sono ricristallizzati lungo microfrature, ma sono solo leggermente impoveriti nell'isotopo pesante dell'ossigeno. Al momento della dolomitizzazione la selce era già litificata e pertanto è stata affetta dai fluidi dolomitizzanti solo superficialmente.

I risultati raccolti indicano un'origine idrotermale della dolomitizzazione durante l'Oligocene superiore - Miocene inferiore, età ricavata dai valori isotopici dello stronzio e dalle inclusioni fluide. Il modello idrodinamico proposto consiste nella circolazione di acqua marina calda attraverso i calcari brecciati in celle convettive, attivate dal gradiente geotermico collegato con l'attività vulcanica. Considerazioni idrologiche dimostrano che la circolazione attraverso i corpi di brece è fattiva per la dolomitizzazione.
Table of Contents

Abstract 3
Zusammenfassung 5
Riassunto 7
Table of contents 9
List of figures 13
List of tables 19
List of abbreviations 20

Chapter 1. Introduction 21

1.1. Introduction 21
1.2. Modern base line 1: The dolomite problem 23
  1.2.1. The dolomite crystal and its composition 23
  1.2.2. Dolomite synthesis - theoretical and experimental 24
  1.2.3. Replacement of calcium carbonate by dolomite 25
  1.2.4. Kinetics of dolomitization 26
  1.2.5. Other factors influencing dolomitization 28
  1.2.6. Summary 28
  1.2.7. Dolomitization models 29
1.3. Modern base line 2: Tectonics and geological boundary conditions 34
  1.3.1. Paleogeography and alpine tectonics 34

Chapter 2. Field analysis of the Lessini area 37

2.1. Region of study 37
2.2. Regional stratigraphy 37
  2.2.1. Late Triassic stratigraphy 37
  2.2.2. Jurassic and Cretaceous stratigraphy 38
  2.2.3. Tertiary stratigraphy 39
2.3. Faulting of the Lessini area 40
2.4. Tertiary volcanic rocks 42
2.5. Structural features in the field 44
  2.5.1. Tectonic breccia 44
  2.5.2. Extensional structures 47
  2.5.3. Volcanic/host rock relationships 47
Chapter 3. Dolomite and dolomitization

3.1. Introduction 50
3.2. Regional distribution of the dolomite and dolomitization 50
3.3. Macroscopic description of the Lessini and Feltre area dolomites 52
3.4. Petrographic description of dolomite
   3.4.1. Introduction 52
   3.4.2. Preparation 52
   3.4.3. Observations 56
3.5. Ultrastructural sedimentary fabric
   3.5.1. Introduction 56
   3.5.2. Preparation 63
   3.5.3. Observations 63
3.6. Cathodoluminescence 63
   3.6.1. Introduction 63
   3.6.2. Preparation 64
   3.6.3. Observations 64
3.7. Microscopic analysis interpretation 70
3.8. Mineralogical composition of the dolomitized rock and composition of the dolomite
   3.8.1. Introduction 71
   3.8.2. Preparation 74
   3.8.3. Observations 74
   3.8.4. Interpretation 76
3.9. Trace element geochemistry 80
   3.9.1. Introduction 80
      3.9.1.1. Strontium 80
      3.9.1.2. Sodium 81
      3.9.1.3. Manganese 81
      3.9.1.4. Iron 81
   3.9.2. Preparation 82
   3.9.3. Observations 82
   3.9.4. Interpretation 82
Chapter 4. Stable isotopes

4.1. Introduction
4.2. Oxygen and carbon isotopes
  4.2.1. Introduction
  4.2.2. Preparation
  4.2.3. Observations
  4.2.4. Interpretation
4.3. Strontium isotopes
  4.3.1. Introduction
  4.3.2. Preparation
  4.3.3. Observations
  4.3.4. Interpretation
4.4. Oxygen and strontium isotopes in the basalt

Chapter 5. Fluid inclusions

5.1. Introduction
  5.1.1. Determination of the volatile phase
  5.1.2. Determination of the salt content in the fluid
  5.1.3. Trapping temperature
  5.1.4. Daughter minerals
5.2. Preparation
5.3. Observations
5.4. Interpretation

Chapter 6. Non-carbonate mineral analysis

6.1. Introduction
6.2. Clay minerals
  6.2.1. Introduction
    6.2.1.1. Kaolinite
    6.2.1.2. Illite
    6.2.1.3. Chlorite
    6.2.1.4. Mixed-layered clays
  6.2.2. Preparation
  6.2.3. Observations
  6.2.4. Interpretation
LIST OF FIGURES

Figure 1: Stability relations in the Ca\(^{2+}\)-Mg\(^{2+}\)-CO\(_3\)-H\(_2\)O system. 25
Figure 2: Stability fields of calcite and dolomite as result of variation of Mg/Ca ratio, salinity and the CO\(_3\)/Ca ratio. 27
Figure 3: Relationship between rock composition, depth of burial, system openness to allochtonous magnesium, and dolomite stoichiometry. 30
Figure 4: Theoretical saturation relationships between dolomite and calcite in mixtures of seawater and meteoric water at 25°C, for ordered dolomite (K = 10\(^{-17}\)). 31
Figure 5: Distribution of the tectonic units in the Mediterranean area. 34
Figure 6: Palinspastic cross section through the Ligurian ocean during the Upper Jurassic. 35
Figure 7: Stratigraphic correlation through the Southern Alps. 38
Figure 8: Stratigraphic column of the Lessini Mounts. 40
Figure 9: Simplified geological map of the Lessini Mounts. 41
Figure 10: Distribution of the volcanic rocks in the Venetian Tertiary Province. 43
Figure 11: Photograph of a brecciated, dolomitized rock from Crespadoro, Chiampo Valley, Lessini. 45
Figure 12: Photograph of the "listric" faults in the Maiolica at the contact with the dolomite. 45
Figure 13: Photograph of a brecciated Maiolica in a yellow dolomitized matrix. 45
Figure 14: Photograph of a small-scale normal fault, which is open and filled with chert fragments. 46
Figure 15: Map to show the orientation of the extensional structures observed in the Lessini Mounts. 48
Figure 16: Map to show the distribution of the volcanics with its relationship with the tectonics during the Tertiary. 49
Figure 17: Map of the Southern Alps with the location of areas where the dolomitization occurs. 51
Figure 18: Photograph of a thin section of sample M6. 53
Figure 19: Photograph of a thin section of the yellow material filling the fractures in the Maiolica at the contact with the dolomitized rock. 53
Figure 20: Photomicrograph of sample VN14 (Val di Non, Trentino), showing scattered dolomite rhombs in micrite. 53
Figure 21: Example of fluid inclusion-rich cores of dolomite crystals (sample PR10/11).

Figure 22: Example of fluid inclusion-rich cores of dolomite crystals (sample M6).

Figure 23: Example of fluid inclusion-rich cores of dolomite crystals (sample PR10/11).

Figure 24-28: Mosaic of 5 photomicrographs, showing a profile through a vein, from the dolomite host rock to the calcitic spar (sample M6).

Figure 29: Photomicrograph of the surface of a dolomite crystal with clays and iron-oxides needles (sample M6).

Figure 30: Photomicrograph showing a contact between calcite and ankerite with EDAX (sample M6).

Figure 31: Photomicrograph showing a general view of Figure 30.

Figure 32: Photomicrograph of large dolomite crystals against smaller calcite microcrystals (sample RA3).

Figure 33: Photomicrograph showing a close-up view of Figure 32 (sample RA3).

Figure 34: Photomicrograph of dolomite crystals in dolomicrite (Hauptdolomit, sample HDT19).

Figure 35: Photomicrograph of a close-up view of the iron-oxides (goethite?) needles from Figure 34 (Hauptdolomit, sample HDT19).

Figure 36: Photomicrograph of a close-up view of iron-oxide needles on the surface of a dolomite crystal (sample M6).

Figure 37: Photomicrograph of a ghost of dolomite rhombohedron in dedolomitized yellow fracture filling (sample PB21/87).

Figure 38: Photomicrograph to show another example of dolomite rhombohedron in the yellow filling (sample PB21/87).

Figure 39: Photomicrograph of sparry calcite in fractured Maiolica (sample PB21/87).

Figure 40: Back-scattered photomicrograph of a fracture in the dolomite (sample M6).

Figure 41: Close-up view of back-scattered photomicrograph of Figure 40 (sample M6).

Figure 42: Photomicrograph of a fracture in the dolomite (sample M6).

Figure 43: Photomicrograph showing the elemental distribution of Mg for Figure 42.

Figure 44: Photomicrograph showing the elemental distribution of Fe for Figure 42.

Figure 45: Photomicrograph of an example of backscattered images of fractures in dolomite (sample SG2b).

Figure 46: Photomicrograph of an example of backscattered images of fractures in dolomite (sample SG2b).
Figure 47: Photograph of a thin section of a dolomitic rock showing a typical dull orange-red colour through cathodoluminescence (sample SG2b).

Figure 48: Photograph of a thin section of a vein with typical sequence of crystals, in dolomitic host rock (sample M6).

Figure 49: Photograph of a thin section of the vein of Figure 48 through cathodoluminescence.

Figure 50: Photograph of a thin section of a crystalline vein filling in dolomite (sample M6) in normal light.

Figure 51: Photograph of a thin section of a crystalline vein filling in dolomite of Figure 50.

Figure 52: Photograph of a thin section of Figure 50, through cathodoluminescence.

Figure 53: Photograph of a thin section through a fracture filled with sparry calcite in dolomitized rock (sample MS9).

Figure 54: Photograph of a thin section through a fracture in dolomitized rock of Figure 53, through cathodoluminescence.

Figure 55: Photograph of a thin section across the contact limestone- dolomite, in Rosso Ammonitico formation (sample RA3).

Figure 56: Photograph of a thin section across the contact limestone-dolomite of Figure 55, through cathodoluminescence.

Figure 57: Photograph of a cross section of a calcitic vein in dolomitized rock.

Figure 58: Photograph of a cross section of a calcitic vein of Figure 57, through cathodoluminescence.

Figure 59: Calibration curve for the determination of percent dolomite in carbonate rocks and sediments by X-ray diffraction.

Figure 60: Variation of $d_{104}$ for Ca-Mg carbonates.

Figure 61: X-ray basal reflections of standard dolomite and calcite.

Figure 62: Histogram of the distribution of percent dolomite and percent magnesium in dolomite as measured from XRD analysis.

Figure 63: Graph to show the shifts of the dolomite (104) peak with increasing Ca-content in X-ray diffractogramm.

Figure 64: Graph to show % dolomite against % Mg in dolomite for the AL/87 sample series.

Figure 65: Graph to show % dolomite against % Mg in dolomite for the C sample series.

Figure 66: Graph to show % dolomite against % Mg in dolomite for the M sample series.

Figure 67: Graph to show % dolomite against % Mg in dolomite for the MS sample series.
Figure 68: Graph to show % dolomite against % Mg in dolomite for the PB sample series.

Figure 69: Graph to show % dolomite against % Mg in dolomite for the PR sample series.

Figure 70: Graph to show % dolomite against % Mg in dolomite for the RA sample series.

Figure 71: Graph to show % dolomite against % Mg in dolomite for the SG and P sample series.

Figure 72: Photomicrograph of back-scattered image of sample M6 (scale shown by bar) with corresponding EDAX analyses of the three different phases observable.

Figure 73: EDAX analysis of the yellow material filling the fractures in proximity to the contact with the dolomitized rock.

Figure 74: Graphical representation of the oxygen isotopic equilibrium between dolomite (in PDB), $\delta^{18}O$ water (SMOW) and temperature, using the empirical relationship $10^6 \ln a = 2.78 \times 10^6 T^2 (\text{°K}) + 0.91$.

Figure 75: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the measured samples.

Figure 76: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the AL and AL/87 sample series.

Figure 77: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the C sample series.

Figure 78: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the M sample series.

Figure 79: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the MS sample series.

Figure 80: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the P sample series.

Figure 81: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the PB sample series.

Figure 82: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the PR sample series.

Figure 83: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the RA sample series.

Figure 84: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the SG sample series.

Figure 85: Graph to show a contour plot of the spatial distribution of $\delta^{13}C$ against height above the road surface at the outcrop of Crespadoro, Chiampo Valley.

Figure 86: Graph to show a contour plot of the spatial distribution of $\delta^{18}O$ against height above the road surface at the outcrop of Crespadoro, Chiampo Valley.

Figure 87: Variation of $\delta^{13}C$ and $\delta^{18}O$ in dolomitized rock with age.

Figure 88: Phanerozoic strontium isotope ratio variation curve for seawater.

Figure 89: $^{87}Sr/^{86}Sr$ values of seawater with compared ratios for its different sources.

Figure 90: Flow diagram of the geochemical cycle of Sr from seawater into the continental and oceanic crust.

Figure 91: Plot of the analysed samples on the $^{87}Sr/^{86}Sr$ seawater curve for the last 200 ma.

Figure 92: $^{87}Sr/^{86}Sr$ seawater variation curve for the Eocene-Miocene age.

Figure 93: Diagram to show primary and secondary inclusions in a quartz crystal.

Figure 94: Diagram to show the appearance of inclusions with various volume percentages of gas compared to the total volume of the inclusion.
Figure 95: Graph to compare the size and weight of spherical inclusions.

Figure 96: Graph to show the phase transitions during heating of fluid inclusions with high and low density one-component fluids.

Figure 97: Photograph of a thin section showing primary and secondary fluid inclusions in dolomite (sample AL10/87).

Figure 98: Photograph of a thin section showing primary and secondary inclusions in dolomite crystals (sample AL10/87).

Figure 99: Photograph of a thin section showing first and second generation of dolomite in veins (sample C30/B/87).

Figure 100: Photograph of thin section showing one- and two-phases inclusions in dolomite (sample M8).

Figure 101: Photograph of a thin section showing a daughter mineral in the inclusion in the middle (sample C30/B/87).

Figure 102: Photograph of a thin section showing a view of the different mineral phases (sample M8).

Figure 103: X-ray diffractogramm of non-carbonate phases in limestone and dolomitized samples.

Figure 104: Photomicrograph of a clay mineral aggregate in dolomite (sample C9).

Figure 105: Photomicrograph of clays on a dolomite crystal (with EDAX analysis) (sample C9).

Figure 106: Photomicrograph of a close-up on clay minerals in dolomitized rock (sample C9).

Figure 107: Photomicrograph of a detrital K-feldspar in the silt fraction of limestone (sample M1S).

Figure 108: Photomicrograph of an aggregate of microcrystals of quartz in limestone (sample M1S).

Figure 109: Photomicrograph of clay minerals from the clay fraction of a dolomitized sample (sample C13T).

Figure 110: Photomicrograph of a close-up of clays in limestone (sample M1S).

Figure 111: Photomicrograph of kaolinite (with EDAX) in the clay fraction of the limestone.

Figure 112: Photomicrograph of a view of the clay fraction in limestone (sample M1T).

Figure 113: Photomicrograph of a view of the clay fraction in a dolomitized rock sample (sample C13T).

Figure 114: Photomicrograph of a view of clays in a dolomitized rock sample (sample M6T).

Figure 115: Photomicrograph of a clay mineral in limestone (with EDAX analysis) (sample M1T).

Figure 116: Photomicrograph of a lamina of aggregated clay minerals from dolomite (sample C13T).

Figure 117: Photomicrograph of a close-up on the clays of Figure 116.

Figure 118: Photomicrograph of a close-up of Figure 117 with EDAX analysis (sample C13T).

Figure 119: Photomicrograph of clay aggregates (sample C13T).

Figure 120: Photomicrograph of clay aggregates (sample C13T).
Figure 121: Photomicrograph of a view of clay minerals from limestone, as they look “sprayed" on the sample holder (sample M1T).

Figure 122: Photomicrograph of a view of “sprayed” clays from dolomite, to compare with Figure 121.

Figure 123: Photomicrograph of a view of clays from dolomitized rock (with EDAX analysis)(sample C13T).

Figure 124: Photomicrograph of a view of clays from limestone (with EDAX analysis) (sample C5T).

Figure 125: Photomicrograph of carbonate dissolution features in yellow filling material (sample PB21/87).

Figure 126: X-ray diffractogramms of the different silica phases.

Figure 127: Photograph of a thin section of chert in limestone (sample PB21).

Figure 128: Photograph of a thin section of chert included in dolomitized rock (sample C77/87).

Figure 129: Photograph of a thin section of chert included in dolomite (sample C77/87).

Figure 130: Photomicrograph of silica crust in dolomitized sample (sample C13T).

Figure 131: Photomicrograph of aggregate of clays with quartz fibers (sample C13T).

Figure 132: Photomicrograph of microcrystalline quartz from chert in limestone (sample M1S).

Figure 133: Isochore (on P-T diagram) of the studied system, calculated from the fluid inclusion analysis.

Figure 134: Paleogeographic reconstruction of the Western Mediterranean for 30 and 5 Ma.

Figure 135: Kohout-type convection fluid circulation in a platform.

Figure 136: Hydrodynamic model proposed for the dolomitizing fluid circulation.

Figure 137: Location map of the series of collected samples.

Figure 138: Photograph to show the contact between Maiolica and dolomite.

Figure 139: a) Photograph of a close-up on the Maiolica of Figure 138 at the contact.

b) Diagram of the photograph in Figure 139a.

Figure 140: Photograph of undolomitized Maiolica included in the dolomitized rock.

Figure 141: Photograph of undolomitized Maiolica of Aptian age included in the dolomitized rock (Crespadoro, Chiampo Valley).

Figure 142: Photograph of the outcrop of the MS series (San Liberale Valley, Grappa area).

Figure 143: Photograph of dolomitized rock of the P series (Seren del Grappa, near Feltre).

Figure 144: Photograph of brecciated Maiolica at the contact with dolomite.

Figure 145: Photograph of a sample of brecciated Maiolica of the series PB (Ferrazza, Chiampo Valley).

Figure 146: Drawing of the hand specimen of Figure 145.

Figure 147: Photograph of the subvertical contact between Rosso Ammonitico and dolomitized breccia (series PR, Ferrazza, Chiampo Valley).
### List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Dolomite geochemical data</td>
<td>24</td>
</tr>
<tr>
<td>3.1</td>
<td>Chemical composition of a selection of calcite and dolomite samples</td>
<td>82</td>
</tr>
<tr>
<td>4.1</td>
<td>Stable isotope ratios in limestone and dolomitized breccia</td>
<td>90</td>
</tr>
<tr>
<td>4.2</td>
<td>Stable isotope ratios of the fracture fillings</td>
<td>90</td>
</tr>
<tr>
<td>4.3</td>
<td>Strontium isotope ratios of different materials</td>
<td>101</td>
</tr>
<tr>
<td>4.4</td>
<td>Strontium isotope composition of the analysed samples</td>
<td>103</td>
</tr>
<tr>
<td>5.1</td>
<td>Triple points and critical points of some one-component systems</td>
<td>111</td>
</tr>
<tr>
<td>5.2</td>
<td>Eutectic temperatures and compositions of some selected chloride and non-chloride aqueous solutions</td>
<td>112</td>
</tr>
<tr>
<td>5.3</td>
<td>Fluid inclusions analyses</td>
<td>117</td>
</tr>
<tr>
<td>6.1</td>
<td>Percentage clay and silt fraction in the studied samples</td>
<td>124</td>
</tr>
<tr>
<td>6.2</td>
<td>Partial elemental composition of bulk clay minerals in calcite and dolomite samples</td>
<td>133</td>
</tr>
<tr>
<td>6.3</td>
<td>Oxygen isotope values of chert from both limestone and dolomite</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>(Crespadoro, Chiampo Valley)</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF ABBREVIATIONS

%: percent
%o: per mil
a: activity ratio
AAS: atomic absorption spectrometry
aq: solution
cal: calorie
cc: cubic centimeters
CRT: crystal roughening temperature
EDAX: energy dispersion analysis system
kb: kilobars
Kc: solubility product of calcite
Kd: solubility product of dolomite
kV: kilovolts
ma: million years
mg/kg: milligrams per kilogram
mg/l: milligrams per liter
ml: milliliters
μm: micrometers
mol %: mole %
NaCl eqv: NaCl equivalents
PDB: Pee Dee Formation Belemnite
ppm: parts per million
ρ: density
rpm: rotations per minute
SEM: scanning electron microscope
SMOW: standard mean ocean water
Te: eutectic temperature
Th: homogenization temperature
Tm,Pm: melting temperature and pressure
Tt,PT: trapping temperature and pressure
wt%: weight percent
xl: crystal
XRD: X-ray diffraction
CHAPTER 1

INTRODUCTION

1.1 Introduction

In the Lessini Mounts, the hills situated in the northern part of the provinces of Verona and Vicenza, North-East Italy, dolomite has been first recognized over 150 years ago by Maraschini (1824). Geologically, the area is situated in the Southern Alps, the remains of the southern Tethyan continental margin. The Southern Alps have only marginally been involved in the alpine orogenesis, not showing a metamorphism of alpine age, due to its distance from the suture zone, but only a brittle tectonism.

During the Late Jurassic and the Cretaceous, carbonates of pelagic origin were deposited along the southern continental margin of the alpine Tethys. They are overlain by shallow water carbonates in the Tertiary. The pervasive dolomitization of the pelagic carbonates in the central-eastern part of the present Southern Alps has been explained by two different scenarios: (1) the dolomitization was related to a Mesozoic carbonate buildup or coral reef. This interpretation was in line with the interpretation on dolomitization in the Dolomites (Bittner, 1877; Secco, 1883; Dal Lago, 1899; Dal Piaz, 1912); (2) dolomitization was related to metasomatic alteration of carbonates by volcanic waters (Maraschini, 1824; Balestra, 1897). The first scenario found support in more recent studies by Ferasin (1956) and Carraro (1964). Since then, the enigmatic dolomitization of the Mesozoic limestones of the Southern Alps has been only sporadically mentioned, but it has never been deeply studied, in order to define its occurrence, conditions of formation and position in the geological framework of the Southern Alps. With this aim the present study started in 1986. I will define occurrence and geologic framework of dolomitized sediments. I will use new tectonic and geochemical information to establish a model of dolomitization.

Modern analytical and tectonic ideas, associated with the evolution of the Alpine orogenic belt, have led not only to a greater understanding of its formation, but also new insights into more specific problems such as the formation of dolomite. The discovery of dolomite forming today led to a new framework in the understanding and formulation of the various dolomitization models, that can be interpreted from the present into the past. This particular example of dolomitization in the Southern Alps can indicate a variety of tectonic features that can be related to the paleogeography of the pre-collisional southern continental margin of the Tethys, and the post-collisional effects with their relation to the basic volcanism of Tertiary age. This example of dolomitization of pelagic limestone during their diagenesis allows to test modern analytical techniques to see whether a greater understanding of dolomitization process can be found.
The study has been divided into two parts: field observations, followed by petrographical and chemical analyses. The field work consists principally of the identification of dolomitized areas and their relationship to the stratigraphic sequence, as well as structural observations correlated with the tectonic framework of the studied area. The petrographical and chemical analyses have been performed with the aim of collecting information on the characteristics of the dolomite, necessary to the formulation of a probable genetic model.

Single pieces of information provide a fragment to the answer of a puzzle, and only at the end, when all the parts are available and can then be compared, it is possible to formulate a genetic hypothesis: thin sections provide information on the crystallisation process; the chemical composition of the dolomite depends directly on the chemistry of the deposition environment; fluid inclusions are powerful means to reconstruct the chemistry of the fluids, from which the crystals have been precipitated, and the temperature reached by the system; oxygen and carbon isotopic composition of dolomite depends also from the physical conditions during the crystallisation and from the nature of the formation fluids. Strontium isotopes can provide a more or less accurate dating of the dolomitization, in specific formation conditions. The mineralogy of the non-carbonate fraction may have also been affected by the dolomitization process, and can therefore be a useful means of comparison with the results obtained from the carbonate fraction.

For a long time, dolomite has been considered as an indicator of an evaporitic environment, or the product of hydrothermal fluids. Recent studies on Holocene dolomite improved our knowledge of the origin and history of dolomitized sediments and led to the formulation of different dolomitization models. Dolomitization is controlled by specific geochemical and hydrological boundary conditions. The chemical conditions, a high Mg:Ca ratio and/or sulphate-reducing conditions, are reached both in shallow water marine environments and in deep sea sediments. Specific hydrological conditions, favouring the establishment of these conditions include evaporative pumping (Hsu and Siegenthaler, 1969; McKenzie et al., 1980) and hydrothermally induced flow of pore fluids (Land, 1985; Lister, 1983).

The second pillar where this study is founded is the tectonics. The new insights on the alpine orogenesis in general, and on the tectonics of the Southern Alps in particular, have been fundamental for the hydrodynamic model, an essential part of the study of dolomitization phenomena. The recognition in the field, that dolomitization affects almost exclusively brecciated limestones, revealed the importance of the study of tectonic features to this particular sedimentological problem. An attempt to correlate the structures connected with the dolomite in the framework of the tectonic evolution of the Tethyan continental margin provided further information on the mechanism and occurring of the dolomitization.

In the introductory part of this work, a brief review of the modern ideas on both dolomitization processes and tectonics will be made.
1.2. Modern base line 1: The dolomite problem

Although there are many different kinds of dolomite, it can be asserted that dolomitization is almost exclusively a diagenetic process. Only a small amount of dolomite of primary precipitation has been found in modern environments (i.e. Deep Spring Lake, California, and Coorong Lagoon, Australia (von der Borch and Jones, 1976), which is negligible compared to the huge bulk of ancient dolomite.

The problem of the origin of the dolomite began in 1791, when Déodat de Dolomieu discovered in the Dolomites an unknown mineral, similar to calcite, but not reacting with hydrochloric acid. He unintentionally started 200 years of controversy on one of the most interesting and studied problems in sedimentology. Up to the present, an incredible amount of literature has been written on dolomite and dolomitization. There is, of course, a considerable range of opinions regarding the mechanism or mechanisms of dolomitization.

The discovery of penecontemporaneous Holocene dolomite in marine, mostly supratidal, environments, as in the Coorong area in Australia (Von der Borch et al., 1964), in the Bahamas (Shinn et al., 1965), in the Persian Gulf (Illing et al., 1965), and in Bonaire, Netherlands Antilles (Deffeyes et al., 1965) generated new interest in the problem. Many comparisons between examples of ancient dolomite and Holocene dolomite have been made (e.g. Laporte, 1967; Matter, 1967; Roehl, 1967). However the consideration of the small volume and areal distribution of the Holocene dolomite does not allow a generalisation; there may have been other processes involved in the massive dolomitization of ancient carbonates (Zenger, 1972).

The essence of the "dolomite problem" is the application of the knowledge collected with the study of recent dolomitization examples to the ancient dolomite sequences.

1.2.1. The dolomite crystal and its composition

The mineral dolomite has an ideal chemical composition of CaMg(CO₃)₂ and a symmetry structure in the trigonal subsystem of the hexagonal crystal system. The unit cell is a rhombohedron, elongate parallel to the "c" crystallographic axis. The crystal is built up of layers of Ca²⁺ and Mg²⁺ cations alternating with anions (CO₃²⁻), perpendicular to the c-axis. The resulting oxide analysis is 21.9% MgO, 30.4% CaO and 47.7% CO₂ by weight. This is the composition of a stoichiometric dolomite, with 50 mol% Ca²⁺ and 50 mol% Mg²⁺ in the cationic position. In nature and in the laboratory synthesized dolomite does not normally show a complete segregation of Ca²⁺ ions and Mg²⁺ ions in the respective layers, i.e. the dolomite is not stoichiometric and is better represented by the formula Ca₁₋ₓMgₓ(CO₃)₂. The possible explanations for this non-ideal crystalline structure are many. The Mg²⁺ has a thick hydration
shell and the Ca\(^{2+}\) enters preferentially into the crystalline structure. Moreover, foreign cations of Fe, Sr, Mn, Na can substitute Ca\(^{2+}\) or Mg\(^{2+}\) in many dolomites. Assuming a relative slow precipitation in equilibrium, the process of inclusion of trace elements in a crystal can be represented as:

\[ A_{\text{aq}} + B_{\text{aq}} \rightleftharpoons A_{\text{sl}} + B_{\text{sl}} \]

where, A is the structurally preferred ion and B the foreign ion (Veizer, 1983).

Graf and Goldsmith (1956) used first the term "protodolomite" for a disordered or non ideal dolomite. Land's suggestion (1980) of a general name "dolomite" for all the phases with a composition near CaMg(CO\(_3\))\(_2\) seems to be the most acceptable. Ideal dolomite has the lowest free energy possible for any combination of CaCO\(_3\) and MgCO\(_3\) under sedimentary conditions. This means that ideal dolomite is the least soluble, i.e. the most stable, form.

1.2.2. Dolomite synthesis - theoretical and experimental

In marine environments, dolomite is thermodynamically stable, but because of kinetic factors it does not precipitate, and the deposition of aragonite or low-magnesium calcite is normally observed (e.g. Stehli and Hower, 1961). The experiments of precipitation of dolomite from solutions at low temperatures, with conditions of temperature and partial pressure of CO\(_2\) close to the conditions existing at the earth’s surface, have not been particularly successful. Moreover, there is no general consensus regarding the chemical conditions required for the dolomitization process: the difficulty of precipitating dolomite under controlled laboratory conditions is the essence of the problem of the origin of the dolomite (Hsu, 1967).

To determine whether sea water is saturated with respect to dolomite, one needs to calculate the solubility product in sea water. Once the molar concentration in the sea is known, the activity coefficient and the percentage of the species present as free ion for the three ionic species involved in the reaction (Ca\(^{2+}\), Mg\(^{2+}\) and CO\(_3\)\(^{2-}\))(Table 1.1)(Blatt et al., 1980), a value can be obtained of 10\(^{-15.01}\). This indicates that the sea water is supersaturated with respect to dolomite by almost two orders of magnitude (Figure 1).

Table 1.1: Dolomite geochemical data (from Blatt et al., 1980)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Molality in seawater (c)</th>
<th>Activity coefficient (g)</th>
<th>Activity (gc)</th>
<th>Percentage free ion</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>9.98 x 10(^{-3})</td>
<td>0.26</td>
<td>2.59 x 10(^{-3})</td>
<td>90</td>
<td>2.34 x 10(^{-3})</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>5.23 x 10(^{-2})</td>
<td>0.29</td>
<td>1.52 x 10(^{-2})</td>
<td>87</td>
<td>1.32 x 10(^{-2})</td>
</tr>
<tr>
<td>CO(_3)(^{2-})</td>
<td>2.70 x 10(^{-4})</td>
<td>0.20</td>
<td>5.30 x 10(^{-5})</td>
<td>9</td>
<td>4.80 x 10(^{-6})</td>
</tr>
<tr>
<td>(CO(_3)(^{2-})(_2))</td>
<td>2.30 x 10(^{-11})</td>
<td></td>
<td></td>
<td></td>
<td>2.30 x 10(^{-11})</td>
</tr>
</tbody>
</table>

\[ K = (2.34 x 10^{-3})(1.32 x 10^{-2})(2.3 x 10^{-11}) = 7.1 x 10^{-16} \approx 10^{-15.01} \]

The possible kinetic reasons for this apparent lack of dolomite growth from sea water can be caused by the thick shell of water molecules tightly bound to magnesium (Christ and
Figure 1: Stability relations in the Ca²⁺- Mg²⁺- CO₂⁻- H₂O system. This is based on the solubility product of dolomite $K_s = 2 \times 10^{-17}$ (25°C, 1 atm). Seawater is within the thermodynamic predominance of dolomite as a solid phase (from Stumm and Morgan, 1970).

Hostetler, 1970). In addition, the nucleation of dolomite is a slow process at low temperatures. At higher temperatures, however, the water of hydration surrounding the magnesium ions is easily removed and the nucleation can be accelerated by the accreted thermal energy of the ions, that can now migrate rapidly to ordered positions (Morrow, 1982a).

Dolomite can be quite easily precipitated by solutions at temperatures higher than "normal", particularly in the hydrothermal environment. Graf and Goldsmith (1956), starting with magnesium-rich calcite in the presence of $H_2O$ and $H_2O + CO_2$, at temperatures over 200°C, produced stable dolomite of 1:1 composition, ordered with respect to Ca and Mg. On the other hand, already at temperatures of about 70°C the product is a calcium-rich, imperfectly ordered "protodolomite". Most of the attempts to synthesize dolomite at low temperatures produced only a nearly 50 mole % magnesian calcite, material that cannot be called dolomite (Berner, 1971). Glover and Sippel (1967) suggest that the time available in the natural environments might make the difference between order and disorder.

1.2.3. Replacement of calcium carbonate by dolomite

Diffusion of ions in crystals, at low temperature, is an extremely slow process, and therefore it seems impossible that dolomitization can be a solid-state reaction. The process is a simultaneous dissolution of calcium carbonate and precipitation of dolomite from a solution passing through the rock.

The necessity of the use of "special waters" for the dolomitization characterized most of the studies of the past two decade. In the last years the idea of normal seawater as dolomitizing solution became more and more accepted. The review of thermodynamic considerations, presented in Appendix 1, leads to the statement that seawater is a potentially dolomitizing
1.2.4. Kinetics of dolomitization

Much has been written on the possible influence of environmental chemical factors in dolomitization. The carbonate ion activity is related to pH by the relation:

\[(aH^+)^2(aCO_3^2)/aH_2CO_3 = KH_2CO_3\]  

(Equation 1)

where, \(KH_2CO_3\) is a constant at any given pressure and temperature.

An increase in the pH should favour the precipitation of a carbonate phase, but there is no theoretical basis or experimental evidence that the precipitation of dolomite instead of calcite can be favoured. In the dolomitization reaction the hydrogen ion does not appear. For this reason and for the evidences showed before, the conditions of replacement of calcite by dolomite are only controlled by the magnesium-calcium ion activity ratio, at any temperature and pressure (Hsu, 1967). However, any change in pCO_2 in a solution can result in change in the pH, since the two factors are related. It is then possible that this influences the kinetics of dolomite formation.

The dolomitization reaction, not being an oxidation-reduction reaction, is not directly related to the redox potential, Eh. The Eh may, however, influence the stability of ions or minerals that do not appear in the reaction, but can act as inhibitors or catalysts in the kinetics of the dolomitization process.

The relation between the CO_2 partial pressure (pCO_2) and dolomitization is controversial. It could be possible that the ratio of the equilibrium activities of the magnesium and calcium ions can be altered by variation in the partial pressure of CO_2, in systems involving the precipitation of hydromagnesite or other hydrated carbonate minerals which could eventually be altered to dolomite (Hsu, 1967).

Several kinetic factors hinder the precipitation of dolomite. They have been well resumed in Morrow’s review (1982a). The first major kinetic barrier is the velocity of the crystallisation. The rapid precipitation from highly saline, supersaturated solutions does not give time for the calcium and magnesium ions to reach the respective ordered positions, leading to the formation of disordered Ca-Mg carbonates (Graf and Goldsmith, 1956; Folk, 1974; Folk and Land, 1975; Lippman, 1973). Some authors imagine the crystallisation of dolomite as an adding of cationic and ionic layers parallel to the "c" crystallographic axis (e.g. Deelman, 1975). Studies on recent dolomite have observed that the growth of the dolomite crystal proceeds contemporarily in all directions (Morrow, 1982b). As already mentioned, the problem of the hydration shell of the magnesium ions also plays an important role in the lack of precipitation of ordered dolomite instead of calcium-rich phases (Lippman, 1973; McKenzie, 1981). The third important factor is the low concentration of CO_3^2- relative to Ca^{2+} or Mg^{2+} in most natural solutions (e.g. in seawater Ca^{2+} = 400 mg/l, Mg^{2+} = 1350 mg/l, CO_3^{2-} = 140 mg/l)[Lippman, 1973]. Figure 2 shows that an increase in either the magnesium/
calcium ratio, the carbonate ion concentration, or a decrease in salinity favours the precipitation of dolomite. The explanation of this behaviour is simple: an increase in the Mg²⁺/Ca²⁺ ratio and carbonate ions increases the probability of the magnesium and carbonate ions to enter in the structure and a dilution of the solution slows down the crystallisation, favouring the formation of an ordered crystalline structure.

Figure 2: Stability fields of calcite and dolomite as result of variation of Mg/Ca ratio, salinity and the CO₃/Ca ratio (from Morrow, 1982).

The need of particularly high Mg²⁺/Ca²⁺ ratios in the dolomitizing solutions is disputed. In fact solutions with high Mg²⁺/Ca²⁺ ratio tend to precipitate aragonite, not dolomite because of kinetic hindrance (Baker and Kastner, 1981). Zenger (1972) points out the evidence of many ancient dolomites that appear to be formed in a normal marine environment. The analysis of interstitial waters in the dolomite of the Andros Island, Bahamas, shows essentially normal chlorinities and magnesium/calcium ratios. The importance of seawater as a source of dolomitizing solution has been reexamined in the latest publications on the dolomite problem (e.g., Land, 1985) and seems to be probable, considering, for example, the appropriate magnesium/calcium ratio.
1.2.5. Other factors influencing dolomitization

Other factors that influence the kinetics of dolomitization are obviously the temperature, reducing, for example, the hydration layer of the magnesium ion, and the time available for the reaction (e.g. Mattes and Mountjoy, 1980). Conditions of supersaturation promoting dolomitization can only be maintained if magnesium ions are supplied to the system until the process has proceeded to completion. It must not be forgotten that any aqueous solution supersaturated with respect to dolomite (seawater, lake waters, groundwaters, hypersaline waters, mixing-zone waters) is a potential dolomitizing solution (Hardie, 1987). Furthermore, it has been demonstrated experimentally that calcite can be converted into dolomite in presence of solution containing Mg²⁺, with appropriate Mg²⁺/Ca²⁺ activity greater than the equilibrium constant K (see A1.3), in days, at 100°C (Baron, 1960). As a result, almost any groundwater with a Mg/Ca ionic activity ratio greater than the equilibrium ratio is a potential dolomitizing fluid, and no “special waters” are needed; the dynamics of the groundwater movement insures a continuous supply of Mg²⁺.

The possible influence of the presence of certain cations, such as lithium (Carpenter, 1980), urease-producing and/or uric-acid-fermenting bacteria (Mansfield, 1980; Gunatilaka, 1987) and Fe(II)-chelates (Mirsal and Zankl, 1985), acting as catalysts for the dolomitization, have also been discussed. Whether these catalysts did play a significant role in nature has not been demonstrated.

More important are the inhibiting factors. Baker and Kastner (1981) experimentally demonstrated the negative influence of the presence of sulphate ions for the formation of dolomite. This means that, in a reducing environment and with the action of sulphate-reducing bacteria, the precipitation of dolomite is strongly favoured. Recent geochemical works (Gunatilaka et al., 1985) indicates that not only a low sulphate ions concentration is essential for dolomite nucleation, but the reduced S²⁻ should also be removed to cause carbonate precipitation. This explains the often mentioned association of pyrite with recent dolomite in some marine sediments.

A critical factor is, of course, a continuous supply of Mg²⁺ to maintain the reaction toward complete replacement of CaCO₃ by CaMg(CO₃)₂, which needs the presence of a driving force that moves the necessary amount of Mg-bearing solution through the pore of the sediments or rocks (Hsu, 1966; Blatt et al., 1980; Hardie, 1987).

1.2.6. Summary

It is thermodynamically demonstrated that dolomite is the stable carbonate in many natural solutions at earth surface conditions. A thermodynamic drive exists for the dolomitization of calcite and aragonite in the presence of subsurface water. The precipitation of dolomite seems, however, inhibited by kinetic factors, such as a hydration shell of Mg²⁺, crystallisation velocity, CO₃²⁻/Ca²⁺ ratios and sulphate concentration in the solution, porosity and permeability of the original sediment/rock, time available for the transformation. Chemical factors can act as catalysts of dolomite (e.g. FeII-chelates, Li), or inhibitors (e.g.
sulphate ions). It is the net effect of all involved (thermodynamic and kinetic) factors that
determines whether or not dolomite precipitates. Most important of all is, however, whether
a driving force makes the dolomitizing fluid circulate through sediments.

1.2.7. Dolomitization models

If both thermodynamic and kinetic considerations are combined, the following conditions
and environments are considered chemically favourable to dolomitization:

1) Environments of any salinity above thermodynamic saturation with respect to dolomite
and kinetically not inhibitive (freshwater/seawater mixing zones, normal saline to hypersal-
ine subtidal or supratidal environments, schizohaline environments).

2) Alkaline environments (under the influence of bacterial reduction and/or fermentation
processes, or alkaline continental groundwater, enriched in CO$_3^{2-}$ and HCO$_3^-$).

3) Environments with temperatures higher than about 50°C (subsurface and hydrother-
mal environments) (Machel and Mountjoy, 1986).

The deposition of unstable high-magnesium calcite in a marine environment is quite
common. If magnesian calcite dissolves in the presence of a small amount of fluid, or if calcite
and dolomite co-precipitate from this same fluid, or if the process is rapid in comparison to
the rate of flow through the carbonate, the system can be considered closed during the
diagenetical stabilization. The result will be low-magnesium calcite with floating euhedral
dolomite rhombohedra (Sperber et al., 1984).

Given that marine magnesian calcites rarely contain more than 18 mol% MgCO$_3$, in a
closed diagenetic environment, this would stabilize to about 36% stoichiometric dolomite and
64% low-magnesium calcite. These considerations reasonably agree with the abundance of
dolomite in dolomitic limestones, ranging between 12 and 27% (Sperber et al., 1984).

The formation of dolomite rocks from limestone requires sufficient influx of magnesium,
occurring therefore, necessarily in an open system, such as, for example, an evaporitic or
hydrothermal environment, with a sufficiently high hydrodynamic potential to induce a
continuous flow of magnesium-bearing fluids through sediments or rocks with a sufficiently
high primary or secondary permeability.

It seems that, at the time scale of the dolomitization process, the hydrodynamic potential
or the carbonate permeability must have been adequate to allow for the flow of dolomitizing
fluids that are rapidly dolomitized, or dolomitic limestones are formed in hydrodynamic
inactive or hydrostatic conditions. The scarcity of rock with dolomite content intermediate
between dolomitic limestones and dolostones suggests that dolomitization is a relatively
rapid process at the scale of Phanerozoic time (Sperber et al., 1984).

Figure 3 summarizes the distribution of the abundance and stoichiometry of dolomite. The
lower horizontal axis represents the composition of the dolomite, the upper horizontal axis
the increasing diagenetic grade (age, burial depth, temperature), the left vertical axis the
One of the first models emphasizing the hydrodynamic aspect of dolomitization on a large scale was the *Seepage Refluxion Model* (Adams and Rhodes, 1960; Deffeyes et al., 1965). Evaporation in a lagoon increases the density of marine water, that is induced to infiltrate the underlying sediments and move seaward by reflux. Magnesium is continually transported through the sediments by the continuous support of marine water in the lagoon. Murray (1969) demonstrates that the flux is confined in the most permeable conduits: therefore, extensive dolomitization of large, relatively impermeable carbonate bodies through seepage is impossible (Hsu and Siegenthaler, 1968).

Since 1929 the Coorong Lagoon in Australia has been known as a dolomite formation area (Mawson, 1929). Fine grained calcian dolomite (protodolomite) precipitates in ephemeral lakes from continental groundwater or in a zone of mixing between sea water and continental water. Precipitation seems to be related to the high CO$_3^{2-}$ concentration of the alkaline groundwater and Mg$^{2+}$ may have been derived from the weathering of basic volcanic rocks (Von der Borch et al., 1975).

Another example of penecontemporaneous dolomite is the sabkha dolomite observed in the Persian Gulf, associated with evaporite minerals (Illing et al., 1965). The intense evaporation of the marine water that infiltrates the tidal flat, activates the process of *evaporative pumping* (McKenzie et al., 1980). New data on the strontium isotopic content of the sabkha dolomite suggest that the source of Mg$^{2+}$ for dolomitization was seawater recharged after the flooding of sub-sabkha (D. Müller, in press). It is still controversial if the
dolomite is the product of substitution of preexisting aragonite (e.g. McKenzie, 1981) or of direct precipitation (Hardie, 1987).

Another hydrodynamic model was first suggested by Hanshaw et al. (1971) for the deep confined Tertiary carbonate aquifer of Florida, the *mixed-water* or the *dilution model*. Badiozamani (1973) called it the *Dorag-model*, from the name given in Arabic to the mongrel people. This suggestion was then taken up by many authors (e.g. Land, 1973; Land et al., 1975; Veizer et al., 1978 among others). It is based on the principle that dolomitization could proceed preferentially with a continuous supply of waters undersaturated with respect to calcite, but supersaturated with respect to dolomite. The dolomitization occurs within the zone of mixing of meteoric groundwater with phreatic seawater. Groundwater does not carry enough magnesium ions for extensive dolomitization (Hsü, 1967); the magnesium is derived primarily from marine water and the flow of fresh groundwater induces the circulation of seawater (Land, 1973). The necessity of the dilution of the seawater has been proposed to cause a slow precipitation which favours dolomite precipitation (Folk and Land, 1975; Morrow, 1982b). Hardie (1987) finds serious reasons to doubt the efficacy of this model for extensive dolomitization. Presuming the formation of poorly ordered, more soluble dolomite (which is the dolomite that forms at surface temperature) the range of mixed-waters that complies with the assumption of supersaturation of dolomite and undersaturation of calcite is very narrow (Figure 4). Furthermore, no active modern examples of this dolomitization are documented (Hardie, 1987, p. 170), nor is there any theoretical quantitative model ever proposed that the supply of Mg^2+ could be adequate.

![Figure 4: Theoretical saturation relationships between dolomite and calcite in mixtures of seawater and meteoric water at 25°C, for ordered dolomite (K = 10^-17). The starting water composition is the same as that used by Badiozamani (1973) (from Hardie, 1987).](image-url)
The increase of the temperature related to the burial of sediments and the longer time available, should promote the formation of dolomite; the compaction of clay sediments associated to carbonates expulses pore water, which contains magnesium ions (Illing, 1959; Mattes and Mountjoy, 1980), or magnesium can be released by pressure solution (Wanless, 1979). The burial compaction model is based on these observations. It seems unlikely that the amount of fluids expelled is enough to produce regionally extended dolomitized sequences and that the circulation of fluids is sufficiently active at these depths to transport the magnesium into, and to remove calcium from the dolomitization situ (Morrow, 1982b; Wells, 1985).

The most recent models involve seawater as a dolomitizing solution in a hydrothermal environment (e.g. thermal convection, Saller, 1984; Kohout convection, Kohout et al., 1977; Simms, 1984). The thermal convection model operates with a convection "half-cell" with seawater acting as an infinite reservoir. Thermal convection probably takes place in Florida (Kohout et al., 1977) and Enewetak Atoll (Saller, 1984) and may also occur in isolated platforms that are not in hydrologic communication with groundwater flow systems (Simms, 1984). Hydrothermal dolomite associated with fractures has been described for example by Zenger (1976), Pichugin et al. (1977), Black et al. (1981).

Several modern models proposed for dolomitization all consider a supply of magnesium, from alkaline lakes, hypersaline brines or marine water. This is a necessary but not sufficient consideration. The hydraulic drive to supply the source of magnesium to the dolomitization system is the key of the problem. Most of the models have been tested in the laboratory, but only a few could reproduce natural geological conditions, like sediments permeability, Mg-bearing fluid supply and circulation, and time. Among the proposed models, only the evaporative pumping and the thermal convection models could be considered valid scientific hypotheses because they have formulated quantitative relations for verification or falsification. Other models which cannot be tested are speculations.

Hydrodynamic models which potentially can supply magnesium for dolomitization are subduction-induced pore fluid venting and hydrothermal, gravity-driven, circulation in convection cells.

The first model is observed in accretionary prisms of subduction zones, e.g. in Oregon. The deforming, ancient accreted deposits de-water through fracture permeability associated with faults. The accretionary wedge and underthrust sediments comprise distinct fluid domains separated by a permeability barrier above the decollement zone. The vents of pore fluids cause precipitation of calcium carbonate in chimneys and cementation of the accreted sediments, probably as results of migration and oxidation of biogenic methane, which provides a pool for the carbonate ion, advected through the underthrust sediment from beneath the accretionary wedge. The surrounding waters, enriched in organic carbon, allows for the proliferation of microorganisms and molluscs communities. Temperature anomalies of 0.3°C were observed in the bottom water surrounding the vents. It is suggested that pore fluid venting in subduction zones may also act as global sink or source for other than Ca elements (Kulm et al., 1986; ODP Leg 110 Scientific Party, 1987).
Hydrothermal circulation in convective cells is documented in mid-ocean ridge regions. At the ridge axis, magma maintains steep horizontal temperature gradients in the crust, driving vigorous, "forced" convection. This produces the "black smoker" vents observed at or near the ridge axis. A weaker "free" convection continues in the ridge flank region in an area as wide as 1000 km, where the crust is permeable enough to allow for a circulation in free convective cells. The estimated flux of seawater through this area is of a few hundreds of cubic kilometers per year, whereas the circulation in ridge axis region involves only few tens of km$^3$ of seawater per year.

The aim of this thesis is to make a base-hystory study to test the viable models of dolomitization.
1.3. Modern base line 2: Tectonics and geological boundary conditions

1.3.1. Paleogeography and alpine tectonics

The Southern Alps are a major structural subdivision of the Alps, located to the south of the Insubric Lineament. They are unaffected by the alpine metamorphism and considered a South-vergent thrust-belt (Castellarin, 1979; Gaetani and Jadoul, 1979; Laubscher, 1985; Doglioni and Bosellini, 1987) (Figure 5).

The present geometry of the Alps is the result of several stages of deformation that have occurred since the late Paleozoic. The Permian sediments are continental and shallow marine (e.g. Arenaria di Val Gardena and Bellerophon Formation), with their detritus derived from the erosion of the Variscan massif. Active rifting of the Tethys associated with their deposition led in the Middle Triassic to the intrusion and extrusion of volcanics (alkali-volcanics of the Monzoni area, South Tyrol). This led to the formation of extensional structures (i.e. basins and swells), breaking up the preexisting carbonate platform, as the future southern continental margin of the Tethys experienced mainly rifting and subsidence, creating the set of roughly N-S oriented platforms and basins with hemipelagic-pelagic sedimentation (Winterer and Bosellini, 1981). Among them, of major interest for the present study are, from west to east, the Lombard Basin, the Trento Plateau and the Belluno Trough (Figure 6). Differential subsidence of the shallow-water carbonate blocks gave rise to the seamount-and-basin topography that closely controlled the facies developments. Extensional tectonics
persisted throughout the Jurassic in many parts of the Tethys. Sinking of the seamounts led to progressive facies changes from biosparites to red nodular limestones (Rosso Ammonitico-type). By Mid- to Late Jurassic time the Tethyan drifting begins and pelagic sediments are deposited in the Tethyan ocean and along its southern continental margin (radiolarites, nannofossil limestones) (Bernoulli and Jenkins, 1974).

The opening of the Tethys coincided with the opening of the Atlantic Ocean in the Jurassic. Therefore, in the Cretaceous the relative movement of African and European plate changes. The Adriatic sub-plate, which was either caught between the two continents, or was just a promontory of the African plate, collided with the Eurasian continent after the subduction of the Tethyan oceanic crust in the Cretaceous. The complex collision between Eurasian and the Adriatic plate generated the alpine chain between the Cretaceous and Lower Tertiary in three main stages: Eoalpine (Late Cretaceous), Mesoalpine (Paleogene) and Neoalpine (Neogene) (Trümpy, 1973, 1982; Hsü, 1989). During the eoalpine stage the subduction of the Tethyan oceanic crust took place, a tectonic pattern that persisted until the Middle Eocene. The evidence for the Cretaceous deformation suggests that the Adriatic plate was independent from the African plate (Hsü, 1989). At the end of the Cretaceous, the ocean basin was probably partly closed, with pelagic sedimentation continuing in some areas, whereas flysch was becoming progressively more widespread as orogenic movements proceeded

![Diagram](https://example.com/diagram.png)

**Figure 6:** Palinspastic cross section through the Ligurian ocean during the Upper Jurassic (from Laubscher and Bernoulli, 1977).

(Bernoulli and Jenkins, 1974). Hemipelagic sediments of the Scaglia Rossa, Scaglia Variegata and Scaglia Grigia formations are deposited in this time in the deep water Trento Plateau, while terrigenous turbidites with a thickness of up to 2000 m are deposited in the Lombard Basin (Doglioni and Bosellini, 1987). The collision of the southern margin of Europe and the northern edge of the Adriatic plate took place in late Eocene, earlier in the east and later in the west (Hsü, 1989). In the Neoalpine stage, post-collision deformation takes place, the African plate overrides the European plate. The intrusion of the alpine plutons, like the Adamello, attest to the post-collision magmatism. Oligocene extensional tectonics active in the Southern Alps, related to collision tectonics, has been described by Laubscher (1983) and Ratschbacher et al. (1989).

In the Venetian Alps, south of the main suture zone between Europe and the Adria plate, shallow water nummulitic limestones and rare coral reef deposits were deposited on top of
the Mesozoic pelagic sequence. The area was affected at the same time by mafic volcanism. This volcanic activity was firstly explosive, with deposition of breccias and tuffs, and then evolved in the eruption of basaltic lava flows from localised vents.

The presence of dolomitic rocks in the Lessini Mounts, the hills situated in the northern part of the provinces of Verona and Vicenza, in North-East Italy, has been mentioned already in the last century (Maraschini, 1824; Balestra, 1832; Bittner, 1877; Secco, 1883; Dal Lago, 1899; Dal Piaz, 1912). In the "Foglio Verona, # 49" of the Carta Geologica d'Italia (1:100 000) the dolostones are named "Complesso dolomitico indifferenziato". The dolomite is widespread, mostly in the central part of the Lessini Mounts. The dolomitization affects the Jurassic and Cretaceous sequence, some 700 m thick carbonates above the Norian Hauptdolomit formation. The geometry of the dolomitized bodies is discordant with respect to the regional trend of the bedding, oriented parallel to the major tectonic disturbances in the area. The interesting proximity with the basaltic rocks which extruded in the Paleogene gives rise to consideration about a possible connection between the two phenomena, as already suggested by Carraro (1964).
CHAPTER 2

FIELD ANALYSIS

2.1. Region of study

The study was carried out in the Veneto region, NE-Italy. The dolomitization in this area is widespread in the central-western part of the Lessini Mounts, north of Verona and west of Vicenza. The Lessini Mounts are a group of elongated, ridge-shaped hills varying their orientation from NNW-SSE to N-S to NNE-SSW, moving from west to east. They are a few hundred of meters high and are cut by deep valleys, with a fan structure, closing and bordered to the north by the Recoaro area. Similar examples of dolomitization were found NE of the Lessini Mounts in the Grappa Mount region between Bassano del Grappa, at the southern edge of the Prealpi (about 40 km north of Padua) and Feltre (30 km SW of Belluno).

2.2. Regional stratigraphy

Above the transgressive deposits of the Early Triassic that covered the Variscan basement, the Permian volcanics and the sandstones of the Val Gardena formation, the Southern Alps evolved into a carbonate platform. Ladinian and Carnian pelagic sediments show, in the Dolomites, the beginning of the fragmentation of the carbonate platform (Bosellini and Rossi, 1974). The dolomite-evaporites association of the Strati di Raibl and the Hauptdolomit gives evidence of the return to more uniform sedimentation conditions. This stratigraphic sequence is exposed in the Recoaro anticline, northernmost to the Lessini Mounts.

2.2.1. Late Triassic Stratigraphy

The Norian Hauptdolomit (Dolomia Principale) of the Triassic extends from the Lombardia (NW-Italy) to Yugoslavia. The 900 m (in the Lessini area) thick dolomitic limestones and dolostones have been deposited in a shallow sea, with a cyclic carbonate sedimentation oscillating between subtidal, intertidal and supratidal (Bosellini, 1965, 1967). It is possible to subdivide the Hauptdolomit in two parts. The lowermost 500-600 m are a classic peritidal cyclic sequence at a m-scale (1-3 m), the uppermost 200-300 m are represented by a white subtidal dolomite, sucrosic and massive, interrupted every 3-5 m by 20-100 cm thick pedogenetic levels with pisolites and tepees (Bosellini and Hardie, 1985).

The cycles present in the Hauptdolomit can be explained as authigenic sedimentary cycles (Ginsburg’s model), as the result of eustatic variations of the sea level or intense subsidence (Bosellini, 1967) or as climate cycles.
2.2.2. Jurassic and Cretaceous stratigraphy

Varied paleogeography ensured that the Jurassic period was the time of maximum facies variety in the Alpine Tethys. On the Trento platform, above the Norian Hauptdolomit, a thick sequence of tidal-flat sediments (Calcari Grigi di Noriglio formation, mostly limestones and dolomitic limestones) were deposited during Liassic, followed by the oolitic limestone and pelagic pelletal limestones of the San Vigilio formation (Toarcian - Aalenian). This last formation is locally missing (e.g., high Chiampo Valley) because of local emersions of the carbonate platform (Bosellini and Broglio Loriga, 1971). To the east, in the Belluno Trough coeval are Liassic pelagic limestones and chert of the Formazione di Igne. The Vajont formation is formed by redeposited oolithes on top of the Igne formation. From the Late Dogger, the sediments in the trough are not distinguishable from those on the Trento Platform (Weissert, 1979)(Figure 7). However, variations in formation thickness indicate a persisting seafloor morphology. The Lombardian Basin, west of the Trento platform, is subdivided into internal basins, where thick turbiditic sequences are deposited, and swells with intertidal and neritic sedimentation (Gaetani, 1975).

![Stratigraphic correlation through the Southern Alps](image_url)

Figure 7: Stratigraphic correlation through the Southern Alps (from Winterer and Bosellini, 1973).
The beginning of pelagic sedimentation on the Trento Platform is marked by the Rosso Ammonitico Veneto, a red condensed, nodular limestone rich in ammonites, that reaches thicknesses of 30 m in the area (Sturani, 1964). In Middle-Upper Jurassic pelagic limestones (Rosso Ammonitico Lombardo, Gaetani, 1975) are sedimented in the Lombardian Basin. The sedimentation continues with radiolarites and cherty limestones (Rosso ad Aptici) (Lombardian Basin, western Trento Platform) and white nodular limestones (rest of the Trento Platform and Belluno Trough) (Weissert, 1979). The white, micritic, nannofossil limestones of the Maiolica Veneta formation (Tithonian - Early Aptian) and the greenish-gray marls and marly limestones (biomicrites) of the Scaglia Variegata (Late Aptian - Cenomanian) (Cita, 1964; Weissert, 1979) overlays the Rosso Ammonitico in the Trento Platform. Characteristically, its lithology includes grey chert layers and nodules. In the Lombardian Basin, the Maiolica Lombarda is not distinguishable from the Maiolica Veneta lithologically but the thickness difference suggests the existence of a structural difference between the two areas. The flasered marls of the hemipelagic Scaglia Rossa formation (Turonian - Maastrichtian) finally close the Mesozoic sedimentary sequence in the studied area (Bosellini et al., 1967). This is associated with the Scaglia Grigia and Scaglia Variegata formations at the edges of the Trento Plateau (Trentino, Bellunese), which range in age from Paleocene to Middle Eocene.

2.2.3. Tertiary stratigraphy

A stratigraphic hiatus, from the Late Maastrichtian to the Late Paleocene, at the top of the Scaglia Rossa, is marked by a hard-ground (Malaroda, 1962; Medizza, 1965). In the Late Paleocene begins the extrusion of volcanic breccias and tuffs of basaltic composition, which are intercalated with Upper Paleocene to Lower Eocene marls and fossiliferous limestones, as well as Middle Eocene nummulitic limestones (Medizza, 1965). The paleogeogeographic situation in the Early Eocene in the northern part of the Lessini can be deduced by the presence of fine grained limestones rich of perfectly preserved fossils of tropical fishes and plants like coconut palms, found in the well known fossiliferous locality of Bolca (Verona) (Bosellini et al., 1967). The limestone deposited in an anoxic lagoon, with conditions that allowed the perfect conservation of the fossils, adjacent to an emerged area which provided the continental debris.

The Middle Eocene basalts are locally subaerial (e.g. Mount Calvarina) (Barbieri et al., 1981). The presence of lignite intercalated with the upper part of the basalts of Middle Eocene age testifies the establishment of lagoons during rests of the volcanic activity, where a continental flora, characteristic of a tropical climate, has been deposited (De Visiani and Massalongo, 1856). Transgressive on the subaerial basalts, fossiliferous marls and algal limestones (calcari nulliporici) of the Marnie di Priabona formation (Upper Eocene), Oligocene calcarenites (Calcareniti di Castelgomberto), Miocene sandstones and limestones (Arenariga di S. Urbano) are deposited in a shallow sea. Coral reefs are frequent, especially during the Oligocene (Figure 8).
2.3. Faulting of the Lessini area

A prominent tectonic feature, and the oldest observed in the area, is the Marana Fault, at the northern margin of the Lessini Mounts (Fig. 9). This ENE-WSW oriented normal fault, and a sheaf of minor faults with the same orientation, is the result of an extensional tectonism. It dips to the south with a throw variable between 1000 and 2000 m (Zanferrari, 1972).
Figure 9: Simplified geological map of the Lessini Mounts (modified from Carta Geologica d'Italia, Foglio # 49 [Verona] 1:100 000). 1: Quaternary alluvial deposits; 2: Tertiary sediments (limestones, marls, sandstones); 3: Tertiary volcanic rocks; 4: dolomitized breccias; 5: Mesozoic limestones and Hauptdolomit.
The NNW-SSE oriented fault system (Castelvero Fault) seems to be active in two distinct times: during an extensive stage, faults with throws of few hundreds meters took place, and a later that was a less important, mainly dextral transcurrent event (Barbieri et al., 1980).

The latest faulting is a strike-slip fault, the Schio-Vicenza Fault, NW-SE oriented. The movement is sinistral (Figure 10).

In the volcanoclastic rocks of Late Paleocene-Early Eocene age are common inclusions megablocks of sedimentary rocks, such as poorly consolidated Scaglia Rossa and nummulitic limestones, which may range up to a few thousands cubic meters in size.

2.4. Tertiary volcanic rocks

The only important manifestations of the Tertiary volcanism in the Southern Alps are found in the area defined by the Garda Lake, Bassano del Grappa and Padua, especially in the Lessini Mountains, in the Marosticano area, north of Vicenza, and in the Euganean Hills, west of Padua. The volcanics are extended beneath the Po Plain, southernmost of the Lessini Mountains and underneath the Euganean Hills (Cassano et al., 1986) and between Padua and Bassano del Grappa (Illiceto, unpubl. data). Volcanic rocks are of Late Paleocene to Oligocene age. Radiometric dating of basalt of two necks in the Chiampo Valley gives an Early Miocene age (Savelli and Lipparini, 1980)(Figure 10).

Only the volcanics in the Euganean Hills are predominantly acid. The rest of the area are products of basic volcanics (nephelinites and ankaratrites with less than 40% SiO₂; alkali-olivin basalts, latibasalts), with an alkaline character (both sodic and potassic) in the earliest ones and a tholeiitic trend in the youngest ones. The genesis of the alkaline magma can be described as the result of partial melting in the upper mantle (60-70 km)(Green and Ringwood, 1967). Subaqueous volcanoclastic rocks of Late Paleocene age (Globorotalia pseudomenardii zone) are exposed only in the Chiampo Valley (Medizza, 1965). Between the Paleocene and the end of the Middle Eocene basaltic tuffs, breccias and lavas are mainly found in the Lessini area. During the Early Eocene (Globorotalia subbotinae and Globorotalia aragonensis zones) basaltic breccias of Early Eocene age are found in the western part of the Lessini (Veronese) and NNW of the Lessini (Rovereto and Trento area)(Castellarin and Piccoli, 1966).

Two layers of Middle Eocene subaqueous basaltic lavas are widespread in both the Lessini and the Trentino (west of the Adige River). The second layer, dated in the Nummulites
Figure 10: Distribution of the volcanic rocks in the Venetian Tertiary Province (from Conedera et al., 1972). 1 = Mountain border; 2 = Faults; 3 = Overthrusts; 4 = Anticline axes; 5 = Syncline axes; 6 = Tertiary volcanics and main volcanic necks; 7 = Triassic volcanics; 8 = Permian volcanics; 9 = Plutons; 10 = Pre-Permian crystalline basement; 11 = Marls and sandstones (Miocene); 12 = Paleogene nummulitic limestones and Lower Miocene limestones; 13 = Marls of Eocene and Oligocene age; 14 = Mesozoic limestones and dolostones; 15 = Permian sandstones, limestones and evaporites.
brogniartii zone is up to 300 m thick (Barbieri et al., 1981). These basalts are, in the late Middle Eocene, locally reddish, oxidized during subaerial exposure.

Late Eocene-Early Oligocene age basaltic rocks are found exclusively in the Euganean Hills (Globorotalia cerroazulensis cerroazulensis and G. c. cocoaensis zones) (Dieni and Proto Decima, 1963; Piccoli et al., 1976). Acidic to intermediate, mainly alkaline volcanic rocks (rhyolites, alkali-rhyolites, trachytes and latites) are found in this area. Geochronological dating gives these products an age of 30-34 million years, i.e. Oligocene.

In the Marosticano area (east of the Lessini) basaltic rocks of mainly tholeiitic composition have a Middle to Late Oligocene age (Piccoli, 1967). In the Lessini, necks of this age are found. In the Marosticano and in the eastern Lessini, the youngest products of this volcanic activity, two necks of Early Miocene age (Savelli and Lippiari, 1980) are found.

Spinel lherzolite xenolithes included in the basic rocks, give evidence for the primitive, not differentiated, character of the melt. This can be explained with a quick ascent of the magma in conditions of extensive tectonism. Gravimetric and seismic data of the area show the presence of a high-density (3.15 g/cm³) body at a depth of 30-40 km. The chemistry of the Venetian alkaline basic volcanics shows some similarities with the post-orogenic, essentially basic, volcanism in the Western USA, connected with extensive tectonism and partly caused by a mantle plume (Wilson, 1973; De Vecchi et al., 1976). The possible origin of the acid products from a differentiation of the mafic magma is unviable, because of the Sr isotope data (Barbieri et al., 1978). They are originated from a distinct “trachytic” magma.

2.5. Structural features in the field

The dolomitic bodies which are widespread in the Jurassic-Cretaceous limestones are distinctly related to the tectonic framework of the area. Dolomitization affects brecciated limestones. Throughout the area various structures were formed which can be related to a specific stage in the tectonic history. The main structures observed are tectonic breccias, minor listric faults, and cross cutting vertical fractures.

2.5.1. Tectonic breccias

Tectonic breccias were observed throughout the area where dolomite is found and dolomitization particularly only affects brecciated limestones. The breccia tectonic bodies are up to hundred meter wide, generally crosscutting the original bedding. Macroscopically the brecciation consists the grey-buff coloured dolomitic rock with scattered angular chert fragments (Figure 11). Clasts are generally from 1 to 2 cm. Field contacts with the unaffected rock is sharp, subvertical and often marked by a fracture. At one field location (Crespadoro, Chiampo Valley) it was noticed that no displacement took place along this fracture.
Figure 11: Photograph of a brecciated, dolomitized rock from Crespadoro, Chiampo Valley, Lessini.

Figure 12: Photograph of the listric faults in the Maiolica at the contact with the dolomite (right in the photo) (Crespadoro, Chiampo Valley). The orientation of the tectonic features is $320^\circ/60^\circ$.

Figure 13: Photograph of a brecciated Maiolica in a yellow dolomitized matrix. Note the extensional features in the central fragment (Chiampo Valley). (Orientation: $330^\circ/50^\circ$)
Figure 14: Photograph of a small-scale normal fault, which is open and filled with chert fragments (Novale, Agno Valley) (Orientation: 020°/30°)
2.5.2. Extensional structures

Small scale listric faults, of about 20 cm length, are found (Figures 12-14). They show the characteristic extensional domino-structure where the beds are successively downthrown to the north or south. The listric faults do not seem to detach along one common horizon, but rather anastomose along a detachment plane. Figure 15 shows the field observations of these faults, which can be seen to be striking predominantly east-west and dipping to either the north or south at angles of approximately 60 to 70°. They are found at the contacts of the limestone and the tectonic breccia and cut the already lithified and stylolithized limestone, which can be seen to allow for the precipitation of dolomite into the adjacent veins. These faulting has the same orientation as the contact limestone-dolomitized breccia and seems the oldest tectonic feature affecting the Jurassic-Cretaceous limestones.

2.5.3. Volcanic / host rock relationships

Basaltic volcanic dykes were seen to cut discordantly across and throughout the Mesozoic limestones in the Lessini area. However, they were not found to intrude into the tectonic breccia where the dolomitization had taken place. The dykes were generally a few meters wide and were only seen to extend at outcrop scale. The fine grained, dark basalt was highly altered, fragmented and intruded by a late stage calcitic veins. It usually contains small, 1-3 mm, almond-shaped amigdales containing zeolites and calcite. The contact of the dykes were typically chilled, and there are rare stringers of volcanics into the host rock. In places, where the dykes are over 5 to 10 meters wide, significant recrystallization of the country rock can be seen where the heat generated from the intrusive dyke has altered the textural features. The dykes show mainly two orientations, ENE-WSW and NNE-SSW. Crosscutting relationships were not observed.

2.5.4. Crosscutting vertical (extensional?) fractures

Small scale (10 cm to 1 m) fractures were found which crosscut the listric faults and sometimes the basaltic dykes. They are oriented NW-SE, dipping to the east by a high angle, i.e. almost vertical and show little evidence of movement. They are rarely filled with fibrous calcite and essentially look like joints.

2.6. Interpretation of the structures observed

Field observations demonstrate that the dolomitized rock is brecciated and that the brecciation is earlier than the dolomitization. This conclusion is reached by noticing that the the whole breccia is homogeneously dolomitized and the dolomite is not disturbed itself. That the breccia is associated with a phase of extensional tectonism is indicated by the fact that their occurrence is intrinsically related to the listric faults at the contact with the unaffected limestone. The occurrence of the east-west striking faults can be seen to parallel the Marana Fault system (see 1.2.3). This suggests that the minor listric faults are syntectonic to the
Figure 15: Map to show the orientation of the extensional structures observed in the Lessini Mounts (see Figure 10). Equal area stereoplot projection, unshaded half moon represents hanging wall.
Marana Fault and formed because of a major phase of extension. The age of the beginning of the extensional movements is probably Paleocene (Zanferrari, 1972) and led to the extrusion of the volcanic products. The tectonism, brecciating the limestones, opened the way not only to the magma but also to the circulation of potentially dolomitizing fluids.

Barbieri (1972) and Barbieri et al. (1981) suggested the existence of a roughly N-S oriented Chiampo graben, which was active in the Paleogene and apparently controlled the extrusion of these basalts. They found that the regional distribution pattern of the volcanics suggests an active tectonism during the volcanic activity. The presence of megablocks of unconsolidated sediments of Scaglia Rossa formation and nummulitic limestones which slid in the volcanics testify of the tectonic instability of the area. Furthermore, they point out that the orientation of volcanic necks and dikes is mostly NW-SE. But ENE-WSW oriented dikes are also quite common (Barbieri et al., 1980: Carta Geologica dell'area di Recoaro). As the dykes in the Lessini area only cut the Mesozoic limestones and not the dolomitized breccia, it suggests that the breccia formed later than the main phase of volcanic activity (Figure 16).

The late stage cross cutting fractures, which cross the listric faults, suggest a new stage of extensional tectonics (?), or at least a further stage of progressive deformation which can be associated with the NW-SE Castelvero Fault system. Further evidence of this is the absence of lava flows west of the Castelvero line which can be explained by erosion. Upper Paleocene volcanic breccias are present north of Verona and the occurrence of volcanic vents cross-cutting the Mesozoic carbonates testifies the occurred extrusion of magma also in this part of the area. The general distribution of the volcanic rocks in the whole area between the Paleocene and the Miocene shows a E-W pattern. This suggests that the graben, related to the volcanism, was east-west elongated, generated by N-S extension, limited to the north by the Marana Fault.

Figure 16: Map to show the distribution of the volcanics with its relationship with the tectonics during the Tertiary.
CHAPTER 3

Dolomite and dolomitization

3.1. Introduction

The aim of the present work is to define a plausible genetic and hydrological explanation for the dolomitization. In addition to the field analysis, detailed petrographic and geochemical analysis was carried out on various samples. Techniques such as thin section analysis, X-ray diffraction, scanning electron microscopy and cathodoluminescence were utilized.

3.2. Regional distribution of the dolomites and dolomitization

Dolomites are found extensively in the Southern Alps, ranging in age from Middle Triassic to Cretaceous. The nature of the Triassic dolomites (Middle Triassic dolomite in the Dolomites and the Norian Hauptdolomit) is distinctly different from the dolomite breccias found in the Trentino plateau. These are found in the Mesozoic limestones overlying the Hauptdolomit, from the Liassic Calcari Grigi di Noriglio formation up to the lowermost part of the Scaglia rossa formation. The uppermost Scaglia rossa and the Tertiary limestones are neither brecciated or dolomitized. Locally, in the Trentino plateau, the dolomitized rocks are widespread in most of the Lessini Mounts area to the south (Figure 10) and near Feltre (Belluno) to the north-east (Figure 17). Dolomite has also been sporadically found in Trentino, more exactly in the Val di Non, north-west of Trento. Here, dolomitization affects the Rosso Ammonitico and Maiolica Veneta Formations which are here few meters thick because of a stratigraphic hiatus, and directly overlie the Hauptdolomit. In this case, dolomitization does not affect brecciated limestones. A few examples have been collected in this area and, although macroscopically they look quite similar to the dolomite from the Lessini and Feltreino, the dolomite from the Trento area is not comparable to the samples collected in the Lessini and Feltre area (see 4.2.3 and 4.3.3). For this reason, these dolomitized rocks have not been taken into consideration for the development of the dolomitization model.

In this study, only the upper 250 m of Upper Jurassic to Upper Cretaceous age of the dolomitized sequence in the Lessini and Feltre areas have been analysed in detail. The lower part was strongly karstified and altered by late meteoric processes. An advantage of using pelagic limestones as the starting material for the dolomitization, simplifies the problem,
Figure 17: Map of the Southern Alps with the location of areas where the dolomitization occurs (asterisks).
since the original sediments are an almost pure calcium carbonate.

3.3. Macroscopic description of the Lessini and Feltre area dolomites

In the Lessini and Feltre areas, the dolomitization affects only the brecciated limestones. The consistence of the brecciated rock before the dolomite should have been the one of a cataclasite, a very fine carbonatic breccia with included bigger chert fragments. These bodies are from a few meters to few kilometers wide and usually few tens of meters thick. Only in the Lessini area, the volume of outcropping dolomitized breccias is about 28 km³, i.e. at least about 5% of the Mesozoic carbonate rocks overlying the Hauptdolomit.

The dolomite rock is massive with a grey-yellow colour, consisting mainly of anhedral dolomite and subordinated calcite. No fossils are found in the dolomitized rock. In one case, two fragments of undolomitized rock have been found included in the dolomite. The rock is fine to medium grained, homogeneous with a granoblastic texture. No relic textures of the earlier limestone could be found, as it was obliterated by dolomitization. The rock weathers to a poorly cemented material of a light buff to dark brown colour, probably due to the oxidation of the iron. Chert fragments are widespread in the host rock. Veins and vugs filled by ankerite and sparry calcite also cut the dolomite host rock. The limestone next to the contact with the dolomitized breccia is also fractured and the brecciated zone has a width of two meters maximum. The fractures in the brecciated limestone in these zones are filled with yellowish-brown calcite, chert fragments, diagenetic pyrites and clay minerals, and, later, with calcitic spar.

3.4. Petrographic description of dolomite

3.4.1. Introduction

Thin section analysis of both limestone and dolomite samples from the Lessini Mounts, Feltre area and Trentino (see Appendix 2), of Upper Jurassic to Upper Cretaceous age, allows for a detailed examination of the granular and intergranular relationships within a specific sample.

3.4.2. Preparation

The dolomite rock samples were studied on standard 30 µm thin sections. The thin sections have been stained with a mixture of one part of potassium ferricyanide (1 gr in 100 ml 0.12N HCl) and 1.5 part of Alizarin Red-S (0.1 gr in 100 ml 0.12N HCl)(Friedman, 1959; Dickson, 1966) to facilitate the distinction between calcite and dolomite: calcite assumes a
Figure 18: Photograph of a thin section of sample M6; the dark material is the dolomite bulk rock, the lighter area is a vein with a typical dolomite-ankerite (or Fe-rich dolomite, the yellow crystals)-calcite (the big crystals in the middle) sequence.

Figure 19: Photograph of a thin section of the yellow material (see text) filling the fractures in the Maiolica at the contact with the dolomitized rock. Note the ghosts of dolomite rhombohedra, as shown by the white arrows.

Figure 20: Photomicrograph of sample VN14 (Val di Non, Trentino), showing scattered dolomite rhombs in micrite.
Figure 21: Example of fluid inclusion-rich cores of dolomite crystals (sample PR10/11). Base of photograph is 0.27 mm.

Figure 22: Example of fluid inclusion-rich cores of dolomite crystals (sample M6). Base of photograph is 0.27 mm.
Figure 23: Example of fluid inclusion-rich cores of dolomite crystals (sample PR10/11). Base of photograph is 0.27 mm.
distinct reddish-violet coloration, while dolomite is unstained.

### 3.4.3. Observations

The pelagic limestone of the *Rosso Ammonitico, Maiolica* and *Scaglia* Formations is generally a micrite, more or less rich in macrofossil fragments and microfossils (forams, radiolarians, calpionellides). The dolomitized rock in the brecciated zones consists of a mosaic of crystals less than 100 μm across. The dolomite crystals have a cloudy core and a relatively clearer rim. Rhombohedral calcite crystals partially substitute dolomite crystals. Idiomorph pyrite crystals are present. Microfractures and vugs are filled first with slightly coarser dolomite, then with ankerite (Ca-Mg-Fe-carbonate) and sparry calcite, with crystals of few hundreds μm size (Figure 18). The yellowish filling of the fractures in the brecciated limestone at the contact with the dolomitized zone, at a microscopic observation, is a dedolomitized calcite: it is still possible to distinguish ghosts of zoned dolomite rhombohedra (Figure 19). The dolomite crystals are zoned, with a dark core due to a high concentration of fluid inclusions. The size distribution of the dolomite in the matrix is unimodal and the anhedral dolomite crystals are closely packed with irregular intercrystalline boundaries. The samples of Tithonian age collected in Trentino (Val di Non) are constituted by sparse zoned dolomite rhombohedra in the calcitic micrite (Figure 20).

At high magnification fluid inclusions inside the crystals of the dolomite could be observed. They are very abundant in the core but less in the rim of the crystal. Fluid inclusions are widespread in the whole dolomite sample and the abundance of liquid inclusions in the core of the crystals gives an isotropic appearance in the polarized light. Fluid inclusions are widespread in the whole dolomite sample (Figures 21-23). The inclusions are elongated, radiating from the center of the crystal. From their relation to the crystal geometry, it is possible to assert that these inclusions were formed at the time of the formation of the dolomite crystal, i.e. they are primary. Their size is commonly 2-5 μm, but rare inclusions of up to 50 μm across have been found. Their whole volume constitutes up to 10% of the volume of the core. In the veins, primary inclusions are very abundant in the dolomite crystals at the edge of the vein, often separated from later dolomite crystals by an ankerite rim.

Secondary inclusions, formed in microfractures, lined up and cross-cutting the crystals, are also present. The late calcite filling is sterile. The study of the fluid inclusions will be discussed separately (see Chapter 5).

### 3.5. Ultrastructural sedimentary fabrics

#### 3.5.1. Introduction

Generally, a scanning electron microscope (SEM) allows for the detailed examination of rock fragments by the excitement of its surface by electronic rays. The sample can be viewed at sizes to a fraction of a micron, which can then be chemically analysed qualitatively with the aid of an energy dispersive system (EDAX). Some of the most significant dolomite samples
Figure 24-28: Mosaic of 5 photomicrographs, showing a profile through a vein, from the dolomite host rock (left) to the calcite spar (right) [sample M6]. Scale shown by bar.
Figure 29: Photomicrograph of the surface of a dolomite crystal with clays and iron-oxides needles (sample M6). Scale shown by bar.

Figure 30: Photomicrograph showing a contact between calcite and ankerite with EDAX (sample M6). Scale shown by bar.

Figure 31: Photomicrograph showing a general view of Figure 30. Scale shown by bar.

Figure 32: Photomicrograph of large dolomite crystals against smaller calcite microcrystals (sample RA3). Scale shown by bar.

Figure 33: Photomicrograph showing a close-up view of Figure 32 (sample RA3). Scale shown by bar.

Figure 34: Photomicrograph of dolomite crystals in dolomicrite (Hauptdolomit, sample HDT19). Scale shown by bar.
Figure 35: Photomicrograph of a close-up view of the iron-oxides (goethite?) needles from Figure 34 (Hauptdolomit, sample HDT19). Scale shown by bar.

Figure 36: Photomicrograph of a close-up view of iron-oxide needles on the surface of a dolomite crystal (sample M6). Scale shown by bar.

Figure 37: Photomicrograph of a ghost of dolomite rhombohedron in dedolomitized yellow fracture filling (sample PB21/87). Scale shown by bar.

Figure 38: Photomicrograph to show another example of dolomite rhombohedron in the yellow filling (sample PB21/87). Scale shown by bar.

Figure 39: Photomicrograph of sparry calcite in fractured Maiolica (sample PB21/87). Scale shown by bar.

Figure 40: Back-scattered photomicrograph of a fracture in the dolomite (sample M6). See text for explanation. Scale shown by bar.

Figure 41: Close-up view of back-scattered photomicrograph of Figure 40 (sample M6). Scale shown by bar.

Figure 42: Photomicrograph of a fracture in the dolomite (sample M6). Scale shown by bar.
Figure 43: Photomicrograph showing the elemental distribution of Mg for Figure 42. Scale is the same as for Figure 42.

Figure 44: Photomicrograph showing the elemental distribution of Fe for Figure 43. Scale is the same as for Figure 42.

Figure 45: Photomicrograph of an example of backscattered images of fractures in dolomite (sample SG2b). Scale shown by bar.

Figure 46: Photomicrograph of an example of backscattered images of fractures in dolomite (sample SG2b). Scale shown by bar.
especially those collected at the contact with the unaffected rock, were analysed with the SEM.

3.5.2. Preparation

Fragments of some of the studied limestone and dolomite samples (M6 - dolomitized *Scaglia variegata* of Cenomanian age from Molino d'Altissimo, Lessini; RA3 - contact between *Rosso Ammonitico* and dolomitized breccia from Ferrazza, Lessini; PB21/87 - yellow fracture filling in *Maiolica* from Ferrazza, Lessini) were glued to the metal sample holder with liquid graphite and then metallised with gold. Samples were then excited under a voltage of 25 kV and viewed, through the attached computerized screen. An additional technique of analyzing the samples is by the "backscatter" image of a thin section. Some 30% of the electrons that hit the specimen surface in the SEM are scattered out to produce localised pictures of various intensity related to the chemistry of the element concerned. The number of backscattered electrons increases with the atomic number of the hit element. This results in a more or less bright luminescence of the crystal, depending on the presence of lighter or heavier elements in the structure.

3.5.3. Observations

The micrite of the *Rosso Ammonitico, Maiolica and Scaglia* limestones is very fine grained, the single crystals having a size of 3-4 μm. At low magnification, the dolomitic rock shows an irregular surface and the single crystals are small (10-15 μm) and not well distinguishable. With a 2000x to 4500x magnification it is possible to see some impurities on the surface of the crystals or at the interface between two crystals: grouped needles of Fe-minerals (determined with EDAX, Energy Dispersion Analysis System) and leaflets of Al-rich phyllosilicates, clay minerals (Figure 29). The contact between the dolomite and the calcite is extremely sharp, and it is clearly due to the secondary formation of the dolomite, whose crystals grew out from the micrite. Crystals in the veins are a few hundreds of μm across and are well crystallized rhombohedra. The calcite crystals fill the center of the vein, and are divided from the dolomitic host rock by a thin "film" of ankerite, "visible" only by mean of EDAX qualitative analyses (Figures 24-39).

The backscattered images of the samples easily distinguish the dolomite matrix (darker) from the ankerite "film" (brighter) and the calcite filling (intermediate brightness). This is due mainly to the iron content in the different phases, as also proved with EDAX analyses: the higher the iron content, the brighter the mineral is (Figures 40-46).

3.6. Cathodoluminescence

3.6.1. Introduction

Luminescence in minerals is caused or inhibited by the presence of trace elements in solid solution. It also depends on the type of distorted crystal surfaces and cracks, inhomogeneities of composition between different part of a crystal and/or impurities (Gies, 1976). Minerals like calcite and dolomite can be excited in different ways, which lead to the differentiation of
different kinds of luminescence, such as photo-, cathodo-, electro-, radio-, chemo- and thermoluminescence. The element produces an emission band independent from the excitation method which can be analysed (Gies, 1976).

The most common used luminescence method is cathodoluminescence. Without a spectrometer it is only possible to observe and subjectively quantify the cathodoluminescence of a mineral and give a subjective definition, such as "bright", "dull" or "non-luminescent", defining the predominant color. The elements that influence the luminescence can be subdivided into activators (their outer electrons undergo the energy transition upon excitation, "activating" the luminescence; the intensity of the luminescence decreases above a certain activator concentration), sensitizers (they promote the luminescence of the activators) and quenchers (they decrease the luminescence generated by activators and sensitizers, up to the extinction) (Gies, 1976; Marfunin, 1979).

The main activators in calcite and dolomite are Mn$^{2+}$, Pb$^{2+}$ and several rare earth elements. For Mn-activated luminescence, the main sensitizers are Pb$^{2+}$ and Ce$^{2+}$ and the main quenchers are Fe$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ (Machel, 1985). In both dolomite and calcite the Mn-activated luminescence is red-orange. The lowest activation concentration of Mn in carbonates published is 20-40 ppm (Richter and Zinkernagel, 1981); the activity of a sensitizer could take the minimum concentration as low as 10-20 ppm (Gies, 1976). If the Mn-concentration reaches or exceeds 17 mol% (93300 ppm) the luminescence is completely enhanced (Northrup, 1972). The quenching effect of Fe$^{2+}$ for the cathodoluminescence begins at 200 ppm (Machel, 1985). The concentration necessary to cause extinction is up to now still controversial, ranging about 1 wt.% (10000 ppm) Fe$^{2+}$ (Pierson, 1981) or 15 wt.% FeCO$_3$ (72300 ppm Fe) (Richter and Zinkernagel, 1981). Several authors suggested that extinction of the luminescence depends on the Fe/Mn ratio (Machel, 1985; Pierson, 1981).

### 3.6.2. Preparation

Cathodoluminescence microscopy was performed using uncoated, polished thin sections at a Technosyn 8200 Mark 2 cathodoluminescence microscope with an acceleration voltage of 12 kV under vacuum conditions.

### 3.6.3. Observations

The pelagic micrite almost shows no luminescence. In the dolomitized samples, the dolomitic matrix shows a homogeneous, weak, dull orange-red luminescence. The outer rim of the calcitic filling surrounding the late fractures is non-luminescent, though the last crystallisation phase alternates non-luminescent and bright orange-red luminescent stripes (Figures 47-58).
Figure 47: Photograph of a thin section of a dolomitic rock showing a typical dull orange-red colour through cathodoluminescence (sample SG2b). Base of photograph is 5 mm.

Figure 48: Photograph of a thin section of a vein with typical sequence of crystals, in dolomitic host rock (sample M6). Base of photograph is 5 mm.

Figure 49: Photograph of a thin section of the vein of Figure 49 through cathodoluminescence. Note the zonation of luminescence exclusively present in the sparry calcite. Base of photograph is 5 mm.
Figure 50: Photograph of a thin section of a crystalline vein filling (lighter crystals) in dolomite (darker) (sample M6) in normal light. Base of photograph is 5 mm.

Figure 51: Photograph of a thin section of a crystalline vein filling in dolomite of Figure 50 with crossed nicols. Base of photograph is 5 mm.

Figure 52: Photograph of a thin section of Figure 50, through cathodoluminescence. Base of photograph is 5 mm.
Figure 53: Photograph of a thin section through a fracture filled with sparry calcite in dolomitized rock (sample MS9). Base of photograph is 5 mm.

Figure 54: Photograph of a thin section through a fracture in dolomitized rock of Figure 53, through cathodoluminescence. Base of photograph is 5 mm.
Figure 55: Photograph of a thin section across the contact limestone (upper part) - dolomite, in Rosso Ammonitico Formation (sample RA3). Base of photograph is 5 mm.

Figure 56: Photograph of a thin section across the contact limestone-dolomite of Figure 55, through cathodoluminescence. Base of photograph is 5 mm.
Figure 57: Photograph of a cross section of a calcitic vein in dolomitized rock. The brown crystals are ankerite (sample M6). Base of photograph is 5 mm.

Figure 58: Photograph of a cross section of a calcitic vein of Figure 57, through cathodoluminescence. Note that only the calcite shows a bright luminescence. Base of photograph is 5 mm.
3.7. **Microscopic analysis interpretation**

The shape of dolomite crystals in dolomitic rocks is governed in part by the temperature at which a crystal grows (Brice, 1973; Lewis, 1975). At low temperatures, a smooth crystal surface is energetically favoured and atoms are added to crystal faces layer by layer. This results in faceted crystals and euhedral to subhedral crystal mosaics. Thus a distinction can be made between *idiotopic* (rhombic shaped euhedral to subhedral crystals) and *xenotopic* (non-rhombic, usually anhedral crystals) dolomite. A further step subdivides *idiotopic-E* (euhedral), *idiotopic-S* (subhedral), *idiotopic-C* (cement), *idiotopic-P* (porphyrotopic, matrix-supported crystals floating in a limestone matrix), *xenotopic-A*, *xenotopic-C*, and *xenotopic-P* textures.

This idea led Gregg and Sibley (1984) to suggest the concept of *critical roughening temperature* (CRT). Above this CRT, a rough surface is energetically favoured and atoms are randomly added to the crystal surface, resulting in nonfaceted growth and an anhedral crystal mosaic. It has been demonstrated experimentally that xenotopic-A dolomite can be synthesized at temperatures of 250°C and 300°C. This data, together with geological considerations, suggests that the CRT should be between 50°C and 100°C. Some ferroan dolomite and calcium-rich dolomite, due to thermodynamic considerations, may have a lower CRT than stoichiometric dolomite. Calcite has a CRT of about 25°C. The presence of impurities in the substrate may determine the growth of faceted crystals at temperatures above the CRT.

A more recent work (Sibley and Gregg, 1987) classifies dolomitic rocks by combining considerations on the texture with data of crystal size distribution. First of all, "idiotopic" and "xenotopic" are renamed "planar" and "non-planar" respectively, making them more immediately understandable. Secondly, *unimodal* and *polymodal* crystal size distribution is defined. Unimodal size distribution indicates generally a single nucleation event on a unimodal substrate. Polymodal sizes can be formed by multiple nucleation events on a unimodal or polymodal substrate or differential nucleation on an originally polymodal substrate. Kinetic considerations allows the assertion that non-planar boundaries are not only characteristic of elevated growth temperatures (> CRT), but also of high supersaturation.

According to the above classifications, the texture of the studied dolomite is unimodal and nonplanar, which gives rise to the first genetical considerations. The dolomitization affected a homogeneous limestone, therefore unimodal, and the dolomite crystals formed principally during a single growth phase, at relatively high temperature (>50°C) and/or high supersaturation. Later, precipitation of dolomite, iron-rich dolomite (or ankerite) and sparry calcite occurred, with the partial substitution of dolomite crystals with calcite (dedolomitization).
especially in the veins. Ankerite, or generally a Fe-rich dolomite, is a typical low-temperature hydrothermal mineral, forming at temperatures higher than 100°C. This suggests higher formation temperatures for the minerals in the veins than for the bulk of the dolomitic rock.

In the samples of dolomitized Rosso Ammonitico and Maiolica collected in Trentino (VN samples), sparse euhedral dolomite rhombi are present in the calcitic micrite. These partially "dolomitized" rocks could be the result of diagenetic stabilisation of high-magnesium calcite to low-magnesium calcite and dolomite, in a closed system in presence of small amount of fluids. It is possible that the high-magnesium calcite was contained in particles in the sediments, and not necessarily constituted the whole sediment (Sperber et al., 1984).

Photographs from the SEM analysis suggest that the dolomite has a secondary origin, substituting the precursor calcitic micrite. The homogeneity in the back scatter photographs and the element-distribution pictures made with the EDAX, is consistent with the assumption of a single crystallisation event for the dolomitization.

The trace element composition as revealed by the cathodoluminescence of calcite and dolomite can be interpreted in terms of pH and Eh of the dolomitizing solution, if it is sure that no ions, other than Fe and Mn, are effective in the luminescence. Therefore, changes in physical parameters in the diagenetic environment during the formation of the mineral can cause the alternance of intensity of the luminescence (Frank et al., 1982). Another possibility is the variation of trace element concentration in solution (Machel, 1985).

The absence of luminescence shown by the micritic limestone is consistent with the common observations in marine limestones. In the studied dolomite, the homogeneous distribution of the cathodoluminescence in the dolomitic matrix suggests a single nucleation and crystallisation event for the main dolomitization phase. The red-orange colouring indicates the presence of Mn²⁺ in dolomite as an activator of the luminescence and probably a relatively low iron (Fe²⁺) content. The zonation of the luminescence in the secondary calcite could be explained by specific diagenetic environmental variations (pH, Eh, trace elements).

3.8. Mineralogical composition of the dolomitized rock and composition of the dolomite

3.8.1. Introduction

Different methods can be used for the determination of the amount of dolomite in a carbonate rock (staining of thin sections, X-ray diffraction analysis, chemical analysis). For the determination of the relative proportions of coexistent calcite and dolomite, the ratio of
the areas of calcite and dolomite peaks in X-ray diffraction charts have long been used (Tennant and Berger, 1957). The results depend on sample preparation techniques (Graf and Goldsmith, 1963), on analytical techniques and on variations in the composition of the dolomite.

X-ray diffraction (XRD) is a qualitative method of analysis of the mineralogical composition of a sample. After the mineral is excited the electronic beam is diffracted with diffraction angles of the X-rays characteristic for different minerals.

Royse et al. (1971) present a calibration curve for the determination of percent dolomite in carbonate rocks and sediments, using the [104] basal reflection (the largest) of both calcite and dolomite, calculating the ratio between the height of the dolomite peak and the sum of the height of the dolomite and calcite peaks. The curve obtained (Neri Bellanca et al., 1975) (Figure 59) is:

\[
\frac{[DOL]}{[DOL] + [CAL]} = 0.0099 \text{ [weight % dol]} + 0.0077 \quad \text{(Equation 2)}
\]

The value obtained has a reliability of ± 5%.

Figure 59: Calibration curve for the determination of percent dolomite in carbonate rocks and sediments by X-ray diffraction; the dashed lines indicate a 95% confidence interval (from Royse et al., 1971).

Lumsden (1979) compares different analytical procedures for the determination of the amount of dolomite present in 250 samples of carbonate rocks. He finds out that three independent errors affects the X-ray estimates. Using calcite/dolomite [104] peak ratios, each 1% of excess calcium in the dolomite lattice causes approximately a 2% overestimate of the amount of dolomite. Use of the [113] peak would avoid this stoichiometric problem; however, if quartz is present, the interference between the [102] quartz peak (d = 2.282 Å) and the [113] calcite peak (d = 2.285 Å) can cause a serious underestimate of the dolomite.
The grain size of the powder used for the analysis influences the results. Therefore, Lumsden (1979) suggests the use of visual estimation or point count of stained thin sections as simple and reliable technique for visibly crystalline, lithified sediments.

X-ray diffraction can also be used to determine the stoichiometry of dolomite. Calcium in excess of stoichiometry (Ca$_{1.5}$Mg$_{0.5}$CO$_3$) both expands the $d_{104}$ distance and enlarges the [104] (hexagonal crystallographic indices) X-ray reflection of dolomite. The amount of the enlargement is a direct function of the amount of excess calcium (Goldsmith and Graf, 1958). Ferrous iron also influences the $d_{104}$ spacing and peak size (Ronneill, 1970, 1974) (Figure 60). The proportion of calcium in dolomite (in mole percent CaCO$_3$) is determined by measuring the shift in position of the [104] peak relative to an internal quartz standard. The equation of the straight line obtained plotting percent CaCO$_3$ in dolomite versus $d$-spacing of the [104] plane (Goldsmith and Graf, 1958) is (Lumsden, 1979):

$$ N_{CaCO_3} = md + b \quad \text{(Equation 3)} $$

where, $N_{CaCO_3}$ is the percent of CaCO$_3$ in dolomite, $m$ is 333.33, $d$ the observed $d_{104}$ value, and $b$ is -911.99. The standard error of the mean is ±0.15%.

![Figure 60: Variation of $d_{211(104)}$ for Ca-Mg carbonates. Crosses indicate standard measurements made with XRD (from Goldsmith and Graf, 1958).](image-url)
3.8.2. Preparation

All the samples collected (see Appendix 2) have been ground for 1 minute in a mill with steel cylinders, down to less that 200 mesh (Milliman, 1974). A few milligrams of the powder were mixed with ethanol, sufficient for the preparation of smear slides. The samples were then analysed with a Philips PW 1130/00 diffractometer at the speed of 2° 2θ/min, 2θ = 20-40°, with CuKα radiation, a time constant of 1 sec, a 1° divergence slit and a 0.1° receiving slit. The reflections obtained have been compared with diffractograms of standards (Figure 61).

Figure 61: X-ray basal reflections of standard dolomite (upper graph) and calcite (lower graph).

3.8.3. Observations

The dolomitized rock contains usually more than 90% dolomite. In vein fillings the calcite content reaches 35% of the carbonate fraction. The yellow vein filling is calcite with some clay impurities (Figure 73). The distribution of the values obtained is shown in Figure 62.
Figure 62: Histogram of the distribution of percent dolomite and percent magnesium in dolomite as measured from XRD analysis.

The shift of the dolomite peak in the diffractograms can be calculated by a comparison with standard diffractograms. The d$_{[104]}$ in the measured samples varies between 2.89 (stoichiometric dolomite, Ca$_{0.5}$Mg$_{0.5}$, in Goldsmith and Graf (1958) the exact value would be 2.886 Å, but this accuracy cannot be reached from the diffractograms) and 2.92 Å (about Ca$_{0.6}$Mg$_{0.4}$) (Figure 63). Stoichiometric dolomite coexists randomly with calcian dolomite in the dolomitized bodies. Generally, it can be said that the partially dolomitized samples are calcian, although the vice versa is not valid. The percentage of dolomite in the samples of the series was plotted versus the percentage of magnesium in the dolomite crystals: as it can be seen in Figures 64-71, there is no definite correlation.
3.8.4. Interpretation

The results show that the dolomitization of the limestone in the brecciated zones is mostly complete, with 90% to 100% dolomite found in the rock. This confirms the assumption that dolomitization is a reaction that proceeds to completion.

The dolomite can be either stoichiometric or non-stoichiometric (up to 60% CaCO₃), relating appropriately to the chemistry of the dolomitizing solution, and the chemistry of the dolomite mineral does not seem to depend on the amount of magnesium available for the dolomitization.
Figure 64: Graph to show % dolomite against % Mg in dolomite for the AL/87 sample series (see reduced map of Appendix 2 (Figure 137) for the location of the symbols).

Figure 65: Graph to show % dolomite against % Mg in dolomite for the C sample series.

Figure 66: Graph to show % dolomite against % Mg in dolomite for the M sample series.
Figure 67: Graph to show % dolomite against % Mg in dolomite for the MS sample series.

Figure 68: Graph to show % dolomite against % Mg in dolomite for the PB sample series.

Figure 69: Graph to show % dolomite against % Mg in dolomite for the PR sample series.
Figure 70: Graph to show % dolomite against % Mg in dolomite for the RA sample series.

Figure 71: Graph to show % dolomite against % Mg in dolomite for the P and SG sample series.
3.9. Trace element geochemistry

3.9.1. Introduction

Quantitative analyses of the trace element composition of the studied samples has been performed using Atomic Absorption Spectrometry. A qualitative analysis of the chemical composition of the dolomite crystals and vein fillings can also be performed with the Energy Dispersion System (EDAX) connected with the scanning electron microscope.

The trace element content of dolomite, precipitating at equilibrium from a given solution, is related to the ionic concentrations of the solution. The concentration ratio of a minor element in the crystal \( x_l \) relative to the major element for which it substitutes is proportional to the concentration ratio of the two elements in the solution \( (aq) \) from which precipitation occurs at constant temperature and pressure (McIntire, 1963). For the dolomite there is, considering \( X \) the mole fraction in the crystal or the molality in solution of an element:

\[
\frac{X}{Ca} = K_c \times \frac{X}{Ca}_{aq} \quad \text{(Equation 4)}
\]
\[
\frac{X}{Mg} = K_m \times \frac{X}{Mg}_{aq} \quad \text{(Equation 5)}
\]
so,
\[
\frac{X}{Ca+Mg} = (K_c + K_m) \times \frac{X}{Ca+Mg}_{aq} \quad \text{(Equation 6)}
\]

where, the distribution coefficients \( K_c \) and \( K_m \) contain terms for the thermodynamic equilibrium constant and activity coefficients for each of the species in the equation for \( CaC_0_3 \) and \( MgC_0_3 \) respectively.

A review of strontium (Sr), sodium (Na), manganese (Mn) and iron (Fe) contents in carbonates was carried out.

3.9.1.1. Strontium

The average \( Sr^{2+}/Ca^{2+} \) ratio in seawater is 0.86 ±0.04 x 10^{-2}, i.e. the concentration of Sr is about 10 ppm. Groundwater contains an average of less than 0.5 ppm (Veizer, 1983). Strontium concentration in modern aragonite ranges between 4,000 and 6000 ppm in aragonite corals in the Barbados (Pingitore, 1978), between 7,000 and 8,000 ppm in corals in Persian Gulf and Bahamas, and between 9,000 and 10,000 ppm in marine oolites in the Bahamas and Persian Gulf (Kinsman, 1969). In planktonic foraminifera (calcitic Globigerina) the measured content is about 1,100 ppm (Emiliani, 1955a). The strontium content in calcite corals from the Barbados ranges between 500 and 3,000 ppm (Pingitore, 1978). Freshwater calcites are generally depleted in strontium (few tens of ppm).

Average strontium content in dolomite that have been reported: recent marine dolomite has 650 ppm strontium, early diagenetic dolomite's content varies between 1862 ppm (Pleistocene) and 120 ppm (Paleozoic). Shallow burial dolomite has about 100 ppm strontium. The Miette dolomite studied by Mattes and Mountjoy (1980) contains about 50 ppm strontium.
3.9.1.2. Sodium

Sodium, with 10,000 ppm, is one of the major components of seawater. Sodium can be present both in the carbonate crystal lattice and as inclusions of NaCl. Ideally, in a sodium-rich bulk fluid host, Na⁺ can occupy Mg²⁺ sites (Land, 1973) and dolomite should thus incorporate more sodium than calcite. The Na⁺ partition coefficients in calcite and dolomite are not known (Mattes and Mountjoy, 1980). The behaviour of sodium during the diagenesis is unknown. In addition, the preparation of the carbonate solution for the analyses can easily leach clay minerals, contaminating the results.

Equilibrium concentration of sodium in marine calcites is about 200-300 ppm, in marine aragonites 1500 ppm (Veizer, 1983). Sodium concentrations of 300 - 400 ppm in late diagenetic dolomite have been reported by Mattes and Mountjoy (1980) for the Miette Buildup (Alberta, Canada). Badizamani (1973) reports an average content of 190 ppm for his "Dorag" dolomite. From a review of data available from the literature, recent marine dolomites are reported to have an average sodium content of about 2000 ppm, early diagenetic dolomite from 380 ppm (Pleistocene and Paleozoic) to 140 (Tertiary), shallow burial dolomite 250 ppm (Mattes and Mountjoy, 1980).

3.9.1.3. Manganese

The distribution coefficient of manganese is greater than one, i.e. it is concentrated in the crystal phase during the diagenesis (Land, 1980). Manganese, in its reduced ionized form (Mn²⁺) builds complete solid solution with Mg²⁺ in dolomite lattice. An enrichment in the manganese content in the dolomite can suggest the formation under reducing conditions.

The manganese content in calcite corals from the Barbados ranges between 11 and 68 ppm, in aragonite corals from 9 to 22 ppm (Pingitore, 1978). The average manganese content in early diagenetic dolomite is about 50-60 ppm, in the Miette dolomite (Canada) ranges from 35 to 95 ppm (Mattes and Mountjoy, 1980).

3.9.1.4. Iron

Little data is available on the substitution of iron into dolomite under sedimentary conditions, and the partition coefficient K_{Fe_{dolomite}} is unknown. It seems anyway that large iron concentrations are associated with late phases formed from saline formation waters under reducing conditions (Land, 1980).

The iron content in marine calcite is of a few ppm (2-39), whereas iron is absent in marine aragonite (Veizer, 1983). Weber (1964) found the average iron content in diagenetic dolomite to be close to 2000 ppm. In early diagenetic phases the iron content is lower, a few hundreds of ppm (Mattes and Mountjoy, 1980).
3.9.2. Preparation

A sample of 1 g of powder was reacted with 30 cc of HCl 8% and heated for 20 minutes. After cooling, the solution was filtered and distilled water was added to reach a volume of 250 cc. The samples were then analysed in a Perkin Elmer PC 420 atomic absorption spectrophotometer.

3.9.3. Observations

The following quantitative results were obtained from the analyses of the selected samples (Table 3.1).

Table 3.1: Chemical composition of the analysed samples.

<table>
<thead>
<tr>
<th></th>
<th>CaO %</th>
<th>MgO %</th>
<th>FeO %</th>
<th>Sr ppm</th>
<th>Na ppm</th>
<th>Mn ppm</th>
<th>Ba ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR1</td>
<td>54.95</td>
<td>0.41</td>
<td>0.05</td>
<td>72</td>
<td>55</td>
<td>57</td>
<td>n.m.</td>
</tr>
<tr>
<td>PR12</td>
<td>29.19</td>
<td>16.68</td>
<td>0.90</td>
<td>48</td>
<td>62</td>
<td>315</td>
<td>n.m.</td>
</tr>
<tr>
<td>C1</td>
<td>53.96</td>
<td>0.34</td>
<td>0.18</td>
<td>146</td>
<td>37</td>
<td>255</td>
<td>n.m.</td>
</tr>
<tr>
<td>C14</td>
<td>30.39</td>
<td>20.42</td>
<td>0.66</td>
<td>72</td>
<td>92</td>
<td>312</td>
<td>n.m.</td>
</tr>
<tr>
<td>SG15</td>
<td>46.77</td>
<td>0.60</td>
<td>0.07</td>
<td>167</td>
<td>n.m.</td>
<td>n.m.</td>
<td>294</td>
</tr>
<tr>
<td>SG14</td>
<td>27.18</td>
<td>21.85</td>
<td>0.11</td>
<td>45</td>
<td>n.m.</td>
<td>n.m.</td>
<td>176</td>
</tr>
<tr>
<td>AL1/87</td>
<td>54.95</td>
<td>0.29</td>
<td>0.07</td>
<td>231</td>
<td>57</td>
<td>330</td>
<td>412</td>
</tr>
<tr>
<td>AL8/87</td>
<td>28.26</td>
<td>20.11</td>
<td>1.18</td>
<td>43</td>
<td>52</td>
<td>500</td>
<td>176</td>
</tr>
<tr>
<td>M1</td>
<td>50.94</td>
<td>0.25</td>
<td>0.14</td>
<td>244</td>
<td>30</td>
<td>455</td>
<td>n.m.</td>
</tr>
<tr>
<td>M6</td>
<td>28.61</td>
<td>19.81</td>
<td>1.38</td>
<td>52</td>
<td>72</td>
<td>550</td>
<td>n.m.</td>
</tr>
</tbody>
</table>

(n.m. = not measured)

The qualitative determination (with EDAX) of the elements present in the dolomite crystals and in the veins is shown in Figures 72 and 73.

3.9.4. Interpretation

As it can be seen from the comparison of the analyses of limestone and correspondant dolomite, dolomitization reduces the strontium content of the carbonate phase. Strontium occupies calcium sites in the calcite crystals because of its ionic radius (1.12 Å) close to that of Ca\(^{2+}\) (1.02 Å). The results obtained are consistent with those obtained by Mattes and Mountjoy (1980). The values obtained for the limestones are notably lower than the ones expected for marine carbonates: a depletion affected both the limestone and the dolomite. It is probable that a depletion took place during the diagenetic process, independently from the dolomitization.

The sodium content is only of few tens of ppm, much lower than the expected values (Mattes and Mountjoy, 1980). The difference between the limestone values (30-40 ppm) and the dolomite values (70-90 ppm) is very slight. It can be expected that the sodium measured is present in liquid inclusions in the crystals and not in the crystalline lattice.
Figure 72: Photomicrograph of back-scattered image of sample M6 (scale shown by bar) with corresponding EDAX analyses of the three different phases observable:

a) the bright mineral (ankerite) adjacent to the contact
b) the medium shaded mineral (calcite) in the vein
c) the dark coloured mineral (dolomite) of the host rock.
Figure 73: EDAX analysis of the yellow material filling the fractures in proximity to the contact with the dolomitized rock. Note the high Si and Al content, due to the clay minerals present.
Manganese and iron are concentrated in the dolomite. This can be easily explained considering the very close ionic radius of magnesium (0.78 Å), ferrous iron (0.83 Å) and manganese (Mn$^{2+}$ = 0.91 Å), and the same ionic charge (2+). Therefore, manganese and ferrous iron can easily substitute magnesium in the crystalline structure of dolomite. The 300 ppm of manganese found in the dolomite suggest that the dolomitization took place in a reducing environment, which favoured the incorporation of Mn$^{2+}$ in the dolomite lattice. The iron is present in the dolomite almost exclusively in its reduced form (Fe$^{2+}$). The iron content reaches, in some cases, 1% of the carbonate fraction. The comparison of the iron content in the whole rock and in the carbonate fraction shows that the iron is almost completely contained within the dolomite. These values also support the assumption of a precipitation from saline waters in a reducing dolomitization environment (Land, 1980).
CHAPTER 4

STABLE ISOTOPES

4.1 Introduction

The geochemistry of isotopes studies the causes of the variation in isotopic composition in natural environments, their related processes, consequences and their possible use for the understanding of geological events. Urey (1947) theorized that some thermodynamic properties of molecules depend on the mass of the atom: light isotopes have a higher oscillation frequency than heavier ones, in molecules and crystals; they build therefore weaker chemical bonds, and their molecules are more reactive.

It has been stated that the isotopic ratios depend on variations in chemical, physical and biological factors. The stable isotopes, contrary to the radioactive isotopes, keep constant their relative abundance through the time. Several isotopic pairs are used in geology: Carbon (\(^{13}\)C/\(^{12}\)C), Oxygen (\(^{18}\)O/\(^{16}\)O), Hydrogen (H/D), Sulphur (S/\(^{33}\)S) and Strontium (\(^{87}\)Sr/\(^{86}\)Sr).

4.2. Oxygen and carbon isotopes

4.2.1. Introduction

Stable isotope fractionation occurs in different processes: physical processes, like evaporation, condensation, melting, crystallisation, diffusion; chemical reactions where the difference in mass influences the velocity of the reaction (e.g. photosynthesis of carbon). These properties have been used, for example, to determine paleotemperature from mollusks and forams (e.g. Epstein et al., 1951; Emiliani, 1955b) or to make paleoecological considerations.

The measurements are effectuated relative to a standard:

\[
\delta_{\text{sample}} = \left[ \frac{R_{\text{sample}} - R_{\text{stand.}}}{R_{\text{stand.}}} \right] \times 10^3 \text{ (in %)} \quad \text{(Equation 7)}
\]

where, \( R \) is the ratio between the heavier and the lighter isotope.

The element oxygen is present in nature with 3 stable isotopes, respectively with mass 16 (99.759 atoms %), 17 (0.0374%) and 18 (0.2039%). The isotope 17 is usually neglected and a correction to the measured ratios is applied. The standards used for the oxygen isotopes are PDB (a belemnite from the Pee Dee Formation, S. Carolina; today this standard has been totally used and it is substituted by secondary standards) for carbonates and SMOW (Standard Mean Ocean Water) for water. Oxygen in CO\(_3^2\)- in solution is 28.6% richer in \(^{18}\)O
relative to SMOW: the relation between PDB and SMOW is (Friedman and O’Neil, 1977):

\[
\delta_{\text{SMOW}} = 1.03086 \delta_{\text{PDB}} + 30.86 \quad (\text{Equation 8})
\]

\(\alpha\) is the isotopic fractionation factor:

\[
\alpha = (^{18}O/^{16}O) \text{ CO}_2 \text{ from PDB} / (^{18}O/^{16}O) \text{ oxygen from } \text{CaCO}_3 \text{ PDB} \quad (\text{Equation 9})
\]

Measured in \(\delta\) notation:

\[
\delta^{18}O = \left(\frac{([^{18}O/^{16}O]_{\text{unknown}} / [^{18}O/^{16}O]_{\text{standard}}) - 1}{[^{18}O/^{16}O]_{\text{unknown}}} \right) \times 1000 \quad (\text{Equation 10})
\]

so,

\[
\alpha = 1000 + \delta^{18}O_{\text{CO}_2 \text{ from PDB}} / 1000 + \delta^{18}O_{\text{oxygen from PDB}} \quad (\text{Equation 11})
\]

Marine organisms that build a carbonate shell take the \(\text{CO}_3^{2-}\) (in equilibrium with \(\text{HCO}_3^-\)) from the seawater; the oxygen isotopic composition of their shell reflects therefore the isotopic composition of the hydrocarbon ions present in the seawater. The hydrocarbon ions in solution exchange oxygen atoms with water molecules. In this exchange the oxygen isotopes will be fractionated in dependence of the temperature:

\[
\text{C}^{16}\text{O}_3^{2-} + \text{H}^{16}\text{O}_2 + \text{H}_2^{18}\text{O} \iff \text{C}^{16}\text{O}_3^{2-} + \text{H}^{16}\text{O}_2^{18}\text{O} + \text{H}_2^{16}\text{O} \iff \\
\iff \text{C}^{16}\text{O}_2^{18}\text{O}^{2-} + \text{H}^{16}\text{O}_3 + \text{H}_2^{16}\text{O} \quad (\text{Equation 12})
\]

During the building of the shell, carbonate ions will be included proportionately to their isotopic abundance in the water:

\[
2\text{Ca}^{2+} + \text{C}^{16}\text{O}_3^{2-} + \text{C}^{16}\text{O}_2^{18}\text{O}^{2-} \iff \text{CaC}^{16}\text{O}_3 + \text{CaC}^{16}\text{O}_2^{18}\text{O} \quad (\text{Equation 13})
\]

The isotopic composition of a foram, for example, depends from both the oxygen isotope composition of the seawater and the temperature of the water.

Because dolomite has yet to be synthesized at 25°C, it is still impossible to determine directly the equilibrium oxygen isotopic fractionation dolomite-water at sedimentary temperature. Values obtained at high temperature have been extrapolated, obtaining that at 25°C dolomite should be enriched in \(^{18}O\) relative to coexisting calcite at equilibrium by between 4 and 7‰ (O’Neil and Epstein, 1966; Northrop and Clayton, 1966; Sheppard and Schwarcz, 1970; Friedman and O’Neil, 1977). Further, it is necessary to take into consideration that the \(\delta^{18}O\) of the dolomite depends not only from the temperature and \(\delta^{18}O\) of the water from which it is precipitated, but also from the \(\delta^{18}O\) of the precursor limestone.

Various relationships between the isotopic composition of dolomite, temperature (\(T\) in kelvins) and isotopic composition of water have been determined. One of them (Matthews and Katz, 1977) is:

\[
10^3 \ln \alpha_{\text{dol-water}} = 3.06 \times 10^6 T^2 - 3.24 \quad (\text{Equation 14})
\]
Given a dolomite analysis, assuming an open system reaction, the range in uncertainty of temperature is about 15°C (given a δ¹⁸O for the water), and it is about 4% in δ¹⁸O water (given a temperature) (Land, 1983) (Figure 74).

\[ 10^3 \ln \alpha = 2.78 \times 10^6 T^{-2} (°K) + 0.91 \]  

(from Land, 1981)

Carbon is composed of two stable isotopes of mass 12 (98.892 atoms%) and 13 (1.108 atoms%), and one radioactive isotope of mass 14. δ¹³C is the ratio \(^{13}\text{C}/^{12}\text{C}\), referred to the PDB standard. Fractionation of the carbon isotopes occurs through organic processes, like photosynthesis, and it depends very slightly on the temperature (about 0.035‰ each 1°C (Emrich et al., 1970)).

Due to the relative insolubility of carbonate, it is very difficult to alter the carbon isotopic composition of carbonate sediments very much from their initial value. Considering the size of the carbon reservoir constituted by the precursor limestone, the carbon in solution in the dolomitization fluids can hardly affect the original isotopic signal (Land, 1980).

Many dolomitized rocks have probably undergone one or more recrystallisations to a more stable phase and this obviously affects the isotopic composition. It is therefore difficult to interpret absolutely the isotopic values, if no other data are available. Considering δ¹⁸O, the majority of ancient dolomites is depleted with respect to the Holocene examples. Dolomite depleted in \(^{18}\text{O}\) must have formed, either at an elevated temperature or from fluids depleted in \(^{18}\text{O}\) relative to seawater (or both) (Land, 1980).
4.2.2. Preparation

Bulk rock analyses were made, since individual crystals could not be isolated. Most of the samples (see Appendix 3) have been collected by hand with a diamond drill on polished rock cuts, with an attempt to sample homogeneous parts of the rock. Where it was possible, some distinguishable breccia fragments were also sampled. From the powder, 10 mg were weighed and heated to 400°C in a vacuum for 30 minutes, to transform the organic matter eventually present into unreactive graphite. The sample was then reacted in a water bath at 25°C with anhydrous phosphoric acid (McCrea, 1950). Limestone samples were reacted for 24 hours and dolomite samples for 72 hours. For those samples that contained both calcite and dolomite, their gas was extracted in 2 stages: first after 20 minutes and then again after 72 hours. The results were not satisfactory for a calcite sample content lower than 30%.

The CO₂ gas, resulting from the reaction, was measured with a VG 903 Mass Spectrometer, using as laboratory standard Carrara Marble (δ¹³C = +2.04‰, δ¹⁸O = -1.62‰). The precision of the instrument (2 σ) is ±0.025‰, the standard deviation on duplicated measurements is ±0.08‰ for δ¹³C and ±0.16‰ for δ¹⁸O. The correction for the possible phosphoric acid fractionation factor has not been applied (Sharma and Clayton, 1965; Land, 1980).

4.2.3. Observations

About 200 stable isotope analyses were performed on both dolomite and calcite from the Lessini, Feltre and Trento area. The values are given relative to the PDB standard (Appendix 3). The δ¹³C values obtained from the limestone vary between +1.16 and +2.64‰ (with one exception), with an average over 38 analyses of +1.63‰ ± 0.15. The δ¹⁸O values vary between -0.98 and -6.74‰, with an average value of -3.33‰ ± 0.20. In the dolomitized samples (except the Rosso Ammonitico samples) the δ¹³C varies between -2.95 and +2.89‰, with a mean value (over 117 analyses) of +1.59‰ ± 0.07. The δ¹⁸O varies between -0.53 and -12.64‰, with an average of -5.40‰ ± 0.22.

Due to the very negative oxygen values obtained from the dolomitized Rosso Ammonitico samples, their values are considered separately: δ¹³C varies between -0.68 and +1.61‰ (average of 7 samples: +1.15‰ ± 0.15), δ¹⁸O varies between -8.97 and -11.71‰ (average: -10.72‰ ± 0.36).

The samples of Maiolica of Tithonian age collected in the Val di Non, Trentino (VN14, B.L. 88/16), show values around +1.7‰ for the carbon isotope and -2.3‰ for the oxygen.

The fragments of undolomitized Maiolica included in the dolomite in the outcrop of the series C have an isotopic ratio in agreement with the bulk of the unaffected limestone, δ¹³C = +2.04‰ and δ¹⁸O = -3.43‰.
Table 4.1: **Stable isotope ratios in limestone and dolomitized breccia**

<table>
<thead>
<tr>
<th>Sample Series</th>
<th>δ13C%o range</th>
<th>δ18O%o mean</th>
<th>Sample Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jurassic limestone</td>
<td>+2.39 - +2.64</td>
<td>+2.52 (-2.80) - (-0.98)</td>
<td>FR</td>
</tr>
<tr>
<td>Lower Cret. limestone</td>
<td>+0.95 - +2.04</td>
<td>+1.60 (-4.89) - (-1.75)</td>
<td>C,MS,PB,P,SG</td>
</tr>
<tr>
<td>Upper Cret. limestone</td>
<td>+1.44 - +2.34</td>
<td>+1.80 (-6.74) - (-2.67)</td>
<td>M,AL</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample Series</th>
<th>δ13C%o range</th>
<th>δ18O%o mean</th>
<th>Sample Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>dolom. Jurassic limestone</td>
<td>+0.76 - +2.61</td>
<td>+1.36 (-12.06) - (-0.86)</td>
<td>F,PR,P8-27,RA, SG1-12a,VV</td>
</tr>
<tr>
<td>dolom. Lower Cret. limestone</td>
<td>[-1.37] - [+2.89]</td>
<td>+1.60 (-12.64) - (-2.88)</td>
<td>C,MS,PB,SG13-14</td>
</tr>
<tr>
<td>dolom. Upper Cret. limestone</td>
<td>[-0.66] - [+2.45]</td>
<td>+1.71 (-8.12) - (-4.78)</td>
<td>-6.00 AL,M</td>
</tr>
</tbody>
</table>

| Maiolica Trentino | +1.70 - +1.75 | +1.72 (-2.79) - (-2.31) | 2.55 VN14,B.L.88/16 |

The isotopic ratios of the yellow dedolomitized fracture filling are not uniform: the δ13C varies between +2.21 and -6.90%o (average of 8 samples: -1.75%o ± 1.08) and the δ18O varies between -5.19 and -7.39%o (average: -6.53%o ± 0.32). The sparry calcite filling the vugs in the dolomite has δ13C = +0.87 and δ18O = -14.90%o (Table 4.1). It has been impossible, because of their minor occurrence, to measure the calcite substituting the dolomite in the host rock.

Table 4.2: **Stable isotope ratios of the fracture fillings**

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Nature</th>
<th>Location</th>
<th>% calcite</th>
<th>δ13C %o PDB</th>
<th>δ18O %o PDB</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL7'/87</td>
<td>yellow</td>
<td>Scaglia r. (Lessini)</td>
<td>0</td>
<td>+1.78</td>
<td>-7.27</td>
</tr>
<tr>
<td>C23'/87</td>
<td>yellow</td>
<td>Maiolica (Lessini)</td>
<td>70</td>
<td>-2.21</td>
<td>-6.03</td>
</tr>
<tr>
<td>C54'/87</td>
<td>yellow</td>
<td>Maiolica (Lessini)</td>
<td>95</td>
<td>-6.90</td>
<td>-5.19</td>
</tr>
<tr>
<td>C59'/87</td>
<td>spar</td>
<td>Maiolica (Lessini)</td>
<td>43</td>
<td>-4.38 (20')</td>
<td>-7.36 (20')</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+1.84(72h)</td>
<td>-3.60(72h)</td>
</tr>
<tr>
<td>C73b</td>
<td>spar</td>
<td>Maiolica (Lessini)</td>
<td>35</td>
<td>-1.79(20')</td>
<td>-7.39(20')</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+0.55(72h)</td>
<td>-7.67(72h)</td>
</tr>
<tr>
<td>C76g</td>
<td>yellow</td>
<td>Maiolica (Lessini)</td>
<td>85</td>
<td>-3.05</td>
<td>-6.09</td>
</tr>
<tr>
<td>PB21cc</td>
<td>spar</td>
<td>Maiolica (Lessini)</td>
<td>100</td>
<td>+0.87</td>
<td>-14.90</td>
</tr>
<tr>
<td>PB21g</td>
<td>yellow</td>
<td>Maiolica (Lessini)</td>
<td>100</td>
<td>-0.55</td>
<td>-7.33</td>
</tr>
</tbody>
</table>

The data obtained for the different series of samples are plotted in δ13C against δ18O diagrams (Figures 75-84). The carbon isotopic composition does not vary considerably from the limestone to the dolomitized rock, as expected. The carbon isotope signal of the precursor limestone buffered the influence of fluids with probably a low carbonate and bicarbonate content.
Figure 75: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the measured samples (see reduced map of Appendix 2 (Figure 137) for the location of the symbols).

Figure 76: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the AL and AL/87 sample series.
Figure 77: Graph to show the $\delta^{13}$C against $\delta^{18}$O of the C sample series.

Figure 78: Graph to show the $\delta^{13}$C against $\delta^{18}$O of the M sample series.
Figure 79: Graph to show the $\delta^{13}$C against $\delta^{18}$O of the MS sample series.

Figure 80: Graph to show the $\delta^{13}$C against $\delta^{18}$O of the P sample series.
Figure 81: Graph to show the $\delta^{13}$C against $\delta^{18}$O of the PB sample series.

Figure 82: Graph to show the $\delta^{13}$C against $\delta^{18}$O of the PR sample series.
Figure 83: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the RA sample series.

Figure 84: Graph to show the $\delta^{13}C$ against $\delta^{18}O$ of the SG sample series.
The oxygen isotopic composition is more significant, showing a sharp change toward more negative values. As it can be seen, no trends are observable and the values are quite randomly distributed.

The samples of the series C (Crespadoro, Chiampo Valley) have been plotted in two-dimensions on a 3-D diagram (the third dimension being the oxygen and carbon isotope values) (Figures 85-86). The graphs give an idea of the distribution of the values in the outcrop. The most negative values are concentrated in the middle of the dolomitized area and along the contact with the unaffected rock.

### 4.2.4. Interpretation

The isotopic values in the limestone are consistent with values from pelagic limestones. Data from DSDP cores show that limestones become more depleted in $^{18}O$ with increasing age and burial because of the increased recrystallisation temperature (Bernoulli et al., 1978). This trend is also found in the analysed samples (Figure 87).

The variation of the oxygen isotope ratios in a vertical cross section of a dolomitized breccia shows an high $\delta^{18}O$ at the contacts with the limestone and in the core of the breccia (Figure 86). The observed heterogeneity in the values, varying between -5.5‰ and -3‰ could suggest local variation of the temperature or a different situation in the limestone. The more negative values denote a higher temperature, and therefore a later formation of the dolomite with respect to the sample with less depleted ratios. This suggest that, where more negative values are found, were located more permeable areas in the breccia. In these areas, a more active water circulation led to higher formation temperatures for the dolomite.

The dolomitization does not notably affect the original carbon isotopic signature, especially considering that variations in the order of 1‰ are not particularly significant in rocks that have been subjected to late recrystallisation phases. On the other hand, the oxygen isotope values show a remarkable depletion in the heaviest isotope. A weak trend towards more negative values can be found to occur with increasing age of the precursor limestone. This could be interpreted as due to differences in the original signature, which were not observed in this order of magnitude, or with temperature differences, local or otherwise, influenced by the burial depth.

It can be seen that the dedolomitized yellow fracture filling shows various values, some depleted in both $^{13}C$ and $^{18}O$, which could suggest a late origin, probably influenced by late hydrothermal meteoric processes. The oxygen isotope values of the sparry calcite in vugs are the most negative ones measured, suggesting a higher precipitation temperature or changing fluid composition.

If it is assumed that an almost constant isotopic composition of the fluid is involved, then the dolomitization occurred at an increasingly higher temperature in the presence of fluids, which were not particularly rich in carbonate or bicarbonate ions, therefore excluding
Figure 85: Graph to show a contour plot of the spatial distribution of $\delta^{13}C$ against height, in m, above the road surface at the outcrop of Crespadoro, Chiampo Valley. Each symbol represents the result of a sample analysis. The contours are 0.5‰ $\delta^{13}C$ apart.

Figure 86: Graph to show a contour plot of the spatial distribution of $\delta^{18}O$ against height, in m, above the road surface at the outcrop of Crespadoro, Chiampo Valley. Each symbol represents the result of a sample analysis. The contours are 0.5‰ $\delta^{18}O$ apart.
Figure 87: Variation of $\delta^{13}C$ and $\delta^{18}O$ in dolomitized rock with age. Only a few of the samples are represented.
meteoric waters. The temperature calculated from Equation 15, considering a marine water with a δ18O 0-2‰ SMOW, is about 70°C for -6‰ PDB in the dolomite and 110°C for -12‰ PDB. The fact that the samples of the Ammonitico Rosso and the overlying Maiolica from Ferrazza (Lessini) show the most negative values does not seem to comply with a regional trend, but rather it is a local factor, i.e. the area in which the highest temperature was reached.

4.3. Strontium isotope

4.3.1. Introduction

The concentration of strontium in seawater is 0.1 μM (8 mg/kg), with an oceanic residence time of about 4 x 10^6 years. The element strontium (atomic number: 38) is present in nature with four isotopic modifications with masses of 88 (82.6%), 87 (7.0%), 86 (9.9%) and 84 (0.5%). ^87Sr is a radiogenic, stable, isotope formed from β decay of ^87Rb with a half life of 4.99 x 10^10 years. The abundance of the isotope ^87Sr is, by convention, expressed relative to the abundance of the stable ^86Sr (Elderfield, 1986). The isotope geology of strontium concerns the increase over time of the amount of ^87Sr produced by the radioactive decay of ^87Rb (Peterman et al., 1970; Hawkesworth and Elderfield, 1978; Burke et al., 1982; DePaolo and Ingram, 1983; Palmer and Elderfield, 1985; Hess et al., 1986). On the general assumption that the earth's crust differentiated from the mantle early in geologic time, the general behaviour of Rb and Sr during the differentiation has been markedly different. The large Rb+ ion would be concentrated, like K+, in the silica-rich crust. The smaller Sr^2+ behaves like Ca^2+, distributing more evenly between crust and mantle. The greater concentration of Rb in the crust means that production of ^87Sr has been faster in crustal material than in the mantle, and samples of rock that has been part of the crust for most of its history should have generally higher ^87Sr/ ^86Sr than samples from the mantle. The ratio for mantle rocks ranges between 0.702 and 0.706 (Krauskopf, 1979).

The Sr isotopic composition of seawater is determined by the isotopic ratios in the various source materials. In general, two sources are involved, continental crust and upper mantle. The continental crust supplies Sr through chemical weathering and river input. Material from the upper mantle can be brought through hydrothermal activity at middle ocean ridges, submarine weathering of basalts and chemical weathering of continental basalts (Elderfield, 1986).

The isotopic composition of the source materials depends on their age and on the ratio of their elemental abundances of the radioactive parent isotope to the radiogenic daughter isotope. Due to the long half life of its parent isotope and the low oceanic Rb/Sr ratio, no significant production of ^87Sr occurs during the residence of Sr in the oceans. Therefore, the ^87Sr/ ^86Sr ratio of seawater is determined only by the ratios of the source materials. Moreover, the Sr residence time in the oceans is much longer than the oceanic mixing time of about 10^7 years, allowing us to say that the ^87Sr/ ^86Sr ratio of seawater is the same everywhere at any one time. Thus, the oceanic Sr isotope record through time is the tracer of the relative
importance of the different sources of Sr (Elderfield, 1986). The homogeneity of Sr isotopes in seawater means that there is a single temporal Sr isotope record for the oceans. When Sr-bearing minerals are precipitated from seawater, their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are the same as those of the seawater because Sr isotopes are not measurably fractionated in nature (Jones and Faure, 1978). For example, a decrease in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of a sequence of non-marine carbonate rocks may be caused by the weathering of volcanic rocks with a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (Faure and Powell, 1972).

Burke et al. (1982) provide the most comprehensive set of data showing the variation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater through the Phanerozoic. The curve (Figure 88) summarizes the values of 786 samples of marine origin and has been consequently modified by Elderfield and Gieskes (1982). The results show that the $^{87}\text{Sr}/^{86}\text{Sr}$ has ranged between 0.7092 (present and late Cambrian) and 0.7068 (Jurassic and Late Permian). These values are intermediate between the values for continental crust (~0.716) and submarine basalts (~0.703) (Table 4.2 and Figures 89-90). Two main trends are recognizable: a slow decrease from the Cambrian to the Jurassic and a relative rapid increase from the Jurassic to the present.
Table 4.3: $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in different materials (from Elderfield, 1986):

<table>
<thead>
<tr>
<th>Strontium host</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>modern seawater</td>
<td>0.709211</td>
</tr>
<tr>
<td>volcanic materials</td>
<td>0.7027 - 0.705</td>
</tr>
<tr>
<td>biogenic carbonates</td>
<td>0.7068 - 0.7092</td>
</tr>
<tr>
<td>hydrothermal fluids (MOR)</td>
<td>~0.703</td>
</tr>
<tr>
<td>continental detritus</td>
<td>~0.716</td>
</tr>
</tbody>
</table>

Figure 89: $^{87}\text{Sr}/^{86}\text{Sr}$ values of seawater with compared ratios for its different sources (from Elderfield, 1986).

Figure 90: Flow diagram of the geochemical cycle of Sr from seawater into the continental and oceanic crust (from Elderfield, 1986).
The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can be used to date diagenetic events, provided that no sources of Sr other than those derived from seawater and the original sediments become involved (Sailer, 1984; Swart et al., 1987).

### 4.3.2. Preparation

A sample chosen for Sr isotope stratigraphy must fulfill some basic requirements: the Sr content must be sufficient for a precise isotopic analysis, the sample must contain insignificant amounts of material (e.g. detrital matter) that can contaminate the results. If the presence of $^{87}\text{Rb}$ is determined, the measured ratio must be age-corrected to remove the contribution from the decay of $^{87}\text{Rb}$ since the time of the formation of the sample (the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio in cleaned carbonates is generally of the order of 0.001 and no correction is necessary) (Elderfield, 1986).

Three standards are commonly used for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio: Eimer and Amend (0.70800), NBS 987 SrCO$_3$ (0.71022) and seawater (0.70920). By convention $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are normalised to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$: the normalised ratios are not related to stable isotope fractionation processes such as biological activity (Elderfield, 1986).

Strontium isotope analyses have been performed at the Laboratorio di Geocronologia of the C.N.R. at the University of Padua (Italy) by Giancarlo Cavazzini and its assistants.

A sample of dolomite or calcite of 0.1 g was reacted with 10 cc of HCl 0.1 N in a teflon vessel. After adding a few drops of HNO$_3$ (diluted with distilled water 1:1), the solution was heated up to 100°C until it dried, 5 cc of HCl 6 N were then added to reach the complete dissolution of the carbonate fraction and the solution was dried again. The product was then diluted with 3 cc of HCl 2.5 N and centrifuged. The strontium was separated from 0.3 cc of solution with a chromatography method, adding gradually HCl. The solid strontium was collected in a quartz vessel, dried at low temperature and put on a tungsten or tantalum filament, where it was analysed with a VG 54E mass spectrometer. The NBS 987 standard was used, which was measured with the samples and gave a value of 0.71013 (± 0.00003).

### 4.3.3. Observations

Thirteen samples of both calcite and dolomite from the Lessini [PR4 (Rosso Ammonitico), C3 (Maiolica of Valanginian age), M2 (Scaglia variegata of Cenomanian age), AL1/87 (Scaglia rossa of Turonian age), PB21 (yellow vein filling), C81 (sparry calcite in vein), are calcite, FR12, C8, M5, AL8/87, are dolomite], Feltre area (SG15, Maiolica, and SG14, dolomite), Trentino (VN14, partially dolomitized Tithonian Maiolica) and Euganean Hills (BB1, Maiolica) were analysed. The $^{87}\text{Sr}/^{86}\text{Sr}$ in the limestone samples range between 0.70686 (Rosso Ammonitico) and 0.70742 (Maiolica of Lower Cretaceous age). Sample BB1 of Maiolica was collected in the Euganean Hills, west of Padova, where dolomitization was not observed. This allows a comparison with coeval samples from the Lessini area to be made. The obtained value
of 0.70746 is consistent with the values obtained for the Maiolica in the area affected by dolomitization.

The dolomite samples values vary in a narrow range between 0.70839 and 0.70867. The yellow dedolomitized calcite in the veins has a value of 0.70951 (Table 4.3). The standard error 2σ varies between 0.00002 and 0.00007.

| Table 4.4: Strontium isotope ratios of the analysed samples |
|-------------|----------------|----------|--------------------------|
| Sample #    | Formation      | Approx. age | Nature       | 87Sr/86Sr ± 2s           |
| PR4         | Rosso Ammon.   | Malm      | calcite      | 0.70686 ±0.00003         |
| PR12        | Rosso Ammon.   |           | dolomite     | 0.70850 ±0.00002         |
| VN14        | Maiolica       | Tithonian | calcite and dolomite | 0.70743 ±0.00002 |
| SG15        | Maiolica       | Berriasian| calcite      | 0.70713 ±0.00002         |
| SG14        | Maiolica       |           | dolomite     | 0.70839 ±0.00002         |
| C3          | Maiolica       | Valanginian| calcite    | 0.70742 ±0.00002         |
| C8          | Maiolica       |           | dolomite     | 0.70855 ±0.00002         |
| BB1         | Maiolica       | Valanginian| calcite    | 0.70746 ±0.00002         |
| (Euganean Hills) |
| M2          | Scaglia varieg.| Cenomanian| calcite      | 0.707371 ±0.000004       |
| M5          | Scaglia varieg.|           | dolomite     | 0.708672 ±0.000005       |
| AL1/87      | Scaglia rossa  | Turonian  | calcite      | 0.70718 ±0.00002         |
| AL8/87      | Scaglia rossa  |           | dolomite     | 0.70843 ±0.00003         |
| PB21        | vein in Maiolica|         | yellow calcite| 0.70951 ±0.00007         |
| C81         | vein in Maiolica|         | calcite      | 0.70657 ±0.00003         |

4.3.4. Interpretation

The results obtained from the limestones are consistent with the Jurassic - Cretaceous marine water values (Burke et al., 1982) (Figure 91). The comparison of the Maiolica sample collected in the Euganean Hills and the coeval sample from the Chiampo Valley (Lessini Mounts) shows the reliability of the original isotopic ratio. The dolomitic rock values all lie around 0.70845.

The value of 0.70743, obtained for the sample VN14, from the Trentino, is the expected value for marine carbonate of Upper Jurassic age. This confirms the previous data, i.e. the sparse dolomite crystals found in the Trentino area have a diagenetic origin and can be excluded a relation to the dolomitization process which affects brecciated limestones in the Venetian Alps.
Figure 91: Plot of the analysed samples on the $^{87}\text{Sr}/^{86}\text{Sr}$ seawater curve for the last 200 ma (see Figure 88).

The strontium isotopes were first measured in the attempt to check if there was a relationship between the dolomitizing fluids and the volcanic rocks, which have a characteristic isotopic ratio very different from that of marine carbonates. Considering that the Tertiary basaltic rocks (Barbieri et al., 1978) are strongly depleted in the strontium radiogenic isotope with respect to the limestones, it excludes the contamination of the carbonate rocks with volcanic fluids. In fact, if the volcanic fluids have influenced somehow the dolomitization process, the dolomite values would be lower than those of the limestone. On the other hand, the values obtained are not as enriched in $^{87}\text{Sr}$ as it would be expected for meteoric carbonates (which show $^{87}\text{Sr}/^{86}\text{Sr}$ values around 0.716) and therefore an exclusion of a meteoric origin of the fluids is likely. In fact, the sample of yellow dedolomitized calcite filling (sample PB21) has a value (0.7095) higher than that of the present marine water and can therefore be interpreted as result of precipitation from waters of at least partial continental origin.
The results (0.7084-0.7085) obtained for the studied dolomite give rise to another interpretation. Dolomitization of the Jurassic-Cretaceous carbonates of the Trentino Platform is likely to have occurred under the influence of marine water: they lie in the isotopic range of marine carbonate of Phanerozoic age (0.707-0.709, Figure 88) and therefore can be used for an approximate dating of the dolomitization, giving the oldest possible age of the dolomitization and the youngest age of the sediments. The gap existing between the limestone and the dolomite values allows for the clear distinction of the two events: the deposition of the sediments and their dolomitization. Comparing the data with the Phanerozoic curve, a Late Oligocene-Early Miocene age can be deduced (DePaolo, 1986) [Figure 92]. The differences between the values do not depend upon the original lithology, stratigraphic position or geographic location. It can be therefore explained as a difference in the dolomitization time. The range of data corresponds to a time interval of about 7 ma, a reasonable value for the dolomitization process.

![Graph showing Sr/86Sr seawater variation curve for the Eocene-Miocene age.](image)

Figure 92: $^{87}$Sr/$^{86}$Sr seawater variation curve for the Eocene-Miocene age. The continuous line is from Miller et al. (1988); the dashed line is extrapolated from the data of DePaolo (1986). Results of the plotted samples are extrapolated relative to the seawater variation curve.

### 4.4. Oxygen and strontium isotopes in the basalt

The stable isotope ratios of the basaltic rocks of the Lessini Mounts and Marosticano area have been measured in order to define their origin and to reconstruct the post-eruption history (Barbieri et al., 1978). The basalts of the southern part of the area are generally strongly altered, as indicated by the high water content and the occurrence of secondary
calcite. The oxygen isotope ratios of the carbonates in the groundmass vary between -3 and -4‰ PDB, whereas the carbon isotope varies between -6 and -7‰ PDB: these values are typical of low-temperature fresh-water carbonates. This meteoric influx seems to have affected also the $\delta^{18}O$ of the fine-grained silicates in the groundmass, increasing the whole rock $^{18}O$ content ($\delta^{18}O = +7.71 - +9.19\%_o$ SMOW). Samples of basalts from the northern part of the area (Lessini and Marosticano) are relatively fresh, and show average $\delta^{18}O$ values of $+7.4\%_o$ SMOW, close to those typical of unaltered basalts ($+5.5 - +6.5\%_o$: Taylor, 1968; Anderson et al., 1971; Pineau et al., 1976). These basalts underwent secondary alteration processes (Barbieri et al., 1978).

The strontium isotope ratios in the basaltic rocks of the Lessini Mounts are uniform (0.7028-0.7036) and characteristic of basalts originated from the upper mantle and not contaminated by crustal material during the ascent (Faure and Powell, 1972; Barbieri et al., 1978).
CHAPTER 5

FLUID INCLUSIONS

5.1. Introduction

Direct evidence about the composition of the fluid from which one crystal precipitated is given by the fluid inclusions, although the information that we can obtain from these traces are difficult to interpret, due to their complex nature, minuscule size and fragmentary appearance. When crystals grow or recrystallise in presence of a fluid, growth irregularities trap portions of the fluid in the solid phase. Fluid inclusions are present in most minerals, but are often overlooked because of their small size: inclusions larger than 50 μm are rare; most of them are between 1 and 30 μm and with the SEM it is possible to reveal the presence of inclusions as small as 2 x 10⁻⁵ mm (Roedder, 1979b). The percentage of volume of a crystal constituted by fluid inclusions is generally less than 1%: common minerals like quartz and calcite generally contain 10⁹ inclusions/cm³, constituting only 0.1% of the mineral.

Any process that interferes with the growth of a crystal may cause the trapping of primary fluid inclusions, for example a rapid growth phase. For studies of synthetic crystals, it has been observed that even a change in the concentration of a constituents affects the perfect growth of a crystal (Roedder, 1979b). Primary inclusions are distributed within crystals along growth faces, edges and corners (Mullis, 1987).

Secondary inclusions are formed after the complete formation of the host mineral. If a crystal is fractured in the presence of a fluid in which it is partially soluble, the fluid will enter the fracture, starting the dissolution and recrystallisation of the host crystal, and so trapping new secondary inclusions in the process (Roedder, 1979a). They usually crosscut grain and crystal boundaries (Figure 93).

Figure 93: Diagram to show primary (1 older than 2) and secondary (3 older than 4) inclusions in a quartz crystal.
Inclusion trails terminated at growth boundaries of a host crystal are named *pseudosecondary* (Yermakov, 1949). The cracks along which they occurred were healed during further crystal growth.

The criteria that can be used for the determination of the primary origin of inclusions are reviewed in Roedder (1979, Table 14-1, p. 689-691). They are usually large, randomly distributed in three dimensions in the crystal, isolated or in the core of the crystal. Secondary inclusions occur on the other hand as planar groups outlining healed fractures that come to the surface of the crystal, and are very thin and flat.

The inclusions can be originally of different phases: i.e. liquid, liquid-liquid, liquid-solid or liquid-gaseous. These can be hardly distinguished from phase changes that occurred after the trapping. The fluid phase is commonly H$_2$O, HHc (higher hydrocarbons than methane), CH$_4$ and CO$_2$, but also N$_2$ and H$_2$S are sometimes significant components (Mullis, 1987).

A two-phase inclusion is commonly observed: a vapour or gas bubble in a liquid phase (Figures 94-95). After the trapping of an originally homogeneous fluid by cooling the system down to room temperature, the host mineral contracts less than the fluid inside, because of its volume coefficient of thermal expansion, which is one to three orders of magnitude lower than that of water. As soon as the pressure in the inclusion drops below the total vapour pressure of a multicomponent fluid at that temperature, a bubble nucleates and grows (Roedder, 1979b). Occasionally, the originally homogeneous fluid in the inclusion becomes saturated with respect to phases, other than those constituting the walls of the inclusion, and nucleates new crystals in the inclusion. These crystals are called *daughter minerals* and the most common of these is NaCl, although carbonates or sulphates are also found (Roedder, 1972).

![Figure 94: Diagram to show the appearance of inclusions with various volume percentages of gas compared to the total volume of the inclusion. The gas bubble and the inclusion are assumed to be spherical. The shaded area is the gas phase (from Roedder, 1984).](image)
Sorby (1858) stated that any reversible phase change that occurs on cooling an originally homogeneous fluid phase (formation of a gas or vapour phase, crystallisation of daughter minerals) acts as a thermometer. This characteristic makes the use of fluid inclusions a precious help in the study of low-grade metamorphic rocks. The determination of the composition and molar volume of the fluid is often the only direct evidence of fluid composition that we can have in the study of diagenetic processes.

However, it is necessary to make some important assumptions for the use of fluid inclusions:
1. Fluid trapped with the sealing of the inclusion was a single, homogeneous phase: therefore, analyses of many inclusions apparently belonging to the same trapping event must be made;
2. After the sealing of the inclusions, the volume of the cavity in which the fluid is trapped did not change;
3. No or very minor chemical exchange between the trapped fluid and the host must have occurred;
4. Nothing has been added or taken away from the inclusion.

Fluid inclusions can be studied by means of optical examinations and a non-destructive analytical method called microthermometry. The principle is simple and based on the property that the inclusions which homogenize the gas and liquid phase at a certain temperature is defined as the minimum trapping temperature, i.e. the minimum temperature at which the fluid was homogeneous. To explain the principle of microthermometry, it is easier to assume a one-component system.
If a liquid-like fluid A trapped at temperature $T_{tA}$ and pressure $P_{tA}$ is considered and the inclusion is cooled at a constant density until it reaches the liquid-vapour curve, a small bubble will show up. The bubble grows, with further cooling, until below the triple point ($T_m$ and $P_m$) the liquid freezes. If we consider a vapour-like fluid trapped in an inclusion B, when the inclusion cools and reaches the liquid-vapour curve, a thin liquid film forms at the walls of the inclusion, increasing with further cooling. Also, in this case, the liquid freezes below the triple point. With an increase in temperature, the ice melts at the triple point ($T_m$ and $P_m$). In both cases, the bubble disappears at the homogenization temperature ($T_h$) characteristic for the system (Mullis, 1987)(Figure 96).

**Figure 96:** Graph to show the phase transitions during heating of fluid inclusions with high (A) and low (B) density one-component fluids. $T_p =$ triple point; $C_p =$ critical point. Inclusions: black = solid phase; hatched = liquid phase; white = vapour phase; stippled = fluid phase. Phase transitions: $T_m$, $P_m =$temperature and pressure of melting; $T_h$ and $P_h =$temperature and pressure of homogenization; $T_t$ and $P_t =$temperature and pressure of trapping.

### 5.1.1. Determination of the volatile phase

If a volatile component is present in a fluid, temperature and pressure of solid-vapour or liquid-vapour phase transitions may vary, but the sequence is the same as the one explained for a one-component system (see 5.1)(Mullis, 1987). It is possible to determine the nature of the volatile phase present in the bubble by means of slow heating: the frozen volatile phase melts at temperature characteristic of each gaseous phase (Table 5.1).
Table 5.1: **Triple points and critical points of some selected one-component systems**
*(data from Mullis (1987))*

<table>
<thead>
<tr>
<th>Gas</th>
<th>Triple point</th>
<th>Critical point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>P (bar)</td>
</tr>
<tr>
<td>N₂</td>
<td>-210.00</td>
<td>0.13</td>
</tr>
<tr>
<td>CH₄</td>
<td>-182.47</td>
<td>0.12</td>
</tr>
<tr>
<td>CO₂</td>
<td>- 56.57</td>
<td>5.18</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>-183.27</td>
<td>0.11x10⁻⁴</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>-187.68</td>
<td>3.3x10⁻⁶</td>
</tr>
<tr>
<td>H₂S</td>
<td>- 87.50</td>
<td>0.23</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>-138.29</td>
<td>4x10⁻⁶</td>
</tr>
<tr>
<td>H₂O</td>
<td>+ 0.015</td>
<td>6.11x10⁻³</td>
</tr>
</tbody>
</table>

5.1.2. **Determination of the salt content in the fluid**

The melting point of ice in a saline, volatile-free solution is related to its salt content; therefore we can use freezing studies to determine the salinity of a solution trapped in an inclusion. By measuring the Tm (melting temperature), it is possible to deduce a salinity expressed in weight% of NaCl equivalents (Roedder, 1963; Potter et al., 1978). For most natural brines, the error in estimating the salt content in terms of NaCl equivalents is lower than 5%.

The eutectic temperature (Te), at which the whole fluid freezes, depends upon the type of dissolved salts present (Table 5.2). An addition of other salts to an existing water-salt system lowers the Te. Therefore, it is possible to use the eutectic behaviour to provide constraints on the salt-system present in the inclusions. Eutectic temperatures are also used to distinguish chlorides from other salts present in a solution: for aqueous chloride solutions, the eutectic temperature is lower than -10°C, whilst for aqueous solutions of sulphates, carbonates or hydrocarbonates it is higher than -10°C (Mullis, 1987).
Table 5.2: Eutectic temperatures and compositions of some selected chloride and non-chloride aqueous solutions (from Mullis, 1987)

<table>
<thead>
<tr>
<th>Dissolved salt</th>
<th>Eutectic temperatures (°C)</th>
<th>Eutectic composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>-10.7</td>
<td>19.5</td>
</tr>
<tr>
<td>NaCl</td>
<td>-20.8</td>
<td>32.2</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>-33.6</td>
<td>20.6</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>-49.8</td>
<td>30.2</td>
</tr>
<tr>
<td>NaCl-KCl</td>
<td>-22.9</td>
<td>20.2% NaCl, 5.8% KCl</td>
</tr>
<tr>
<td>NaCl-MgCl₂</td>
<td>-35.0</td>
<td>1.6% NaCl, 22.7% MgCl₂</td>
</tr>
<tr>
<td>NaCl-CaCl₂</td>
<td>-52.0</td>
<td>1.8% NaCl, 29.9% CaCl₂</td>
</tr>
<tr>
<td>NaCl-CaCl₂-MgCl₂</td>
<td>-57.0</td>
<td>?</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>- 1.2</td>
<td>4.0</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>- 2.1</td>
<td>5.9</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>- 2.3</td>
<td>6.3</td>
</tr>
<tr>
<td>NaF</td>
<td>- 3.5</td>
<td>4.1</td>
</tr>
<tr>
<td>NaBr</td>
<td>- 28.0</td>
<td>40.3</td>
</tr>
</tbody>
</table>

5.1.3. Trapping temperature

The temperature at which the bubble homogenizes within the liquid phase (Th) can be considered as the minimum trapping temperature and thus a minimum estimation of the temperature at which the crystal was formed. If we consider the fluid inclusions as a closed system with a constant composition and volume, geothermometric and geobarometric information can be derived if composition and density (or molar volume) of a given fluid is known and if the experimental P-V-T-X (pressure, volume, temperature and composition) properties of the fluid are known. In this case, it is possible to construct the isochores of that fluid, i.e. the lines of constant volume in a P-T diagram (Roedder, 1984).

It can be presumed that the hydrostatic pressure at the time of trapping was greater than the vapour pressure of the solution at that temperature otherwise the fluid would have boiled. In this case, a temperature correction based on the volumetric properties of the solution in the inclusion is required to obtain the true trapping temperature. Since entrapment must lie somewhere along the evaluated isochore at a temperature higher than the homogenization temperature, the true trapping temperature can be evaluated along the isochore using an independent pressure estimation. On the other hand, if it is possible to estimate the formation temperature with another method, it is possible to calculate the trapping pressure using the pressure correction (Potter, 1977; Mullis, 1988). Curves of temperature correction against homogenization temperature for different trapping pressures, calculated for solutions with 1, 5, 10, 15, 20, 25% NaCl are available (Potter, 1977). A construction of the isochore for a given fluid on a P-T diagram, using the available curves, allow for the calculation of pressures corresponding to different temperatures.
5.1.4. Daughter minerals

Daughter minerals are generally found as well formed crystals and the crystalline shape can suggest the nature of the mineral. The determination of the exact composition of a daughter mineral present in an inclusion can be made by Raman Spectroscopy or with destructive analytical methods. With non-destructive analytical methods, it can only be stated if it is a carbonate or a chloride. In fact, during the heating of the inclusion, a chloride should dissolve in the fluid phase, whilst a carbonate resists to a higher temperature.

5.2. Preparation

The preparation of the thin sections for the fluid inclusions analysis must be very accurate. First, samples must be chosen that contain an adequate number of inclusions and distinguish the "real" inclusions from the artificial "bubbles" that form in the adhesive during the preparation of the section. The surface of the rock sample must be accurately polished before to be glued to the glass with Cementit or another glue soluble in acetone. It is important not to use the glues normally used for the preparation of the thin sections because they are not soluble in acetone and therefore it is necessary to heat up the rock section to detach it from the glass. After completing the sticking of the rock slice to the glass, it must be polished very accurately, keeping it relatively thick (50-100 μm depending upon the transparency of the slice and the size of the observed inclusions). At the end it suffice to put the thin section for few hours in acetone until it detaches from the glass. The immersion in the acetone bath is also necessary for the removal of the glue from the section, traces of which could affect the quality of the observations.

"Chips" of the sample of 3-4 mm across can be examined. In this study, the microthermometric measurements have been performed on the Chaix-Meca freezing-heating stage, designed to work in the -180°C to +600°C temperature range (Poty et al., 1976). The stage is then mounted on a Zeiss transmitted light microscope. The precision of the measurements is on the order of ±0.1°C in the -60° to +40°C range and ±1°C outside this range.

5.3. Observations

The presence of fluid inclusions both in the studied dolomite and in the vein fillings has been already mentioned in the Chapter 3.4.3. In the dolomitic host rock, inclusions of primary and secondary origin are very abundant. Primary inclusions are concentrated in the core of the crystals, radiating from the center. Their size varies from 2 μm to a maximum of 50 μm. They constitute, at the most, 2% of the volume of the crystal, with rare peaks of 10%. Secondary inclusions are lined along healed cracks, and are few μm across. In the veins primary inclusions are present in the dolomite, mainly behind the ankerite rim. The late calcite spar is free of inclusions (Figures 97-102).
Figure 97: Photograph of a thin section showing primary and secondary fluid inclusions in dolomite (sample AL10/87). Base of photograph is 0.27 mm.

Figure 98: Photograph of a thin section showing primary and secondary inclusions in dolomite crystals (sample AL10/87). Base of photograph is 0.27 mm.
Figure 99: Photograph of a thin section showing first and second generation of dolomite in veins. Note the ankerite and the distribution of fluid inclusions (sample C30/B/87). Base of photograph is 0.95 mm.

Figure 100: Photograph of thin section showing one- and two-phases inclusions in dolomite (sample M8). Base of photograph is 0.27 mm.
Figure 101: Photograph of a thin section showing a daughter mineral in the inclusion in the middle (sample C30/B/87). Base of photograph is 0.95 mm.

Figure 102: Photograph of a thin section showing a view of the different mineral phases. Note the inclusion-free calcite crystals in the vein (sample M8). Base of photograph is 0.27 mm.
Most of the inclusions are single-phase inclusions, filled only with liquid. Some inclusions are filled with two phases: solid-liquid and liquid-gas. Originally, the bubble present in the inclusions was too small for the determination of the eutectic temperature. However, the relative instability of the carbonates during the heating process or the preparation of the sections enables the artificial mechanical or thermal “stretching” to leak some of the inclusions, provoking the loss of a minimum quantity of the trapped fluid and enlarging the bubble. As the pressure inside the inclusion is higher that the atmospheric pressure at which we normally work, it is possible to assert that no contamination from the outside occurred during this process.

Five samples of dolomitized rock were analysed by microthermometry for fluid inclusions, M6 and M8/87, dolomitized Scaglia variegata (Cenomanian) from Molino d’Altissimo (Lessini); AL10/87, dolomitized Scaglia rossa (Turonian) from Altissimo (Lessini); C30/B/87, dolomitized Maiolica (Valanginian) from Crespadoro (Lessini); PR10/11, dolomitized Rosso Ammonitico from Ferrazza (Lessini). The results are presented in Table 5.3.

Table 5.3: Fluid inclusion analysis.
The volume of the bubble in the "stretched" inclusions is given in brackets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Size +Vol%gas</th>
<th>Inclusion location</th>
<th>T_{hem} -&gt; trapping</th>
<th>T_{eut} -&gt; salt cont.</th>
<th>T_{mel} -&gt; salinity</th>
<th>Mother Mineral</th>
</tr>
</thead>
<tbody>
<tr>
<td>M8/87</td>
<td>8-36 μm</td>
<td>cal in veins</td>
<td>69-73°C</td>
<td>-36°C -&gt; -0.8 -1.0</td>
<td>NaCl-MgCl₂ -&gt; 17%</td>
<td>NaCl-MgCl₂</td>
</tr>
<tr>
<td></td>
<td>3%(25%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>AL10/87</td>
<td>7-17 μm</td>
<td>dolomite</td>
<td></td>
<td>-2.6 -3.0</td>
<td>&gt; 46-49%</td>
<td>carbonate (cal)</td>
</tr>
<tr>
<td></td>
<td>(10-25%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>M6</td>
<td>&lt; 50 μm</td>
<td>dolomite</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>C30/B/87</td>
<td>&lt; 20 μm</td>
<td>dolomite</td>
<td></td>
<td></td>
<td></td>
<td>carbonate (cal)</td>
</tr>
<tr>
<td></td>
<td>in vein</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>PR10/11</td>
<td>core of dolomite</td>
<td>x1</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>(single-phase, liquid)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

From the two-phase inclusions in the veins, it was possible to determine a homogenization temperature of 71°C ±1. Unfortunately, the inclusions are unstable i.e. either they crack contemporaneously during the heating of the sample or the bubble does not re-nucleate during cooling, making this observation particularly difficult. From their characteristics, it can be seen that the true trapping temperature was not higher than +120°C. The homogeni-
zation temperature could not be determined in the inclusions present in the matrix because the gas content was too low. In fact, they are mostly one-phase, liquid inclusions. Therefore it can be suggested that, because of this characteristics, the trapping temperature in the matrix was lower than that in the veins.

During the heating and cooling of the samples between -180°C and +100°C, no melting of the frozen substance occurred at the critical point characteristic of the most common volatiles (CO₂, CH₄, N₂, C₂H₆, C₃H₈).

The eutectic temperature and the melting point have been determine in the "stretched" inclusions. Cooling the sample between 0°C and -70°C, the eutectic point was met at a temperature of -36°C.

Heating slowly the inclusion from -70°C to 0°C, the ice melting point was met at -2.9°C in the fluid included in the dolomite host rock and at -1.0°C in the veins.

Daughter minerals are present, trapped in the inclusions in the dolomite matrix. The rhombohedral crystals have been heated up to +250°C and no changes in their size or shape have been observed.

5.4. Interpretation

The determination of the critical point of the fluid inclusions suggest that the gaseous phase in the bubble is water vapour. By comparing the measured eutectic point of -36°C of the solution trapped in the dolomite crystals with the standard eutectic temperatures of different chloride solutions (Table 5.2), it can be seen that the eutectic temperature of the system H₂O-NaCl-MgCl₂ is -35°C, very close to the measured value. The eutectic composition is 1.6 weight% NaCl + 22.7 weight% MgCl₂. By comparing these values with those of Potter et al. (1978), a salinity of 49 wt% NaCl and 17 wt% NaCl can be calculated. The daughter mineral analysis shows stability at temperatures as high as 200°C and can, therefore, be described as a carbonate, probably calcite. This assertion is supported by the observation of its rhombohedral shape.

From the data obtained from the fluid inclusions, it can be ascertained that the dolomite precipitated rapidly from a relatively high saline (44% NaCl), aqueous solution, whilst the dolomite in the veins precipitated from a more dilute solution. The calcite filling the veins precipitated slowly. The dominant Mg-chloride and subordinate NaCl which are still present in the solution, were probably associated with the calcium and carbonate ions, which now build the daughter minerals. The trapping temperature of the inclusions lies between +70°C and +120°C, which is higher in the veins than in the bulk dolomite rock. These values coincide with the temperature estimated from the oxygen isotope ratios.
Chapter 6

NON-CARBONATE MINERAL ANALYSIS

6.1. Introduction

The non-carbonate minerals, which constitute 2 to 20% of the dolomitized rock, were also analyzed to provide additional information on the dolomitization process. Two main non-carbonate minerals were present: clay minerals and silica. The clay minerals were analyzed with the aid of the scanning electron microscope and X-ray diffraction. Silica was analyzed by the optical microscope, scanning electron microscope and X-ray diffraction.

6.2. Clay minerals

6.2.1. Introduction

Clay minerals are phyllosilicates with a two-dimensional disposition of the SiO₄ tetrahedra and an hexagonally symmetric network. Their crystalline structure is simply an alternance of tetrahedra layers, bonded on one side with layers of cations in octahedric coordination (Mg²⁺, Fe²⁺, Al³⁺) with oxygen and on the other with larger cations (K⁺, Na⁺, Ca²⁺) that coordinate 12 oxygens. Essential, is the presence of hydroxyl (OH⁻) in the middle of the hexagons of Al-O. The amount of H₂O in the crystalline lattice is relatively high and depends on the number of exchangeable cations.

In the clay minerals, dioctahedral and trioctahedral minerals can be distinguished, the former if the octahedric layer is occupied only in 2 of the 3 sites (the element in coordination 6 is in this case usually Al³⁺), or if it is completely occupied.

A classification of the clays is very difficult because of their complex structure and chemical composition. They can be divided into two-layer clays (one layer of tetrahedra and one of octahedra, e.g. kaolinite: Al₄(Si₂O₇)(OH)₂), three-layer clays (tetrahedra-octahedra-tetrahedra, e.g. illite: K₂⁺Al₄(Si₆xAl₄-xO₂₀)(OH)₄, where x may vary between 0.5 and 1, and montmorillonite or dioctahedral smectite), four-layer clays (chlorites, constituted by a three-layers structure plus a trioctahedric layer, where Mg²⁺, Fe²⁺ or Fe³⁺ has 6 (OH⁻) coordinated, with the general formula [Mg, Fe, Al]₁₂[Si,Al]₈O₂₀(OH)₁₆] and mixed-layer clays (complex combination of regularly or irregularly distributed tetrahedric and octahedric layers that can be explained as mixture of other clay minerals, e.g. chlorite-vermiculite, illite-montmorillonite, kaolinite-montmorillonite, etc.).

The geological environments which form clay minerals can be divided into five groups: weathering, sedimentation, burial, diagenesis and hydrothermally altered environments. In
the sedimentation, burial and weathered groups, the clay minerals often reflect the mineralogy of the source area from which the sedimentary material has been derived. The reactions that take place in diagenetic environment, mostly dissolution and precipitation of material from an aqueous solution, are controlled by the supply and quality of the detrital material. The diagenetic and hydrothermally altered groups are more complicated and show a wide range of processes in the formation or transformation of the clay minerals. As the fluid penetrates the rock, certain elements are removed and others deposited as a function of the temperature of the fluid, the composition of the fluid relative to the host rock and the duration of the phenomenon (Velde, 1985).

Certain clay minerals, that are found in carbonates, have distinguishable characteristics. The most common clay minerals are kaolinite, illite, chlorite and mixed-layered clays.

6.2.1.1. Kaolinite

Kaolinite can be considered as an aluminum-silicate with a “neutral lattice”, i.e. it has practically no tendency to build solid solutions. It is one of the most important constituents of sediments, sedimentary rocks and hydrothermal alterations. It has an extreme chemical stability that restricts its usefulness as a diagnostic in tracing the history of a rock. It is stable throughout the range of most clay mineral environments at its bulk composition (Velde, 1985).

6.2.1.2. Illite

Illite represents the dominantly potassic, dioctahedral, aluminous, mica-like fraction of clay-size materials, with a wide range of compositionally solid solutions. It is apparently stable and unaffected by transport in fresh water for relatively short periods of time (Hurley et al., 1961), but changes somewhat in presence of seawater (Carroll and Starkey, 1960). It has been reported to be converted in chlorite or other expandable minerals upon marine sedimentation (Powers, 1959). A minor portion of illite is found in sedimentary rocks with a detrital origin (Velde and Hower, 1963). Illite can be crystallised from an aqueous gel (Harder, 1974). Montmorillonite tends to lose potassium and aluminum, while it relatively gains silica: it is thus converted into an illite (Lin and Clemency, 1981). During the lithification process, illite seems to remain stable or at least it is slow to react with other minerals. Deeply buried sediments show an increase in illite as pressure and temperature increase (Weaver and Beck, 1971). Illite-rich sediments develop the assemblage chlorite-illite-quartz or chlorite-illite-biotite-quartz upon epi-metamorphism (Nicot, 1981). Studies on hydrothermal alteration products in acidic rocks show the tendency of the original minerals to be substituted by illite and kaolinite (e.g., Lowell and Guilbert, 1970).

6.2.1.3. Chlorite

The chemical composition of chlorites which are found in sedimentary rocks is not well understood. It seems that authigenic chlorites in low temperature environments are iron-rich (Grim, 1968), but their exact composition cannot be determined even with the most common
analytical method (X-ray diffraction) and they are rarely separable from the other clay minerals. Chlorite is not stable in weathering profiles, especially under oxidizing conditions (Bain, 1977). It can form during weathering in a temperate climate (Ducloux et al., 1976). It is also common in deep-sea sediments, where it is considered to be a detrital material (Griffin et al., 1968). Siever and Kastner (1972) observed in the Ordovician Lewis Shale, Quebec, Canada and in the Triassic Newark Series Shale, New Jersey, the replacement of Mg$^{2+}$ for Fe$^{3+}$ in clays to form Mg-rich chlorite and pyrite during late diagenesis. During burial metamorphism, chlorite is present at temperatures near or below 100°C (Hower et al., 1976). Mg-chlorite is stable at temperature higher than 150°C (Velde, 1985).

Chlorite can be precipitated from solutions containing the necessary amount of magnesium, aluminum and silica at a pH between 6 and 8, or from reactions of aluminous sediments and seawater (Velde, 1985). It has also been experimentally produced at 2 Kb pressure and 300°-400°C from natural illites and expandable mixed-layered minerals (Velde, 1977). This reinforces the observation that chlorite of variable composition within a sample is an early product of diagenetic, or low grade “metamorphic” change in pelitic rocks.

6.2.1.4. Mixed-layered clays

The natural occurrence of mixed-layered clays is varied and complex. They are particularly chemically variable and have a wide range of mineralogical compositions. They are common weathering products and are proved to be authigenic products of sedimentation on the deep-sea ocean floor (Lerman and MacKenzie, 1975). They are found in sedimentary rocks, especially near the surface. Their stability depends on the geothermal gradient with which the rocks are associated. They are unstable above 100°C and at depths of 2 km or more (Perry and Hower, 1970). In zones of hydrothermal alteration, the formation of mixed-layered clays is limited by temperature, although the composition of the fluids and of the host rock may be important. It seems, in fact, that high magnesium concentrations could form chlorite instead of mixed-layered clays (Velde, 1985).

6.2.2. Preparation

A 15 g calcite or dolomite sample powder is coarsely ground for 1 minute in a mill. It was reacted with 100 ml of concentrated (85%) formic acid (HCOOH) which was diluted 1:1 with distilled water. The carbonate fraction in the calcitic samples were completely dissolved after a few minutes reaction at room temperature. The solutions of the dolomite samples were boiled for 20 minutes. The cooled solutions then deposited the insoluble fraction. After removing the acid, the samples were then washed with distilled water and centrifuged for 10 minutes at 2000 rpm. This process was repeated 3 to 4 times. The samples were then put for 5 minutes into a water bath with ultrasonic waves passed through, which facilitated the separation of the agglomerated particles. Samples were then transferred into glass cylinders of 500 cc size, prepared for separation. Two lines, one 10 cm distant from the top and the other 20 cm from the top, are drawn to aid the observation of the separation. The cylinders were then filled with distilled water and shaken. It is important that the solution does not flocculate: if it does, the sample has not been washed accurately and some acid or carbonate
is still present which builds flocules of clay minerals. If this happens, it is therefore necessary either to rewash the samples or to add to the solution a few ml of Calgon (sodium-hexa-metaphosphate) which is a dispersing agent.

After 15 hours and 40 minutes, the first 20 cm of liquid is removed and transferred into a porcelain bowl. The bowl is placed in an oven at 60°C throughout the whole process. The cylinder is filled again, shaken and let to deposit for 8 hours and 20 minutes, before the first 10 cm of liquid is removed and put into a bowl. The whole operation is repeated again after 2 or 3 days, removing another 20 cm of liquid after 15h40m and 10 cm after 8h20m. At the end of the process, the solution must be clear. When the water in the bowl has evaporated completely, it is possible to scratch away the clay fraction. This fraction that is deposited in the cylinder is the silt fraction of the insoluble residue (> 2µm). The part in the bowl is the clay fraction (< 2µm).

The smear slides of both the silt and the clay fraction were prepared for the XRD with water and a small quantity of the sample. The analyses have been performed with a Philips APD 1700 Diffractometer at standard work conditions. The 2θ range analysed is between 5° and 45°.

The clay minerals were also observed with the scanning electron microscope (SEM) on the surface of the dolomite rhombohedra. Samples of both dolomitized and unaffected rocks from the same horizontal profiles have been compared. Qualitative analysis was performed by X-ray diffraction and the energy dispersion system (EDAX) connected with the SEM. The best method for the preparation of the samples for the SEM observations, is with the use of a spray gun. A highly dispersed suspension of the clays in water has been sprayed for 12 hours on a graphite sample holder (neutral for the EDAX analysis, because the light carbon is out of the range) from a distance of about one meter. From this distance, the suspension was vaporized and no drops were formed on the surface of the sample holder. This optically invisible coat of clays represents a statistically optimal distribution of differently oriented clay packets. A less elaborate, but also less exact, preparation method is the smearing of a suspension of clays in water, alcohol or by sticking the clays and silt by means of an organic glue on a metal sample holder. For the metallisation of the prepared samples an alternative is to use gold (more suitable for photos) or carbon (more suitable for analyses).

A quantitative analysis of some samples has been performed with the atomic absorption spectrometer in an attempt to determine the nature of the dolomitizing fluids. The solutions for the analyses were prepared by dissolving 200 mg of the sample in 30 ml of a solution of concentrated hydrofluoric acid (HF) and nitric acid (HNO₃). The solution was then dried, whilst contained in a platinum evaporating dish on a hot sand bath; 5 ml of nitric acid was then added, evaporated, and a further 5 ml of nitric acid subsequently added. After this acid was then evaporated, the dish was washed with distilled water and a further 1 ml of nitric acid was added. It was then heated for 10 min to obtain the complete dissolution. Finally distilled water was added to obtain 100 ml of solution. The samples were measured with a Perkin-Elmer PC 420 Atomic Absorption Spectrophotometer alternatively with an air-acetilene flame or an air-N₂O flame.
Figure 103: X-ray diffractogramm of non-carbonate phases in limestone and dolomitized samples (comparison of sample M1, calcite (black line) and M6, dolomite (red line)).
6.2.3. Observations

Most of the samples collected for this study do not have enough non-carbonate phases (<5%) to allow for a separation of the clay fraction. 9 samples of both calcite and dolomite were found suitable for this method and chosen for the clay fraction analysis: C5 (calcite) and C13 (dolomite) are Maiolica samples of Valanginian age from Crespadoro (Lessini); M1 (calcite) and M6 (dolomite) are Scaglia variegata of Cenomanian age from Molino d’Altissimo (Lessini); AL1/87 (calcite) and AL8/87 (dolomite) are Scaglia rossa samples of Turonian age from Altissimo (Lessini); PR12 is a dolomitized sample of Rosso Ammonitico from Ferrazza (Lessini); SG15 (calcite) and SG14 (dolomite) are Maiolica samples from the Grappa area.

Non-carbonate phases were seen to constitute from 2 to 20% of the carbonates. The silt fraction has a tendency to constitute a major part of the residue of the dolomite samples, whilst the clay fraction is dominant in the calcite samples (see Table 6.1).

Table 6.1: Percentage clay and silt fraction in the studied samples

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Main dissolved carbonate</th>
<th>% Silt fraction</th>
<th>% Clay fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5 calcite</td>
<td>0.73</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>C13 dolomite</td>
<td>2.22</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>M1 calcite</td>
<td>0.32</td>
<td>17.93</td>
<td></td>
</tr>
<tr>
<td>M6 dolomite</td>
<td>11.08</td>
<td>3.77</td>
<td></td>
</tr>
<tr>
<td>AL1/87 calcite</td>
<td>6.20</td>
<td>2.64</td>
<td></td>
</tr>
<tr>
<td>AL8/87 dolomite</td>
<td>2.19</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>SG14 dolomite</td>
<td>3.32</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>SG15 calcite</td>
<td>1.82</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>PR12 dolomite</td>
<td>14.45</td>
<td>1.42</td>
<td></td>
</tr>
</tbody>
</table>

The diffractograms of the dolomitized and unaffected samples were plotted and compared (Figure 103). In some of the diffractograms the peaks of the carbonates, not completely leached, are still observable. The silt fraction is, in both cases, constituted by microcrystalline quartz and chert. The basal reflections of the clays are well defined. The clay fraction of the calcite samples is constituted by kaolinite and, sometimes illite. In some of the dolomite samples (e.g. M6), mixed-layered clays and chlorite peaks are present. In the same sample, an abnormally high background between 20° and 40°, i.e. in the range where the quartz peaks are registered, is observable.

The SEM photographs of the silt and clay fractions are shown in Figures 104-125. The corresponding EDAX analyses, when available, were also shown. The quality of the
Figure 104: Photomicrograph of a clay mineral aggregate in dolomite (sample C9). Scale shown by bar.

Figure 105: Photomicrograph of clays on a dolomite crystal (with EDAX analysis) (sample C9). Scale shown by bar.

Figure 106: Photomicrograph of a close-up on clay minerals in dolomitized rock (sample C9). Scale shown by bar.

Figure 107: Photomicrograph of a detrital K-feldspar in the silt fraction of limestone (sample M1S). Scale shown by bar.

Figure 108: Photomicrograph of an aggregate of microcrystals of quartz in limestone (chert fragment) (sample M1S). Scale shown by bar.
Figure 109: Photomicrograph of clay minerals from the clay fraction of a dolomitized sample (with EDAX analysis) (sample C13T). Scale shown by bar.

Figure 110: Photomicrograph of a close-up of clays in limestone (sample M1S). Scale shown by bar.

Figure 111: Photomicrograph of kaolinite (with EDAX analysis) in the clay fraction of the limestone (sample M1S). Scale shown by bar.

Figure 112: Photomicrograph of a view of the clay fraction in limestone (sample M1T). Note the detrital aspect of the minerals. Scale shown by bar.

Figure 113: Photomicrograph of a view of the clay fraction in a dolomitized rock sample (sample C13T). Note the large, well formed, probably recrystallized, clay minerals (QV Figure 112). Scale shown by bar.
Figure 114: Photomicrograph of a view of clays in a dolomitized rock sample (sample M6T). Also in this case the clays look well crystallized. Compare with Figure 112 and 113. Scale shown by bar.

Figure 115: Photomicrograph of a clay mineral in limestone (with EDAX analysis) (sample M1T). Scale shown by bar.

Figure 116: Photomicrograph of a lamina of aggregated clay minerals from dolomite (sample C13T). Scale shown by bar. This photo shows the necessity to prepare the sample for the SEM photographs with a spray gun in order to separate the layers.

Figure 117: Photomicrograph of a close-up on the clays of Figure 116. Scale shown by bar.

Figure 118: Photograph of a close-up of Figure 117 (sample C13T). Scale shown by bar.

Figure 119: Photomicrograph of clay aggregates (sample C13T).
Figure 120: Photomicrograph of clay aggregates (sample C13T).

Figure 121: Photomicrograph of a view of clay minerals from limestone, as they look "sprayed" on the sample holder (sample M1T). Note the detrital aspect of the minerals. Scale shown by bar.

Figure 122: Photomicrograph of a view of "sprayed" clays from dolomite, to compare with Figure 121. The same enlargement has been used (sample M6T).

Figure 123: Photomicrograph of a view of clays from dolomitized rock (with EDAX analysis)(sample C13T). To compare with Figure 121. Scale shown by bar.

Figure 124: Photomicrograph of a view of clays from limestone (with EDAX analysis)(sample C5T). The scale bar is the same as Figure 123.

Figure 125: Photomicrograph of carbonate dissolution features in yellow filling material. The material still remaining is clays (sample PB21/87). Scale shown by bar.
photographs associated with the EDAX analyses is not very satisfactory, due to the carbon coating where the electric charge concentrates on the surface, thus affecting the contrast effect.

In the silt fraction, microcrystalline quartz, sometimes aggregated with clay, is almost the exclusive mineral present. Detrital feldspars are rare. It is interesting to compare an overview of clays from limestone and dolomite (Figures 123 and 124). The degree of differential crystallinity is visible: the clay minerals in the dolomite are larger and better crystallised. With the SEM, it is difficult to distinguish the different clay minerals with their morphology, this being the characteristic sheeted aspect common to all the clays. This analysis is best carried out by the EDAX. The clays in the calcite samples contain mainly calcium, a small amount with potassium and iron, associated, of course, with silicon and aluminum. The clays in the dolomite contain mainly magnesium, potassium, calcium, iron, with minor sodium, sulphur and phosphorus.

The barium, magnesium, strontium and iron content of 4 samples of clay fractions were analysed by means of the AAS. The results are shown in Table 6.2.

Table 6.2: Partial elemental composition of bulk clay minerals in calcite and dolomite samples

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Ba (ppm)</th>
<th>Sr (ppm)</th>
<th>MgO (%)</th>
<th>Fe$_2$O$_3$ + FeO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M 1T (cal)</td>
<td>1360</td>
<td>315</td>
<td>0.95</td>
<td>0.49</td>
</tr>
<tr>
<td>M 6T (dol)</td>
<td>423</td>
<td>171</td>
<td>2.46</td>
<td>2.02</td>
</tr>
<tr>
<td>C 5T (cal)</td>
<td>345</td>
<td>207</td>
<td>1.76</td>
<td>1.72</td>
</tr>
<tr>
<td>C 13T (dol)</td>
<td>402</td>
<td>211</td>
<td>2.62</td>
<td>1.86</td>
</tr>
</tbody>
</table>

It can be seen that, almost uniformly, magnesium and iron are concentrated in the clays present in the dolomitized samples, whilst strontium tends to depletion. The data on barium concentrations are controversial. This behaviour is similar to the trace element behaviour in the carbonates: strontium prefers to concentrate in the fluid phase, iron in the solid phase. The high magnesium content in the dolomitizing solution influences also the composition of the clay minerals.

6.2.4. Interpretation

The clay minerals present in the dolomite rock are well crystallised. The good preservation of clays suggests that the temperature never exceeded 200°C. The presence of chlorite exclusively in the dolomitized samples, allows us to reject a detrital origin. The neoformation of chlorite occurs at temperatures higher than 100°C (Hower et al., 1976; Bowers and Taylor, 1985), whilst Mg-rich chlorite forms at 100°C to 150°C. By using EDAX analyses, a Mg-rich mineral was found, which is probably chlorite. It can, therefore, be suggested that a formation temperature for this chlorite is between 100°C and 150°C.
The higher content of clays in the dolomitized rock, with respect to the limestone, is probably due to homogenisation that occurred in the rock during the dolomitization: in fact, the unaffected bulk rock is constituted by almost pure micritic limestone strata interposed with clay-rich interstrata, whilst the dolomitic rock is more or less homogeneous.

However, it is not possible to generalize on the fluid composition from the chemical composition of the clays and there is even less evidence concerning the influence of these solutions on the clays (Velde, 1985). The only information that can be deduced from the bulk composition of the clays in the dolomitized rock is that it was possibly influenced by hydrothermal fluids which enriches the clays in elements like barium, characteristically present in all hydrothermal vent fields (Von Damm et al., 1985).
6.3. Silica

6.3.1. Introduction

In sediments and sedimentary rocks, several forms of SiO₂, stable at near surface conditions, are found: quartz, chalcedony, opal and amorphous gels. Silica is in solution at surface temperature and pressure and at pH lower than 9 in the monomeric form Si(OH)₄ (Stumm and Morgan, 1970). Solutions containing 5-15 ppm SiO₂ in solution at 25°C may be saturated with respect to quartz (Morey et al., 1962). Seawater, however, which contains less than 1 ppm SiO₂ in solution, is always undersaturated with respect to amorphous silica and cristobalite (Kastner, 1981).

The solubility of silica is a function of the crystalline state of the phase, except with respect to temperature and pressure conditions: it increases with temperature and pressure. Surface impurities like Al, Fe or organic matter have been experimentally shown to lower the solubilities of the silica phases (Krauskopf, 1956). Quartz is the stable phase at surface temperature and pressure; all other phases are metastable (Stöber, 1967). For this reason, it is not correct to consider the “solubility” of the amorphous silica phases, but an “apparant solubility”. Quartz, chalcedony, cristobalite and amorphous silica are, therefore, in order, increasingly soluble (Kastner, 1981). The solubility of quartz at 25°C and 1 bar is about 6 ppm (100 µM) (Morey et al., 1962). Chalcedony is more soluble than quartz, because of the presence of opal-CT which is not stable (Kastner, 1981). The “apparant solubility” of silica gel at 25°C and 1 atm yields 114 ppm SiO₂ (1900 µM) (Krauskopf, 1956). In seawater the “apparant solubility” of amorphous silica at 2°C and 1 atm yields 56 ppm SiO₂, at 100 atm 70 ppm (1167 µM) (Jones and Pytowicz, 1977).

Silica has not been experimentally precipitated from a solution at temperatures below 80°C (Velde, 1985): it is necessary to elude the kinetic barriers to quartz equilibria at low temperatures, for example, using abraded quartz grains as crystallisation nuclei (MacKenzie and Gees, 1971).

The silica present in the sediments has been formed from dissolved silica mainly through biogenic processes, like secretion of silica of phyto- and zooplankton. Biogenic silica, in the present oceans, is extracted from seawater by diatoms, radiolarians, sponges and silicoflagellates, in order of decreasing importance. Inorganic silica precipitation may occur in connection to hydrothermal vents (Kastner, 1981).

The authigenic silica phases are opal-A, opal-CT, opal-C and quartz. Opal-CT and quartz are the most common phases respectively in porcelanite and in chert (Figure 126). The terms chert and porcelanite are widely used for this description. Chert is a rock constituted mainly of authigenic quartz (Smith, 1960) whilst porcelanite is a rock mainly composed of opal-CT (Calvert, 1971). Chert and porcelanite are present in nodules in carbonate sediments, replacing the carbonate matrix, and in beds in siliceous and clay-rich sediments, replacing the original amorphous silica (Kastner, 1981).
6.3.1.1. Opal-CT

It has a characteristic X-ray diffraction pattern (Figure 124), with three broad peaks near 4.3, 4.1 and 2.5 Å (Jones and Segnit, 1971). It can be massive or occur as lepispheres of the size of a few μm (e.g. 4 to 30 μm; Wise and Kelts, 1972), spherical to elliptical bodies built of intersecting platy or bladed euhedral to subhedral crystals (Kastner, 1981). The water content of the opal-CT can reach 13 wt% (Keene, 1975; Kastner, 1981).

6.3.1.2. Opal-C

Opal-C is a well ordered α-crystobalite. It is found in opals associated with lava flows.

6.3.1.3. Quartz

Deep-sea cherts are mainly composed of quartz. Quartz occurs as subhedral to euhedral megacrystals (>20μm, e.g. drusy quartz), microcrystals (<20μm) forming massive structures
and as chalcedony, a cryptocrystalline variety of quartz (Kastner, 1981). Quartz is inert in
many weathering and sedimentary environments. Silica is unstable in the crystalline form
under conditions of intense weathering (bauxites contain no quartz).

6.3.1.4. Silica occurrence in sedimentary environments

After deposition, silica undergoes diagenetic transformations that depend on the nature
of the initial phase: the silica concentration in interstitial fluids, its pH, the nature of
associated rock types, temperature and pressure. The transformation sequence of a siliceous
ooze (opal-A) to porcelanite (opal-CT) to chert (chalcedony, micro- and macroquartz) has been
observed in the Monterey Formation, California (Bramlette, 1946). Both the opal-A to opal-
CT and the opal-CT to quartz transformations involve a solution step (Kastner et al., 1977;
Murata et al., 1977; Kastner and Gieskes, 1983). The transformation from opal-A to quartz
in deep-sea siliceous sediments proceeds always through the intermediate formation of opal-
CT (Kastner, 1981). Temperature and pressure mainly influence the different steps of the
transformation (e.g. Campbell and Fyfe, 1960).

Kastner et al. (1977) demonstrated experimentally that the formation of “nuclei” of Mg²⁺
and OH⁻ in the ratio 1:2 enhances the formation of opal-CT from opal-A. The presence of
carbonates indirectly influences the transformation, providing with its dissolution the
necessary alkalinity, together with seawater that provides magnesium for the formation of the
Mg²⁺ nuclei. Therefore, the transformation should proceed slower in freshwater environments
than in deep-sea sediments. In carbonates, opal-CT would transform in quartz earlier than
in clay-rich sediments. This transformation is strongly influenced by temperature, pressure
and pH of the solution (Kastner and Gieskes, 1982).

Silica is mobilized during diagenesis and moves over short distances. In limestones and
chalks, silica migrates to silicification horizons to form porcelanite or chert beds and nodules.
For this reason, limestones and chalks interbedded with chert or porcelanite are frequently
poor in silica (Kastner, 1981).

Summarizing, the diagenesis of silica in deep-sea sediments proceeds from the dissolution
of siliceous tests and frustules to the formation of opal-CT, to the grain growth of opal-CT to
the formation of quartz, mainly as chalcedony and microcrystalline quartz (Kastner, 1981).
The transition temperature of opal-crystobalite to quartz in Tertiary sediments ranges from
22°C to about 70°C (Iijima and Tada, 1981; Aoyagi and Kazama, 1980). It has been suggested
(Kastner, 1981) that, it has been possible to formulate two equations correlating the time (t
in million years) to the temperature (T in °C) for the formation of porcelanite from siliceous
ooze in oceanic sediments:

\[ t = 80 - 2T + 0.01T^2 \quad (\text{Equation 15}) \]
\[ t = 83 - 4.15T + 0.1T^2 - 0.001T^3 \quad (\text{Equation 16}) \]

This equation (15) is valuable for areas with lower sedimentation rates and/or lower
geothermal gradient and/or less carbonate-rich sediments than the areas represented by
equation (16). It can be seen that opal-A needs 20 my or 5-10 m.y. respectively, for areas at low or high sedimentation rates, to transform in opal-CT at temperatures of 20-50°C. The transformation opal-CT to quartz takes 40-50 ma after deposition to occur in areas of average oceanic heat flow and moderate sedimentation rates (Keene, 1975). At temperatures around 80°C, the transformation would take only 10 m.y. (Murata et al., 1977).

6.3.2. Preparation

The silt fraction, and a minor part of the clay fraction of the non-carbonate phase of both dolomites and limestones, is constituted by silica. These samples have been observed and photographed with the scanning electron microscope.

Smear slides of bulk chert samples and silt and clay fractions were analysed with the X-ray diffraction. The analytical method is described in Chapter 6.2.2.

The oxygen isotope contents of few samples of chert from both dolomite and limestone have been measured by Prof. A. Longinelli and his assistants at the Laboratorio di Geologia Isotopica at the University of Trieste (Italy). Oxygen was extracted using BrF₅ and converted to CO₂ by reaction with heated carbon as described by Taylor and Epstein (1962). The isotopic ratios were determined by conventional mass spectrometric analysis and are reported in δ-values relative to the SMOW standard. Reproducibility for quartz is 0.2‰.

6.3.3. Observations

The pelagic limestones of the Rosso Ammonitico, Maiolica Veneta and Scaglia Rossa Formations contain chert in beds and nodules. The Maiolica Veneta is characteristically silica-rich, containing nodules and lenses of greychert of cm- to dm-size. The nodules show a white shell of a few mm thickness and a dark grey core. In spite of their different appearance, both parts have the same composition and show differences only under the microscope. The chert in the Rosso Ammonitico and in the Scaglia Rossa occurs in scattered reddish nodules. In the dolomitized rock the chert is mechanically deformed and strongly fractured. The nodules are brecciated and the white edgy fragments are scattered in the dolomitic host rock.

In thin section, it is possible to observe the optical difference between the white and grey part of the chert fragments. The grey part is grey-brown, dense, almost opaque material, homogeneous and contains scattered radiolaria. The white part is more or less well crystallised cryptocrystalline quartz with rare radiolaria ghosts preserved. In the dolomite, the chert which is almost exclusively white, is mainly constituted of locally crystallised opaque material with radiolaria. The fragments are crossed cut by microfractures, along which the chert is cryptocrystalline (Figures 127-129).

In the SEM photographs, it has been observed that the chert fragments are constituted by aggregates of tiny quartz crystals. It was impossible to distinguish between the above mentioned white and grey part. In the clay fraction of the sample C13T a silica crust has been
Figure 127: Photograph of a thin section of chert in limestone. Note the ghosts of radiolaria in the opaque material (sample PB21).

Figure 128: Photograph of a thin section of chert included in dolomitized rock. Note the fracture along which the chert is microcrystalline (sample C77/87).
Figure 129: Photograph of a thin section of chert included in dolomite (sample C77/87).

Figure 130: Photomicrograph of silica crust in dolomitized sample. See text for explanation (sample C13T). Scale shown by bar.

Figure 131: Photomicrograph of aggregate of clays with quartz fibers (sample C13T). Scale shown by bar.

Figure 132: Photomicrograph of microcrystalline quartz from chert in limestone (sample M15). Scale shown by bar.
observed, probably the result of a partial dissolution of amorphous silica in ethilic alcohol used for the preparation of that sample (Figures 130-132).

With the X-ray diffraction, no substantial difference has been noticed between the white and grey part of the chert: both show the characteristic basal reflections of chalcedony or quartz. In the diffractograms of the clay fraction of some dolomite samples, it has been possible to state the presence of amorphous silica from the higher background in the 2θ range 20-40°.

Six samples of chert from the *Maiolica Veneta* Formation in Crespadoro (Chiampo Valley, Lessini, series C and CH) were analysed for the oxygen isotope ratio. A part of the samples of chert, included in the dolomitized rock, are slightly depleted in 18O (1 to 2‰), with respect to the chert in the original limestone (Table 6.3).

**Table 6.3: Oxygen isotope values of chert from both limestone and dolomite (Crespadoro, Chiampo Valley)**

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Host rock</th>
<th>Colour</th>
<th>Location</th>
<th>δ18O %o SMOW</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH2</td>
<td>limestone</td>
<td>grey</td>
<td>nodule</td>
<td>+32.54</td>
</tr>
<tr>
<td>C39/A/87</td>
<td>dolomite</td>
<td>white</td>
<td>fragment</td>
<td>+32.20</td>
</tr>
<tr>
<td>C62/D/87</td>
<td>dolomite</td>
<td>white</td>
<td>fragment</td>
<td>+31.92</td>
</tr>
<tr>
<td>CH1</td>
<td>dolomite</td>
<td>white</td>
<td>fragment</td>
<td>+30.97</td>
</tr>
<tr>
<td>CH3</td>
<td>dolomite</td>
<td>white</td>
<td>fragment</td>
<td>+31.18</td>
</tr>
<tr>
<td>CH4</td>
<td>dolomite</td>
<td>grey</td>
<td>lens</td>
<td>+32.86</td>
</tr>
</tbody>
</table>

6.3.4. Interpretation

The grey core of the chert nodules in the limestone shows a less complete equilibration with the diagenetical environment than the white coating. Ionic diffusion transport caused by concentration gradient is more active at the surface of the nodule. This suggests that once the silica migrated to the silicification sites, the outer part is more subject to influence by the surrounding environment, "protecting" as a barrier the ionic diffusion in the internal part once it reached a stable state. The fact that both these parts are chalcedony or quartz indicates that the diagenetic process of the chert is more or less complete, as to be expected in Cretaceous sediments.

Chert fragments are found widespread in the dolomitized breccia: therefore, the chert was already lithified at the time of the dolomitization. Contemporaneous to the dolomitization, a partial dissolution of the silica and formation of amorphous silica has occurred. In hydrothermal environments, with high water flux and higher temperatures, silica is mobilised and precipitated as an amorphous gel (Humphris and Thompson, 1978).
The oxygen isotope values are not very significant, although the chert in the dolomitized rock has slightly more negative $\delta^{18}O$ values than the chert in the unaffected rock, indicating a slightly higher formation temperature. This negligible difference can be easily explained by suggesting that the chert was already at an advanced diagenetised stage when the dolomitization occurred: a maximum of 20-30 ma after the deposition are necessary for the transformation opal-A to opal-CT to chalcedony (Kastner, 1981). Successive environmental changes (e.g. temperature, fluids) could not, therefore, notably affect the chert.
Chapter 7

Synopsis

The simple fact that dolomite has been found in the Southern Alps proves that the environment, in a precise interval of time, fulfilled the requirements for the formation of dolomite, thus overcoming the kinetic barriers to provide favourable physical conditions (e.g. temperature), fluids with a suitable composition (e.g. Mg/Ca ratio, pH, Eh) and a drive for the dolomitizing fluids. The bulk of the data collected on the studied dolomite provides information on the conditions at the time of formation and allows some speculations on the time at which the dolomitization occurred.

The approximate estimated volume of the dolomitized rocks is 28.2 km³, weighing roughly 7 x 10¹⁶ g (28.2 x 10¹⁵ g x 2.5 g/cm³). Assuming a stoichiometric dolomite, the amount of Mg contained in the dolomite is 9.13 x 10¹⁵ g. One liter of marine water contains 1.2 g Mg. 7.6 x 10¹⁸ cm³ marine water (260 times the volume of the dolomite) would provide the necessary amount of Mg for the dolomitization.

At the time of the dolomitization, the limestones were at least partially lithified, whilst the chert was already at an advanced diagenetic state. The brecciation occurred contemporaneously with the extensive north-south oriented tectonism, which was previous or contemporaneous to the volcanism. It facilitated the flux of the dolomitizing water through the limestones and the transformation of the original material. The character of the extruded basalts (non differentiated, xenolith-rich basalts of mantle origin) supports the assertion of the existence of extension, beginning in the Upper Cretaceous-Paleocene, as observed in the field.

The dolomite is not stoichiometric (up to Ca₉₀Mg₄₀) suggesting, together with other petrographic observations, a rapid crystallisation especially at the beginning. The crystallisation occurred in one single phase from a homogeneous substrate in a reducing environment. The water/rock ratio must have been quite high, considering the amount of fluid
trapped mostly in the core of the dolomite crystals. The successive precipitation of dolomite - ankerite (or iron-rich dolomite)- calcite in the veins occurred more slowly, probably contemporaneously to the partial dedolomitization of yellow dolomite in the brecciated limestone. The chert, included in the dolomitized rock, has been slightly affected (recrystallised) by the dolomitizing solutions.

A temperature (T) estimation has been made from the oxygen isotope values in the dolomite, with the simplified dolomite-water fractionation formula (Mathews and Katz, 1977), where 

\[
8^{18}O_{\text{O}_{\text{w}}} - 8^{18}O_{\text{H}_{2}O} = 3.06 \times 10^6 T^2 - 3.24 \quad \text{(Equation 17)}
\]

As both the \(8^{18}O_{\text{H}_{2}O}\) and the temperature are unknown, it can be assumed that an oxygen isotopic ratio for the water varies between 0 and -2% SMOW (seawater). A value of \(8^{18}O_{\text{O}_{\text{dol}}} = -6\%_{\text{vdpb}}\) (roughly the mean value of the studied dolomite) corresponds respectively to a temperature of 62°C (0%o) or 51°C (-2%o). A value of \(8^{18}O_{\text{O}_{\text{dol}}} = -12\%_{\text{vdpb}}\) (the most negative value, obtained for the Rosso Ammonitico samples) corresponds respectively to a temperature of 106°C (0%o) or 90°C (-2%o).

The temperature at which the dolomitization occurred ranged between 70° and 120°C, which was higher for the vein fillings than for the dolomite host rock. This is suggested by the petrography of the dolomite, the \(8^{18}O\) data, the fluid inclusions trapping temperature and the clay mineralogy.

Assumptions on the chemistry of the dolomitizing fluids can be made from the chemical composition of the fluids trapped in the crystals. The fluid is now constituted by an aqueous solution of NaCl and MgCl\(_2\). The presence of carbonate as a daughter minerals suggests the original existence of calcium and bicarbonate in small quantities. These precipitated during the cooling of the fluid. The salinity of the solution included in the dolomite host rock is 49% NaCl eqv, whilst the fluid trapped in the dolomite crystals in the veins is 17%. The fluids that dolomitized the bulk of the limestone were therefore saline, marine-like waters, as suggested also by the stable isotope ratios. A meteoric influence is probable for the latest phase of
crystallisation. The conclusion that the involved dolomitizing solution was marine water allows us to use the strontium isotope ratios for a rough dating of the phenomenon. The obtained Late Oligocene-Early Miocene age agrees with the calculation made from the pressure correction in the fluid inclusions.

In fact, from the trapping temperature and the calculated salts content, the isochore for the system can be constructed (Roedder, 1984; Mullis, 1988) (Figure 133). Using the pressure correction, assuming an average temperature of 100°C, a trapping pressure of about 250 bars can be obtained. Knowing the density of the rocks overlying the dolomite at the moment of the formation of the inclusions, a reconstruction of the approximate geothermal gradient can
the formation of the inclusions, a reconstruction of the approximate geothermal gradient can be made: 390 m of sediments with a density of 2.6 g/cm³ exerts a pressure of 100 bars; 500 m of basalts (ρ = 3.0 g/cm³) exerts a pressure of 150 bars. This corresponds roughly to conditions in the Oligocene of the studied area. The geothermal gradient would, therefore, have been of about 8°C/100 m, anomalously high, which is to be expected for a volcanically active area.

In conclusion, it is possible to ascertain that the dolomite is the product of hydrothermal alteration of the precursor limestone. The higher temperature associated with the volcanism facilitated the dolomitization reaction, overcoming some of the kinetic barriers (e.g. the hydration shell of the magnesium ion) and accelerating the reaction.
CHAPTER 8

Physical model for the formation of hydrothermal dolomite

8.1. Tectonic considerations

There are many different hypothesis for the formation of dolomite, which has been found in various geological environments. As such there is no single type of dolomite, but a collection of dolomites which can form under completely unrelated conditions. Therefore, no single physical model for the formation of dolomite will ever be found. However, for the formation of dolomite, similarities can be found in most of the preexisting models, i.e. the need of magnesium, the presence of chemical conditions favouring the precipitation of dolomite, a water circulatory force etc. Any new model for the formation of dolomite will usually incorporate these conditions although they may be active in different environments.

New insights into the tectonic evolution of the Alpine realm (Hsü, 1989; Dewey et al., 1989; Hill and Hayward, 1988) has provided data that can constrain a physical model to a realistic situation. Extension can be generated in various ways, e.g. transtension, rifting, crustal thinning, gravity sliding, etc. Extension in a compressional regime, such as the Alps in the Tertiary, has long been identified in both the Alpine foreland (Rhine graben and extensional basins in the Molasse) and in the back-arc (Ligurian-balearic basin)(Laubscher, 1983). Such back-arc extension between Southern France and the Corsica-Sardinia-Calabria (CSC) block is associated with the subduction beneath Europe during the Late Oligocene (Figure 134). Whereas the Adria plate moved northwards and rotated counterclockwise resulting in compression in the western Alps and initial collision with Corsica, the rifting developed a transitional crust between France and the Corsica-Sardinia-Calabria block. The CSC microplate rotated counterclockwise about a pole situated in the NW-Apennines, and led to the formation of oceanic crust beneath the Ligurian Sea (Hill and Hayward, 1988). By 15 Ma, the CSC block had locked between Sicily and Italy and the major deformation of the Apennines occured. Subduction to the WNW , beneath Calabria in the Late Miocene, combined with the movement of Africa to the north, resulted in the extrusion of Calabria to the southeast, such that compression on northern Sicily migrates progressively to the east. The southeastward movement of Calabria results in the formation of the Tyrrhenian Sea oceanic crust in a back-arc basin. The opening of the Tyrrhenian Sea caused reactivation of thrusts as normal faults in the Northern Apennines and N-S extension of the Sardinian margin (Figure 134)(Hill and Hayward, 1988; Dewey et al., 1989).
Figure 134: Paleogeographic reconstruction of the western Mediterranean for 30 and 5 Ma (from Hill and Hayward, 1988).
Crustal thinning took place during the Oligocene-Early Miocene in the Lessini area, as testified by the mineralogical and chemical characteristics of the basalts (see Chapter 2.4). This suggests a situation of rifting that fits in the general alpine tectonic framework. The orientation and the age of the Marana graben roughly coincides with the back-arc extension that led to the opening of the Ligurian-Balearic basin. The rifting in the Lessini aborpted because of the counterclockwise rotation of the CSC block about the pole in the NW Apennines. The later Castelvero fault extension can be related to the opening of the Tyrrhenian Sea in the Pliocene.

With the tectonic information as support, the study of dolomite in the Lessini area with modern geological analytical methods led to the production of new data about the formation of dolomite. Such results have been interpreted individually for each analytical method but eventually it is necessary to amalgamate the interpretations and produce a model for the conditions suggested. As a result, a hydrothermal model of dolomite formation is suggested and outlined below.

8.2. The hydrothermal model

The dolomite of the Venetian Alps is the product of a Late Oligocene to Early Miocene hydrothermal activity that subsequently altered a Jurassic to Cretaceous sedimentary series. Favourable chemical conditions related to structural and volcanic activity led to the formation of the dolomite. To understand how the hydrological/thermally induced model occurs, it is necessary to firstly explain how to quantify the amount of water necessary to dolomitize a carbonatic unit and secondly how the temperature of this water is caused and resulted in dolomitization.

An essential feature for any dolomite model is the amount of water necessary for the process of dolomitization. A typical modern sediment contains about 6.3 mole % MgCO₃ (Land, 1973) with about 40 % porosity. To calculate the amount of water needed for dolomitization the following procedure can be followed, assuming that the dolomitizing agent is seawater saturated with respect to calcite. A cubic meter of typical modern sediment contains in total:

1) 400 liters of seawater x 1.025 Kg/l = 4.1 x 10² Kg seawater

2) 600,000 cm³ of sediments consisting of 570,885 cm³ of CaCO₃ (or 1.545 x 10⁴ moles, since one mole are 36.95 cm³) and 29,115 cm³ of MgCO₃ (or 1.039 x 10³ moles, since one mole are 28.02 cm³).
Therefore, \(4.1 \times 10^2\) Kg of seawater contains 4.26 moles of \(\text{Ca}^{2+}\) and 22.1 moles of \(\text{Mg}^{2+}\). This sediment may react with the water according to the equation:

\[
2\text{CaCO}_3 + \text{Mg}^{2+} \leftrightarrow \text{CaMg(CO}_3)_2 + \text{Ca}^{2+} \quad \text{(Equation 18)}
\]

At equilibrium (calcite plus dolomite plus a solution with a Mg/Ca ratio of about one), the interstitial water provides 8.92 additional moles of magnesium (as the reaction occurs, the total amount of calcium and magnesium must remain approximately constant \(4.26 + 22.1 = 26.36\)). At equilibrium, the concentration of calcium must equal the concentration of magnesium (both \(26.36 : 2 = 13.18\)). Therefore, \(22.1 - 13.18 = 8.92\) moles magnesium is available to form dolomite from the pore water in each cubic meter of sediment. The resulting sediment will contain 6.7\% dolomite, derived almost entirely from the original Mg-calcite and, for a small part, from the interstitial water. To dolomitize the rest of the sediment, \(7.19 \times 10^3\) moles of \(\text{Mg}^{2+}\) must be added. Each pore volume of new seawater can provide only 8.92 moles of \(\text{Mg}^{2+}\). Therefore, \(7.190 : 8.92\) (moles Mg necessary for complete dolomitization : moles Mg provided by seawater) produces 807 pore volumes required to dolomitize completely each cubic meter of sediment (Land, 1985).

This problem is more complex, if one takes into consideration that, due to the dolomitization process and the resultant release of calcium in the solution, calcite will precipitate. In this case, 648 pore volumes of seawater is necessary to dolomitize the same volume of sediment. If a calcium-rich dolomite was formed, the amount of water decreases only slightly. By comparison, in a mixing-water zone (i.e. seawater diluted ten times with fresh water) dolomitization requires at least 6500 pore volumes. However, seawater evaporated to halite saturation needs only 30 pore volumes for dolomitization.

However, if a different reaction took place (Equation 19), instead of the reaction (Equation 18), the amount of seawater necessary for the dolomitization increases dramatically:

\[
\text{CaCO}_3 + \text{Mg}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaMg(CO}_3)_2 \quad \text{(Equation 19)}
\]

To have an idea of the order of magnitude of the different amount of seawater necessary for both reactions, 0.25 liters of seawater are necessary for the dolomitization of 1 g \(\text{CaCO}_3\) according to the equation (18) and 1000 liters will be necessary for the reaction (19).

In the case of the dolomitization that occurred in the Venetian Alps, the seawater necessary for the complete dolomitization would range around \(22 \times 10^{12}\) pore volumes.

The chemical and physical conditions of the formation of the examined dolomite have been suggested in accordance with the data obtained. There are two factors still necessary to complete the definition of a dolomitization model: the limestones must have been permeable to the fluids and a driving force for the dolomitizing fluids must have been active. The dynamics of groundwater-flow provide the link between the interpreted physical conditions and the patterns of dolomitization within it.
The first part of the problem is quite easily resolved, taking into account the field observation of the dolomitized rock: the dolomitization occurred in areas where the limestone was intensely tectonized, having, therefore, a discrete secondary porosity. In the presence of an adequate driving force, the fluids would flow through distinct patterns, generated by the combined action of extensive tectonic disturbance and volcanic activity, thus dolomitizing the limestone where the physical and chemical conditions were achieved. The flow of fluids through these tectonic channels has been widely discussed, sometimes associated with dolomitization (Pichugin et al., 1977; Vroljik, 1987).

However, the driving force for the dolomitization process is more complicated. Flows can be generated by a pressure gradient, by a thermal gradient or by a density gradient. After a platform is buried, a variety of subsurface flows may act on the system, such as compaction-driven flow (e.g. Sharp and Domenico, 1976), cellular thermal convection (Wood and Hewett, 1982), regional topography-driven flow (Garven and Freeze, 1984) or seismic pumping (Sibson et al., 1975). Among the models proposed for these fluid movements, thermal convection can be related to the situation in the Venetian Alps.

*Thermal convection* or *Kohout convection* (named after Francis Kohout (1965, 1967; Kohout et al., 1977) who discovered an open-cycle thermal convection in half-cells in the subsurface of South Florida) is a flow that develops due to the strong horizontal density gradient between the cold ocean water surrounding a platform and the warmer porewaters heated by a geothermal gradient. The cold water migrates in the platform through the margin (Figure 135). This is a long-lived process, generating pervasively dolomitized platform margins. The analysis of the chemical composition of the fluids escaping the Florida Platform shows a depletion in Mg, which has been interpreted as due to dolomitization occurring inside the platform (Fanning et al., 1981). The geothermal gradient, essential for this model, can be generated by volcanic activity, and/or associated hydrothermal activity or, more or less locally, by chemical reaction (e.g. the reduction of sulphate by hydrocarbons which is a strongly exothermic process: the amount of heat released by the bacterially induced reaction is seen below:

\[
\text{hydrocarbon} + \text{CaSO}_4 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{H}_2\text{S} + \text{S etc.} \quad (\text{Equation 20})
\]

or by the non-biological reaction:

\[
\text{C}_6\text{H}_{14} + 6\text{CaSO}_4 \rightarrow 6\text{CaCO}_3 + 6\text{H}_2\text{O (gas)} + \text{H}_2\text{S} + 5\text{S} \quad (\text{Equation 21})
\]

The amount of head produced by these reaction is considerable, especially if the water produced is in the liquid state (Gunatilaka, 1987)).

In the Paleogene, the central-eastern part of the Southern Alps was a platform in a shallow sea. Volcanic islands, with tropical flora, emerged from time to time, creating lagoons with an anoxic bottom water. In this geological situation, dolomitization took place in the underlying Mesozoic limestones. The chemical features of the dolomite suggest a relationship
between the dolomitization and the volcanic activity. The geothermal gradient linked with the volcanism could have been the driving force that made fluids flow through the brecciated limestones.

![Figure 135: Kohout-type convection fluid circulation in a platform (from Simms, 1984)](image)

The fluids necessary for the dolomitization must have been of marine origin, being the sea overlying the area and being the only available magnesium-reservoir with enough Mg-carrying potential. However, the salinity measured in the fluid inclusions (49‰) is markedly higher than the normal marine salinity, but not much different from the seawater salinity measured in the Bahamas (Simms, 1984). The increased salinity could be the effect of the high temperatures caused by the volcanism, although no evidences of this have been found. Temperature also has a quite considerable effect on the fluid pressure, increasing it of from 1 to 18 bars for every degree centigrade rise (Norton, 1984). This pressure rise, combined with the temperature gradient, can contribute to the activation of the fluid circulation.

To prove the validity of a model, it is necessary to quantify the associated hydrodynamics. The Darcy-Hubbert equation states that the water flux \(q\) (in cm\(^3\)/sec/cm\(^2\)) , the volume of water that flows through a unitary surface per second, is proportional to the hydraulic gradient which induces the flow \(\text{dh/dl}\). The proportionality constant is the permeability of the material \(K\) (in cm\(^2\)), multiplied by the product of the density of the water \(\rho\) (in g/cm\(^3\)) and the gravity acceleration \(g\) (in cm/sec\(^2\)), divided by the viscosity of the water \(\eta\) (in centipoise = 10\(^{-2}\) g/cm/sec). The formula is:

\[
q = K \left(\frac{\rho \ g}{\eta}\right) \frac{\text{dh}}{\text{dl}} \quad \text{(Equation 22)}
\]

In the case of the dolomitization in the Trento platform, the hydraulic gradient is mainly due to density variation related to the increased temperature. The original density of marine water is 1.03 g/cm\(^3\), the density of water at about 90-100°C, the temperature deduced from...
the isotopic and fluid inclusions data, decreases to 0.96. To calculate the $\Delta h$ in the hydraulic gradient, the equation 23 was used:

$$(p_i - p_o) g h_o = p_o g (h_1 - h_o) \quad \text{(Equation 23)}$$

where, $p_o$ is the original density, $p_i$ the density at about $100^\circ C$, $g$ the gravity acceleration, ($h_1 - h_o$) the $\Delta h$. $h_o$ is assumed to be the thickness of the dolomitized sediments, 750 m.

The resulting $\Delta h$ is 51 meters. The horizontal component of the gradient ($\Delta l$) is difficult to quantify. It would be the distance between the point from where the water infiltrates and the dolomitization site: an extreme value of 50 km (the width of the area where the dolomitization is widespread) is assumed. The hydraulic gradient across a 50 km wide platform is thus $1.02 \cdot 10^{-3}$.

Considering that the dolomitization affects almost exclusively tectonic brecciated limestones, we could assume as permeability coefficient, the permeability of the breccia, which could be about $10^{-2}$ to $10^{-4}$ cm$^2$. However, for this calculation the permeability of the limestone has been considered, though it is impossible to ascertain that the water flew exclusively through the breccia. Therefore, a value of $10^{10}$ cm$^2$ is considered. The viscosity of water $\eta$ is about $10^2$ g/cm/sec. Using the Darcy law (Equation 23), the water flux $q$ can be calculated:

$$q = 10^{10} \cdot 1.03 \cdot 9.8 \cdot 10^2 \cdot 1.02 \cdot 10^{-3} / 10^2 = 10^8 \text{ cm}^3/\text{sec per cm}^2$$

The flux per year is $3.15 \cdot 10^3$ cm$^3$/year. The water would move more or less vertically, along tectonic patterns, upwards, in the direction of the decreasing temperature. This movement would recall water from the surroundings, sustaining a convective circulation. The amount of magnesium transported by this water flux would dolomitize about $10^2$ cm$^3$ of sediments per year per cm$^2$.

An example of dolomitized breccia body of unitary cross section and a thickness of 750 m is considered. The water flux calculated with the Darcy equation would necessitate $7.5 \times 10^6$ years to dolomitize it, a reasonable value, if we consider the 7 million years time span available for the dolomitization, as calculated from the strontium isotope data. Of course, these calculations are very simplified and hypothesize an idealized situation; anyhow, the flux of marine water through brecciated limestone is a plausible suggestion for a dolomitization model.

It is suggested that the convective circulation was triggered by the temperature gradient generated by the basaltic volcanism. The second important factor to consider is whether the heat connected with the volcanic activity is enough to heat the circulating waters up to over $100^\circ C$. Heat transport by conduction from the magma chamber is a relatively slow process, especially considering the rapidity of the heat transport through the quickly ascending basaltic magma. The magma chamber was probably lying at a depth of about 60 km, considering the 20 kbar pressure deduced from the petrographical character of the rock (De Vecchi et al., 1976); probably, however, the magma stationated for a more or less long period
at an intermediate depth, but this cannot be demonstrated or quantified. The attempt is only to try, very simplistically and approximately, to quantify the quantity of water that could be heated up to the measured temperature of about 120°C, the maximum temperature calculated from the isotopic data and suggested by the fluid inclusion trapping temperature in the veins. Considering that the average temperature measured is about 70°C, the first approximation is made. This and the other necessary approximations will anyway lead to a minimum value.

The ascent of the magma occurs mainly along distinct patterns, fractures, discontinuities, bedding. The influence of the magma to the crossed sediments depends, for example on the distance between the single conduits and from their width. Another important factor is the dispersion of the heat, depending from the thermal capacity of the surrounding rocks, their lithological and stratigraphic characteristics (bedding, thickness of the strata) and the degree of fracturation; moreover, the thermal characteristic of both magma and rocks depend from the pressure, i.e. from the burial depth. Considering the purpose of this estimation, it is impossible to consider all the involved factors. Therefore, a very simplistic example will be considered, based on the physical principle that, in an isolated system, at constant pressure the heat loss by a body is equal to the heat gained by a body in contact with it. Three units are considered: the basaltic magma, the water and the sedimentary rocks in which the water is contained. The heat capacity \( Q \) is expressed as:

\[ Q = mcT \quad \text{(Equation 24)} \]

or, considering variation of temperature,

\[ \Delta Q = mc \Delta T \]

where, \( m \) is the mass of the body, \( c_p \) is the specific heat at constant pressure, a value characteristic for a material (in cal/g °C), \( T \) the temperature in °C.

Considering the system as closed, the \( \Delta Q \) lost by the basaltic magma must be equal to the \( \Delta Q \) gained by the water+rock system:

\[ m_b \cdot c_b (T_b - T) = (m_r \cdot c_r + m_w \cdot c_w)(T_e - T_w) \]

where, \( m \) is the mass, \( c \) the specific heat, \( T \) the initial temperature, \( T_e \) the equilibrium temperature, respectively of the basaltic magma (b), rocks (r) and water (w).

The mass of the basaltic magma is estimated to be the volume of the basaltic rocks outcropping today in the Lessini-Marosticano area (about 6 \( \cdot \) 10\(^{17}\) cm\(^3\)) multiplied the mean density of a basaltic magma (2.65 g/cm\(^3\)). The specific heat of a basaltic magma is difficult to determine absolutely, but a value of 0.25 cal/g °C is a good approximation; the specific heat of sedimentary rocks is 0.21, that of water is 1 cal/g °C. The temperature of a basaltic magma extruding at the surface is about 1100°C; we assume the temperature of the water to be about 10°C, whereas the equilibrium temperature is the maximum temperature calculated from
fluid inclusion and stable isotope data, i.e. 120°C. We can calculate the thickness of sedimentary rocks with about 15% porosity and 2.5 g/cm³ density, that can be heated up to 120°C by the estimated amount of basaltic magma, considering an area of 1200 km², which is the surface where the dolomitization is widespread.

\[ 6 \cdot 10^{17} \cdot 2.65 \cdot 0.25 (1100° - 120°) = (x \cdot 2.5 \cdot 0.21 + 0.15 \cdot x)(120° - 10°) \]

The resulting x, i.e. the volume of sedimentary rocks affected, is 5 \cdot 10^{18} cm³, which corresponds to a thickness of 4.1 km. Considering the geothermal gradient estimated from the fluid inclusion results (8°C/100 m), at a depth of 1.5 km the temperature would be 120°C. Therefore, the heat transported by the basaltic melt would be more than enough to reach the requested temperature in both water and reservoir rocks.

The model proposed can not be a Kohout-type circulation, observed e.g. in the Florida plateau. The Kohout-convection is induced by density difference between cold seawater surrounding the platform and the warmer pore fluids in the sediments. The existence of an active volcanism and tectonism in the Eastern Southern Alps creates different boundary conditions, a higher density gradient and brecciated areas where the fluid circulation is facilitated.

A hydrodynamic regime induced by tectonic compaction, with expulsion of pore fluids and their pressure-driven circulation along overthrust planes, is also to exclude. The chemical and physical characters of the dolomitizing fluids and the estimated age of the dolomite speak against this type of circulation. Modern examples of pressure-driven fluids in accretionary prisms (e.g. Oregon subduction zone) show that we are dealing with cool, relatively old, organic carbon-rich, pore fluids. In the dolomitized breccias studied in the Southern Alps, the temperature deducted from liquid inclusion analyses and oxygen isotope ratios are high, up to 120°C. Moreover, the dating of the dolomitization made with the strontium isotope data suggest the influence of marine water of Late Oligocene to Early Miocene age, much younger than the sediments involved in the dolomitization and of eventually present pore fluids. The fluid trapped in the liquid inclusions found in the crystals of the dolomitized breccia is a marine-like saline solution. No traces of methane gas or other organic carbon-rich substances were found. This also contrasts with the characteristics of the fluids expelled from accretionary prisms.
Figure 136: Hydrodynamic model proposed for the dolomitizing fluid circulation.
It is suggested that the dolomitizing fluids responsible for the dolomitization observed in the Southern Alps circulated in a convection in half-cells, driven by the geothermal field induced by the volcanic activity. The existence of the platform could have been decisive for the fluid circulation, allowing the infiltration of cold marine fluids through the slopes of the platform. The fluids could then have been successively modified by the physical conditions present in the platform (i.e. high temperature) and then escape the system after having dolomitized the permeated rocks (Figure 136). The absence of dolomite above the lower part of the Cretaceous Scaglia Rossa Formation can be explained. The overlying sediments could have been un lithified, reacting plastically to the tectonic disturbances and not having, therefore, the permeability necessary for the fluid flow. Also, the chemical composition of the sediments (e.g. sulphate content) at that time could have inhibited the dolomitization. The fluid circulation stopped when the platform ceased to exist, i.e. when the surrounding marine basin filled up with sediments, or simply when one of the catalyzing factors of the dolomitization failed.
APPENDIX 1

Chemistry of dolomite

A1.1. Stability of dolomite

The Gibbs's energy equation is:

\[ dE = TdS - pdV + \mu_1dm_1 + \mu_2dm_2 + \ldots + \mu_ndm_n \quad \text{(Equation 25)} \]

where, \( E \) is the total energy of the homogeneous part, \( T \) the absolute temperature, \( S \) the entropy, \( p \) the pressure, \( V \) the volume, \( m_1, m_2 \ldots m_n \) are the quantities of the various substances and \( \mu_1, \mu_2 \ldots \mu_n \) are the chemical potentials of the various substances or the differential coefficients of \( E \) taken with respect to \( m_1, m_2 \ldots m_n \).

If three homogeneous substances are present, \( s_1, s_2 \) and \( s_3 \), which are parts of a whole mass, each consisting of the same two components, then the variation of energy of the system is:

\[ dE' + dE'' + dE''' \geq 0 \quad \text{(Equation 26)} \]

Substituting in the equation (25), a value for the necessary and sufficient conditions of equilibrium can be obtained:

\[ T' = T'' = T''' \]
\[ p' = p'' = p''' \]
\[ \mu_1' = \mu_1'' = \mu_1''' \]
\[ \mu_2' = \mu_2'' = \mu_2''' \]

If the substance \( s_3 \) is composed of \( s_1 \) and \( s_2 \) with a ratio 1/1, then the equilibrium conditions are:

\[ T' = T'' = T''' \]
\[ p' = p'' = p''' \]
\[ \mu' + \mu'' = \mu''' \]
So, considering the reaction:

\[ \text{CaCO}_3 + \text{MgCO}_3 \iff \text{CaMg(CO}_3)_2 \]  
(Equation 27)

The conditions of equilibrium are:

\[ T^* = T^" = T^"^\prime \]

\[ p^* = p^" = p^"^\prime \]

\[ \mu^*_{\text{CaCO}_3} + \mu^*_{\text{MgCO}_3} = \mu^*_{\text{CaMg(CO}_3)_2} \]

If dolomite forms spontaneously from calcite and magnesite, under a given T and p, then:

\[ \mu^*_{\text{CaCO}_3} + \mu^*_{\text{MgCO}_3} > \mu^*_{\text{CaMg(CO}_3)_2} \]  
(Equation 28)

The same considerations can be made when considering nesquehonite \((\text{MgCO}_3 \times 3 \text{H}_2\text{O})\) or hydromagnesite \((\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \times 3 \text{H}_2\text{O})\) as a possible stable magnesium-carbonate phase at 25°C and 1 atm (Hsu, 1967).

The chemical potential of a one-component pure substance, in J/mole, is equal to its molar Gibbs free energy (F):

\[ F = F^o + RT \ln a \]  
(Equation 29)

where, \(F^o\) is the free energy of a solution in a standard state.

The change of free energy for the reaction (27) is:

\[ \Delta F_A = F^" - (F^* + F^") \]  
(Equation 30)

where, \(F^*, F^\prime\) and \(F^\prime\) represent respectively the molar free energies of calcite, magnesite and dolomite.

Calculating \(F^*, F^\prime\) and \(F^\prime\) from the equation (29), it can be deduced that:

\[ \Delta F_A = RT \ln \frac{K_d}{K_c K_m} \]  
(Equation 31)

where, \(K_d\) is the solubility constant of dolomite, \(K_c\) the one of calcite and \(K_m\) the one of magnesite (Hsu, 1967).

\(\Delta F_A\) must be negative if dolomite forms spontaneously from calcite and magnesite at any temperature and pressure. Experiments for the estimation of \(K\) values (Halla, 1935; Garrels et al., 1960; Halla et al., 1962; Hsu, 1963) led to different values of \(K\) for the dolomite. Nevertheless, calculated \(\Delta F_A\) values are all negative, ranging from -0.5 to -4 kcal at 25°C and 1 atm. The experimental evidence shows that dolomite, rather than the pair calcite-magnesite, is the stable phase at 25°C and 1 atm.
A1.2. Solubility and precipitation of dolomite

The equilibrium dolomite - solution is:

\[ \text{CaMg(CO}_3\text{)}_2 \rightleftharpoons \text{Ca}^{2+}\text{aq} + \text{Mg}^{2+}\text{aq} + 2 \text{CO}_3^{2-}\text{aq} \]  (Equation 32)

The activity of this reaction is:

\[ \mu = \mu^o + RT \ln a \]  (Equation 33)

where, \( \mu^o \) is the chemical potential in a standard state, i.e. the partial molal free energy, \( a \) the activity, \( R \) the gas constant and \( T \) the temperature, expressed in kelvins.

At equilibrium for the reaction (32):

\[ \mu^{\text{Ca}^{2+}} + \mu^{\text{Mg}^{2+}} + 2\mu^{\text{CO}_3^{2-}} = \mu^{\text{CaMgCO}_3\text{}} \]  (Equation 34)

and then, expressed in activities,

\[ (a_{\text{Ca}^{2+}})(a_{\text{Mg}^{2+}})(a_{\text{CO}_3^{2-}})^2 = K_d \]  (Equation 35)

where, \( K_d \) is the equilibrium activity product or the solubility product.

Attempts to calculate the value of \( K_d \) at 25°C and 1 atm pressure range from \( 10^{-17} \) to \( 10^{-20} \). The value calculated from ground waters in dolomite is close to \( 10^{-17} \) (Hsü, 1963; 1967). The Mg/Ca activity in the dolomite largely affects the dolomite solubility (Carpenter, 1980):

\[ K_d \quad \text{[Mg}^{2+}\text{]/[Ca}^{2+}\text{]} \]

| Fully ordered dolomite          | \( 10^{-18.06} \) | 0.10 |
| "Partly" ordered dolomite      | \( 10^{-17.00} \) | 1.00 |
| "Weakly" ordered dolomite      | \( 10^{-16.75} \) | 1.85 |
| Disordered "dolomite"          | \( 10^{-18.52} \) | 3.31 |

A1.3. Replacement of calcium carbonate by dolomite

Diffusion of ions in crystals, at low temperature, is an extremely slow process and, therefore, it seems impossible that dolomitization can be a solid-state reaction. It is more logical to view the process as a simultaneous dissolution of calcium carbonate and
precipitation of dolomite from a solution passing through the rock (Blatt et al., 1980). The commonest dolomitization reaction is:

\[ 2 \text{CaCO}_3 + \text{Mg}^{2+} \leftrightarrow \text{CaMg(CO}_3)_2 + \text{Ca}^{2+} \]  

(Equation 18)

The standard free energy variation (\(\Delta G^\circ\)) for this reaction has been calculated:

\[ \Delta G^\circ = \text{products-reactants} = (-518.7 - 132.2) - (2(-269.9) - 108.9) = -2.2 \text{ kcal/mole} \]

Adjusting this standard free energy value for the composition of seawater:

\[ \Delta G_r = \Delta G^\circ + RT \ln \frac{\text{products}}{\text{reactants}} \]  

(Equation 36)

So, \(\Delta G_r = -2.2 \text{ kcal/mole} + (1.987 \text{ cal/mole degree})(298.15) \times \ln 2.34 \times 10^7/1.32 \times 10^2 = -3.2 \text{ kcal/mole} \)

where, \(\Delta G_r\) is the free energy at a determined temperature (T).

The free energy for the reaction is more negative in seawater than in standard conditions because the magnesium ion is more abundant than the calcium ion in seawater. Thus, the calculation of the free energy allows us to say that the reaction proceeds from left to right, i.e. dolomitization of calcite is thermodynamically favoured in seawater.

In the reaction (18) the magnesium is supplied from an external source. It is also possible that \(\text{CO}_3^{2-}\) in dolomite may have been supplied from an external source (Lippman, 1973). The proposed reaction, therefore, is:

\[ \text{CaCO}_3 + \text{Mg}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaMg(CO}_3)_2 \]  

(Equation 19)

A non-marginal advantage of this formulation of the dolomitization reaction is that it is not necessary to remove the calcium ions out of the dolomitization site. The free energy of this reaction, for the dolomitization of aragonite, is -13.24 kcal/mole, favouring the formation of dolomite even more strongly than reaction (18) (Morrow, 1982a).

Also of major interest, is the calculation of the \(\text{Mg}^{2+}/\text{Ca}^{2+}\) required for dolomitization. The equilibrium constant for calcite (\(K_c\)) and dolomite (\(K_d\)) is expressed as:

\[ (a\text{Ca}^{2+})(a\text{Mg}^{2+})(a\text{CO}_3^{2-})^2 = K_d \]  

(Equation 37)

\[ (a\text{Ca}^{2+})(a\text{CO}_3^{2-}) = K_c \]  

(Equation 38)

where, \(a\) is the activity ratio.

Solving these equations to eliminate carbonate as a variable, the following is obtained:

\[ \frac{(a\text{Mg}^{2+})}{(a\text{Ca}^{2+})} = K_d/K_c^2 = K_{ds} \]  

(Equation 39)
where, $K_{\text{dz}}$ represents the ratio of magnesium to calcium above which the reaction will proceed in the direction of dolomite formation at the expense of preexisting calcite.

By calculation:

$$K_{\text{dz}} = \frac{10^{-17}}{(10^{-8.4})^2} = 10^{-0.2}$$

or a magnesium/calcium activity of 0.6 is obtained. The $K_{\text{dz}}$ value in seawater is $1.32 \times 10^2 / 2.34 \times 10^{-3} = 5.6$.

It is then thermodynamically demonstrated that seawater is a dolomitizing solution.
Appendix 2

Sample locations

Around 200 samples were collected from the Venetian Alps area. They were mostly taken from horizontal profiles which cut across the contact of the affected and unaffected rock. This was necessary for comparisons between the rocks, before and after dolomitization. It should also be noted that only the upper 250 m of the affected sequence, i.e. the pelagic limestones, were studied in detail, as the lower part of the sequence was strongly karstified and altered by late meteoric processes. Thus, any obtained values were not reliable, due to the high grade of contamination overprinting the original composition. Also, the advantage of using pelagic limestones as a start material, simplifies the problem, since the dolomitization affects an almost pure calcium carbonate.

Samples were collected in 19 main groups, divided by analytical profiles (Figure 137):

**AL:** This group consists of two series of 3 and 11 samples (AL1-AL3 and AL1/87-AL11/87). AL1, AL2, AL1/87-AL6/87 are calcitic. The series has been collected in the lower part of the Scaglia Rossa Formation, directly above the contact with the Scaglia Variegata, on the road between Molino di Altissimo, in the Chiampo Valley, and Altissimo, at a height of about 550 m a.s.l.. The AL1-AL3 samples were collected from the same level. The sampling of the series AL1/87-AL11/87 covers a thickness of 8 meters, the upper 5 meters being dolomitized (AL7/87-AL11/87). The contact is oblique, with a dip of 50° to the east, strike horizontal N-S. The Scaglia Rossa consists of alternated levels of thin, flasered, red marls and whitish carbonate-richer banks of 20-30 cm thickness. The dolomitized rock is variegated, yellow-reddish. The age of the Scaglia at the contact (samples AL2 and AL6/87) is determined micropaleontologically as Turonian (H. helvetica zone).

**C:** Consists of 77 samples from Crespadoro, at the base of the Chiampo Valley, underneath the church, on the road going in direction Ferrazza. The first group of 15 samples was collected from the same stratum (C1-C14): samples C1 to C6 are calcitic, C7 to C14 are dolomite. The formation sampled is the Maiolica Veneta of Middle Valanginian-Hauterivian
Figure 137: Location map of the series of collected samples (see Appendix 2 for the symbols).
Figure 138: Photograph to show the contact between *Maiolica* and dolomite (series C, Crespadoro, Chiampo Valley).

Figure 139:

a) Photograph of a close-up on the *Maiolica* of Figure 138 at the contact. The listric faults are well visible. Observe the yellow fracture filling and the deformed chert layer in the upper part.

b) Diagram of the photograph in Figure 139a. In black is the yellow dedolomitized filling. (Striped = secondary sparry calcite). Scale bar = 5 cm.
Figure 140: Photograph of undolomitized Maiolica included in the dolomitized rock. This fragment is of Valanginian age (Crespadoro, Chiampo Valley).

Figure 141: Photograph of undolomitized Maiolica of Aptian age included in the dolomitized rock (Crespadoro, Chiampo Valley).
Figure 142: Photograph of the outcrop of the MS series (San Liberale Valley, Grappa area).

Figure 143: Photograph of dolomitized rock of the P series (Seren del Grappa, near Feltre).
Figure 144: Photograph of brecciated *Maiolica* at the contact with dolomite (on the right). The yellow vein filling is visible (series PB, Ferrazza, Chiampo Valley, Lessini).

Figure 145: Photograph of a sample of brecciated *Maiolica* of the series PB (Ferrazza, Chiampo Valley).

Figure 146: Drawing of the hand specimen of Figure 145. Dotted symbol represents the micritic limestone; black and stippled symbols show two generations of sparry calcite; white represents yellow dedolomite; acute symbol represent the chert; dispersed dots are pyrite crystals.

Figure 147: Photograph of the subvertical contact between *Rosso Ammonitico* (left) and dolomitized breccia (right)(series PR, Ferrazza, Chiampo Valley).
The stratification is subhorizontal and the contact is dipping subvertical to the N, striking E-W, and is marked by a fracture (Figure 138). The limestone is an almost pure white micrite with grey chert layers and nodules. The dolomite is grey and it is widely cross-cut by veins or vugs of ankerite and calcite. The limestone next to the contact shows the best example of small scale “listric” faults observed in the area (Figure 139). The outcrop is about 100 m long (of which only 5 m are undolomitized) and is up to 5 m high. A second group of samples, covering the whole outcrop in 2 dimensions, was also taken. These samples are numbered from C22/*/87 to C65/*/87 (the asterisk can be an “A” (the series at the bottom of the outcrop), a “B” (the series 60 cm higher than “A”) or a “D” (the series 1 m higher than “B”)). Particularities, like veins or inclusions, are the samples numbered from C71 to C77. This outcrop also contains two fragments (C50/B/87 and C48/B/87) of about 60 cm width of undolomitized Maiolica, that were micropaleontologically dated: the age of one of the samples (C50/B/87) is consistent with the age of the Maiolica cropping out at the contact (Valanginian); the other sample (C48/B/87), darker and marly is Aptian (Figures 140 and 141).

CH: These samples are 4 grey cherts located as for the C series. CH1 and CH2 come from the limestone. CH3 and CH4 are fragments included in the dolomitized rock.

F7: This is a sample of dolomitized Calcare oolitico di S.Vigilio. It comes from the quarry Fainetti (Campofontana, northern Alpone Valley).

M: This series belongs to the Scaglia Variegata, underlying the Scaglia Rossa in the location where the “AL” series was collected. Nine samples (M1-M9) were collected from the same level, which is of Cenomanian age. The samples from M1 to M5 are a white micritic limestone, very similar to the Maiolica, with black marks, denoting the presence of organic material. The samples M6-M9 are dolomitized and show the same marks, but on a yellowish matrix.

MS: This profile consists of 12 samples, collected from the Maiolica Formation along the road Bassano del Grappa - Crespano del Grappa (NE of the Lessini Mounts in the Venetian Alps), in the S. Liberale Valley, after the the village of Fletta. The stratification is quite steep.
(the dipping varies between 20 and 70° N-S, strike E-W). The sampling has been made from N to S, covering a thickness of about 75 m. The dolomitized part is a breccia (MS1-MS9). The samples MS10 and MS11 are unaffected and the limestone is generally very fractured (Figure 142).

**P:** In the Feltre area, more exactly in Forcen del Grappa (road to Colle La Croce), the rocks underlying the Maiolica and part of the Maiolica itself are completely dolomitized, affecting also a brecciated rock. It is impossible to reconstruct the original stratigraphic sequence, since the dolomite is homogeneously massive and grey. Sample P1 to P7 were not analysed as they showed no dolomitization. The samples P8 to P33 are distributed on a profile of about 185 m thickness. The distances between the samples vary between normally 5 m to, when the conditions do not allow a thicker sampling, 20 m. From a very indistinct residual stratification, it is possible to state that the lowermost 50 m of the Maiolica Formation are included in the dolomitized part. P32 and P33 are undolomitized Maiolica (Figure 143).

**PB:** These samples are located on the same road of the "PR" series, on the partly dolomitized overlying Maiolica. The Maiolica is white and fractured, whereas the dolomite is massive and grey. The age is Valanginian. Two contacts are present, both subvertical and marked by a fracture. The 9 samples were collected on a horizontal profile. PB2 and PB10 are taken from the limestone, PB3-PB5, PB7-PB8 and PB11-PB12 are from the dolomitized rock. Additional samples (PB20/87, PB20a/87, PB21/87, PB30 and PB31) were collected from veins fillings, chert fragments and fractured areas in the limestone (Figures 144-146).

**PR:** This series has been collected in the uppermost Rosso Ammonitico Formation. The locality, next to Ferrazza, is in the Chiampo Valley, on the road to Case Pozza. It consists of 12 samples (PR1-PR12) collected from the same level. The contact, subvertical and very sharp, is between PR5 and PR6. The samples from PR1 to PR5 are taken from a whitish nodular limestone. The dolomitized rock is a fine breccia with grey clasts in a yellow-red ground, both completely and homogeneously dolomitized (PR6-PR12)(Figure 147).

**RA:** This sample has been collected at the contact between limestone and dolomite in the locality of "PR", which is, in this case, not marked by a fracture. Four parts of this sample were
made (RA3/1-RA3/4), which are either clasts (RA3/2 and RA3/4) or matrix (RA3/3) of the dolomitized breccia, or the limestone (RA3/1).

**SG:** The locality of the profile “P” was sampled with the aim to collect different kinds of dolomitized features. There are 17 samples in total: SG1 to SG14 are dolomitized (15 samples); SG15 and SG16 are *Maiolica*.

**VN14:** This series of samples was collected in the Val di Non (Trentino). Only one sample has been analysed (VN14), but the result does not relate to the values found in the dolomitic rocks of the Lessini and Feltre areas. It is an example of micritic limestone (Tithonian-Berriasian, upper part of the *Crassicollaria* zone) with scattered dolomite crystals, more abundant as a filling of fractures. Another sample collected (B.L.88/16) from the same region, is consistent with the sample VN14 (personal comm. B. Lehner).

**VV7:** This sample is a dolomitized *Calcari Grigi di Noriglio*. It is found on the road from Selva di Progno to Velo Veronese (Illasi Valley, central Lessini). It is very altered, with a sandy consistency, and is therefore not reliable.
## APPENDIX 3

### Sample Analyses

<table>
<thead>
<tr>
<th>Sample#</th>
<th>% Dolomite</th>
<th>% Mg in Dolomite</th>
<th>δ¹³ C (PDB)%</th>
<th>δ¹⁸ O (PDB)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL1</td>
<td>0</td>
<td>-</td>
<td>1.78</td>
<td>-3.33</td>
</tr>
<tr>
<td>AL2</td>
<td>0</td>
<td>-</td>
<td>1.7</td>
<td>-3.54</td>
</tr>
<tr>
<td>AL3</td>
<td>46.2</td>
<td>40</td>
<td>-0.66</td>
<td>-8.12</td>
</tr>
<tr>
<td>AL1/87</td>
<td>0</td>
<td>-</td>
<td>1.73</td>
<td>-3.51</td>
</tr>
<tr>
<td>AL2/87</td>
<td>0</td>
<td>-</td>
<td>2.34</td>
<td>-2.67</td>
</tr>
<tr>
<td>AL3/87</td>
<td>0</td>
<td>-</td>
<td>1.93</td>
<td>-3.1</td>
</tr>
<tr>
<td>AL4/87</td>
<td>0</td>
<td>-</td>
<td>1.87</td>
<td>-3.11</td>
</tr>
<tr>
<td>AL5/87</td>
<td>0</td>
<td>-</td>
<td>1.68</td>
<td>-4.26</td>
</tr>
<tr>
<td>AL6/87</td>
<td>0</td>
<td>-</td>
<td>1.79</td>
<td>-6.74</td>
</tr>
<tr>
<td>AL7/87</td>
<td>100</td>
<td>40</td>
<td>1.68</td>
<td>-6.6</td>
</tr>
<tr>
<td>AL7'/87</td>
<td>100</td>
<td>40</td>
<td>1.78</td>
<td>-7.27</td>
</tr>
<tr>
<td>AL8/87</td>
<td>100</td>
<td>46</td>
<td>1.46</td>
<td>-5.21</td>
</tr>
<tr>
<td>AL9/87</td>
<td>100</td>
<td>48</td>
<td>2.45</td>
<td>-5.58</td>
</tr>
<tr>
<td>AL10/87</td>
<td>100</td>
<td>50</td>
<td>2.03</td>
<td>-5.22</td>
</tr>
<tr>
<td>AL11/87</td>
<td>100</td>
<td>50</td>
<td>2.32</td>
<td>-4.78</td>
</tr>
<tr>
<td>B.L.88/16</td>
<td>100</td>
<td>39</td>
<td>1.7</td>
<td>-2.79</td>
</tr>
<tr>
<td>C1</td>
<td>0</td>
<td>-</td>
<td>1.97</td>
<td>-2.8</td>
</tr>
<tr>
<td>C2</td>
<td>0</td>
<td>-</td>
<td>1.83</td>
<td>-2.83</td>
</tr>
<tr>
<td>C3</td>
<td>0</td>
<td>-</td>
<td>1.79</td>
<td>-3.38</td>
</tr>
<tr>
<td>C3a</td>
<td>0</td>
<td>-</td>
<td>1.45</td>
<td>-4</td>
</tr>
<tr>
<td>C4</td>
<td>0</td>
<td>-</td>
<td>1.51</td>
<td>-3.49</td>
</tr>
<tr>
<td>C5</td>
<td>0</td>
<td>-</td>
<td>1.75</td>
<td>-3.22</td>
</tr>
<tr>
<td>C6</td>
<td>0</td>
<td>-</td>
<td>1.21</td>
<td>-4.08</td>
</tr>
<tr>
<td>C7</td>
<td>100</td>
<td>46</td>
<td>2.01</td>
<td>-8.37</td>
</tr>
<tr>
<td>C8</td>
<td>100</td>
<td>42</td>
<td>1.57</td>
<td>-6.47</td>
</tr>
<tr>
<td>C9</td>
<td>100</td>
<td>39</td>
<td>1.48</td>
<td>-5.9</td>
</tr>
<tr>
<td>C10</td>
<td>100</td>
<td>42</td>
<td>1.62</td>
<td>-4.33</td>
</tr>
<tr>
<td>C11</td>
<td>100</td>
<td>42</td>
<td>1.39</td>
<td>-4.78</td>
</tr>
<tr>
<td>C12</td>
<td>100</td>
<td>44</td>
<td>1.37</td>
<td>-5.07</td>
</tr>
<tr>
<td>C13</td>
<td>100</td>
<td>46</td>
<td>1.39</td>
<td>-4.71</td>
</tr>
<tr>
<td>C14</td>
<td>100</td>
<td>42</td>
<td>1.65</td>
<td>-4.8</td>
</tr>
<tr>
<td>C21/A/87</td>
<td>100</td>
<td>43</td>
<td>2.1</td>
<td>-5.4</td>
</tr>
<tr>
<td>C22/A/87</td>
<td>100</td>
<td>40</td>
<td>1.7</td>
<td>-4.19</td>
</tr>
<tr>
<td>C23/A/87</td>
<td>100</td>
<td>45</td>
<td>1.72</td>
<td>-4.5</td>
</tr>
<tr>
<td>C23'/A/87</td>
<td>30</td>
<td>45</td>
<td>-2.21</td>
<td>-6.03</td>
</tr>
<tr>
<td>C24/B/87</td>
<td>100</td>
<td>45</td>
<td>1.75</td>
<td>-4.75</td>
</tr>
<tr>
<td>C25/A/87</td>
<td>100</td>
<td>40</td>
<td>-1.37</td>
<td>-3.4</td>
</tr>
<tr>
<td>C26/B/87</td>
<td>100</td>
<td>45</td>
<td>1.28</td>
<td>-3.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C27/A/87</td>
<td>100</td>
<td>42</td>
<td>1.46</td>
<td>-5.18</td>
</tr>
<tr>
<td>C28/B/87</td>
<td>100</td>
<td>45</td>
<td>1.67</td>
<td>-4.9</td>
</tr>
<tr>
<td>C29/A/87</td>
<td>100</td>
<td>40</td>
<td>1.76</td>
<td>-4.15</td>
</tr>
<tr>
<td>C30/B/87</td>
<td>100</td>
<td>40</td>
<td>1.76</td>
<td>-4.55</td>
</tr>
<tr>
<td>C31/A/87</td>
<td>100</td>
<td>45</td>
<td>1.63</td>
<td>-5.07</td>
</tr>
<tr>
<td>C32/B/87</td>
<td>100</td>
<td>45</td>
<td>1.33</td>
<td>-4.84</td>
</tr>
<tr>
<td>C33/A/87</td>
<td>100</td>
<td>45</td>
<td>1.39</td>
<td>-5.64</td>
</tr>
<tr>
<td>C34/B/87</td>
<td>100</td>
<td>45</td>
<td>1.62</td>
<td>-4.35</td>
</tr>
<tr>
<td>C35/A/87</td>
<td>100</td>
<td>50</td>
<td>2.76</td>
<td>-2.88</td>
</tr>
<tr>
<td>C36/B/87</td>
<td>100</td>
<td>50</td>
<td>2.5</td>
<td>-3.79</td>
</tr>
<tr>
<td>C37/A/87</td>
<td>100</td>
<td>45</td>
<td>2.45</td>
<td>-3.34</td>
</tr>
<tr>
<td>C38/B/87</td>
<td>100</td>
<td>45</td>
<td>2.27</td>
<td>-3.89</td>
</tr>
<tr>
<td>C40/B/87</td>
<td>100</td>
<td>50</td>
<td>2.44</td>
<td>-3.31</td>
</tr>
<tr>
<td>C41/A/87</td>
<td>100</td>
<td>45</td>
<td>1.84</td>
<td>-4.41</td>
</tr>
<tr>
<td>C42/B/87</td>
<td>100</td>
<td>43</td>
<td>2.55</td>
<td>-3.39</td>
</tr>
<tr>
<td>C43/A/87</td>
<td>90</td>
<td>45</td>
<td>2.42</td>
<td>-2.79</td>
</tr>
<tr>
<td>C44/A/87</td>
<td>100</td>
<td>35</td>
<td>2.25</td>
<td>-4.29</td>
</tr>
<tr>
<td>C45/B/87</td>
<td>88</td>
<td>45</td>
<td>1.27</td>
<td>-3.9</td>
</tr>
<tr>
<td>C46/A/87</td>
<td>100</td>
<td>47</td>
<td>2.03</td>
<td>-5.31</td>
</tr>
<tr>
<td>C47/A/87</td>
<td>100</td>
<td>52</td>
<td>2.13</td>
<td>-5.16</td>
</tr>
<tr>
<td>C48/B/87</td>
<td>0</td>
<td>-</td>
<td>2.04</td>
<td>-3.43</td>
</tr>
<tr>
<td>C48'/B/87</td>
<td>65</td>
<td>43</td>
<td>1.23 (20')</td>
<td>-5.48 (20')</td>
</tr>
<tr>
<td>C48'/B/87</td>
<td>65</td>
<td>43</td>
<td>1.20 (72h)</td>
<td>-6.16 (72h)</td>
</tr>
<tr>
<td>C49/A/87</td>
<td>90</td>
<td>43</td>
<td>1.91</td>
<td>-4.81</td>
</tr>
<tr>
<td>C51/A/87</td>
<td>100</td>
<td>43</td>
<td>2.04</td>
<td>-6.84</td>
</tr>
<tr>
<td>C52/B/87</td>
<td>100</td>
<td>45</td>
<td>1.92</td>
<td>-5.37</td>
</tr>
<tr>
<td>C53/A/87</td>
<td>100</td>
<td>43</td>
<td>2.89</td>
<td>-4.79</td>
</tr>
<tr>
<td>C54/D/87</td>
<td>0</td>
<td>-</td>
<td>1.55</td>
<td>-3.64</td>
</tr>
<tr>
<td>C54'/D/87</td>
<td>5</td>
<td>45</td>
<td>-6.9</td>
<td>-5.19</td>
</tr>
<tr>
<td>C55/D/87</td>
<td>100</td>
<td>45</td>
<td>2.56</td>
<td>-2.19</td>
</tr>
<tr>
<td>C56/D/87</td>
<td>90</td>
<td>40</td>
<td>2.36</td>
<td>-3.65</td>
</tr>
<tr>
<td>C57/D/87</td>
<td>35</td>
<td>40</td>
<td>-3.19 (20')</td>
<td>-7.16 (20')</td>
</tr>
<tr>
<td>C57/D/87</td>
<td>35</td>
<td>40</td>
<td>-0.16 (72h)</td>
<td>-6.45 (72h)</td>
</tr>
<tr>
<td>C58/D/87</td>
<td>100</td>
<td>45</td>
<td>2</td>
<td>-3.98</td>
</tr>
<tr>
<td>C59/D/87</td>
<td>100</td>
<td>43</td>
<td>1.9</td>
<td>-4.18</td>
</tr>
<tr>
<td>C59'/D/87</td>
<td>57</td>
<td>45</td>
<td>-4.38 (20')</td>
<td>-7.36 (20')</td>
</tr>
<tr>
<td>C59'/D/87</td>
<td>57</td>
<td>45</td>
<td>1.83 (72h)</td>
<td>-3.60 (72h)</td>
</tr>
<tr>
<td>C60/D/87</td>
<td>100</td>
<td>45</td>
<td>2.05</td>
<td>-4.77</td>
</tr>
<tr>
<td>C61/D/87</td>
<td>100</td>
<td>45</td>
<td>1.73</td>
<td>-4.54</td>
</tr>
<tr>
<td>C63/D/87</td>
<td>100</td>
<td>43</td>
<td>1.77</td>
<td>-4.6</td>
</tr>
<tr>
<td>C64/D/87</td>
<td>90</td>
<td>50</td>
<td>1.53</td>
<td>-8.14</td>
</tr>
<tr>
<td>C65/D/87</td>
<td>100</td>
<td>40</td>
<td>1.76</td>
<td>-3.81</td>
</tr>
<tr>
<td>C65'/D/87</td>
<td>95</td>
<td>40</td>
<td>1.69</td>
<td>-3.24</td>
</tr>
<tr>
<td>C71a</td>
<td>0</td>
<td>-</td>
<td>1.42</td>
<td>-2.94</td>
</tr>
<tr>
<td>C71b</td>
<td>90</td>
<td>40</td>
<td>1.84</td>
<td>-5.74</td>
</tr>
<tr>
<td>C72</td>
<td>100</td>
<td>45</td>
<td>2.05</td>
<td>-6.42</td>
</tr>
<tr>
<td>C73</td>
<td>100</td>
<td>43</td>
<td>1.77</td>
<td>-3.95</td>
</tr>
<tr>
<td>C73b</td>
<td>65</td>
<td>40</td>
<td>1.79 (20')</td>
<td>-7.39 (20')</td>
</tr>
<tr>
<td>C73b</td>
<td>65</td>
<td>40</td>
<td>0.55 (72h)</td>
<td>-7.67 (72h)</td>
</tr>
<tr>
<td>C76</td>
<td>0</td>
<td>-</td>
<td>2.34</td>
<td>-2.62</td>
</tr>
<tr>
<td>C76g</td>
<td>15</td>
<td>40</td>
<td>-3.05</td>
<td>-6.09</td>
</tr>
<tr>
<td>C77</td>
<td>0</td>
<td>-</td>
<td>-1.33</td>
<td>-5.56</td>
</tr>
<tr>
<td>F7</td>
<td>100</td>
<td>45</td>
<td>2.01</td>
<td>-4.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>----</td>
<td>----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>M1</td>
<td>0</td>
<td>-</td>
<td>1.44</td>
<td>-4.99</td>
</tr>
<tr>
<td>M2</td>
<td>0</td>
<td>-</td>
<td>1.77</td>
<td>-3</td>
</tr>
<tr>
<td>M4</td>
<td>90</td>
<td>46</td>
<td>1.53</td>
<td>-7.54</td>
</tr>
<tr>
<td>M5</td>
<td>100</td>
<td>47</td>
<td>2</td>
<td>-5.25</td>
</tr>
<tr>
<td>M6</td>
<td>100</td>
<td>39</td>
<td>2.12</td>
<td>-5.59</td>
</tr>
<tr>
<td>M7</td>
<td>100</td>
<td>43</td>
<td>2.07</td>
<td>-5.36</td>
</tr>
<tr>
<td>M8</td>
<td>100</td>
<td>45</td>
<td>1.82</td>
<td>-5.64</td>
</tr>
<tr>
<td>M9</td>
<td>100</td>
<td>45</td>
<td>1.64</td>
<td>-5.89</td>
</tr>
<tr>
<td>MS1</td>
<td>100</td>
<td>45</td>
<td>1.78</td>
<td>-3.52</td>
</tr>
<tr>
<td>MS2b</td>
<td>53</td>
<td>45</td>
<td>-0.2</td>
<td>-3.26</td>
</tr>
<tr>
<td>MS2g</td>
<td>95</td>
<td>45</td>
<td>1.25</td>
<td>-3.81</td>
</tr>
<tr>
<td>MS3</td>
<td>5</td>
<td>47</td>
<td>-3.48</td>
<td>6.62</td>
</tr>
<tr>
<td>MS4</td>
<td>48</td>
<td>47</td>
<td>-5.57(20')</td>
<td>6.97(20')</td>
</tr>
<tr>
<td>MS4</td>
<td>48</td>
<td>47</td>
<td>0.14(72h)</td>
<td>-6.46(72h)</td>
</tr>
<tr>
<td>MS5</td>
<td>77</td>
<td>45</td>
<td>0.16(20')</td>
<td>9.24(20')</td>
</tr>
<tr>
<td>MS5</td>
<td>77</td>
<td>45</td>
<td>0.85(72h)</td>
<td>-7.42(72h)</td>
</tr>
<tr>
<td>MS6</td>
<td>90</td>
<td>47</td>
<td>1.55</td>
<td>-4.8</td>
</tr>
<tr>
<td>MS7</td>
<td>40</td>
<td>45</td>
<td>-2.25(20')</td>
<td>6.11(20')</td>
</tr>
<tr>
<td>MS7</td>
<td>40</td>
<td>45</td>
<td>0.98(72h)</td>
<td>-5.09(72h)</td>
</tr>
<tr>
<td>MS8</td>
<td>65</td>
<td>47</td>
<td>-1.65(20')</td>
<td>6.09(20')</td>
</tr>
<tr>
<td>MS8</td>
<td>65</td>
<td>47</td>
<td>1.38(72h)</td>
<td>-4.24(72h)</td>
</tr>
<tr>
<td>MS9</td>
<td>0</td>
<td>-</td>
<td>1.73</td>
<td>-2.54</td>
</tr>
<tr>
<td>MS10</td>
<td>0</td>
<td>-</td>
<td>1.67</td>
<td>-2.23</td>
</tr>
<tr>
<td>MS11</td>
<td>0</td>
<td>-</td>
<td>1.72</td>
<td>-1.75</td>
</tr>
<tr>
<td>NV1</td>
<td>100</td>
<td>46</td>
<td>2.39</td>
<td>-1.68</td>
</tr>
<tr>
<td>NV2</td>
<td>100</td>
<td>49</td>
<td>2.51</td>
<td>-1.12</td>
</tr>
<tr>
<td>PR1</td>
<td>0</td>
<td>-</td>
<td>2.64</td>
<td>-2.8</td>
</tr>
<tr>
<td>PR2</td>
<td>0</td>
<td>-</td>
<td>2.49</td>
<td>-1.67</td>
</tr>
<tr>
<td>PR3</td>
<td>0</td>
<td>-</td>
<td>2.58</td>
<td>-0.98</td>
</tr>
<tr>
<td>PR6</td>
<td>70</td>
<td>42</td>
<td>-3.55(20')</td>
<td>9.09(20')</td>
</tr>
<tr>
<td>PR6</td>
<td>70</td>
<td>42</td>
<td>1.25(72h)</td>
<td>-11.48(72h)</td>
</tr>
<tr>
<td>PR7</td>
<td>65</td>
<td>39</td>
<td>-3.55(20')</td>
<td>8.87(20')</td>
</tr>
<tr>
<td>PR7</td>
<td>65</td>
<td>39</td>
<td>1.08(72h)</td>
<td>-10.70(72h)</td>
</tr>
<tr>
<td>PR8</td>
<td>80</td>
<td>39</td>
<td>1.57</td>
<td>-10</td>
</tr>
<tr>
<td>PR9</td>
<td>81</td>
<td>40</td>
<td>0.76</td>
<td>-11.71</td>
</tr>
<tr>
<td>PR10</td>
<td>92</td>
<td>40</td>
<td>1.61</td>
<td>-8.97</td>
</tr>
<tr>
<td>PR11</td>
<td>81</td>
<td>39</td>
<td>1.5</td>
<td>-11.5</td>
</tr>
<tr>
<td>PR12</td>
<td>90</td>
<td>46</td>
<td>0.84</td>
<td>-11.31</td>
</tr>
<tr>
<td>PB2</td>
<td>0</td>
<td>-</td>
<td>0.95</td>
<td>-4.89</td>
</tr>
<tr>
<td>PB3</td>
<td>94</td>
<td>40</td>
<td>-0.91</td>
<td>-9.01</td>
</tr>
<tr>
<td>PB4</td>
<td>90</td>
<td>42</td>
<td>1.21</td>
<td>-12.01</td>
</tr>
<tr>
<td>PB5</td>
<td>95</td>
<td>42</td>
<td>1.4</td>
<td>-12.64</td>
</tr>
<tr>
<td>PB7</td>
<td>100</td>
<td>39</td>
<td>1.83</td>
<td>-11.57</td>
</tr>
<tr>
<td>PB8</td>
<td>100</td>
<td>40</td>
<td>2.02</td>
<td>-11.41</td>
</tr>
<tr>
<td>PB10</td>
<td>76</td>
<td>42</td>
<td>1.25</td>
<td>-3.85</td>
</tr>
<tr>
<td>PB11</td>
<td>80</td>
<td>40</td>
<td>0.3</td>
<td>-11.17</td>
</tr>
<tr>
<td>PB12</td>
<td>80</td>
<td>40</td>
<td>1.28</td>
<td>-10.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>PB21</td>
<td>0</td>
<td>-</td>
<td>1.81</td>
<td>-3.22</td>
</tr>
<tr>
<td>PB21 cc</td>
<td>0</td>
<td>-</td>
<td>0.87</td>
<td>-14.9</td>
</tr>
<tr>
<td>PB21g</td>
<td>0</td>
<td>-</td>
<td>-0.55</td>
<td>-7.33</td>
</tr>
<tr>
<td>P8</td>
<td>100</td>
<td>39</td>
<td>1.63</td>
<td>-3.07</td>
</tr>
<tr>
<td>P9</td>
<td>90</td>
<td>46</td>
<td>1.97</td>
<td>-4.53</td>
</tr>
<tr>
<td>P10</td>
<td>100</td>
<td>50</td>
<td>1.77</td>
<td>-6.14</td>
</tr>
<tr>
<td>P11</td>
<td>100</td>
<td>46</td>
<td>1.87</td>
<td>-1.56</td>
</tr>
<tr>
<td>P12</td>
<td>100</td>
<td>46</td>
<td>2.02</td>
<td>-0.86</td>
</tr>
<tr>
<td>P13</td>
<td>100</td>
<td>50</td>
<td>2.29</td>
<td>-1.65</td>
</tr>
<tr>
<td>P14</td>
<td>100</td>
<td>46</td>
<td>2.61</td>
<td>-1.26</td>
</tr>
<tr>
<td>P15</td>
<td>100</td>
<td>39</td>
<td>1.87</td>
<td>-0.75</td>
</tr>
<tr>
<td>P16</td>
<td>100</td>
<td>47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P17</td>
<td>100</td>
<td>46</td>
<td>0.87</td>
<td>-5.82</td>
</tr>
<tr>
<td>P18</td>
<td>85</td>
<td>42</td>
<td>-2.95</td>
<td>-10.27</td>
</tr>
<tr>
<td>P19</td>
<td>100</td>
<td>47</td>
<td>0.91</td>
<td>-8.53</td>
</tr>
<tr>
<td>P20</td>
<td>100</td>
<td>46</td>
<td>1.74</td>
<td>-7.77</td>
</tr>
<tr>
<td>P21</td>
<td>100</td>
<td>47</td>
<td>0.97</td>
<td>-8.37</td>
</tr>
<tr>
<td>P22</td>
<td>100</td>
<td>46</td>
<td>1.15</td>
<td>-6.78</td>
</tr>
<tr>
<td>P23</td>
<td>100</td>
<td>40</td>
<td>1.35</td>
<td>-9</td>
</tr>
<tr>
<td>P24</td>
<td>100</td>
<td>44</td>
<td>1.37</td>
<td>-5.8</td>
</tr>
<tr>
<td>P25</td>
<td>94</td>
<td>42</td>
<td>1.36</td>
<td>-5.33</td>
</tr>
<tr>
<td>P26</td>
<td>100</td>
<td>42</td>
<td>1.33</td>
<td>-4.7</td>
</tr>
<tr>
<td>P27</td>
<td>100</td>
<td>46</td>
<td>1.46</td>
<td>-5.27</td>
</tr>
<tr>
<td>P28</td>
<td>100</td>
<td>46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P29</td>
<td>100</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P30</td>
<td>100</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P31</td>
<td>100</td>
<td>46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P32</td>
<td>0</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P33</td>
<td>0</td>
<td>-</td>
<td>1.16</td>
<td>-3.28</td>
</tr>
<tr>
<td>RA3/2</td>
<td>100</td>
<td>42</td>
<td>1.79</td>
<td>-4.16</td>
</tr>
<tr>
<td>RA3/3</td>
<td>90</td>
<td>42</td>
<td>0.85</td>
<td>-12.06</td>
</tr>
<tr>
<td>RA3/4</td>
<td>90</td>
<td>39</td>
<td>1.74</td>
<td>-11.29</td>
</tr>
<tr>
<td>SG1</td>
<td>95</td>
<td>40</td>
<td>1.51</td>
<td>-3.37</td>
</tr>
<tr>
<td>SG2a</td>
<td>95</td>
<td>45</td>
<td>2.13</td>
<td>-7.63</td>
</tr>
<tr>
<td>SG3</td>
<td>100</td>
<td>50</td>
<td>1.62</td>
<td>-7.32</td>
</tr>
<tr>
<td>SG4</td>
<td>100</td>
<td>47</td>
<td>1.64</td>
<td>-2.35</td>
</tr>
<tr>
<td>SG5</td>
<td>100</td>
<td>47</td>
<td>2.06</td>
<td>-0.9</td>
</tr>
<tr>
<td>SG6</td>
<td>100</td>
<td>50</td>
<td>1.35</td>
<td>-5</td>
</tr>
<tr>
<td>SG7</td>
<td>100</td>
<td>47</td>
<td>1.15</td>
<td>-0.53</td>
</tr>
<tr>
<td>SG8</td>
<td>100</td>
<td>47</td>
<td>1.51</td>
<td>-5.98</td>
</tr>
<tr>
<td>SG9</td>
<td>100</td>
<td>49</td>
<td>1.43</td>
<td>-5.47</td>
</tr>
<tr>
<td>SG10</td>
<td>100</td>
<td>49</td>
<td>1.29</td>
<td>-6.02</td>
</tr>
<tr>
<td>SG11</td>
<td>85</td>
<td>45</td>
<td>1.06</td>
<td>-5.48</td>
</tr>
<tr>
<td>SG12</td>
<td>100</td>
<td>45</td>
<td>1.51</td>
<td>-5.65</td>
</tr>
<tr>
<td>SG12a</td>
<td>100</td>
<td>45</td>
<td>1.02</td>
<td>-5.96</td>
</tr>
<tr>
<td>SG13</td>
<td>100</td>
<td>47</td>
<td>1.69</td>
<td>-10.08</td>
</tr>
<tr>
<td>SG14</td>
<td>95</td>
<td>45</td>
<td>1.35</td>
<td>-5.37</td>
</tr>
<tr>
<td>SG15</td>
<td>0</td>
<td>-</td>
<td>1.41</td>
<td>-2.68</td>
</tr>
<tr>
<td>SG16</td>
<td>0</td>
<td>-</td>
<td>1.35</td>
<td>-3.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>VV7</td>
<td>90</td>
<td>39</td>
<td>-0.05</td>
<td>-4.91</td>
</tr>
<tr>
<td>VN14</td>
<td>38</td>
<td>50</td>
<td>1.15 (20')</td>
<td>-4.90 (20')</td>
</tr>
<tr>
<td>VN14</td>
<td>38</td>
<td>50</td>
<td>1.75 (72h)</td>
<td>-2.31 (72h)</td>
</tr>
</tbody>
</table>
Bibliography


Balestra, A. (1897). "Contribuzione geologica al periodo Cretaceo del Bassanese." Boll. ann. Club Alpino Bassanese. 3:


Bittner, A. (1877). "Il territorio montuoso fra Vicenza e Verona." Boll. R. Com. Geol. It. 8:


\(^{87}\text{Sr}/^{86}\text{Sr} \) evolution from Cretaceous to Present - Applications to Paleoceanography." *Science*. **231**: 979-984.


Secco, A. (1883). Note geologiche sul Bassanese.


Acknowledgements

I would like to thank Prof. Kenneth J. Hsü, Dr. Helmut Weissert and Dr. Günther Kahr, ETH - Zürich, for their patient help throughout the preparation of this thesis. Their advice, discussions and suggestions during the past four years taught me a “scientific” way of thinking and opened a new, fascinating world.

I am very grateful to Prof. Hans R. Thierstein, ETH - Zürich, for his direct and inquisitive questions on the usefulness of some of my data and his infinite patience in listening to my “catastrophic” (!) dolomite dilemmas.

Prof. Stefan Schmid, University of Basel, was of immense value with his interpretation of the structural features associated with “my” dolomite, allowing a completely new interpretation of the regional tectonics, which led to the formulation of the dynamic model.

Prof. Daniel Bernoulli, ETH - Zürich, who always patiently found five minutes for me, revised and corrected my ideas of Alpine tectonics.

Discussions with Dr. João Keller, Imperial College, London, about the Tertiary tectonic evolution of Italy were illuminating.

Discussions with Prof. Myriam Kastner, Scripps Institution of Oceanography, and Prof. Robert E. Garrison, University of California Santa Cruz, were sincerely appreciated.

Dr. Hans Fischer, ETH - Zürich, provided the first strontium isotope analyses that suggested to me the possibility of their utilization for the dolomitization problem. Dr. Giancarlo Cavazzini, Roberto Rizzieri and Renzo Battocchio of the Laboratorio di Geocronologia of the C.N.R. at the University of Padova, in spite of the sequence of analytical and instrumental “disasters” that occurred, performed most of the strontium isotope analyses.

Dr. Joseph “Sepp” Mullis, University of Basel, helped with the analysis of the fluid inclusions trapped in the dolomite crystals. How he could provide so much information from so few droplets of fluid is still a mystery to me.

Dr. Dorothee Dietrich, ETH - Zürich, advised me during the preparation of the SEM photographs, suggesting many different ideas on electron microscopy and its various applications.
Dr. Bahattin Ayranci, ETH - Zürich, helped me with the analyses of calcite, dolomite and clay minerals at the Atomic Absorption Spectrometer.

Michael Knappertsbusch, ETH - Zürich, kindly made the micropaleontological dating of the limestones.

Dr. Arnold Stahel availed me of the X-ray diffractometer from the Mineralogisches und Petrographisches Institut, ETH - Zürich, to measure my dolomites and calcites.

Prof. Antonio Longinelli and his technicians at the Laboratorio di Isotopi Stabili, University of Trieste, Italy, kindly provided the oxygen isotope composition of the chert.

I had never thanked properly Gretli Früh-Green and Stefano Bernasconi who courteously provided hospitality when I first arrived in Zürich. They have always remained good friends to me and took an interest in my work.

Peter J. Kindle is one of the best friends I could ever hope to have at the Institute. His trust in my abilities and his support for my work were of immense value. Thank you, Pietsch.

Urs Gerber, ETH - Zürich, advised and processed all the photographs, patiently dealing with my "urgent" requests.

Albert Uhr, ETH - Zürich, was very generous with his time and ability for drafting some of the figures.

Frowin Pirovino, Kurt Ghilardi, Herr Schärli, Toni Willi and the rest of the staff of the Werkstatt, ETH - Zürich, always promptly provided my thin sections and helped me solve other technical problems with my samples.

My brother, Eugenio and his girlfriend, Natascia sacrificed some of their 1989 summer vacation to make most of the wonderful drawings and diagrams with the Macintosh included in this thesis. They assembled the thesis and figures in its final version.

Jon Dobson, Thomas Gubler, Ulrich Henken-Mellies and Hans Mohr, alias the H49, patiently put up with my phone calls and visits for almost three years.
I cannot forget all the friends who were with me during my time in Zürich, especially Federico Zardi and Bruno Rosenberger.

Dr. Nicoletta Piccolrovazzi shared an apartment and three years of life with me: although we now will take different roads, I will always remember the good times we had together. I wish her all the best for the future.

My parents, Ruggero and Luisa, have been wonderful over the last four years and no words can exist to express what I feel for them. They supported me continuously with my studies and I would not have made this achievement if it was not for their love. Questo lavoro è dedicato a voi.

Support for the first 8 months of the research programme came from two “Fondazione Gini” Awards from the University of Padova, and from the “Foundation pour des Bourses Italo-Suisses”, Lausanne. Additional finance from Prof. Hsü is gratefully acknowledged.

Finally, I would like to express my eternal gratitude to my husband, David Spencer. Not only did he correct the English and the format of my thesis in at least four versions, he tried in vain to seem interested in my “non-deformed” dolomites, pushing me with his love and his incredible, never exhausting energy during the drafting of this thesis. I hope I will be able to do the same for you, when it is your turn. Non ce l’avrei fatta senza di te.
Cinzia Spencer-Cervato was born in Padova (Italy) the 29 March, 1961. She attended, from October, 1966 until June, 1971, the Scuola Elementare "Sacro Cuore" in Padova. From October, 1971 until June, 1974, she attended the Scuola Media "G. Pascoli", where she obtained the Diploma di Scuola Media Inferiore with the maximum grade possible. She then studied at the Liceo Classico "Tito Livio" in Padova, from September, 1974 until July, 1979, where she obtained the Maturità Classica degree. In October, 1979 she registered at the Faculty of Natural Science at the University of Padova for a degree in Earth Sciences. On the 5 July, 1984 she graduated as a dottore in Scienze Geologiche with 110/110 cum laude, which included a geological - sedimentological thesis on the Lessini area in the Venetian Alps, Italy. In January, 1988, she passed the National State Examination for the qualification of Dr. geol, enabling her to practice as a professional Geologist in Italy.

Since November, 1985, she is a doctoral student at the ETH - Zürich under the supervision of Prof. Dr. Kenneth J. Hsu, PD Dr. Helmut Weissert and Dr. Günther Kahr. Since August, 1986 she was a teaching assistant at the Geological Institute, ETH - Zürich.

She married on the 10 March, 1990 David A. Spencer, british citizen.