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Oxygen isotope composition of calcite in Alpine ophicarbonates: a hydrothermal or Alpine metamorphic signal?

By HELMUT WEISSERT¹⁾ and DANIEL BERNOUlli²⁾

ABSTRACT

Remnants of the central Tethys with its Jurassic oceanic crust are preserved in South Pennine thrust nappes of eastern Switzerland. Serpentinites, metabasalts, metahyaloclastites and ophicarbonates, associated with radiolarian cherts and Early Cretaceous pelagic limestones and shales are regarded as traces of oceanic fracture zones. However, the question on the origin of ophicarbonates remains controversial, although tectono-sedimentary processes involved in the formation of many of these rocks have been documented.

In order to distinguish carbonate of pelagic origin from possible hydrothermal carbonates within the ophicarbonates, we analyzed the oxygen and carbon isotope composition of various calcite cements and sedimentary carbonates within these rocks. In addition, we analyzed samples from overlying Early Cretaceous pelagic limestones. The samples were taken along a N–S transect between Davos and St. Moritz, where an increase in metamorphism from pumpellyite–prehnite facies to high greenschist facies has been documented petrologically. Although the C-isotope composition of all the measured samples scatters between $-1\text{\textperthousand}$ to $+2.5\text{\textperthousand}$ (PDB), a distinct trend to decreasing O-18 values is observed along the studied transect. Differences in lithology had no influence on the O-18 composition. Values of $-6.7\text{\textperthousand} \pm 0.7\text{\textperthousand}$ (PDB) were measured in calcite cements and in red recrystallized calcite matrix of ophicarbonates as well as in Early Cretaceous pelagic limestones near Klosters. O-18 compositions of $-10\text{\textperthousand}$ to $-11\text{\textperthousand}$ (PDB) are typical for samples taken near Arosa and values of $-12\text{\textperthousand}$ to $-13\text{\textperthousand}$ (Platta nappe) and of $-16\text{\textperthousand}$ were measured in areas with higher metamorphic grades. These data show that original oceanic or hydrothermal isotope signals in the sediments studied were eliminated during Alpine metamorphism. Calcite reequilibrated with penetrative Alpine metamorphic fluids with an isotope composition of $\delta^{18}\text{O} = +12\text{\textperthousand}$ to $+15\text{\textperthousand}$ (SMOW), using petrologic temperature data for calculation. We suggest that oxygen isotope data, therefore, are not reliable tracers for hydrothermal activity along Jurassic oceanic fracture zones within the Alps. Mineralogical information, such as the common impregnation of ophicarbonates by hydrogrossular, may be more significant.

ZUSAMMENFASSUNG

Serpentiniten und ozeanische Sedimente sind in den südpenninischen Decken Graubündens oft mit Serpentinitbreccien (»Ophikarbonaten«) assoziiert, welche als Indizien für intraozeanische Bruchzonen gewertet werden können. Mit Hilfe von isotopengeochemischen Untersuchungen versuchten wir in diesen Ophikarbonaten Calcit pelagischer Herkunft von möglichem hydrothermalem Calcit zu unterscheiden. Sauerstoff- und Kohlenstoffisotopenwerte von verschiedenen Calcitzement-Generationen und von sedimentärem Karbonat wurden mit der Isotopenzusammensetzung von unterkretazischen Kalken, die Ophiolithe, Ophikarbonate und Radiolarite der

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südpenninischen Decken überlagern, verglichen. Die Proben wurden entlang eines N–S-Profils zwischen Klosters und St. Moritz entnommen, wo gegen Süden eine Zunahme der alpinen Metamorphose von Pumpellyit–Prehnit-Fazies bis zu Grünschiefer-Fazies dokumentiert ist. Während die Kohlenstoffisotopenzusammensetzung aller gemessenen Proben zwischen $-1\text{\textperthousand}$ und $+2,5\text{\textperthousand}$ (PDB) streut, erkennt man in den Sauerstoffdaten mit zunehmender Metamorphose einen deutlichen Trend zu negativeren Werten. Unterschiede in der Lithologie zeichnen sich hingegen in den Isotopenresultaten nicht ab. Bei Klosters wurden in den Karbonaten Werte um $\delta^{18}\text{O} = -7\text{\textperthousand}$ (PDB) gemessen, während Werte um $-10\text{\textperthousand}$ (PDB) für die Region Arosa typisch sind. Eine Isotopenzusammensetzung von $-13\text{\textperthousand}$ (PDB) charakterisiert die Karbonate der Platta-Decke im Oberhalbstein, und Werte von $-16\text{\textperthousand}$ (PDB) wurden im Oberengadin gemessen. Diese Daten zeigen, dass urprüngliche marine oder hydrothermale Sauerstoffisotopensignale in den von uns studierten Sedimenten während der alpinen Metamorphose durch metamorphe Wässer eliminiert wurden. Spuren hydrothermaler Aktivität sind in alpinen Ophiokarbonaten deshalb kaum mit Sauerstoffisotopendaten nachweisbar. Die gemessenen Daten geben jedoch wertvolle Hinweise auf alpine metamorphe Prozesse.

Introduction

In eastern Switzerland, remnants of the central Tethys including Jurassic oceanic basement rocks are preserved in the South Pennine Platta thrust nappe and in the Arosa Zone, a highly complex zone comprising imbricates of oceanic and distal continental margin origin sandwiched between Pennine and Austroalpine nappes (SPICHER 1980). Although the major lithologies typical of ophiolite suites, peridotites, gabbros and mafic volcanics, are present in these units, no complete stratigraphic section through oceanic crust and lithosphere has been preserved. An ophiolite suite appears to have been highly dismembered during Alpine orogeny. In contrast, however, to areas, such as Troodos or Oman where a complete ophiolite sequence is preserved (e.g. MOORES 1969; MOORES & VINE 1971; GLENNIE et al. 1974), the Jurassic–Early Cretaceous oceanic sediments occur in stratigraphic contact, not only with mafic pillow lavas, usually the uppermost layer of oceanic crust, but also directly in contact with peridotites and serpentinites. Common, as well is the cooccurrence of serpentinites with complex ophiolitic breccias, known as ophicalcites which comprise various mixtures of fresh or oxidized angular, sand- to boulder-sized fragments of serpentinite or peridotite set in a pink to gray calcareous matrix.

STUDER (1837) published the first map on the geology of the Davos area in eastern Switzerland and already recognized these breccias within the large mass of the Totalp serpentinite. He conceded the difficulties of deciding whether calcite or serpentinite formed the matrix of these rocks. CORNELIUS (1935) not only confirmed STUDERS observations but documented the widespread occurrence of ophicalcites within the South Pennine nappes. The origin of these rocks, however, remained enigmatic.

CORNELIUS and successive authors (GRUNAU 1947; GEES 1956; PETERS 1963) did not recognize the tectonically inverted position of many of the most important ophiolite sequences in the Platta nappe and the Arosa Zone (e.g. Totalp). They thus considered peridotites, serpentinites and pillow lavas as younger than the associated sediments and interpreted the observed primary contacts not as depositional but as intrusive. Consequently, they postulated that ophicalcites were the product of contact metamorphic reactions between peridotite or serpentinite and sediments. They explained the conspicuous scarcity of high temperature minerals by the high water content of the sediments (GEES 1956) or a low temperature emplacement of an already crystallized peridotite

(PETERS 1963). Following the establishment of the new paradigm of plate tectonics, ophiolite complexes were reinterpreted as the remnants of oceanic crust and lithosphere and the concept of an ideal ophiolite stratigraphy developed. In this context, the South Pennine ophicalcites of Graubünden, as well as similar lithologies in the Western Alps and the Ligurian Apennines were related to tectono-sedimentary processes along oceanic fracture zones (DIETRICH et al. 1974; GIANELLI 1977; LEMOINE 1980; CORTESOGNO et al. 1981). Along oceanic fracture zones, fragmented oceanic crust and uplifted mantle commonly occur associated with ultramafic/mafic breccias and pelagic sediments (BONATTI et al. 1974).

In other models developed over the last two decades, the formation of ophicalcites is coupled with the serpentinization process (e.g. BEARTH 1967). PFEIFER (1979) and TROMMSDORFF et al. (1980) suggest in their scenarios that mixing of alkaline fluids from serpentinites with more acidic fluids from areas with felsic or mafic rocks may lead to the precipitation of the calcite found in some ophicalcites.

For our investigation on the origin of ophicalcites in the South Pennine nappes we decided to approach the problem from a sedimentologists point of view. Sedimentological and regional field observation yielded abundant evidence for a tectono-sedimentary origin of the ophicalcites studied and allowed us to substantiate and refine respective models (BERNOULLI & WEISSERT 1983). In addition, we used geochemical parameters in order to distinguish among various carbonate types involved in the formation of ophicalcites. Our initial goal was to discriminate between calcite derived from early hydrothermal processes and calcite from pelagic sediment infill by using the method of oxygen and carbon isotope geochemistry. In this presentation we show, however, that the oxygen isotope composition of carbonates from the South Pennine nappes in Graubünden does not reflect the Jurassic geochemical environment during the formation of the ophicalcites. Instead, the oxygen isotope values correlate well with a progressive signature of Alpine metamorphism which is related to the formation of the nappe edifice.

Ophicalcites and their stratigraphic and tectonic framework

The samples chosen for our oxygen and carbon isotope study were collected from ophicalcites and associated pelagic sediments in the South Pennine Arosa Zone and Platta nappe which are exposed in the Grisonide Alps of eastern Switzerland (Fig. 1). The ophicalcites are associated with elements of a dismembered oceanic crust and with radiolarites and pelagic limestones of ?Middle and Late Jurassic to Early Cretaceous age. Detailed mapping of ophicalcite bodies in the ophiolite complex near Davos reveals that they occur preferentially along distinct zones within the serpentinite host rock. Ophicalcites fill graben-like structures up to several tens of meters wide (Fig. 2). Several generations of calcite veins and fractures filled with pelagic carbonate document a polyphase tectono-sedimentary origin of these lithologies (Fig. 3; BERNOUILLI & WEISSERT 1983). One type of calcite, filling veins and fractures which shows distinct textures of cement, can be distinguished from possibly metasomatic calcite which replaces serpentinite minerals and preserves a mesh structure typical for serpentine minerals (GREENE 1981). Evidence of possible hydrothermal alteration of carbonates is shown by micron-sized red garnet, identified as hydrogrossular which commonly im-

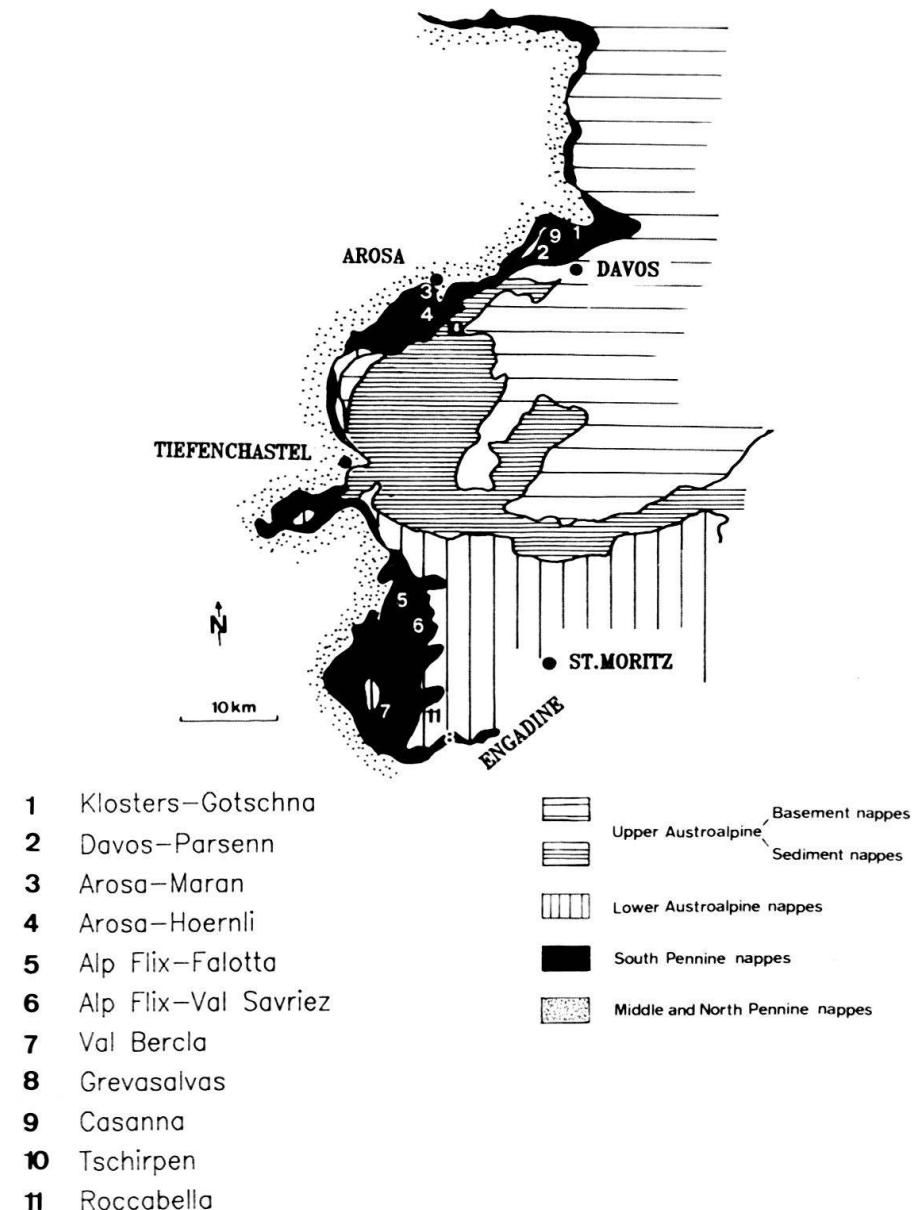


Fig. 1. The South Pennine Arosa and Platta nappes in eastern Switzerland. Samples for isotope study were taken at the South Pennine localities 1-8 and at the Austroalpine outcrops 9-11.

pregnates veins and fracture fillings (CORNELIUS 1935; PETERS 1963; CORTESOGNO et al. 1981; Fig. 4). Ophiolite breccias related to subaqueous gravity slide processes are associated with ophicalcites formed by polyphase fracturing of serpentinite host rock (WEISSERT 1975). In these, components of peridotite and serpentinite and rare fragments of sedimentary rocks are embedded in a matrix of recrystallized carbonate, which is also impregnated by minute crystals of hematite.

A few meters of radiolarian chert of Late Jurassic age overlie the ophiolite and ophicalcite complexes. Pelagic limestones follow the radiolarites in the stratigraphic succession and are of Tithonian and Berriasian age (DIETRICH 1970; WEISSERT 1975).



Fig. 2. Ophicalcite filling graben structure within the Totalp peridotite–serpentinite complex (Davos). Photograph shows peridotite–serpentinite to the right and ophicalcite to the left.



Fig. 3. Geopetal infill in an ophicalcite breccia (Totalp peridotite–serpentinite, Davos). Several generations of calcite cement and of red limestone with serpentinite fragments fill a small fracture (size of the coin: 2 cm).

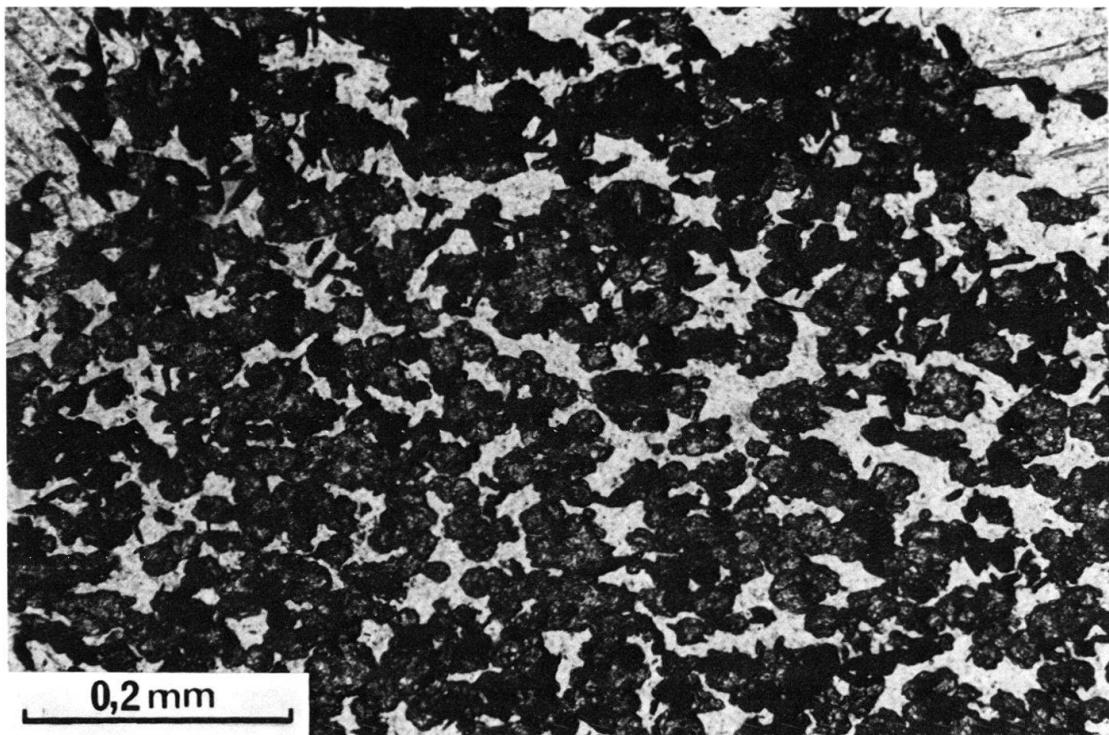


Fig. 4. Thin section photomicrograph showing ophicalcite impregnated with fine-grained hematite and hydrogrossular. From ophicalcite illustrated in Figure 3. Totalp, Davos.

The limestone sequence which is only a few meters thick is known as the Aptychus Limestone or the Calpionellid Limestone formation. It gradually passes upward into a sequence of alternating dark pelagic limestones and siliceous shales formed during the Early Cretaceous. This formation, locally known as Roccabella Formation (DIETRICH 1970) is comparable with the Ligurian Argille a Palombini Formation (e.g. DECANDIA & ELTER 1972).

In our area of study the South Pennine thrust nappes can be traced almost continuously from the Klosters area in the north to the upper Engadine in the south. Along this north-south transect the grade of Alpine metamorphism increases. Low-grade metamorphic conditions (prehnite-pumpellyite facies) are registered near Davos. From there the degree of metamorphism is increasing until greenschist facies conditions have been reached in the Engadine area (DIETRICH et al. 1974). This metamorphism has been related to eo-Alpine deformation and overthrusting of Austroalpine elements onto the South Pennine units during the Cretaceous (DEUTSCH 1983), although evidence for later deformation is ubiquitous. Today, thrust slices of lower Austroalpine origin and sedimentary nappes of upper Austroalpine derivation form the tectonic cover of the Arosa and Platta nappes together with the large crystalline basement nappe of the Silvretta (TRÜMPY 1975).

On the origin of the carbonate: a geochemical approach

The oxygen and carbon isotope composition of carbonates in ophicalcites and ophiolite breccias has previously been used as an indicator of calcite origin in samples

from the Ligurian Apennines (GALLI & TOGLIATTI 1965; BARBIERI et al. 1979) and in the Western Alps (LEMOINE et al. 1983). An earlier study of the isotope composition of interpillar carbonates and associated sediments has been conducted by SCHIDLOWSKI & STAHL (1971) in the South Pennine Arosa Zone. BARBIERI et al. (1979) concluded from their data that all their carbonate samples were of pelagic origin. They suggested that, however, subseafloor-metamorphism had modified the original marine oxygen isotope signature. In fact, traces of early-stage hydrothermal metamorphism have been observed in the related adjacent mafic rocks (SPOONER & FYFE 1973; SPOONER et al. 1974). The carbon isotope composition – less temperature dependent – remained within the range of normal marine values. BARBIERI et al. (1979) interpretation has been supported by LEMOINE et al. (1983). They analyzed ophicalcites samples from the Western Alps and from the South Pennine Arosa Zone for carbon and oxygen stable isotopes. They concluded that the light oxygen isotope values from calcites could best be explained by early hydrothermal alteration processes. They postulated that Alpine metamorphism could not completely mask the original isotopic composition of the carbonates studied. In contrast with these postulates is the hypothesis of SCHIDLOWSKI & STAHL (1971). In their view the light oxygen isotope value from the South Pennine ophicarbonates is a signature of modern meteoric water diagenesis which shifted an original marine isotope composition to more negative values. They further supported the idea that serpentinite and sedimentary carbonates were mixed tectonically as they found no evidence for a magmatic origin of the carbonate fraction in ophicalcites. The few studies mentioned above serve to document the wide range of interpretations possible for isotope data in Alpine carbonates.

In our isotope investigation on South Pennine ophicalcites and associated pelagic carbonates we focus on the controversial question whether the isotopic compositions measured, still reflect geochemical conditions of early diagenetic environments or, if Alpine metamorphism has had a masking effect, resetting the isotope signature of the carbonate. Samples for isotope analysis were collected from ophicalcites and pelagic limestones along a north–south transect between Klosters and the Engadine valley (Fig. 1). Within ophicalcite zones we compared the isotopic composition of various generations of calcite veins with the isotope signature of red recrystallized pelagic sediment filling fractures and forming a matrix for breccias. Pelagic limestones were sampled along continuous stratigraphic sections. For comparative purposes we collected a few additional samples from pelagic limestones from lower Austroalpine tectonic units (Casanna nappe, Tschirpen nappe, Err nappe).

The carbonate was prepared and reacted with H_3PO_4 according to the traditional method for the release of CO_2 gas (MCCREA 1950). The gas was analyzed with a Micro-mass 903 mass spectrometer. The results are expressed in the $\delta\text{\textperthousand}$ notation relative to the PDB isotopic standard.

Oxygen and carbon isotope data

The results of our analyses are tabulated in the table and graphically displayed in Figure 5 to Figure 8. The measured oxygen isotope values cover a wide range from $\delta^{18}O = -5.6\text{\textperthousand}$ to $-16.3\text{\textperthousand}$ in the South Pennine samples and from $\delta^{18}O = -4.4\text{\textperthousand}$ to $-10.5\text{\textperthousand}$ in the pelagic limestones of lower Austroalpine origin. The scatter is minimal,

| | | | ^{13}C (PDB) | ^{18}O (PDB) |
|-------------|------------------------------|--|-----------------------|-----------------------|
| Klosters- | Calpionellid limestone | | +1.03 | -7.43 |
| Gotschna | | | +1.15 | -7.69 |
| | Ophicalcite | | +0.79 | -7.08 |
| | pelagic sediment | | +1.42 | -6.63 |
| | | | +1.05 | -6.66 |
| | | | +1.15 | -7.64 |
| | calcite vein | | +2.12 | -6.03 |
| Davos- | Ophicalcite | | +0.57 | -10.54 |
| Parsenn | pelagic sediment | | +0.72 | -10.26 |
| | oolite component | | +0.56 | -10.53 |
| | hemipelagic marl (component) | | | |
| Arosa- | Calpionellid limestone | | -0.73 | -10.55 |
| Maran | | | -0.17 | -10.04 |
| Arosa-* | Calpionellid limestone and | | +0.48 | - 9.37 |
| Hörnli | Palombini limestone | | +0.69 | -10.07 |
| | | | -0.48 | -10.17 |
| | | | -0.42 | -10.28 |
| | Inter-pillow limestone | | +1.37 | -10.31 |
| | | | +1.40 | -10.34 |
| | | | +1.70 | - 9.98 |
| | Calcite-vein in basalt | | +0.84 | -10.21 |
| | Ophicalcite | | +1.20 | -10.20 |
| | pelagic sediment | | +2.12 | -10.10 |
| Alp Flix- | Calpionellid limestone | | +0.89 | -12.67 |
| Val Savriez | | | +0.29 | -12.53 |
| | | | +1.08 | -11.86 |
| | | | +0.61 | -12.76 |
| | | | +0.66 | -13.18 |
| | | | +0.24 | -12.57 |
| | | | +0.38 | -13.85 |
| | Ophicalcite | | +0.24 | -13.30 |
| | pelagic sediment | | +1.53 | -13.30 |
| | | | -0.66 | -13.10 |
| Val Bercla | Palombini limestone | | -0.85 | -13.63 |
| | | | +0.33 | -12.33 |
| | | | +0.21 | -12.49 |
| Engadine | Calpionellid limestone | | +0.90 | -16.30 |
| Casanna- | Pelagic limestone | | +1.57 | -6.32 |
| Klosters | | | +1.90 | -6.90 |
| | | | +1.05 | -5.61 |
| Tschirpen- | Calpionellid limestone | | +0.57 | -4.84 |
| Arosa | | | +0.87 | -4.42 |
| Roccabella | Calpionellid limestone and | | +1.77 | -10.13 |
| | Palombini limestone | | +1.12 | - 9.37 |
| | | | +1.97 | - 9.14 |
| | | | +1.14 | -10.29 |

* additional data see Greene (1981)

Table: Oxygen and carbon isotope data from South Pennine and Lower Austroalpine units.

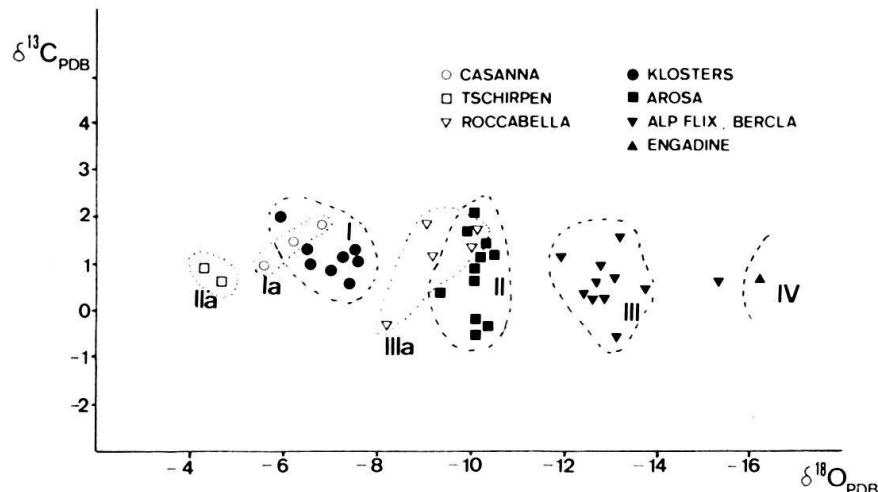


Fig. 5. ^{13}C versus ^{18}O data (PDB) obtained from calcite in ophicarbonates and associated pelagic sediments of the South Pennine Arosa and Platta nappes (full symbols), and from corresponding Austroalpine pelagic sediments (open symbols). Four data groups could be distinguished in each group of nappes along the north-south transect studied:

I: Klosters, Ia: Klosters-Casanna, II: Arosa, IIa: Arosa-Ts chirpen, III: Alp Flix-Bercla, IIIa: Roccabella, IV: Engadine.

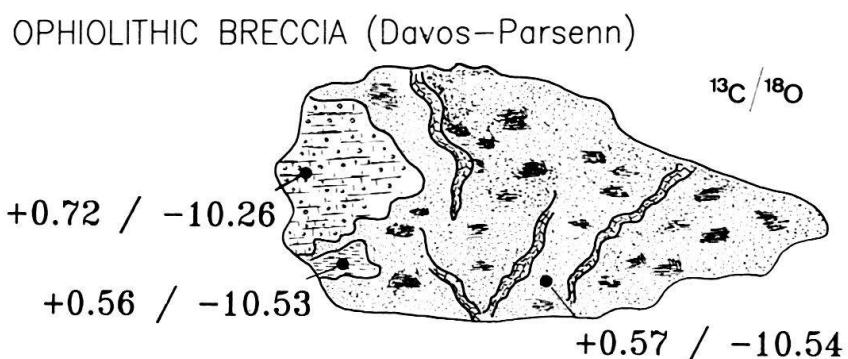
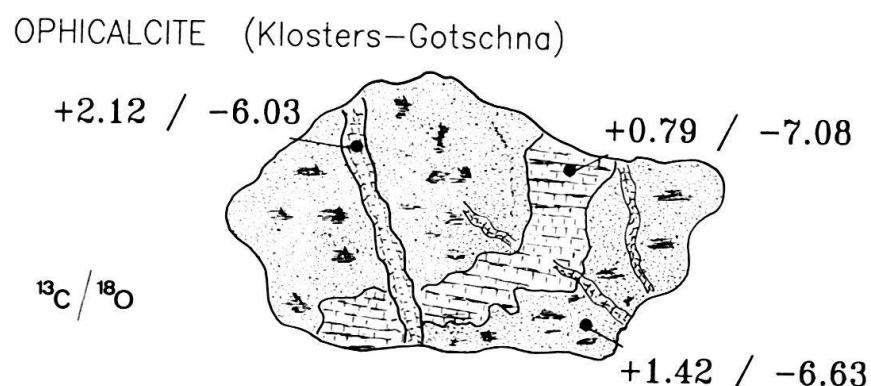


Fig. 6. ^{13}C and ^{18}O data (PDB) from cement and pelagic sediment in an ophicalcite near Klosters and data from sedimentary clasts (oolithic limestone and hemipelagic marl) and the matrix of an ophiolite breccia near Davos (values relative to PDB). Length of ophicalcite: 10 cm, length of ophiolite breccia: 15 cm.

however, if we compare the isotopic composition of various vein cements with the red carbonate matrix from individual ophicalcite specimens (Fig. 6). The values measured in an ophicalcite from Klosters-Gotschna range from $\delta^{18}\text{O} = -6.03\text{\textperthousand}$ to $-7.08\text{\textperthousand}$ and no difference is seen in the oxygen isotopic composition of sedimentary clasts and carbonate matrix in an ophiolite breccia near Davos (Fig. 6). The variations in oxygen isotopic composition between ophicalcites and overlying pelagic limestones along individual stratigraphic sections are also insignificant (Fig. 7). The observed scatter in the oxygen isotope data follows a clear regional pattern along the north-south transect (Fig. 8). In the far north, near Klosters, the least negative values of $\delta^{18}\text{O} = -7.08\text{\textperthousand} \pm 0.6\text{\textperthousand}$ were measured. Compositions of $\delta^{18}\text{O} = -10.1 \pm 0.3\text{\textperthousand}$ and of $\delta^{18}\text{O} = -13.1 \pm 0.42\text{\textperthousand}$ near Arosa and at Alp Flix document the southward trend toward lighter O-18 values. The most negative samples derive from the upper Engadine where a pelagic limestone with a composition of $\delta^{18}\text{O} = -16.3\text{\textperthousand}$ was analyzed. The O-18 compositions of the pelagic limestones from the overlying Austroalpine units are distinctly and consistently more positive, if plotted on a regional map. The O-18 compositions of carbonates from the Casanna nappe near Klosters (WEISSERT 1975) are by 0.8% more positive than values from the underlying South Pennine sediments. Near Arosa the difference noted is $\Delta\delta = +6\text{\textperthousand}$ between South Pennine and Austroalpine values, and in the southern part of our area of study the measured difference is about 2%.

The carbon isotope compositions measured fall within a narrow range of $\delta^{13}\text{C} = -1\text{\textperthousand}$ to $\delta^{13}\text{C} = +2\text{\textperthousand}$. The average value calculated is $+0.67 \pm 0.8\text{\textperthousand}$. This small

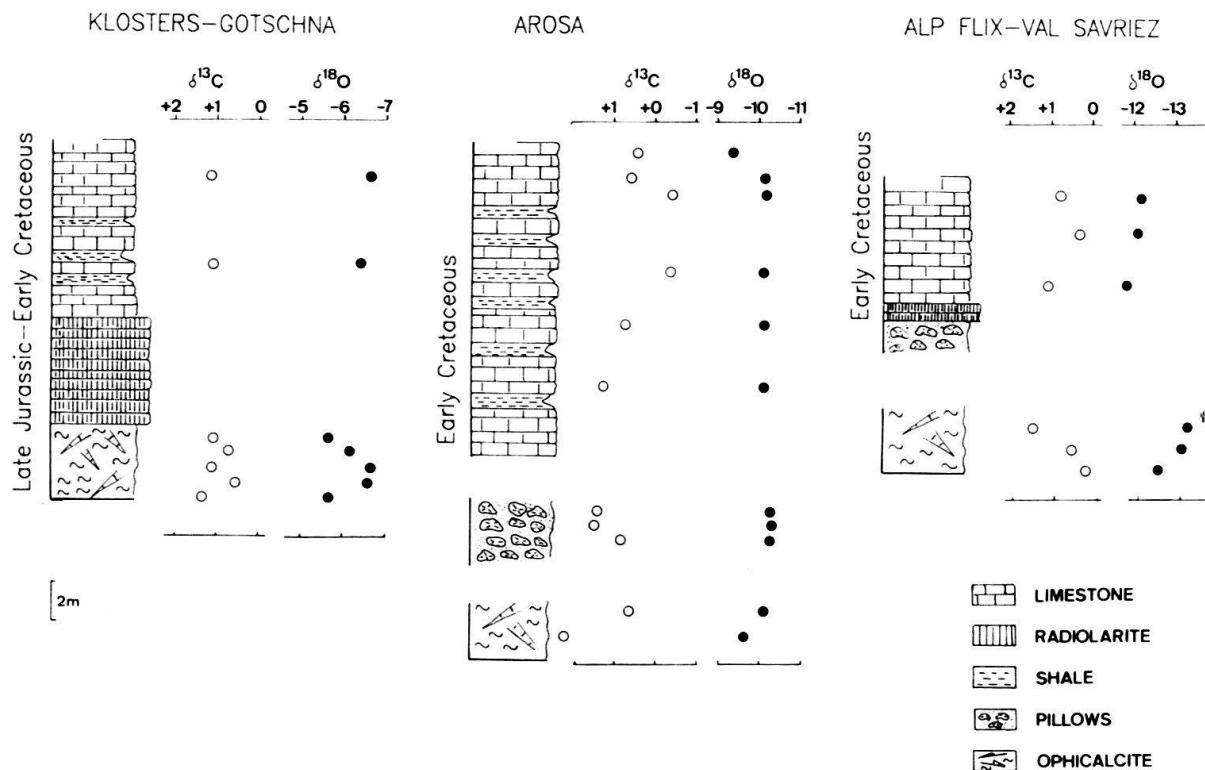


Fig. 7. ^{13}C and ^{18}O (PDB) composition of ophicalcites, interpillow carbonate and associated Early Cretaceous pelagic sediments in three sections along the north-south transect studied.

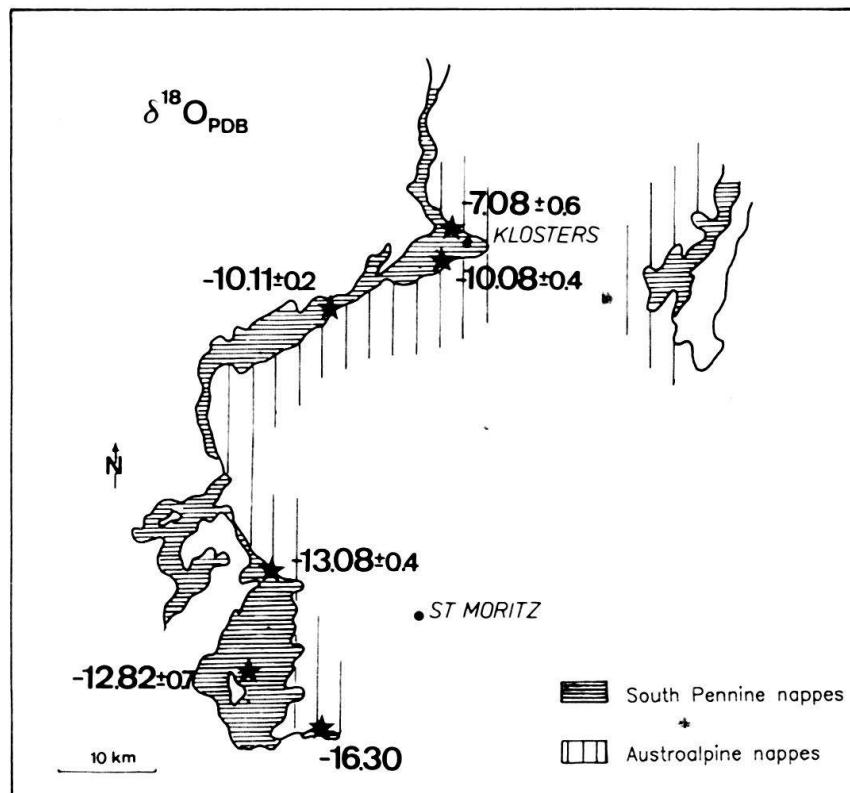


Fig. 8. Average ^{18}O compositions (PDB) for different South Pennine localities along the north-south transect Davos-Engadine, showing a southward trend to more negative values.

variation does not allow any correlation between different lithologies and their C-13 values. No regional trend is recognized in the data and the South Pennine values do not differ from the Austroalpine values.

Discussion: A metamorphic signature

Three important conclusions, drawn from the data presented, must be included in any scenario explaining the isotopic composition of the measured ophicarbonates and pelagic limestones:

1. The C- and O-isotope composition of various carbonates is not controlled by differences in lithology or stratigraphic age. Measured ophicalcites and pelagic limestones from individual stratigraphic sections show little scatter in their isotopic composition.
2. Regional conditions strongly control the O-18 composition of the South Pennine carbonates. This control is documented by a 10‰ decrease in the oxygen isotope values between Klosters and the Engadine.
3. The carbon isotope composition of all the samples analyzed falls within a small range between -1‰ and +2‰ which is typical for marine values.

Difficulties arise if we attempt to integrate our data into previous models for the origin of isotopic signatures in ophicarbonates and associated pelagic sediments. In-

deed, light oxygen isotope values of ophicalcites could have been the result of early hydrothermal alteration and carbonate reequilibration with warm marine pore fluids (BARBIERI et al. 1979; LEMOINE et al. 1983). This could be in fact the case for the extremely negative O-18 values in the ophicalcites of the Chenaillet massif in the Western Alps (LEMOINE et al. 1983; cf. MEVEL et al. 1978). We note, however, that in all other cases the Early Cretaceous pelagic carbonates are equally depleted in the heavy O-18 isotope. Early subseafloor-metamorphism, related to the emplacement of oceanic crust or to tectonic activity along oceanic fracture zones is very unlikely to have affected, on a regional scale, pelagic sediments for several tens of millions of years after the formation of ophicalcites. The measured values from pelagic limestones allow an exact estimate of the size of the postdepositional isotope shift, related to diagenetic and metamorphic processes. Early Cretaceous pelagic limestones from the Southern Alps, an area not affected by Alpine metamorphism, preserve oxygen isotope signatures of $\delta^{18}\text{O} = -1\text{\textperthousand}$ to $-2\text{\textperthousand}$, values which are close to the original marine values, and which have been only slightly altered by burial diagenesis (WEISSERT 1979). A negative shift of 5\textperthousand up to $15\text{\textperthousand}$ in the recrystallized South Pennine pelagic carbonates is therefore best explained by reequilibration processes during Alpine metamorphism. We assume that in both the low-grade metamorphic sequences near Klosters and in the greenschist facies environment of the Upper Engadine a pervasive metamorphic fluid facilitated the modification of an original oxygen isotope composition during peak metamorphism. The shift observed in the oxygen isotope data requires a large fluid/rock ratio in the sediments during metamorphism (SPOONER et al. 1974). The ratio of dissolved carbonate species to sedimentary carbonate was, however, small. A large reservoir of rock carbonate thus controlled the carbon isotope composition of the fluids and remained unchanged even under greenschist metamorphic temperatures. Stable C-13 compositions in burial diagenetic environments, facilitated by a small carbon reservoir in the fluids have been previously documented in studies on carbonate diagenesis (MCKENZIE et al. 1978). In metamorphic environments where CO₂-rich fluids are present, a correlation of decreasing O-18 with decreasing C-13 is observed for increasing metamorphic grades (LATTANZI et al. 1980).

We thus hypothesize that the measured oxygen isotopic composition reflects the thermal conditions at the peak of regional Alpine metamorphism, because isotope ratios are generally preserved during retrograde cooling (O'NEIL 1979). In our area of study, the temperature estimates of regional metamorphism deduced by OTERDOOM (1978) from a study on tremolite- and diopside-bearing assemblages in ultramafic rocks along a north-south profile range from 200°C (Davos) to 400°C (Engadine). These data combined with the measured oxygen isotope data allow us to calculate the isotopic composition of our hypothetical metamorphic fluid. Extremely positive values of $\delta^{18}\text{O} = +12\text{\textperthousand}$ to $+15\text{\textperthousand}$ (SMOW) result from these calculations. If the metamorphic fluids derive from marine pore waters a positive shift in the reservoir of more than $10\text{\textperthousand}$ must have accompanied the reequilibration process. In a study of high-grade diagenetic environments of a deep well located in the Salton Sea geothermal field, CLAYTON et al. (1968) calculated a similar positive O-18 shift for their pore fluids.

Small scatter for measured values from individual localities even including the low-grade metamorphic regions, and the observation that lithic carbonate fragments in ophiolite breccias also show altered isotope signatures which are equivalent to values

for calcite veins, are construed as evidence that homogenizing metamorphic fluids were pervasive. Fluid transport was not restricted to large fractures and veins within these rocks. We may further speculate that the fluid was marine-derived pore water, which was expelled at increasing rates during times with higher heat flow (WALTHER & ORVILLE 1982). A first phase of Alpine metamorphism, dated as middle Cretaceous (DEUTSCH 1983), affected the South Pennine sediments within a few tens of million years after their time of deposition. By the middle Cretaceous for example, the Berriasian pelagic sediments had traversed a short diagenetic history of 40 million years. Today, 40 million years old pelagic sediments commonly show few signs of lithification; they are commonly preserved as a stiff carbonate ooze rich in marine pore fluids (MATTER et al. 1975). Oxygen isotope reequilibration in the South Pennine sediments must be examined within this sedimentological context and the diagenetic stage reached by a pelagic sediment before entering a metamorphic domain may be a main controlling factor on the degree of isotopic change.

The few available oxygen isotope data from lower Austroalpine sediments remain enigmatic within our scenario. Are the distinctly less negative values an indicator for a completely different diagenetic and metamorphic history for tectonic elements which are superimposed today? Oxygen isotope data alone do not give conclusive information on the metamorphic history of these sediments. Additional mineralogical data and measurements of illite crystallinity will show whether a jump postulated between South Pennine and lower Austroalpine units is real (see NIGGLI 1973).

Conclusions

Using methods of oxygen and carbon isotope geochemistry we attempted to trace the early history of calcite in ophicarbonates. The carbon isotope composition of calcite in ophicalcites and in associated pelagic sediments falls within the range of normal marine values. We therefore conclude that the source of all the CO_2 in the studied carbonates is of marine origin. The oxygen isotope data in vein calcites, calcite cements and pelagic carbonates show the imprint of Alpine metamorphism. Along the north-south transect studied in the South Pennine nappes of eastern Switzerland, a decrease from values of $\delta^{18}\text{O} = -6\text{\textperthousand}$ near Klosters to values of $\delta^{18}\text{O} = -16\text{\textperthousand}$ in the upper Engadine is related to an increase in metamorphism along this section. The analyzed carbonates reequilibrated with penetrative fluids at the time of peak metamorphism. At the time of early eo-Alpine metamorphism, the sediments analyzed were still rich in marine-derived pore fluids. A high fluid to sediment ratio facilitated the complete elimination of original oceanic or hydrothermal oxygen isotope values. Calculated equilibrium isotope compositions of the hypothetical fluids fall within a range of $\delta^{18}\text{O} = +12\text{\textperthousand}$ to $+15\text{\textperthousand}$. Oxygen isotope data, we conclude, are therefore not a reliable tracer for possible early hydrothermal activity along Jurassic fracture zones in Alpine environments. Mineralogical information, such as the common impregnation of ophi-carbonates by hydrogrossular, may be of more significance.

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