Diversity of carbonate occurrences at the Fizh massif in the northern part of the Oman ophiolite; a preliminary report

Tomoaki MORISHITA and Shoji ARAI

Department of Earth Sciences, Faculty of Science, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

Abstract: Various occurrences of carbonates can be observed along the wadi (= valley with or without streams) within a mantle section of the Oman ophiolite. The occurrences of carbonates can be divided into three types based on the field observations; (Type 1) precipitates in springs on wadi floors, (Type 2) matrix of wadi sediments and (Type 3) small veins filling cracks in mantle peridotite. These carbonates were identified by X-ray powder diffraction analysis. The precipitates from water on the wadi floors are mainly composed of aragonite with trace amount of calcite. The matrix of the wadi sediments are composed of calcite. The veins in the mantle peridotite are mainly composed of magnesite with trace amount of aragonite. Magnesite was formed by the reaction between the peridotite and CO_2-rich hydrothermal fluid along cracks. The magnesite veins were possibly the conduit for the CO_2-rich aqueous fluid (primary fluid) which has been responsible for serpentinization of the peridotite. The CaO component in the peridotite was selectively removed to fluid (secondary fluid) during serpentinization. Aragonite was precipitated from the secondary fluid, which is the CaO and CO_2-rich spring water, at low-pressure conditions due to high rate of deposition on rapid cooling. Aragonite cemented the wadi sediments and was successively inverted to calcite during diagenesis.

1. Introduction

Various occurrences of carbonates are visible along wadis within the mantle section of the Oman ophiolite. It is possible that the hydrothermal solution circulates through and flows out from the peridotite with precipitation of carbonates. In this paper, we try to identify the carbonate by X-ray powder diffraction analysis to know carbonate species depending on the mode of occurrences. This is the first step to know the formation conditions of the carbonate minerals within the Oman peridotite.

Serpentinization is an extremely common process in ultramafic rocks at the low -temperature regime. Olivine and pyroxenites are converted to serpentine minerals by

reaction with water at low temperatures. The mobility of chemical components from the original peridotite during serpentinization process has been controversial (e.g., Page, 1967 ; Thayer, 1967). The serpentinizaton process is possibly now in progress in ultramafic section of the Oman ophiolite (Barnes et al., 1978). It is highly possible that the solution responsible for the serpentinization in deeper parts precipitate carbonates at the surface. We can get some information about serpentinization from the carbonate minerals which show various modes of occurrence.

2. Geological setting

The Oman ophiolite crops out about 500 km and up to 80 km wide along the stretch of the Oman Mountains and is one of the largest and best-exposed ophiolite complexes in the world (e.g., Coleman, 1981 : Nicolas, 1989). It has been considered as a fragment of oceanic lithosphere, formed in the Tethys ocean at 95-100 Ma and then obducted onto the eastern Arabian margin after a period of 15 m.y. later (Tilton et al., 1981 ; Montigney et al., 1988). We investigated the Fizh massif which is located in the northern part of the Oman ophiolite (Nicolas et al., 1988) (Fig. 1).
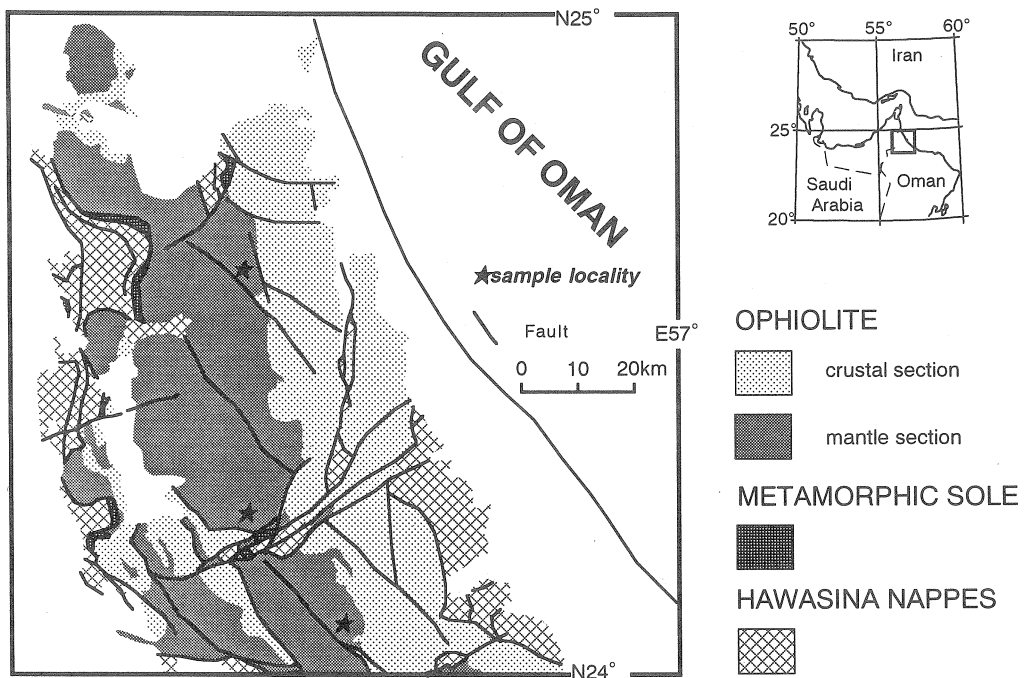

Figure 1. Simplified geological map of the Fizh massif of the northern Oman ophiolite after Ministry of Petroleum and Minerals (1992).

3. Occurrences of carbonates

We can observe various occurrences of leucocratic carbonate minerals along the wadis which cut the Oman ophiolite.   The occurrences of carbonates are divided into three types on the basis of the field observations.

First occurrence (Type 1 carbonate) is precipitates within water on the wadi floor (Plate I).   The carbonate precipitation occurs at water pools (Plate I-a) and on cracks of peridotite exposed on the floor (Plate I-d).   White and soft carbonate mousse typically covers the floor of the pool (Plate I-a).   Some water pools, isolated from the running stream, are partly to completely covered with thin carbonate film (Plates I-e, f).   This type of the water pool has been called "white pool" (Hanna, 1995).   Water temperature is apparently higher in the pool than in stream on the wadi.   The water is sometimes babbling in the pool (Plate I-b).   The gas was suggested as methane (Hanna, 1995). Chimney-shaped carbonate precipitates occur sometimes along the crack of the peridotite open to the stream water (Plate I-c). The water is intermittently vesiculating from the top of the chimney.   This possibly indicates *in situ* carbonate precipitation from the water flowing out from the crack of the peridotite.   Carbonate precipitates are usually dispersed by stream current and are deposited on the wadi bottom (Plates II-a, b, c).   Interstices between pebbles on the wadi floor are partly filled with the carbonate mousse, which consolidates to various degrees.

Second occurrence (Type 2 carbonate) is as matrix of wadi sediments (Plate II-d). These unique sedimentary rocks consist of many gravels (from fine pebble to boulder) within white carbonate matrix, which is hard and very fine-grained.   The sedimentary rocks are characteristically available from the lowest part of the crustal section to the uppermost mantle section in the massif.   The transition from the wadi gravels with soft matrix of carbonate mousse (Plates II-a, b, c) to this type of sediments with hard carbonate matrix (Plate II-d) can be recognized in the field.

Third occurrence (Type 3 carbonate) is as veins in the peridotite body.   The carbonate veins (Plate III-a) or network (Plate III-b) have various dimensions, up to several meters in thickness (Plate. III-c), sometimes forming the carbonate matrix of serpentine breccia. Very hard and purely white porcelain-like boulders are frequently observed on the wadi (Plate III-d).   They are possibly derived from the thick carbonate veins.   The carbonate shows fine-grain aggregate textures (less than 0.02 mm).

4. X-ray powder diffraction (XRD) analysis

XRD analysis for carbonates was performed using a Rigaku goniometry having Cu Kα radiation, operated at 40 kV and 30 mA at Kanazawa University.   The XRD patterns of carbonates are shown in Fig. 2. The precipitates in water pool (Type 1 carbonate) are

composed of aragonite with trace amount of calcite (Figs. 2 A, B). The hard matrix of wadi sediments (Type 2 carbonate) is composed of calcite (Figs. 2 C). The carbonate veins in the peridotite (Type 3 carbonate) body are mainly composed of magnesite with trace amount of aragonite (Figs. 2 D, E, F).

5. Discussion

At normal temperatures and pressures, aragonite is metastable and readily inverts to calcite (e.g., Crawford and Hoersch, 1972 ; Calson, 1980). Aragonite is, however, frequently found in hot springs (e.g., Kitano, 1997). There are some factors controlling the precipitation of aragonite at normal conditions ; temperature, pH value of solution, presence or absent of inorganic ions and certain organic materials, and the rate of precipitation (e.g., Kitano, 1964, 1997). Magnesium-ion (Mg^{2+}) content in the solution is one of the most important factors for the crystallization of aragonite (e.g., Kitano, 1964, 1997). It has never been clear, however, that whether the water in the pool on the wadi floor is rich in Mg^{2+} or not although is expected to be rich in Mg^{2+} because of the Mg-rich environment of the mantle-derived peridotite. It is noteworthy that aragonite is precipitated at both a water pool and on the crack of peridotite where the spring water is in contact with the running water on the wadi floor. This relationship possibly suggests that the CaO and CO_2 -rich hydrothermal solution is abruptly cooled to precipitate the excess carbonate. It can be considered that aragonite (Type 1 carbonate) was crystallized instead of calcite due to high precipitation rate on rapid cooling of the solution. We need to know the composition of water to specify the main factor for the aragonite crystallization at normal conditions.

As described above, aragonite precipitates (Type 1 carbonate) are dispersed by scream current and are deposited at the wadi floor. The calcite matrix of the wadi sediments (Type 2 carbonate) can be interpreted to be of diagenetic origin from the aragonite, because we can observe various transitional sediments from gravels with soft carbonate (aragonite, Type I) mousse matrix to the wadi sediments with hard carbonate (calcite, Type 2) matrix.

The crystal structure of magnesite is similar to that of calcite but with a slightly smaller cell due to the smaller size of Mg^{2+}. Peridotites are commonly transformed to serpentines at low- to medium-grade metamorphic conditions. If CO_2 is available during the serpentinization process, magnesite may be formed with serpentine (e.g., Evans and Trommsdorff, 1974). Origin of the magnesite veins (Type 3 carbonate) are, therefore, due to the penetration of hydrothermal fluids which contain CO_2. Trommsdorff and Evans (1977) showed a T-X_{CO_2} diagram at 2 kbar for the system CaO-MgO-SiO_2-H_2O-CO_2 containing antigorite, talc, forsterite, tremolite, diopside, calcite, dolomite and magnesite. Their diagram shows that the assemblage serpentine+magnesite is stable in higher-X_{CO_2} condition (Fig. 3).

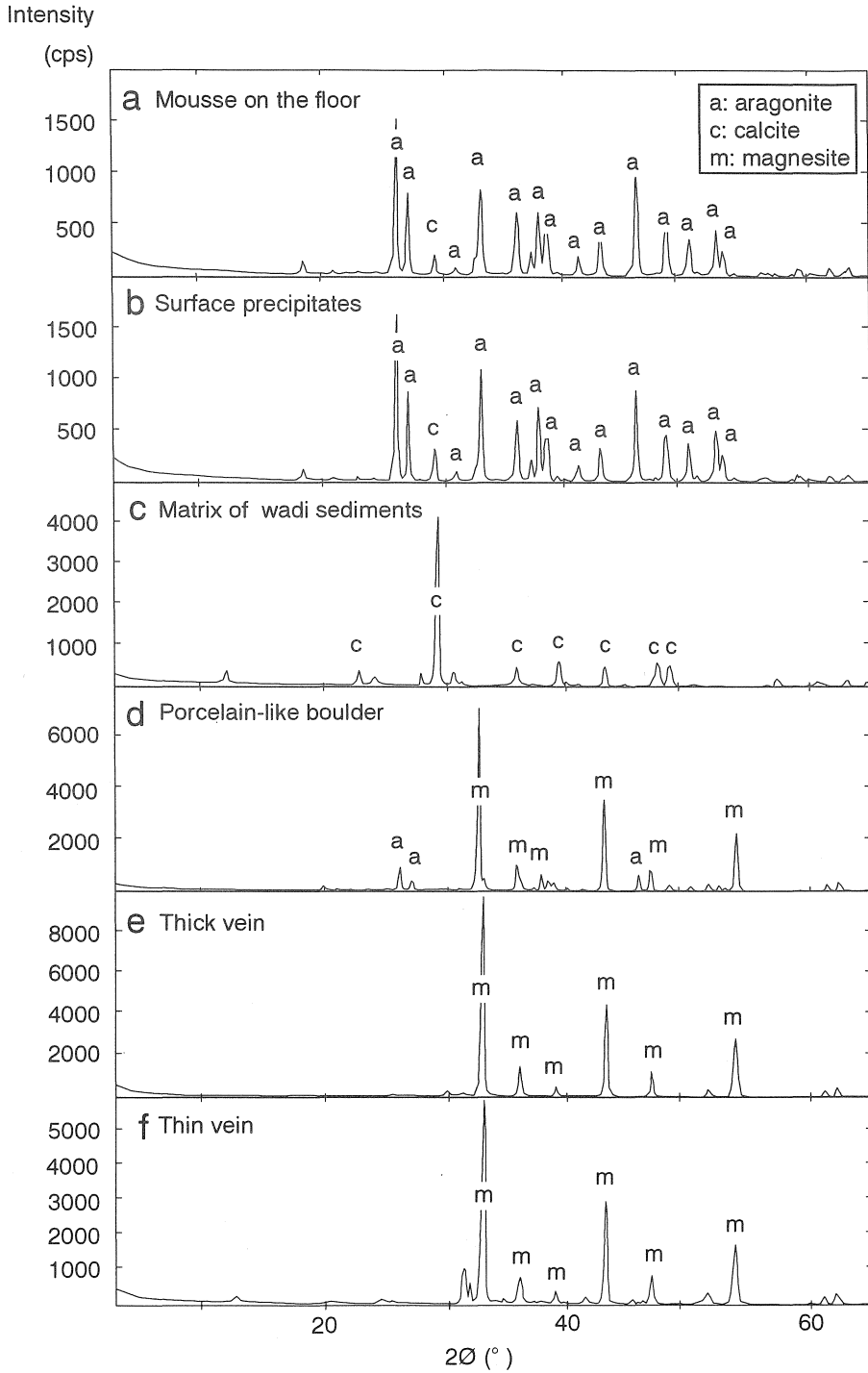Rocks consisting of serpentine and carbonate minerals, which are called ophicar-

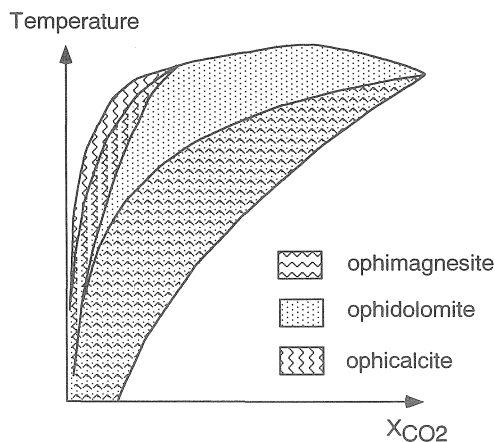Figure 2. The XRD patterns of carbonates.

Figure 3.   Isobaric Temperature-X_{CO_2} in fluid composition diagram showing the relative stability relations
for ophicalcite, ophidolomite and ophimagnesite after Trommsdorff and Evans (1977).

bonates, are characteristic of ophiolitic peridotites (e.g., Ohnmacht, 1974 ; Evans and
Trommsdorff, 1974 ; Trommsdorff and Evans, 1977; Früh-Green et al., 1990).   The origin
of ophicarbonate rocks has been controversial.   Additional data from this area will also
give us information on the origin of ophicarbonate rocks.

The other problem is the relationships between the hydrothermal fluid as an agent of
serpentinization and CaO and CO_2-rich fluid as an agent of aragonite precipitation at the
surface.   The mobility of chemical components from the original peridotite during ser-
pentinization process has been debated by many workers (e.g., Page, 1967 ; Thayer, 1967).
Thayer (1966) suggested that serpentinization is a constant-volume metasomatic process
which requires removal of about 30 wt. % of the original bivalent oxides (MgO, FeO and
CaO) and SiO_2 in peridotite. Page (1967), on the contrary, suggested that the ratio of CaO
to MgO removed is consistently larger than the ratio of these oxides in the original
peridotite.   Barnes et al. (1967), Barnes and O'Neil (1969), and Golding (1971) also
suggested that the CaO component is selectively removed during serpentinization.   Thayer
(1967) argued against Page (1967) that determination of the behavior of CaO during
serpentinization requires precise modal data which might be very difficult to obtain. The
CaO content is lower in serpentinite than in peridotite from the Oman ophiolite (Fig. 4).
Despite some difficulties, schematic reactions are suggested as follows ;
(1)   peridotite + primary fluid (H_2O+CO_2)→serpentinite+$MgCO_3$ (magnesite) +secon-
      dary fluid (CO_2+H_2O+CaO)
          for serpentinization,
(2)   secondary fluid (CO_2+H_2O+CaO)→$CaCO_3$ (aragonite) +H_2O
          for aragonite precipitation, and
(3) $CaCO_3$ (aragonite)→$CaCO_3$ (calcite)

for diagenesis.

The primary CO_2-bearing fluid, the product of reaction (1), is heated due to the exothermic nature of serpentinization reaction.　This relation is consistent with the fact that the water in the pool as an agent of aragonite precipitation is slighly higher in temperature than the stream water.
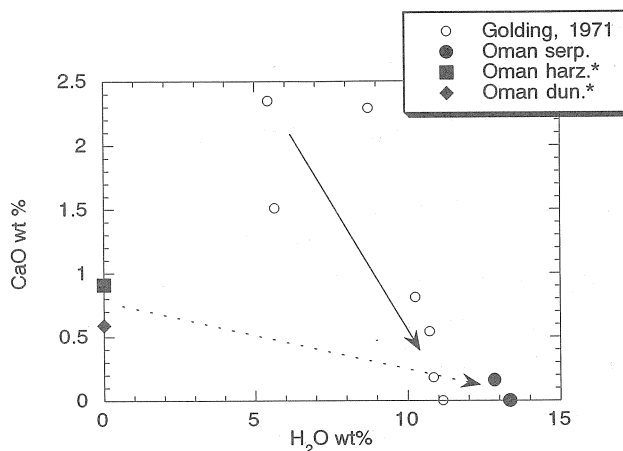

Figure 4. Relationships between H_2O wt. % and CaO wt. % for serpentinites.　The H_2O contents are an
indicator of degree of serpentinization.　Note that the CaO contents in the serpentinites
(Golding, 1971) decrease with increasing H_2O contents (arrow).　Data for serpentinites in the
Oman ophiolite (Oman serp.) are from Stanger (1985).　Data for harzburgite and dunite in the
Oman ophiolite (Oman harz* and Oman dun*, respectively) are from Boudier and Coleman
(1981).　Although the peridotite consists of SiO_2, Al_2O_3, FeO, MgO, CaO Cr_2O_3 and NiO more
than 99 wt. % in total, the H_2O contents were not determined. The CaO content is lower in
serpentinite than in peridotite from the Oman ophiolite (broken arrow).

6. Conclusion

The carbonates within the mantle section of the Oman ophiolite are divided into three types.　Type 1 carbonate is precipitates within water on the wadi floor and consists of aragonite with trace amount of calcite.　Aragonite was crystallized instead of calcite due to high precipitation rate on rapid cooling of the solution at normal conditions.　Type 2 carbonate is as matrix of wadi sediments and consists of calcite.　Calcite was of diagenetic origin from aragonite (Type 1 carbonate) which was dispersed by stream current and was deposited at the wadi floor.　Type 3 carbonate is as veins in the peridotite

body and consists of magnesite with trace amount of aragonite.   Magnesite was formed due to the penetration of hydrothermal fluids which contain CO_2 during serpentinization of the peridotite.

The schematic relationships among these carbonates can be shown as follows ;
(1)   peridotite+ primary fluid (H_2O+CO_2)→serpentinite+$MgCO_3$ (magnesite, Type 3 carbonate) + secondary fluid (CO_2+H_2O+CaO), for serpentinization,
(2)   secondary fluid (CO_2+H_2O+CaO)→$CaCO_3$ (aragonite, Type 1 carbonate)+H_2O, for aragonite precipitation, and
(3) $CaCO_3$ (aragonite)→$CaCO_3$ (calcite, Type 2 carbonate), for diagenesis.

Acknowledgments

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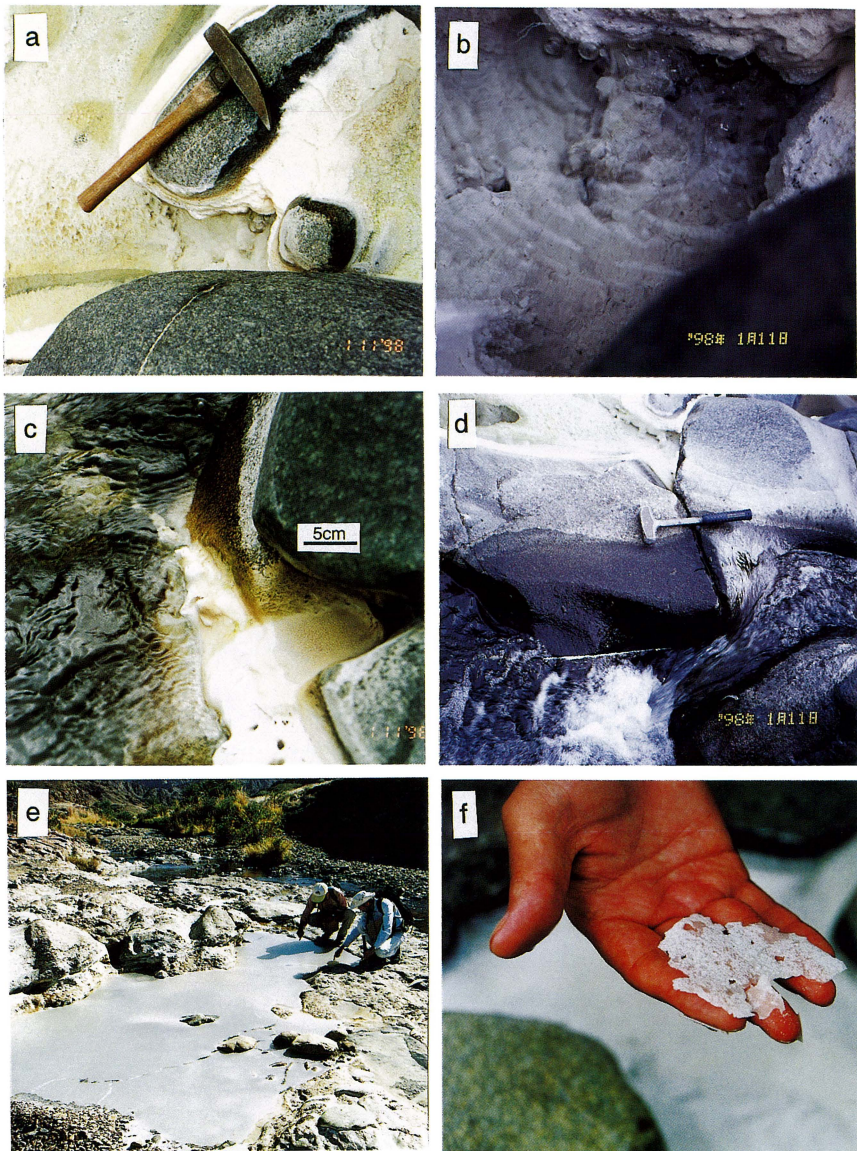
Plate I

(a) Carbonate precipitates. White and soft carbonate mousse typically covers the floor of the pool.
    Note that the water is sometimes babbling.

(b) Babbling in the pool.

(c) Chimney-shaped carbonate precipitates.

(d) Carbonate precipitation occurs on cracks of peridotite exposed on the floor.

(e) Water pool is completely covered with thin carbonate film. It is called "white pool" (Hanna, 1995).
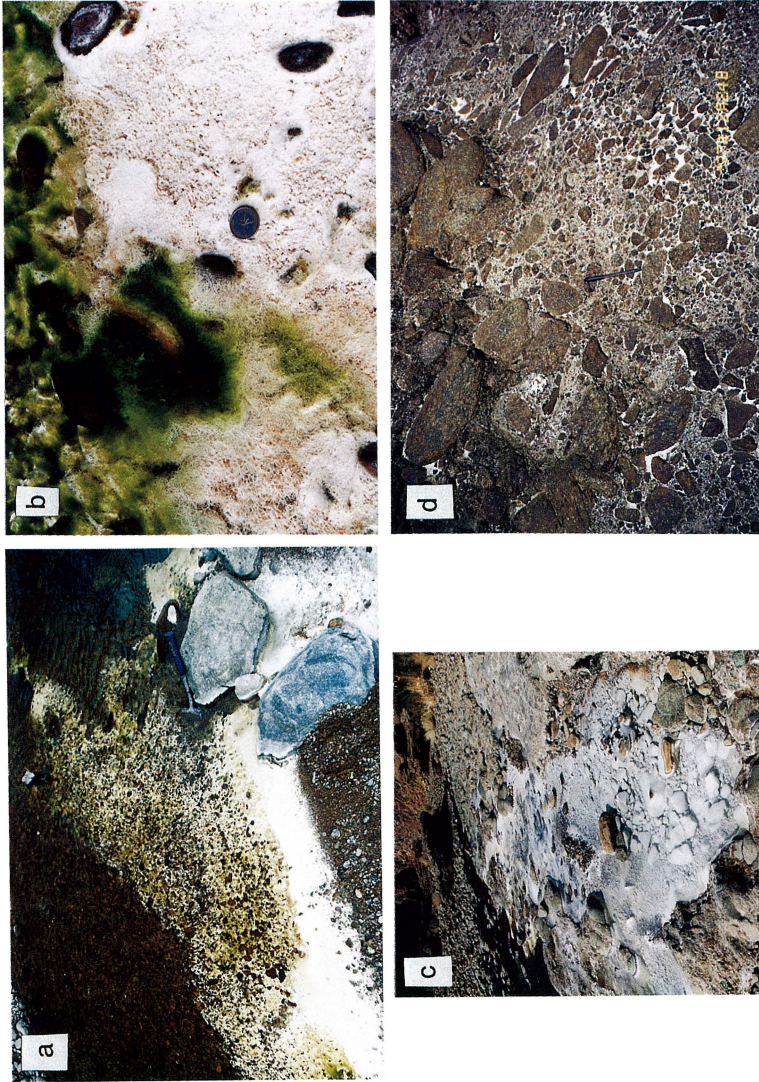
(f) The thin carbonate film of (c).

Plate II
(a) Interstices between pebbles on the wadi floor are partly filled with the carbonate mousse dispersed by
    stream current.
(b) Algae in the water pool are gradually replaced by carbonate precipitates dispersed by stream current.
    Coin is 2.5 cm in diameter.
(c) Interstices between pebbles on the wadi floor are filled with carbonate mousse.
(d) Matrix of wadi sediments. These unique sedimentary rocks consist of gravels (from fine pebble to
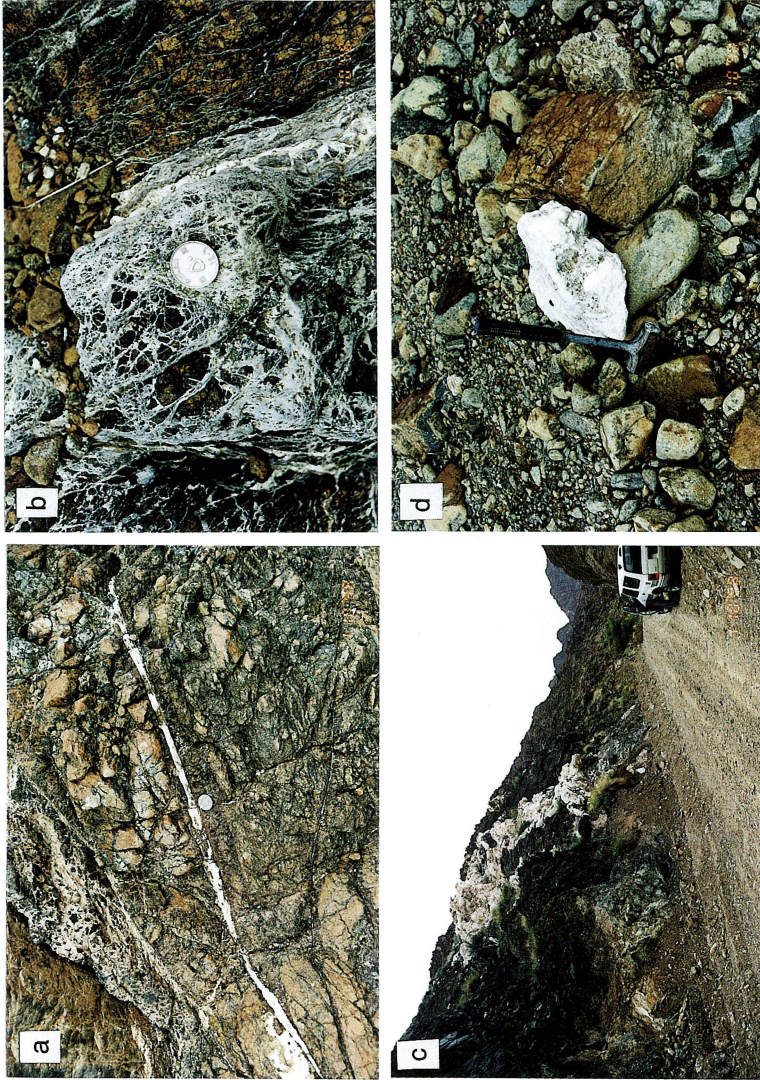   boulder) within white Carbonate-rich matrix.

Plate III
(a)   Thin carbonate vein in the peridotite. Coin is 2.5 cm in length.
(b)   Carbonate network in the serpentine breccia. Coin is 2.5 cm in length.
(c)   Thick carbonate vein in the peridotite.
(d)   Porcelain-like boulder. It is possibly derived from the thick carbonate veins.