

# Diagenetic volume-for-volume replacement: force of crystallization and depression of dissolution

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## Abstract

The concept of force of crystallization is combined with that of depression of dissolution to explain diagenetic volume-for-volume replacement in both cases, either when the pressure is increased in early sedimentary settings, or when it is diminished in a late exposure. Also, a new textural criterion is added to the three classical ones in order to recognize diagenetic volume-for-volume replacement, and calculations are carried out to estimate the speed of the replacement.

**KEYWORDS:** force of crystallization, volume-for-volume replacement, dissolution, diagenesis.

## Introduction

The diagenetic volume-for-volume replacement of one mineral by another through a film located between them is a concept that has attracted scientific attention in the last few years. The first to speak of a force of crystallization mechanism was Ramberg (1947). Some years later, Weyl (1959) wrote about a crystal growing in the region of stress, in which a solution film separates the crystal surface from the limit represented by another mineral. Afterwards, Maliva and Siever (1988*a,b*) developed the volume-for-volume replacement model driven by the overpressure created by the growth of the authigenic crystal as a force of crystallization. Later on, Dewers and Ortoleva (1989, 1990*a,b*) introduced an ambitious quantitative reaction-transport model.

Our aim is to provide a new explanation for the volume-for-volume replacement mechanism, by combining the concept of force of crystallization with the concept of depression of dissolution. We call depression of dissolution the decrease of pressure caused by the dissolution of the host

phase. It is shown that the whole process can be driven by this depression, for it reduces the solubility of the authigenic crystal and, thus, causes its precipitation.

In this work we avoid conventional models for diagenetic replacement based on pore-water undersaturation with respect to the bulk host phase. Instead, all these phenomena are explained as based on the dependence of the solubility of both the authigenic and the host mineral phases upon the pressure. Then, a change in the pressure conditions, as a result of the sedimentary process, can be considered as the origin of the volume-for-volume replacement. This is a simple and powerful model, for it allows us to explain easily the diagenetic replacement process even if it takes place through several consecutive and converse steps, as happens when, once the authigenic crystal has grown, part of it is replaced in a reversely directed process.

Also, we present some examples of diagenetic replacement from the Northern Iberian Peninsula (Elorza and Orúe-Etxebarria, 1985; Elorza and Bustillo, 1989; Elorza *et al.*, (1991), which fully

match the three criteria of Maliva and Siever (op. cit.) for volume-for-volume replacement, and add a fourth criterion for the force of crystallization-controlled replacement. Moreover, we offer an explanation for the observation that, in the same bulk rock, first, a carbonate matrix was replaced by quartz, and later, the reverse took place, when a microquartz matrix was replaced by euhedral carbonate crystals.

### Dependence of solubility upon pressure

From equilibrium thermodynamics theory, it is shown that the maximum concentration  $X_m$  at which a substance can be found dissolved as a solute in a liquid depends on pressure  $P$  and absolute temperature  $T$  according to

$$X_m = X_0 \exp - \left\{ \frac{\Delta \bar{V}(P - P_0)}{RT} \right\} \quad (1)$$

where  $X_0$  is the solubility at pressure  $P_0$  and temperature  $T$  and  $\Delta \bar{V} = \bar{V} - \bar{V}_0$  is the partial molal volume change for dissolution,  $\bar{V}$  and  $\bar{V}_0$  being the partial molal volume of the dissolved substance and of the pure substance respectively. Then, the solubility dependence on pressure can be studied through its derivative

$$\left( \frac{\partial X_m}{\partial P} \right)_T = -X_m \frac{\Delta \bar{V}}{RT} \quad (2)$$

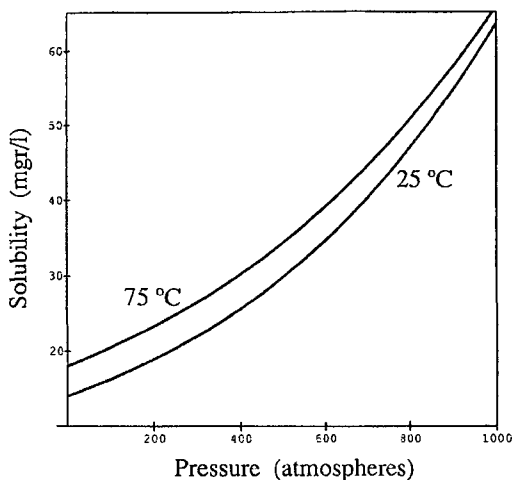


FIG. 1. Solubility of calcite in water as a function of pressure, at 25°C and 75°C. Data of the solubility of calcite at atmospheric pressure have been taken from the CRC Handbook of Chemistry and Physics.

$X_m$  increases or diminishes when  $P$  increases, depending on whether  $\Delta \bar{V} = \bar{V}_o - \bar{V}$  is positive or negative. In our case, we treat the condition that increasing the pressure increases the solubilities  $X_{1m}$  of the host phase and  $X_{2m}$  of the authigenic crystal. Conversely, decreasing the pressure will diminish  $X_{1m}$  and  $X_{2m}$ . This assumption is necessary for our model and, in fact, it includes virtually all the common sedimentary minerals, as pointed out by Maliva and Siever (1988 *a,b*).

Figure 1 shows the solubility of calcite in water as a function of pressure, at 25°C and 75°C, according to equation (1). It has been considered that the water solution does not increase its volume when such small quantities of solute are dissolved, so that the partial molal volume of the dissolved calcite is zero and its partial molal volume change for dissolution is  $\Delta \bar{V} = -\bar{V}_o$ . The solubilities and density of calcite have been taken from the CRC Handbook of Chemistry and Physics (59th edition).

### Depression of dissolution

In this section we describe the process by which the host phase is progressively substituted by an authigenic crystal, using a model driven by the depression created by the dissolution of the host phase.

Before any replacement starts, the two phases can be present subject to certain conditions. The temperature and pressure must be such that the concentration of the host mineral  $X_1$  in the surrounding liquid equals its solubility

$$X_1 = X_{1m} \quad (3)$$

and the concentration of the phase, which is to produce the authigenic crystal,  $X_2$  is less or equal to its own solubility

$$X_2 \leq X_{2m} \quad (4)$$

While relations (3) and (4) hold, no more host phase is dissolved and no authigenic crystal is formed, but a dynamic equilibrium is maintained between the solid and the liquid.

In principle, relations (3) and (4) can be invalidated in two different ways: first, the actual concentrations  $X_1$  and  $X_2$  in the liquid can vary due to transport effects, for instance a diffusion process which changes the liquid composition, and second, the temperature and pressure conditions can vary for any reason which would make the solubilities  $X_{1m}$  and  $X_{2m}$  change, for instance the setting of the sedimentation.

In any case, if  $X_1$  diminishes due to transport effects, or  $X_{1m}$  increases because of some change in the temperature and pressure conditions, relation (3) does not hold any longer and the host phase will start to dissolve in the surrounding liquid. Then, the rate of its grain volume change would be

$$\frac{dV_1}{dt} = K_1 S_1 (X_1 - X_{1m}) < 0 \quad (5)$$

where  $K_1$  is the rate coefficient of the forward dissolution and  $S_1$  the active surface area, both referred to the host phase.

This means that the volume  $V_1$  of the host phase diminishes. Then, if the liquid flow is maintained, the dissolved mineral is carried away, so that  $X_1$  would remain smaller than  $X_{1m}$  and the dissolution of the host phase would progress, giving rise to a negative pressure change.

$$dP = \left( \frac{\partial P}{\partial V} \right)_T dV_1 < 0 \quad (6)$$

With this depression originated by the dissolution of the host phase, the solubility  $X_{2m}$  decreases the relation (4) no longer holds and the authigenic phase starts precipitating. Then, the rate of its volume change is

$$\frac{dV_2}{dt} = \nu_{20} S_2 \frac{dn_2}{dt} > 0 \quad (7)$$

where  $\nu_{20}$  is the molecular volume of the pure authigenic crystal,  $S_2$  its active surface area and  $dn_2/dt$  the number of new molecules which arrive at the surface, either by a hydrodynamic flow or by means of diffusion, and precipitate per area unit and per second.

If the rock is not very viscous, the growing of a new crystal may result in displacement of its surroundings. However, in the case in which we are interested, when the bulk rock does not flow at all due to its high viscosity, this implies a volume constraint condition and the replacement takes place volume-for-volume. Then

$$dV_1 + dV_2 = 0 \quad (8)$$

and the pressure remains constant, because

$$dP = \left( \frac{\partial P}{\partial V} \right)_T (dV_1 + dV_2) = 0 \quad (9)$$

At this pressure, a new dynamic equilibrium is developed, in which the authigenic crystal grows inwards the host phase, in a process driven by the depression caused by the dissolution of the host

phase. Then

$$\frac{dn_2}{dt} = \frac{K_1}{\nu_{20}} (X_{1m} - X_1) \quad (10)$$

as deduced by combining equations (5), (7) and (8) and equating the respective active surface areas  $S_1$  and  $S_2$ .

Equation (10) controls the whole dynamic equilibrium process, since the actual pressure will be a function of the left hand side, whereas the right hand side is a function of that pressure, for  $X_{1m}$  depends on  $P$ . This means that, in order for the process to proceed, it needs the assistance of two transport effects: first, the arrival of a determined number of new molecules of the authigenic crystal per time and area units  $dn_2/dt$ , whose crystallization will result in keeping the pressure above a certain value and so the solubility  $X_{1m}$  above that of the host phase, and second, the evacuation of the dissolved host phase, so that its concentration  $X_1$  in the liquid is not increased, but remains under  $X_{1m}$ .

Both transport effects must take place in the thin space between the two surfaces, within the liquid that fills it. The liquid has a certain composition given by the concentrations  $X_1$  and  $X_2$  of the two phases. In a particular region it may happen that the solubilities  $X_{1m}$  and  $X_{2m}$  of the two components, determined by pressure and temperature conditions, are such that  $X_1 < X_{1m}$  and  $X_2 > X_{2m}$ . Then, while the liquid goes through that region, the host phase is dissolved and the authigenic mineral precipitates, in a dynamic equilibrium controlled by equation (10). Consequently, the liquid composition changes

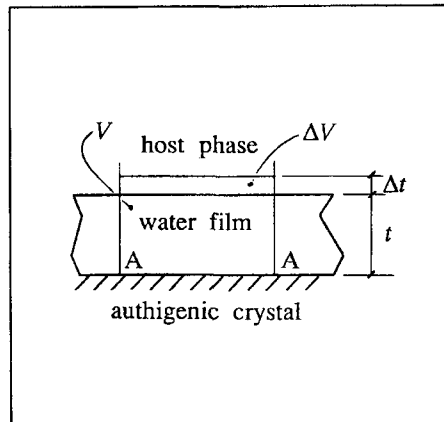


FIG. 2. Diagrammatic representation of a zone of the water film between the authigenic crystal and the host phase.

while it goes through this region, in the sense that  $X_1$  increases and  $X_2$  diminishes. Where relations (3) and (4) are re-established, the two sides of equation (10) are unbalanced, the dynamic equilibrium is not maintained and the volume-for-volume replacement ceases.

### Estimate of the speed of replacement

The diagenetic volume-for-volume replacement depends on parameters such as the concentrations of the dissolved minerals in the flowing water and the speed of the flow, which are impossible to determine. However, in this section we try to get an idea of the order of the speed at which this sort of replacement can occur.

Figure 2 represents a zone A-A of the water film, of thickness  $t$  under a pressure  $P_0 = 1$  atm, located between the calcite of the host phase and the growing crystal. If a high overpressure causes an increase in the solubility of calcite from  $X_0$  to  $X_m$  (see equation 1 and Fig. 1), more calcite will be dissolved and the thickness of the film in that region passes from  $t$  to  $t + \Delta t$ .

The increment  $\Delta t$  provides the water flow with an extra-volume  $\Delta V$ , which is the origin of the so-called 'depression of dissolution' and also provides the necessary volume for the authigenic crystal to grow. If  $V$  is the initial volume of the film in the zone A-A, it can be written straightforwardly that

$$\frac{\Delta V}{V} = \frac{\Delta t}{t} = \frac{X_m - X_0}{\rho} \quad (11)$$

where  $\rho$  is the density of the calcite.

Then if the saturated flowing water of region A-A is renewed by undersaturated water every time period  $H$  so that calcite is replaced by the authigenic crystal, the time needed for this to progress a distance  $d$  against calcite will be

$$T = \frac{\rho}{X_m - X_0} \frac{Hd}{t} \quad (12)$$

The density of calcite is  $\rho = 2.71$  g/cm<sup>3</sup> and its solubility at different pressures can be evaluated from Fig. 1. The value of  $H$  will depend on the length of the region A-A, as well as on the speed of the water flow, variables which are very difficult to estimate accurately. For this reason,  $H$  was given several values in Table 1.

This table, completed by using equation (12), shows the time that the authigenic crystal takes to advance 1 mm, assuming that the thickness of the water film is 10  $\mu$ m.

TABLE 1. The time  $T$  taken by the growing crystal to progress 1 mm against the host phase is estimated for various pressures  $P$  from Eq. (12). It is assumed that the saturated water of the film is renewed every time period  $H$  and that the thickness of the water film is 10  $\mu$ m.

$P$ (at.)	$H$	$T$ (years)
100	1 day	$3.3 \times 10^5$
	1 week	$2.3 \times 10^6$
	1 month	$1.0 \times 10^7$
250	1 day	$1.2 \times 10^5$
	1 week	$8.1 \times 10^5$
	1 month	$3.5 \times 10^6$
500	1 day	$4.7 \times 10^4$
	1 week	$3.3 \times 10^5$
	1 month	$1.4 \times 10^6$
750	1 day	$2.5 \times 10^4$
	1 week	$1.8 \times 10^5$
	1 month	$7.7 \times 10^5$
1000	1 day	$1.5 \times 10^4$
	1 week	$1.1 \times 10^5$
	1 month	$4.6 \times 10^5$

### Examples of diagenetic replacement

In this section we use several examples to illustrate the diagenetic replacement. All are upper Cretaceous, but the tecto-sedimentary domains are different: Basque Arc (deeper marine sediments), Navarro-Cantabrian Trough (distal platform) and Northern-Castilian Platform (proximal platform) (Amiot *et al.*, 1983). All cases are within the Basque-Cantabrian Basin related to the continental margin of the Northern Iberian Peninsula. The examples have been selected from previous works as indicated in the Introduction.

#### *Depositional and biogenic sedimentary structures*

During the early silicification process that affected the carbonate turbidites of the Plentzia Formation, Basque Arc (Elorza and Bustillo, 1989), the different laminations offered by the Bouma's sequence intervals Tb, Tc and Td have been perfectly preserved (Fig. 3). Inside the bedded and nodular cherts, the diagenetic replacement was carried out in such a way that the depositional sedimentary structures were not modified, but remained in continuity with the carbonate host.

Another proof of diagenetic replacement is the selective silicification of *Thalassinoides* burrow networks (Fig. 4). The nodular cherts from the Ribera Alta Formation, Navarro-Cantabrian

Trough (Elorza *et al.*, 1991), with original shapes, stand out without compaction and follow the original bedding. Later, the nodular chert can have suffered a strong tripolization process, allowing an important input of calcium and magnesium carbonates, which would be the origin of the individual euhedral dolomite crystals, as will be seen below.

#### Microscopic evidence

Under the microscope, diagenetic replacement can be observed to satisfy the three textural criteria of Maliva and Siever (1988*a,b*): (1) the restriction of host phase dissolution to authigenic-host crystal contacts, (2) the ghosts of host microstructure features in authigenic crystals; and (3) the euhedral

authigenic faces in planar contact with unreplaced host carbonate matrix. We now add a former criterion: (4) the non-existence of voids with geopetal infills, in which the crystal size is increased from the margins of supposed voids towards the inner parts. This emphasises the difference between the volume-for-volume replacement and the infilling of previously open spaces.

The carbonate bivalve shells (*Gryphaea* sp.) from upper Campanian, Northern-Castilian Platform, collected at Laño, south of Vitoria, (Elorza and Orúe-Etxebarria, 1985.) have been affected by an early replacement process (Fig. 5). The carbonate material has been substituted by euhedral megaquartz and the lamellar microstructure is still preserved. The megaquartz corresponds to the end of a silicification front, when the silica

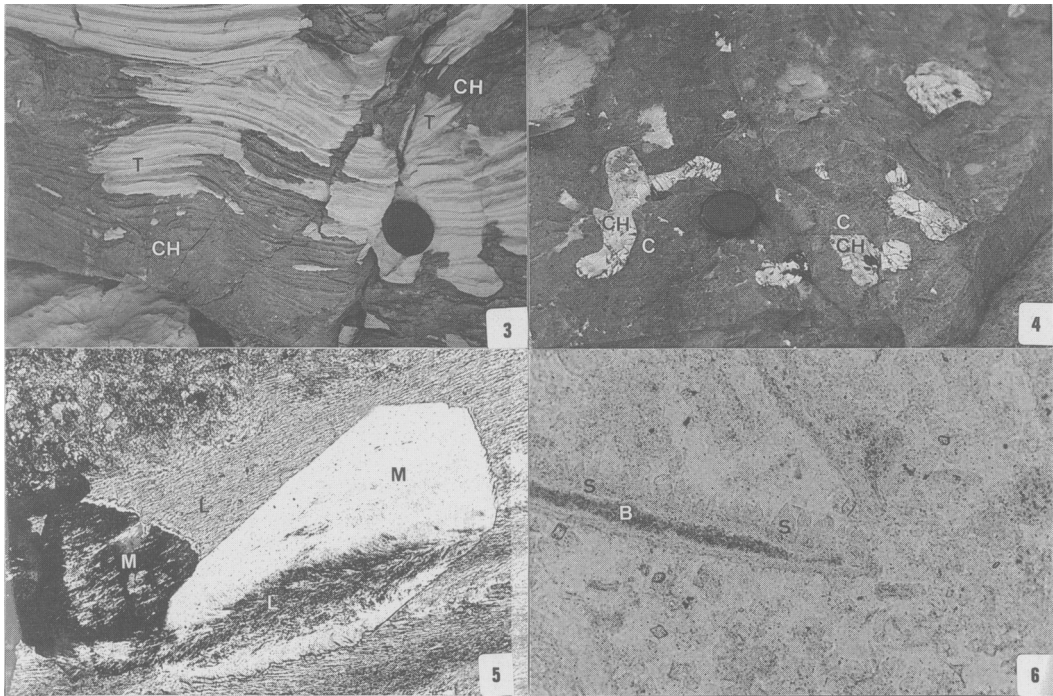


FIG. 3. A detail of the early diagenetic silicification. The convolute lamination is carefully preserved inside the chert (CH) and follows in the host-carbonate turbidite (T). Plentzia Formation, Basque Arc. Lens cap is 5 cm in diameter. FIG. 4. Nodular shapes of chert (CH) controlled by *Thalassinoides* burrow system, inside a calcarenite bed (C). Ribera Alta Formation, Navarro-Cantabrian Trough. Lens cap is 5 cm. in diameter. FIG. 5. Photomicrograph of euhedral megaquartz in a fine morphology replacement (M), in which the lamellar microstructure of the *Gryphaea* sp. shell (L) was preserved. XPL. Photo width = 0.65mm. Upper Campanian, Northern-Castilian Platform. FIG. 6. Bivalve remains (B) with early well developed scalenohedral carbonate cement (S), later completely silicified with different textures, conditioned by the previous original texture. PPL. Photo width = 1.3 mm. Cueva Formation, Northern-Castilian Platform.

concentration is lower (Folk and Pittman, 1971), for which reason the fibrous texture of quartzine-lutecite, very abundant in the outer parts of the shells, is changed to megaquartz. From the Cueva Formation, Northern-Castilian Platform, dated as upper Turonian-lower Coniacian, a bivalve shell fragment can be observed with an early scalenohedral carbonate thoroughly silicified as a large nodular chert (Elorza *et al.*, *op. cit.*). The scalenohedral cement shows a polygonal megaquartz texture and the bivalve fragment a microquartz and fibrous texture (Fig. 6).

In general, the microscope view of many thin sections of nodular cherts from the Cueva Formation (Fig. 7) reveals that a great deal of organic remains (foraminifera, algae, bryozoans, molluscs and other skeletal particles) have been previously silicified and so preserved, before a complete compaction of the host carbonate.

During the middle to late diagenetic stages, the inverse process can take place, of which perfect euhedral dolomite crystals grown within a microquartz matrix of the nodular chert are a common evidence. The nodular cherts from the Ribera Alta Formation, Navarro-Cantabrian Trough, close to the Subijana village (Fig. 8) have been affected by a later 'tripolization process', that generated a macroscopic zonation from concentric tripolized rings in the external crust (2 or more cm thick) to the unaffected inner part. The dolomite crystals are included in the external ring of white highly porous and low density chert, which appears as a 'meeschau'.

In a different sedimentary environment (Fig. 9), the bedded and nodular cherts, together with the host turbidite, from the Plentzia Formation (Basque Arc) have suffered an important distensive fracturing perpendicular to So. The many

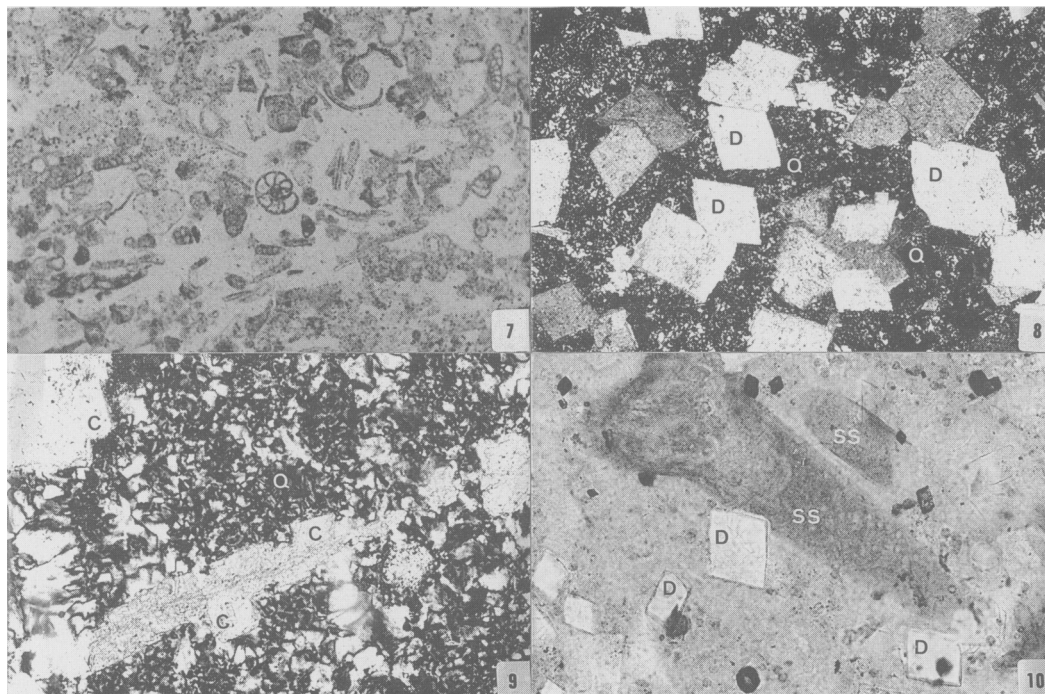


FIG. 7. Microscopic view of a complete silicification in a nodular chert, with micrite-walled benthonic foraminifera, Lituolids, Ataxophragmiids, Ostracodes remains. PPL. Photo width = 3.1mm. Cueva Formation, Northern-Castilian Platform. FIG. 8. Late euhedral dolomite crystals (D) inside a microquartz matrix (Q). XPL. Photo width = 1.3mm. Ribera Alta Formation, Navarro-Cantabrian Trough. FIG. 9. Small fracture infilled by sparry calcite with scarce euhedral calcite crystals (C). These progress from the fracture towards the microquartz matrix (Q) in the carbonate turbidite. XPL. Photo width = 1.3mm. Plentzia Formation, Basque Arc. FIG. 10. Detail of microquartz matrix, with sponge spicule fragments (SS) and euhedral sections of carbonate (D), now replaced by fibrous silica (chalcedonite) indicated by lighter colour. PPL. Photo width = 0.65mm. Cueva Formation, Northern-Castilian Platform.

consecutive cracks are represented by diaclasses infilled by calcite (0.2–2 mm thick). Under the microscope, one can see a massive carbonate phase infilling the cracks and a few euhedral calcite crystals moving towards the microcrystalline quartz matrix. This indicates that the inverse replacement microquartz matrix → euhedral carbonate can happen if the diagenetic conditions are altered.

Alternating conditions can give rise to successive replacements during a long diagenesis. Fig. 10 shows the consecutive steps of the complex sequence carbonate matrix → microquartz (massive chert) → euhedral dolomite → fibrous silica (chalcedonite), which took place in the nodular cherts of the Cueva Formation, Northern-Castilian Platform.

### Discussion

The volume-for-volume replacement starts when either relation (3) or (4) is unbalanced. If

$$X_1 < X_{1m} \quad (11)$$

the host phase starts being dissolved. If the authigenic crystal starts growing, it is because relation (4) does not hold, but

$$X_2 > X_{2m} \quad (12)$$

To determine which of these two processes happens first, one can remember that relations (3) and (4) could be broken in two ways. Effectively, if the liquid composition is altered, the two relations can be unsatisfied. If relation (4) is the first to be broken, the authigenic phase starts precipitating, giving rise to an overpressure (force of crystallization), which increases the solubility of the host phase. This will result in the host phase being dissolved and lead to an equilibrium controlled by equation (10). On the other hand, if relation (3) does not hold first, dissolution of the host phase could start as a consequence of inequality (11). Then, the subsequent depression of dissolution would diminish the solubility of the authigenic phase and cause its precipitation. Again, this would produce an equilibrium controlled by equation (10).

Nevertheless, leaving aside the changes of the liquid composition, relations (3) and (4) can be broken by the change of the pressure conditions that takes place in the successive sedimentary setting and cropping up. In this case, by changing the pressure in any direction, relation (3) is always the first to be unsatisfied.

Until now, it has been shown that, if the pressure increases (early sedimentary setting), relation (3) does not hold and dissolution of the host phase begins as a consequence of inequality (11). Then, a depression is attained which brings down the solubility of the authigenic phase and leads to its precipitation. This makes the authigenic crystal grow and leads to a dynamic equilibrium controlled by equation (10). Examples from early sedimentary settings (Figs 3-7), in which a carbonate matrix is replaced by authigenic quartz, correspond to this situation.

Alternatively, if the pressure diminishes (late sedimentary exposure),  $X_{1m}$  is brought down and relation (3) does not hold. Nevertheless, now the host phase starts precipitating again, as a consequence of the opposite of inequality (11). Then, an overpressure (force of crystallization) is produced, raising the solubility of the authigenic phase and making the authigenic crystal redissolve.

This leads to a new dynamic equilibrium, also controlled by equation (10), now transformed into the form

$$\frac{dn_1}{dt} = \frac{K_2}{\nu_{10}} (X_{2m} - X_2) \quad (13)$$

the meaning of which is evident. Examples shown in Figs. 8–10, from the late diagenetic period, correspond to this reverse case.

As for the estimate of the speed of the diagenetic replacement, it is impossible to obtain accurate and reliable results, since it is not possible to have detailed data with respect to the pressure, or of the characteristics of the liquid flow. However, it is worthwhile noticing from Table 1 how the time taken by the replacement can be very much shortened by an increase in the pressure, as well as by an increase in the flow speed.

### Conclusions

The solubility dependence upon pressure is proposed as the origin of diagenetic volume-for-volume replacement.

The force of crystallization concept has been combined with the depression of dissolution and it has been shown that the two together may drive the diagenetic replacements. In the early sedimentary stages, the depression of dissolution brings down the solubility of the authigenic phase inducing its precipitation, whereas, in the late diagenetic stages, the force of crystallization raises the solubility of the authigenic phase and causes its dissolution.

In this way, the proposed model also explains the observation that a carbonate matrix may have been replaced by authigenic quartz in the early diagenesis, when pressure was increased, and later, when pressure diminishes in the cropping up, the reverse process takes place.

In the Basque-Cantabrian Basin there are many samples that can be recognized as originating from diagenetic volume-for-volume replacements. The distinctive textural criteria and the depositional and biogenic sedimentary structures appear quite clearly in different sedimentary environments (carbonate turbidites, distal and proximal carbonate platforms).

Also, we add a fourth criterion to the three already stated for volume-for-volume replacement. It can be useful to distinguish this sort of replacement from the infilling of open spaces.

Finally, we offer a way to estimate the time taken by these replacements and make some calculations in order to quantify the influence of pressure upon the speed of the replacement as well as the influence of other characteristics of the liquid flow, which influence the speed at which the liquid between the authigenic crystal and the host phase is renewed.

#### Acknowledgement

This work has been financed by a Research Project of the Universidad del País Vasco (UPV 130.310-E136/91).

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[Manuscript received 8 March 1993:  
revised 30 April 1993]