H4.SMR/1011 - 35

## Fourth Workshop on Non-Linear Dynamics and Earthquake Prediction

6 - 24 October 1997

## Mechano-chemistry of Earthquakes

#### D. SORNETTE

University of California at Los Angeles
Department of Earth and Space Sciences &
Institute of Geophysics and Planetary Physics
Los Angeles, California; U.S.A

Université de Nice - Sophia Antipolis Laboratoire de Physique de la Matière Condensée Nice, FRANCE

### Earthquakes: a new way

#### Didier Sornette

Department of Earth and Space Science and Institute of Geophysics and Planetary Physics University of California, Los Angeles, California 90095 and

Laboratoire de Physique de la Matière Condensée CNRS and Université des Sciences, B.P. 70, Parc Valrose 06108 Nice Cedex 2, France

July 21, 1997

**Abstract:** An earthquake is a sudden rupture in the earth's crust or mantle caused by tectonic stress. This premise is usually elaborated by models that attempt to account for seismological and geological data as well as constraints from laboratory experiments. Notwithstanding almost a century of research since the standard rebound theory of earthquakes was formulated [Reid, 1910], the complex nature and many facets of earthquake phenomenology still escapes our full understanding, which is reflected in the on-going controversy on earthquake prediction [Keilis-Borok, 1990; Mogi, 1995; Geller et al., 1997]. There is growing evidence [Kirby, 1984; Hickman et al., 1995; Evans and Chester, 1995; Thurber et al., 1997] of the importance of water as a key participant for decreasing normal lithostatic stress in the fault core and weakening rock materials by stress corrosion. Here, we advance the novel concept that water in the presence of finite localized strain may lead in addition to the phase transformation of pre-existing minerals into other metastable polymorphs of higher free energy density. This new route of "chemical" energy storage is argued in details for the example of the quartz to coesite transformation, based on laboratory and field observations as well as free energy estimations. Under increasing strain, the transformed minerals eventually become unstable, as shown from Landau theory of structural phase transitions, and transform back explosively, creating a slightly supersonic shock wave propagating along the altered fault core leaving a wake of shaking fluidified fragments. As long as the resulting high-frequency waves remain of sufficient amplitude to fluidify the fault core, the fault is unlocked and free to slip under the effect of the tectonic stress, thus releasing the elastic part of the stored energy. We briefly discuss a list of observations that could be rationalize within this theory.

# 1 First phase: mineral alteration and chemical transformation

The preparation for an earthquake starts at the molecular level. Under the action of a slowly increasing tectonic strain and in the presence of water which tends to concentrate in discontinuities within fault zones and within defects in minerals, rocks undergo a progressive hydration and lattice distorsion. This involves the introduction of water molecules both intact and decomposed into hydroxyl and hydrogen components with exchange of electrons with the  $SiO_4^{4-}$  building brick of silicates and also with the impurities within the rock minerals [Jones et al., 1992]. The minerals deform progressively, storing a larger and larger density of dislocations that are nucleated and stabilized by the presence of hydroxyl and other impurities in their cores. Such increasing deformation is both displacive, i.e. corresponds to a distortion of the crystalline mesh as for instance in the local Si - O - Si unit flipping induced by the presence of a single water molecule, and plastic due to the irreversible creation and motion of dislocations. A large rock deformation is progressively concentrated within a few ten-centimeter-thick ultracataclasite zone at the center of fault cores in which the largest amount of water is thought to become available for chemical and hydrolytic attack [Scholz, 1990].

In addition to the slow and diffuse elastic energy storage under tectonic loading, we propose that minerals may act as piezochemical (or mechanochemical [Gilman, 1996]) plants, providing another channel for energy storage. As little is known on chemical and phase transformations for the large variety of relevant minerals in the seismogenic crust, we focus on the case of quartz  $\alpha$ , a main constitutive element of crustal rocks, and its transformation to coesite, its high-pressure polymorph. At equilibrium, coesite is stable above 2000 MPa (compared to the typical pressure of 300 MPa at 10 km depth) at room temperature and at even higher pressures at larger temperatures. Green [1972] showed that quartz becomes metastable at low pressure in favor of coesite when sufficiently strained with a large density of dislocations. The proliferation of dislocations is assisted by defects, inclusions and water molecules. The increase of free energy of strained quartz is roughly  $G_d \approx 10^{-8}~Jm^{-1}$  per unit length of dislocation [Green, 1972]. Neglecting interaction between dislocations, the density d of dislocations such that the increase in elastic energy in quartz  $\alpha$  makes up for the free energy gap  $\Delta G \approx 200~J~mole^{-1}~kb^{-1}$  with coesite is

$$d \approx \frac{\Delta G}{G_d V_d} \approx 10^7 m^{-2} k b^{-1} , \qquad (1)$$

where  $V_d$  is the molar volume of quartz (22.69  $cm^3$  at room conditions). For coesite to form at a pressure which is 17 kb below the equilibrium pressure transition, the dislocation density in quartz must reach about 1.5  $10^{12}$   $cm^{-2}$ . At and above this density, quartz  $\alpha$  has a larger free energy and thus becomes less stable than coesite. The neglect of dislocation interactions (which tends to decrease  $G_d$ ) is probably compensated by incorporating the energy of core dislocations and the effect of anisotropy.

Such high values of dislocation densities are quite plausible for large deformations and have been observed [Green, 1972]. Transformation of both quartz  $\alpha$  and  $\beta$  to coesite has been repeatedly observed experimentally under large deformations and seismogenic pressures [Green, 1972; Hobbs, 1968; Green et al., 1970; Baeta and Ashbee, 1970; Tullis, 1971; Tullis et al., 1973] at strain rates of  $10^{-9}$  s<sup>-1</sup> at 400 C and  $10^{-6}$  s<sup>-1</sup> at 650 C. The competing route of recrystallization of underformed quartz is known, under large strains, to be a very slow growth process in comparison to the faster structural transition to underformed coesite. Instabilities could also control the transformation from quartz to coesite, similarly to alloys which present phase transitions induced by plasticity [Martin and Bellon, 1997], such as ordering, dissolution of precipitates and amorphization.

Relic coesite has been discovered as inclusions in garnet and pyroxene in eclogite and other rocks apparently formed under high pressure in the western Italian alps [Chopin, 1984], in the Norwegian Caledonides [Smith and Lappin, 1989], in the Dabie mountains, central China [Okay et al., 1989; Wang and Liou, 1989]. This coesite is believed to have been formed in its stability domain at depth of about 90 km and then to have come up to the surface. Its observation at the surface is believed to be due to its protection within inclusions. In presence of water, the coesite probably cannot remain metastable and will transform progressively into a quartz pseudomorph [Darling et al., 1997]. If fault are forming coesite due to the presence of water, this coesite would be partly or totally transformed under depressurization in presence of water when coming up to the surface. The detection of coesite would thus be much clearer from a direct and fast access to the internal fault structure shortly after an earthquake.

Deep mines may offer this possibility. Shear ruptures corresponding to large seismic events (up to magnitude 4.7 with displacement of up to 0.4 m) accompanying mining in deep South African gold mine were identified [Ortlepp, 1992; 1997]. The intersection of the fault planes with mine galleries allowed the unique opportunity of analyzing fresh ruptures induced by earthquakes at depth (3 km). Scanning electron microscope studies of the finely-crushed material in the immediate wall of the ruptures showed the existence of fine-grained polyhedral rhombic dodecahedron crystallites of about 40  $\mu m$  in diameter that were filling space in a regular way. The remarkable fact is that the rhombic dodecahedron is not a possible crystal form for quartz. Of the minerals that sometimes occur as accessory minerals in these South African mines, only garnet has the rhombic dodecahedron as a possible crystallographic habit. However, the total amount of garnet is very minute ( $10^{-6}$  in relative concentration) and the probability that the observation of the rhombic dodecahedron crystallites at three different rupture places can be associated to garnet is exceedingly remote  $(10^{-18})$ . The remaining hypothesis is that the crystallites are coesite, which takes indeed the rhombic dodecahedron crystal form. Further analysis of this material in recent ruptures in mines, using X-ray diffraction to ascertain the crystalline structure, is thus called for to confirm this hypothesis [Ortlepp and Sornette, in preparation].

The quartz  $\rightarrow$  coesite transformation at low pressure and temperature might not

be an isolated instance but, rather, the general case. Indeed, there is growing recognition that mineral structures can form at much milder pressures and temperatures than their pure phase diagram would suggest, when in contact with water and/or in the presence of finite anisotropic strain and stress. For instance, diamonds are known to be formed under relatively low pressure (1 kbar) and temperature (500 C) under hydrothermal conditions [Zhao et al., 1997; DeVries, 1997], while the direct transformation route from carbon requires a pressure above 120 kbar and a temperature of about 2000 C. This is yet another striking example of the surprising effect of water which allows for transformations at seismogenic conditions that were thought possible only under much more extreme conditions. These recent discoveries are suggestive of the wealth of new phenomena that are possible when chemistry and/or phase transformations are coupled to finite anisotropic mechanical deformations.

## 2 Second phase: explosive liberation of chemical energy

#### 2.1 Energetics

The forming metastable mineral (coesite in the above example) is submitted to tectonic stress and thus grows with mineralogic orientations governed by those of the applied stress. It also starts to deform until it becomes unstable and converts back to more stable minerals. This instability can be determined by using the Landau theory of phase transitions in minerals [Salje, 1992]. Landau theory uses symmetry constraints to derive the free energy as an expansion of the order parameters, thus minimizing the need for a detailled mineralogic description. Notwithstanding this simplicity, when the order parameters are correctly identified, it reproduces experimental observations of phase transitions in minerals with sufficient accuracy to be useful for many applications [Salje, 1992]. This formalism should apply to any phase transition from one mineral form to another as occurs in quartz but also in feldspars and other crystalline structures found in the crust. To keep the discussion as simple as possible, we use the simplest conceptual model of a coupling between a structural order parameter and the applied strain. In general, minerals and their structural phase transitions involve several coupled order parameters  $Q_i$ , which describe the atomic displacements within the lattice structure. Here, we consider a single scalar order parameter Q which represents for instance a pure shear coupling.

Consider a structural transition described by the following free energy:

$$G = -\frac{1}{2}aQ^2 + \frac{1}{4}bQ^4 + hQ + dQ\epsilon + \frac{1}{2}g\epsilon^2 . (2)$$

 $\frac{1}{2}g\epsilon^2$  is the elastic energy density and  $dQ\epsilon$  is the coupling between the order parameter and strain. In the absence of strain, the critical transition occurs at a=0 and separates a phase with Q=0 (for a<0) from a phase with non-zero Q (for a>0)

possessing the  $Q \to -Q$  symmetry. For a > 0, h = 0 and vanishing strain  $\epsilon = 0$ , the two phases  $Q_{\pm} = \pm \sqrt{\frac{a}{b}}$  have the same free energy. The symmetry between Q and -Q is broken by the field h. Keeping a > 0 and varying h allows one to describe a first-order transition between the two phases  $Q_{\pm}$  and  $Q_{\pm}$  with a jump in order parameter when h goes through zero. Other forms up to  $Q^{6}$  order have been considered to describe tricritical mineral phase transitions [Salje, 1992]. The expression (2) is enough to demonstrate the effect of the coupling with the strain field. In fact, strain is recognized as an essential ingredient in structural phase transitions because elastic strain coupling is the dominant interaction between atoms and mineral cells in structural phase transitions [Marais et al. 1991: Bratkovsky et al., 1995].

For the sake of exposition, the stable undeformed quartz  $\alpha$  corresponds to  $Q_-$  and the metastable undeformed coesite to  $Q_+$ . The presence of strain  $\epsilon > 0$  has, in this model, the same effect as an increase of the field. Other forms of coupling do not have such an exact equivalence but exhibit however the same qualitative properties. In the presence of a finite strain  $\epsilon > 0$ , the two phases have their order parameter which are solution of  $\frac{dG}{dQ} = 0$  (extremum of the free energy) with  $\frac{d^2G}{dQ^2} > 0$  (local stability condition). The first condition gives the cubic equation  $Q^3 + AQ + B = 0$ , with  $A = \frac{a}{b}$  and  $B = \frac{h+d\epsilon}{b}$ . For  $\frac{B^2}{4} + \frac{A^3}{27} < 0$ , i.e.  $\epsilon < \epsilon^* \equiv -\frac{h}{d} + \frac{2}{\sqrt{27}} \frac{a^3}{d}$ , the cubic equation has three real roots, two of which are stable. This is the regime where the two phases  $Q_-$  and  $Q_+$  are locally stable (the phase  $Q_+$  with the highest free energy is metastable). When  $\epsilon$  increases beyond  $\epsilon^*$ , two roots collide and go to the complex plane with only one real solution remaining. At  $\epsilon = \epsilon^*$ , the metastable state  $Q_+$  becomes unstable ( $\frac{d^2G}{dQ^2}|_{Q_+}$  vanishes) and transforms into the stable phase  $Q_-$ . Figure 1 represents schematically the whole process. To sum up, the stable quartz  $\alpha$  becomes metastable to coesite as large plastic deformations accumulate and metastable coesite becomes unstable as strain increases.

The energy released in the chemical transformation is estimated as follows. The free energy difference between the metastable coesite and the stable quartz is approximatly 80  $kJ/kg \approx 2 \cdot 10^8 \ J/m^3$ . Consider a volume of 40 km by 1 km by 1 m, corresponding to the core of a fault activated by an earthquake similar to Loma Prieta (1989 earthquake,  $M_S = 7.1 \pm 0.3$ ) [Kanamori and Satake, 1990], in which alteration has transformed about 10% of the minerals into the energetic metastable phase. This volume can then release 8 10<sup>14</sup> J from the explosive phase transformation (compared to the energy released, say, by the Hiroshima bomb equal to 13 kT of TNT  $\approx 5.2 \ 10^{13} \ J$ ). For Loma Prieta, the radiation energy is in the range [Kanamori et al., 1993; Choy and Boatwright, 1995  $E_S = 10^{15} - 8 \cdot 10^{15} J$ . Another estimate is given by the static elastic calculation using a simple shear rupture model [Knopoff, 1958] giving a total released energy  $E_T \approx \frac{\pi}{8}Gd^2L$ . For  $d \approx 1.6$  m over a rupture length  $L \approx 40 \text{ km}$ , we get  $E_T \approx 1.3 \cdot 10^{15}$ . Thus, the chemical energy storage is comparable to the elastic energy storage. These numbers are susceptible to important variations depending on the heterogeneity of the crust on one hand and the uncertainties in the parameters on the other hand.

### 2.2 Dynamics: explosive shock propagation

The transformation of coesite is a genuine instability governed by the strain as the control parameter, and as such does not involve any energy barrier. We thus expect it to be very fast, similar to an explosion. Indeed, explosive substances are nothing but species storing chemical energy into metastable chemical configurations that become unstable and release it suddenly. Here, an energic solid substance (coesite for instance) releases energy in fast time by transforming to a more stable low energy form. In the core of the shock, large bending and rupture of atomic bonds occur as a consequence in a very narrow zone of atomic scale which can propagate at velocities comparable to or even higher than the velocity of sound in the initial material [Gilman, 1995]. The origin of the supersonic velocity of the explosive front can be explained physically as follows.

The mineral (coesite) must have grown aligned with a coherent crystalline structure in response to the coherent tectonic stress field. We can thus depict the crystalline structure using the following 1D toy model shown in figure 2. A one-dimensional chain is made of atoms of mass m linked to each other by energetic links of spring constant k which, when stressed beyond a deformation threshold  $u_r$ , rupture by releasing a burst of energy  $\Delta g$  converted into kinetic energy transmitted to the atoms. Initially the chain of atoms is immobile. Suppose that the first atom on the left is moved from its rest position by  $u_r$  and thus the first bond ruptures. This rupture liberates the energy  $\Delta g$  shared between the kinetic energy  $K_1$  of the atom fragment expulsed to the left and  $K_2$  of the next atom of the chain:

$$\Delta g = K_1 + K_2 \ . \tag{3}$$

This gives an impulsive boost of velocity  $\sqrt{\frac{K_2}{m}}$  to the boundary atom which accelerates its motion and shortens the time until the rupture threshold  $u_r$  is reached for the next bond. When this occurs, the boundary atom is expulsed and the same process repeats itself along the chain. It is then clear that this leads to a shock propagating at a velocity larger than the sound velocity since the atoms are receiving boots that accelerate their motion faster than what would be the propagation of their motion by the springs with the usual acoustic wave velocity  $\sqrt{\frac{k}{m}}$ . The resulting supersonic shock velocity U is given by an adaptation [Sornette, 1997] of the formula proposed by [Gilman, 1995]

$$U^2 = c^2 + \Delta G \ , \tag{4}$$

where c is the longitudinal velocity (say 5000 m/s), and  $\Delta G \approx 77~kJ/kg$  is the free energy released by the transformation. Expression (4) then yields  $U \approx 1.003~c$ , i.e. an advance of about 6 millisec for a distance of 10 km between source and reception. As the transformation starts at a nucleus within the fault, a genuine shock wave develops as long as there is "fuel", i.e. along a connected part of altered coherently crystallized mineral.

#### 3 Third phase: the genuine rupture

#### 3.1 Explosive fluidization and unlocking of the fault

The explosive transformation of the deformed unstable energetic mineral phase is violent and leads to fragmentation and comminution with the generation of intense shaking due to high frequency sound waves that remain trapped in the loosened low acoustic impedence core of the fault. We argue that this leads to acoustic fluidization [Russo et al., 1995]. Melosh [1996] has proposed acoustic fluidization as a mechanism for the low dynamical friction of faults (the initial unlocking of the fault is not described in his scenario). We differ from him in that the source of the high frequency acoustic modes is not the rupture propagation but rather the explosive phase transformation. Furthermore, the acoustic pressure does not need to reach the overburden pressure to fluidify the fault (which would lead to an unrealistic large acoustic energy in high frequency acoustic waves [Sornette, 1997], larger than the total available energy) but only a rather small fraction of it due to the fact that the gouge material is already significantly loosened by the explosive shock.

The peak deformation strain amplitude  $\epsilon_a$  of the acoustic waves generated by the explosion can be estimated from the density change  $\frac{\rho_{coeste} - \rho_{quartz}}{\rho_{quartz}} \approx 11\%$  during the the explosive transformation from coesite to quartz leading to  $\epsilon_a \approx 3-4\%$ . The acoustic pressure equals to  $\epsilon_a \rho gh$ , i.e. a few percent of the lithostatic pressure. This is almost two order of magnitude less than the value needed in the acoustic fluidization mechanism proposed by Melosh [1996]. The acoustic energy corresponding to this peak pressure is three orders of magnitude smaller and thus only a small fraction of the total available energy.

Now, under the action of such cyclic deformations due to the acoustic shaking, it is a well-established experimental result [Biarez et Hicher, 1994] that the elastic modulii of granular media are much lower than their static values. This effect occurs only for sufficiently large amplitudes of the cyclic deformation, typically for strains above  $10^{-4}$ . At  $\epsilon_a = 10^{-3}$ , the elastic modulii are halved and at  $\epsilon_a = 10^{-2}$  (which is the relevant order of magnitude predicted here) they are more than five times smaller than their static values. The strength of the granular medium is thus drastically decreased by the acoustic shaking and the gouge can slip under the applied tectonic stress. In addition, if the stress-strain curve has a maximum at the pressure and temperature conditions of the seismogenic depth, usually occurring at a deformation of a few percent, the acoustic waves created by the explosive transformation may even lead to an intrinsic shear instability, analogous to the localization instability in sand. A third fluidization mechanism may also add to the instability. When the explosive transformation occurs, the ensuing shaking starts to deform the gouge material. The first stage of the deformation of any granular is compressive, even if it becomes dilatant at larger deformations. As a consequence, any interstitial fluid is first compressed and decreases the friction force between the grains and thus may lead to a release of the fault which may start to rupture. This effect is known as the

#### 3.2 Rupture propagation and seismic radiation

There are two possible contributions to seismic radiation. First, the phase transformation by itself radiates seismic waves: Knopoff and Randall [1970] have shown that a sudden change of shear modulus of the material in the presence of a pre-existing shear strain leads to a "double-couple source" with the correct and usual characteristic radiation pattern found in earthquakes at low frequencies. In fact, it is impossible to discriminate between this source and that of the displacement dislocation from their first motions. The modulus of the corresponding double-couple moment is [Knopoff and Randall, 1970]

$$M = 2\delta\mu \,\,\delta\epsilon \,\,V \,\,, \tag{5}$$

where  $\delta\mu$  is the change in shear modulus,  $\delta\epsilon$  is the change in strain inside the volume V in which the phase transformation has occurred. The change in modulus is very large for coesite (bulk modulus of 9.4  $10^{10}~Pa$ ) to quartz (bulk modulus of 3.7  $10^{10}~Pa$ ) [Liu, 1993]. We take as an upperbound of the change in strain  $\delta\epsilon$  one-third the relative change in density (11 %). The volume V is the surface S of the fault times the width  $w \approx 1$  meter of its core over which the phase transformation occurs. We thus see that this corresponds to the seismic moment of an earthquake with average slip w  $\delta\epsilon$  equal to a few centimeters, irrespective of the size of the fault. This contribution is thus negligible for large earthquakes having slips of meters or more. In addition to this double-couple component, the change in bulk modulus and in density radiates isotropically with radial directions for the first P motions and no first S motions. However, this is again a small effect.

The second contribution to seismic radiation comes from the mechanical fault slip. The shaking of the fault core induced by the mechanical effect of the phase transformation unlocks it; indeed, the fluidization implies that the fault nucleation region can no more support the initial loading stress, since its strength tends to vanish due to the intense acoustic shaking induced by the explosive phase transformation. This explosive transformation triggers the fault slip and the fault starts to slip under the action of the pre-existing shear stress and radiates seismic waves. We insist on the fact that, in the present model, the fault slip is not triggered by reaching a stress threshold (corresponding either to friction unlocking or rupture nucleation), but rather by a chemical instability: as a consequence, any level of stress will activate the fault slip when the explosive phase transformation occurs.

The rupture dynamics is controlled by the usual elasto-dynamic equations. The rupture propagation lasts as long as the high-frequency waves which are trapped within the fluidified material with low-acoustic impedence remain of sufficient amplitude to unlock the fault. The detrapping of these waves control the healing of the fault, and therefore the static stress drop. This mechanism is expected to produce large variations of static stress drops, depending on the degree of chemical alteration

and storage of chemical energy necessary to obtain the unlocking of the fault. This is controlled by the detailled mineralogy in the fault core and the presence of fluids. The total size of the rupture is determined by the extension of the domain over which the supersonic shock has propagated, which is itself controlled by the alteration processes that have matured the material and stored a suitable amount of chemical energy. A fault region which is weakly or not altered plays the role of an energy sink for the explosive shock propagation and will tend to stop it. Such regions are probably associated to geometrical irregularities.

#### 4 Consequences and predictions

The proposed theory allows us to rationalize a large number of observations into a coherent framework. It also leads to a number of testable predictions. We only outline some of them and refer to [Sornette, 1997] for their development.

- Strain, stress and heat flow paradoxes: There is no need for elastic strain concentration over a scale of of about 10 km (which is usually not observed) while very localized plastic-ductile strains are expected. There is no need for large stress to unlock the fault and the low friction is generated dynamically, preventing heat generation and providing a solution to the heat flow paradox [Lachenbruch and Sass, 1980].
- The longer the recurrence time, the larger the stress drop: Several studies have shown recently a remarkable relationship between the average slip rate on faults and the stress drop associated to earthquakes occurring on these faults (see [Kanamori, 1994] for a review). Earthquakes on faults with long repeat times (thousands of years) radiate more energy per unit fault length and have a significant larger dynamical stress drop than those with short repeat times (a few decades to a few centuries). In our framework, a longer period gives more time to saturate the chemical energy storage and leads to more "energetic" earthquakes.
- Shear heating: Direct measurements of heat flux do not exhibit anomalous values and thus no significant frictional heating while the accumulated weight of evidence on the metamorphism of rocks adjacent to faults in higher grades indicates that shear heating can be associated with faulting [Scholz, 1980]. Interpreted with a pure mechanical point of view, this implies shear stresses of about 1 kbar at least at the initiation of slip, posing difficulties to many other interpretations. Within the proposed theory, the observed metamorphism of rocks adjacent to faults could result naturally from the explosive phase transition which launches the rupture propagation. There is no need for large stress once a chemical explosion is triggered.
- Seismic P-wave precursors: Seismic P-wave precursors have been reported [Beroza and Ellworth. 1996] that seem to precede the arrival of the first P-wave (longitudinal compressive acoustic wave). These observations are still controversial [Mori and Kanamori. 1996], not only because the reported signals are weak and the effect is hard to establish, but also because their presence is essentially ruled out

within the standard pictures. The proposed explosive mechanism and resulting shock wave propagating at slightly supersonic velocity (1.003 c according to our estimate) is a natural candidate to rationalize the observation of these seismic P-wave precursors, if they exist. We predict an advance of about 6 milliseconds of the precursor to the first P-wave motion for a propagation over 10 km between source and a seismic station. This seems of the correct order compared to observations [Beroza and Ellworth, 1996]. The finding that the duration of the precursors scale with the size of the earthquake reflects the fact that the mechanical rupture occurs on the length of the fault over which the explosive shock has occurred and thus we should expect them to be proportional to the total size of the rupture.

- Earthquakes occur preferentially in strong rocks: Fault imaging shows the systematic picture that earthquake main ruptures take place in rock with relatively high seismic velocity, while surrounding rock has velocities that are relatively low. The same pattern emerges in images of the 1994 Northridge earthquake [Zhao and Kanamori, 1995], of the 1966 Parkfield shock of 6.0 and of the 1992 Landers earthquake of 7.3. Why do earthquakes regularly take place in strong rock? In our theory, the strength of the rock has not bearing a priori, because neither the rock strength nor its frictional properties control the development of an earthquake. It is rather its chemical composition that controls the preparation and triggering of an earthquake. The chemical route to energy storage and resulting explosion can unlock the fault, independently of the material strength. However, there could be a correlation with the strength of the rock, because stronger rocks are more subjected to structural phase transformation under large deformations. This is due to the higher energy cost of dislocations which makes more favorable the formation of metastable phases. We are thus led to rationalize the long-standing and puzzling observation that earthquakes occur in stronger zones because this is the locus of a more efficient chemical energy storage. While most studies have emphasized softening aspects of shear zones, our theory suggests rather that the upper crust may localize these zones under strain-hardening conditions.
- Creeping sections and slow earthquakes: Some faults appear not to rupture in sudden earthquakes but rather to creep continuously. Slow earthquakes [Linde et al., 1996] are acceleration of creep over a few hours to a few days. This leads to the usual classification in terms of three types of behavior: regions where the seismic coupling is total; those where slip is seismic only when triggered by seismic slip from an adjacent region and which otherwise slip asesimically; and regions where slip is always aseismic. In our theory, the different behaviors can be ascribed to different fluid content, temperature and pressure. As the deformation and alteration becomes highly concentrated in a narrow, weakened, region, several scenarios are possible. If the built-up of dislocations with core defects is not too fast, the strain can be relaxed by rearrangements and flows of the dislocations leading to plastic deformations. The phase transition and storage of chemical energy will not occur in this case. If the alteration and production of dislocations is too slow, point-like defects and partial dislocations will move and accommodate the deformation. This is the regime where a

fault is creeping without triggering large earthquakes. Unsufficient amount of water controls the occurrence of this regime.

- Tilt anomalies have often been reported before earthquakes (for instance before the Haicheng earthquake [Scholz, 1977]). The magnitude of the tilt is usually very small  $(1-20~\mu rad, say)$  and not always present. The slow phase transformation from quartz to coesite (and the other analog mineral transformations) during the alteration process and chemical energy storage leads to a density change that produces a weak surface deformation whose direction and amplitude depend on the mechanical heterogeneity of the earth. This is represented schematically in figure 3. For a phase transformation where 10% of the minerals undergo a relative density change of 11% occurring within the fault core over a depth of 10 km and a width of 1 meter, the expected tilt anomaly is  $\approx 3~\mu rad$ .
- Electric effects: The explosive coherent transformation of aligned crystals presented no-center of symmetry, and thus piezoelectric properties, is expected to lead to significant electric signals and might provide a route for rationalizing recurrent observations [ $Debate\ on\ VAN.\ 1996$ ] and help in improving their investigation. The development of this research is left for another work.
- Deep earthquakes: Finally, our theory suggests that deep earthquake, which have been proposed to be due to unstable olivine-spinel transformations [Green and Houston, 1995], are not so different from superficial earthquakes, not only in the nature of their seismic radiation but also in their source mechanism. This calls for a re-examination of the phase transition route for deep earthquakes in the light of the action of water and other impurities in presence of finite strain.
- Inversion of metamorphic data: The usual inference of tectonic conditions from the examination of minerals and their corresponding equilibrium thermodynamic phase diagrams can be questionned in view of the evidence summarized here on out-of-equilibrium processes in the presence of water and/or finite strain. This calls for a reexamination of the models of crustal motions based on inverting metamorphic patterns.

Acknowledgments: I have benefitted from helpful discussions with J.M. Christie, P.M. Davis, P. Evesque, J. Gilman, H. Houston, D.D. Jackson, W. D. Ortlepp, G. Ouillon and J. Vidale. Useful correspondences with Y. Brechet, J.-C. Doukhan, J. Ferguson, G. Martin, J.P. Poirier are acknowledged. L. Knopoff has been a great teacher of the subtleties of earthquake phenomena and I am greatly indebted to him. Numerous key insights came from discussions with my wife Anne and I cannot express sufficiently strongly how the present work owes to her intuition. I dedicate this work to Jaufray without whom these ideas would not have come to earth.

#### References

Baeta, R.D. and K.H.G Ashbee, Slip systems in quartz, I-Experiments; II-Interpretation, Am. Mineral., 54, 1551-1582, 1970.

Beroza, G.C., and W.L. Ellworth, Properties of the seismic nucleation phase, *Tectonophysics*, 261, 209-227, 1996.

Biarez, J., and P.-Y. Hicher. Elementary mechanics of soil behavior: saturated remoulded soils, Rotterdam: Brookfield, VT: A.A. Balkema, 1994.

Bratkovsky, A.M., E.K.H. Salje, S.C. Marais and V. Heine, Strain coupling as the dominant interaction in structural phase transition. *Phase transitions*, 55, 79-126, 1995.

Chopin, C., Coesite and pure pyrope in high-grade blueschists of the Western Alps: a first record and some consequences, Contributions to Mineralogy and Petrology, 86, 107-118, 1984.

Choy, G.L., and J.L. Boatwright. Global patterns of radiated seismic energy and apparent stress, J. Geophys. Res., 100, 18205-18228, 1995.

Darling, R.S., I.M. Chou and R.J. Bodnar. An occurrence of metastable cristobalite in high-pressure garnet granulite, *Science*, 276, 91-93, 1997.

Debate on VAN, Special issue of Geophys. Res. Lett., 23, 1291-1452, 1996.

DeVries, R.C., Diamonds from warm water, Nature, 385, 485-485, 1997.

Evans, J.P., and F.M. Chester, Fluid-rock interaction in faults of the San Andreas system - Inferences from San Gabriel fault rock geochemistry and microstructures, J. Geophys. Res., 100, 13007-13020, 1995.

Geller, R.J., D.D. Jackson, Y.Y. Kagan and F. Mulargia, Science 275, 1616-1617, 1997.

Gilman, J.J., Chemical reactions at detonation fronts in solides, *Philos. Mag. B* - *Physics of Condensed Matter Structural Electronic Optical and Magnetic Properties*, 71, 1057-1068, 1995.

Gilman, J.J., Mechanochemistry, Science, 274, 65-65, 1996.

Green II, H.W., Metastable growth of coesite in highly strained quartz, J. Geo-phys. Res., 77, 2478-2482, 1972.

Green II, H.W., D.J. Griggs and J.M. Christie, Syntectonic and annealing recrystallization of fine-grained quartz aggregate, in *Experimental and Natural Rock Deformation*, edited by P. Paulitsch, pp. 272-335, Springer. New York, 1970.

Green, H.W., and H. Houston, The mechanics of deep earthquakes, Ann. Rev. Earth Sci. 23, 169-213, 1995.

Hickman, S., R. Sibson and R. Bruhn, Introduction to special section: mechanical involvement of fluids in faulting, J. Geophys. Res., 100, 12831-12840, 1995.

Hobbs, B.E., Recrystallization of single crystals of quartz, Tectonophysics, 6/5, 353-401, 1968.

Jones, R., S. Öberg, M.I. Heggie and P. Tole, Ab initio calculation of the structure of molecular water in quartz. Philos. Mag. Lett., 66, 61-66, 1992.

Kanamori, H., Mechanics of earthquakes, Ann. Rev. Earth Planet. Sci. 22, 207-237, 1994.

Kanamori, H., and K. Satake, Broadband study of the 1989 Loma-Prieta earthquake, Geophys. Res. Lett. 17, 1179-1182, 1990.

Kanamori, H., J. Mori, E. Hauksson, T.H. Heaton, L.K. Hutton and L.M. Jones, Determination of earthquake energy release and  $M_L$  using Terrascope, Bull. Seism. Soc. Am., 83, 330-346, 1993.

Keilis-Borok, V.I., editor, Intermediate-term earthquake prediction: models, algorithms, worldwide tests, *Phys. Earth and Planet. Interiors*, 61, 1-139, 1990.

Kirby, S.H., Introduction and digest to the special issue on chemical effects of water on the deformation and strength of rocks, J. Geophys. Res., 89, 3991-3995, 1984.

Knopoff, L., Energy release in earthquakes, Geophys. J. Roy. Astron. Soc., 1, 44-52, 1958.

Knopoff, L., and M.J. Randall. The compensated linear-vector dipole: a possible mechanism for deep earthquakes, J. Geophys. Res. 75, 4957-4963, 1970.

Lachenbruch, A.H., and J.H. Sass, Heat flow and energetics of the San Andreas fault zone, J. Geophys. Res., 85, 6185-6222, 1980.

Linde, A.T., M.T. Gladwin, M.J.S. Johnston, R.L. Gwyther and R.G. Bilham, A slow earthquake sequence on the San Andreas fault, *Nature 383*, 65-68, 1996.

Liu, L.-G., Bulk moduli of  $SiO_2$  polymorphs: Quartz, coesite and stishovite, *Mechanics of Materials* 14, 283-290, 1993.

Marais, S., V. Heine, C. Nex and E. Salje, Phenomena due to strain coupling in phase transitions, *Phys. Rev. Lett.* 66, 2480-2483, 1991.

Martin, G., and P. Bellon, *Solid State Physics*, 50, 189-331, Ehrenreich and Spaepen eds, Academic press, 1997.

Melosh, H.J., Dynamical weakening of faults by acoustic fluidization, *Nature*, 379, 601-606, 1996.

Mogi, K., Earthquake prediction research in Japan, J. Phys. Earth 43, 533-561, 1995.

Mori, J., and H. Kanamori, Initial rupture of earthquakes in the 1995 Ridgecrest, California sequence, Geophys. Res. Lett., 23, 2437-2440, 1996.

Okay, A.L., X. Shutong and A.M.C. Sengör, Coesite from the Dabie Shan eclogites, central China, Eur. J. Mineral., 1, 595-598, 1989.

Ortlepp, W.D., Note on fault-slip motion inferred from a study of micro-cataclastic particles from an underground shear rupture, *Pure Appl. Geophys.*, 139, 677-695, 1992.

Ortlepp, W.D., Rock Fracture and rockbursts – an illustrative study (S.A. Inst. Min. and Metall. Johannesburg, 1997).

Reid, H.F., The California earthquake of April 18, 1906. The mechanics of the earthquake. Vol. (II of the report of the California state earthquake investigation commission (Carnegie Inst. Wash, Pub n87, vol 2) 192 pp (1910).

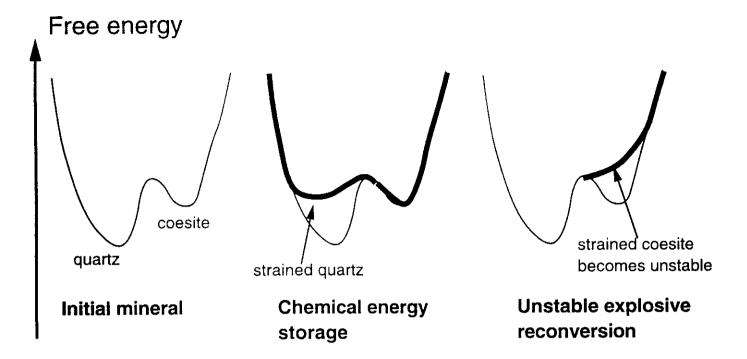
- Russo, P., R. Chirone, L. Massimilla and S. Russo, The influence of the frequency of acoustic waves on sound-assisted fluidization of beds of fine particles, *Powder Technology*, 82, 219-230, 1995.
- Salje, E. K. H., Application of Landau theory for the analysis of phase transitions in minerals,  $Phys. \ Rep., 215, 49-99, 1992.$
- Scholz, C.H., A physical interpretation of the Haicheng earthquake prediction, Nature 267, 121-124, 1977.
- Scholz, C.H., Shear heating and the state of stress on faults, J. Geophys. Res. 85, 6174-6184, 1980.
- Scholz, C.H.. The mechanics of earthquakes and faulting, Cambridge University Press, Cambridge, 1990.
- Smith, D.C., and M.A. Lappin. Coesite in the Straumen kyanite-eclogite pod, Norway, Terra Research. 1, 47-56, 1989.
- Sornette, D., Earthquakes: from chemical energy storage to mechanical rupture, preprint 1997
- Thurber, C., S. Roecker, W. Ellsworth, Y. Chen, W. Lutter and R. Sessions, Two-dimensional seismic image of the San Andreas fault in the northern Gabilan range, central California: evidence for fluids in the fault zone, Geophys. Res. Lett. 24, 1591-1594, 1997.
- Tullis, J.A., Prefered orientation in experimentally deformed quartzites, *Ph.D. Thesis*, *Univ. California*, *Los Angeles*, 344 pp, 1971.
- Tullis, J., J.M. Christie and D.T. Griggs, Microstructures and preferred orientations of experimentally deformed quartzites, Geol. Soc. Am. Bull., 84, 297-314, 1973.
- Wang, X., and J.G. Liou, Coesite-bearing eclogite from the Dabie mountains in central China, Geology, 17, 1085-1088, 1989.
- Zhao, D.P., and H. Kanamori, The 1994 Northridge earthquake 3-D crustal structure in the rupture zone and its relation to the aftershock locations and mechanism, Geophys. Res. Lett., 22, 763-766, 1995.
- Zhao, X.-Z., R. Roy, K.A. Cherlan and A. Badzian, Hydrothermal growth of diamond in metal- $C-H_2O$  systems, Nature, 385, 513-515, 1997.

#### Figure captions:

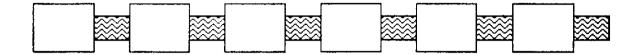
Figure 1: Starting from a double well configuration with  $Q_{-}$  (quartz) more stable than  $Q_{+}$  (coesite), the deformation applied to the  $Q_{-}$  phase creates a higher energy state which eventually becomes comparable to  $Q_{+}$  (this is the effect of inclusion of dislocations in quartz, for instance). As a consequence, the system transforms into the metastable  $Q_{+}$ . As the strain continues to increase, the free energy landscape deforms until a point where  $Q_{+}$  becomes unstable and the mineral transform back into undeformed  $Q_{-}$ .

Figure 2: A one-dimensional chain is made of blocks linked to each other by energetic links which, when stressed beyond a given deformation threshold, rupture by releasing a burst of energy converted into kinetic energy transmitted to the blocks. The figure shows two successive bond ruptures that lead to velocity boosts to the ejected fragments on the left and to the boundary blocks.

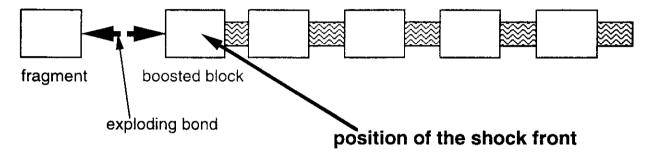
Figure 3: Cartoon of the tilt induced by the change of density during a phase transformation in a narrow fault zone.



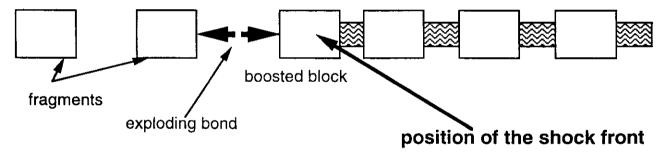
#### Initial energetic crystalline structure

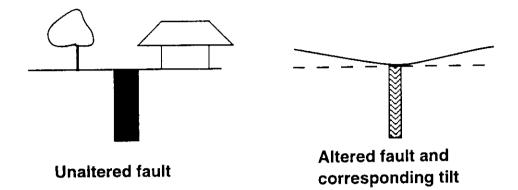


## Rupture of the first energetic bond



#### Rupture of the second energetic bond





f.g. 3