Chemistry in earthquake: the active chemical role of liquid and supercritical waters in microfracturing at depth

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Abstract  The role of water in the nucleation process of an earthquake and its contribution to the mainshock is ascertained by many models in its physical part, as a factor capable of altering the balance of pressures and thus influencing the effective pressure. Assuming that water is present at depth, starting from the observation of its molecular structure at various crustal pressure and temperature conditions, the present paper analyses water's chemical role in relation with the rock matrix, and its response during microfracturing. The creation of a network of new void spaces produces a decrease of the water pressure. Water may respond at molecular scale differently, depending on its aggregation state. Effectively depressurisation has a limited influence on the liquid water, only if it does not cause the transition to the vapour phase. Conversely, depressurisation causes an instantaneous variation in the intermolecular structure of supercritical water (SCW). Specifically, the nearly total disappearance of its ionic characteristics: that means the severe drop of solubility constants. At the same time, the already low viscosity decreases too: SCW intrudes easily into new fissures. When the microcracks tend to close, SCW reacquires adequate ionic characteristics for the rise in density (isothermal pressurisation); hence, an intense water rock interaction starts with freshly opened surfaces. This process influences actively the subcritical crack growth too, again with differences between liquid and SCW: last one participates only when reacquires density. Summarising, it is likely that water plays a fundamental and active role in determining the rock weakening, once earthquake preparation process begin with the development of microcracks are forming, perhaps playing an active role in determining the main rupture. With different modalities according to its aggregation state.

Keywords  Earthquake chemistry · Preseismic scenario · Water molecular structure · Microfracturing · Rock weakening · L’Aquila earthquake example

1 Introduction

According to most models, the opening of microfractures represents the initial stage of the earthquake preparation process leading to a main rupture. The opening of microfractures is normally observed in laboratory during triaxial tests on specimens usually made of homogeneous material (cf. Brace et al. 1966 and Cook...
According to Nishiyama et al. (2002) and references therein, “the deformation and failure of rocks is a culmination of the progressive development of microcrack”. Laboratory tests point out that the evolution of microcracks is a multistep process made by germination, expansion, evolution and coalescence (Zhao et al. 2019; Kandula et al. 2019; Lockner et al. 1991). Grain size of the rock has an important effect in determining the path and behaviour of the crack development, only once microfracturing has started (Eberhardt et al. 1999). Jouniax et al. (2001), however, report that, after the closure of cracks already present, new crack occurs, generally associated to pre-existing intergranular ones; when stress rises, at more than 50% of peak stress, new transgranular cracks appear. The same authors report the interpretation of acoustic emission as being linked to “atomic bond breaking”. Laboratory data highlight the increase of permeability during the development of microcracks (Oda eta al. 2002; Popp et al. 2001), up to a five-order magnitude increase at 99% of peak stress (Homand et al. 2000). In detail, authors report permeability values quite constant between 0 and 60% peak level, (< $10^{-21}$ m$^2$ to $3 \times 10^{-20}$ m$^2$), then an abrupt increase (e.g. at $80\% \ 10^{-19}$ m$^2$, at $90\% \ 10^{-18}$ m$^2$). Temperature has a direct correlation with the development of porosity (Violay et al. 2017) and permeability (Feng et al. 2018) as well. In a similar manner a volume of crustal rock subject to a tectonically induced differential stress, although large lateral and vertical heterogeneities may complicate the pattern, should develop microcracks, which may facilitate deformation and eventually faulting (see Kandula et al. 2019 and references therein). In pointing out the influence of crustal heterogeneities, Main et al. (2012) published a detailed and comprehensive review of the dilatancy, i.e. the volume increase of a portion of rock during microfracturing, when subjected to a differential stress. They focus on the local scale dimension of the dilatant region, rejecting the formerly believed large-scale dilatant region. They conclude that the dilatant small-scale region is localised in proximity of the nucleation zone, or that dilatancy coincides with the nucleation zone, estimated to be in the order of hundreds of meters.

In this framework, the research on the crustal faulting process has focused the attention on the role of water, as reported in Proctor et al. (2020), and more extensively in Yamashita and Tsutsumi (2018) and references therein. They focus principally on the physical capabilities of the water: in particular on its role in transferring stress by varying pressure equilibria so to change the effective stress and, consequently, to trigger earthquakes. Starting from this main mechanism, they analyse and report all possible model and consequences derived by pressure variability. Then, in pointing out the permeability variations and faulting valve mechanism, they mention a chemical aspect involving fluid flow and mineral deposition during the drop of pressure. Here and in general, the chemistry of the water is scarcely present in studies of the earthquake preparation process. Indeed, just few models, e.g. Heinicke et al. (2009) consider the active chemical role of water in triggering seismic swarms due to mineral alteration driven by acid CO$_2$-rich fluids.

Observing that most of models function only if there is free water, Yamashita and Tsutsumi (2018) affirm that the presence of water at depth is ubiquitous. Actually, there is no assurance that water at depth is present everywhere: surely it has been found as a free phase with variable amounts of hydrogen, methane and CO$_2$ in the boreholes of Kola (around 12 km depth, Kozlovsky 1987), and KTB (9 km depth, see e.g. Smithson et al. 2000).

Therefore, assuming the presence of water in active tectonic areas, the fluid pressure can vary in time during tectonic loading. As an example, Zhu et al. (2020) suggest that during inter-seismic periods a complete cycle with a pressure decrease and an increase may occur. Specifically, after the drop of pressure in the first opening of microcracks, a pore pressure increase may take place during the nucleation process of a main shock (Sibson 1991; Doglioni et al. 2014).

Specifically, a consequence never taken into consideration is that the opening of microcracks creates perturbations in the water–rock equilibrium, being a depressurisation. This induces physical and chemical changes in the fluids both at macro and at molecular scales, varying all the chemical relationship between water and solids. In general, these pressure variations act on chemical characteristics of the waters and on the whole water–rock system, varying therefore their mutual relationships. At the same time, the opening of microcracks offers new rock surfaces, available for relationship with the destabilised water.

The present work wants to fill a gap, by integrating water chemistry with physical models. It starts with the description of water molecular characteristics, from standard to thermodynamic conditions typical of middle crustal depth, where water could be in its
supercritical aggregation state. Then, are summarised some highlights on the solubilisation mechanisms of three main mineral classes and on subcritical crack growth in quartz and silicate, both in the liquid and supercritical phase. All these preliminary analyses concur in the comprehension of the model, first by outlining a water phase diagram adjusted to a crustal profile with the presumed temperature and pressure values relative to each depth. These are the basis for the description of the behaviour of different waters subject to isothermal pressure variations happening during the earthquake nucleation process, generally leaving out its ionic content. These approximations are necessary to highlight how pressure variations alone can induce changes on the $\text{H}_2\text{O}$ molecular structure, changing its solvent capability and in turn directly influencing rock shear resistance.

2 Main properties of water

Water is a powerful polar fluid, able to interact with most ionic substances at standard conditions. Among natural liquids, it has the highest dielectric coefficient (close to 80 $\varepsilon$ at standard conditions, decreasing to 55 $\varepsilon$ near 100 °C; Malmberg and Maryott, 1956), and a high dipole moment. It has a $\text{H}–\text{O}–\text{H}$ bond angle between 104.5° and 105°; that allows to bind to other water molecule through hydrogen bonds: one hydrogen of a water molecule, site of positive partial charge, binds the oxygen of a neighbouring water molecule, site of the negative partial charge. The energy of this intermolecular bond, which is only about 20 times smaller than the pure covalent bond (Stumm and Morgan 1996), arises from 90% electrostatic and 10% covalent nature (Isaacs et al. 2000). At standard conditions the configuration is a continuous and infinite network of molecules joined by hydrogen bond; the number of hydrogen bonds ($N_{\text{HB}}$) is at its maximum close to 4 with a near-tetrahedral configuration. A model proposed by Kalinchev and Bass (1997) suggests that an average value of the water hydrogen bonds at 25 °C is 3.19 $N_{\text{HB}}$ with the following speciation: 0.2% monomers, 11% and 22% dimers and over 70% molecules with coordination 4 (Fernandez-Serra and Artacho 2004). The hydrogen bond enthalpy is around 23 kJ/mol (Suresh and Naik 2000), with a vaporisation enthalpy of 44 kJ/mol.

With increasing temperature, this network starts to become a cluster of short-living hydrogen bonds, being continuously destroyed and restored (Ved’ et al. 2010). Above around 200 °C the tetrahedral structure disappears, remaining a linear one (Jedlovsky et al. 1998). Close to the subcritical/supercritical transition region, the $N_{\text{HB}}$ is extremely low (Fig. 1); here takes place the destruction of the infinite-bonded hydrogen clusters (Petrenko et al. 2012) reaching, at low density, a value of $N_{\text{HB}}$ below 1 and not stable (Nakahara et al. 2001). According to Galli and Pan (2013), there is no consensus on the structure of the water in the supercritical field. Apparently, only 15–20% of hydrogen bonds persist, generally up to 600 °C and 134 MPa. It seems that the network is highly distorted, with local zones of well-defined HB with non-HB regions. The formation of HB regions is density dependent that is they are regulated and influenced directly by pressure at fixed temperature (Bruni et al. 1996). Since there is a direct correlation between the formation of local clusters of hydrogen bonds in the supercritical state and density, density will be used as a useful macro-scale parameter for describing the average state of the intermolecular distances per unit volume.

Density, the result of intermolecular distances, is a function of temperature and pressure. In the liquid state, density values have a limited range. Approaching subcritical and supercritical state, at constant pressure, density starts to vary more significantly; near the critical point there’s a sharp decrease in density down to close to 0.1 g/cm$^3$. Beyond this transition zone, and in the supercritical state, small isothermal variations of pressure yield substantial changes in density (Fig. 2). These changes have a fundamental impact on the solvation properties of supercritical water (SCW). In the gas-like domain (i.e. low density), water molecules hardly form hydrogen bonds. Toward the liquid-like domain (i.e. medium high density) through isothermal pressure increases, the formation of HB clusters ($N_{\text{HB}}$ approaching 2) creates a highly reactive fluid: the oxygen in the water has an “unsatisfied” partial negative charge that locally makes it extremely attractive for cations.

Several factors determine the solubility of minerals in water. Hydration is a shielding action that, through the formation of a shell of water molecules, locally neutralises ions in solution; the tendency to bind ions with counter charges, mostly the original with which they were bound in the solid phase,
is therefore prevented. The dielectric constant is a qualitative measure of this shielding ability. Water with a high dielectric value has molecules that are able to solvate and surround ions avoiding that opposite charged ions attract each other again.

Yoshii et al. (2001) started from the equation of the dielectric constant \( \varepsilon \) dividing it into two distinct factors: the squared average of molecular dipole moment and the orientational correlation that can be calculated as

\[
\varepsilon - 1 = \frac{N}{3kTV} \langle \mu_i^2 \rangle G_k
\]  

(1)

where \( N \) is the number of molecules, \( k \) is Boltzmann constant, \( T \) is absolute temperature, \( V \) is volume, \( \mu_i \) is the dipole moment vector of molecule \( i \), and \( G_k \) is the orientational correlation given by

\[
G_k = \frac{\sum_i \sum_j \langle \mu_i \cdot \mu_j \rangle}{N \langle \mu_i^2 \rangle}
\]  

(2)

Equation (1) shows the known general weakening of the dielectric constant with increasing temperatures and the direct correlation of the two factors with the dielectric constant.

Equation (2) assumes the value of unity for no intermolecular orientational correlation. Density acts on both factors of the dielectric constant with different extent: on the molecular moment factor acts causing or removing induced dipole moment up to the extreme low value close to the water gas phase; on the \( G_k \) with more extent, acting on the structuration and orientation on the molecules. In a simulation the same authors observed the behaviour of water: first, at constant density over a wide range of temperature...
(from 27 to 427 °C), and then along the 427 °C iso-
therm (Table 1). Results show that at gas-like density,
the contribution to the dielectric constant is due only
to the single molecular dipole moment ($\mu = 1.87$ D),
a value close to the value found in gaseous state
($\mu = 1.85$ D), with no contribution due to induced
dipole. Here, SCW has no more structured water. In
other words, the factor of the field due to the struc-
tured water molecules is absent. A water molecule is
not any longer forced to bind with its neighbouring
molecule, being the intermolecular forces lower than
the kinetic ones (Nakahara et al. 2001). In this case,
its chemical behaviour becomes similar to the vapour.

At liquid-like density and temperature constant at
427 °C, instead, the SCW is structured with a dielec-
tric constant slightly smaller than that at 327 °C. This
is a consequence of the formation of the local clus-
tering network of hydrogen bonds between molecules
becoming therefore a heterogeneous fluid made of
finite clusters of bonded and free water molecules
(Gorbaty et al. 2017), which makes the liquid-like
behaviour similar to the liquid one. High-density
SCW represents a water that has polar properties: salt
solubilisation, acid–base dissociation and water self-
dissociation (Kritzer 2004).

In the density range from gas-like to 0.9 g/cm$^3$
(see Sakuma et al. 2013) supercritical water is highly
compressible: little pressure variations produce rapid
density variations. Consequently, by isothermally
varying pressure, the ionic character can vary from
gas-like density, with little or no ionic properties, to
liquid-like density that has most of the ionic proper-
ties: that means that these chemical properties are
tuneable by varying pressure at constant temperature.
Above 0.9 g/cm$^3$ the compressibility becomes lower,
since “at higher pressures, the structure of the fluids
is similar to the closest packing of H$_2$O molecules,
and the pressure gradient of the density is lowered.
The low isothermal compressibility was ascribed
to the stiffness of the H$_2$O molecules” (Sakuma and
Ichiki 2016).

### Table 1: Dielectric characteristics of water for
$N=10,648$ molecules at various temperatures, with
fixed density, and at fixed temperature of 427 °C with
decreasing density (from Yoshii et al. 2001)

| Dielectric constant (ε) | Dipole moment (μ) | Density (g/cm$^3$) | Temperature (°C) | $G_K$ |
|-------------------------|------------------|--------------------|------------------|------|
| **Constant density conditions** | | | | |
| 73                      | 2.6              | 1                  | 27               | 3.1  |
| 56                      | 2.44             | 1                  | 127              | 3.57 |
| 40                      | 2.37             | 1                  | 227              | 3.33 |
| 29                      | 2.33             | 1                  | 327              | 2.97 |
| **Isothermal conditions at 427 °C** | | | | |
| 21                      | 2.30             | 1                  | 427              | 2.54 |
| 12                      | 2.15             | 0.66               | 427              | 2.56 |
| 4.3                     | 2.02             | 0.33               | 427              | 1.69 |
| 1.4                     | 1.89             | 0.066              | 427              | 1.14 |
| 1.2                     | 1.87             | 0.033              | 427              | 1.08 |

### 3 Liquid and supercritical water–rock
interaction: rock weakening

The water–rock interaction is a mutual relationship
regulated by numerous factors; among others tem-
perature and, when the water is in supercritical phase,
pressure. In disequilibrium conditions, this interac-
tion results in a flux between solid and fluid phases,
which includes solubilisation (secondary), minerali-
sation and/or simply ion exchange. With increasing
temperature, if the lattice energy of ionic compounds
in the solid-state decreases, and if the hydration
enthalpy is equal or remains even slightly higher than
the lattice energy, ions dissolution occurs with water
molecules surrounding and shielding them.

Below there is a summary of common crustal-min-
erals solubilities, highlighting the density-solubility
correlation experimentally found and/or calculated
with SCW, assuming that the solubility behaviour of
rocks can be compared to the known solubility behav-
ior of specific minerals.
3.1 Quartz

SiO$_2$ is the mineral with the highest covalent characteristics among silicates and at the same time is the last silicate that precipitates with decreasing P and T conditions. The solubility of Quartz in water is a direct function of temperature becoming extremely low at standard conditions. Because of this, it is commonly used as a geothermometer in geothermal exploration (Fournier 1977). Fournier and Potter (1982) analysed the quartz solubility from ambient to supercritical environment, pointing out its direct relationship with SCW density (see Fig. 3A).

Sverjensky et al. (2014) measured quartz, enstatite, forsterite and corundum solubility, and aqueous silica speciation over a wide range of pressures and temperatures. The solubility of SiO$_2$ in water as a function of SCW density at two different isotherms is shown in Fig. 3A. The solubility of NaCl as a function of SCW density (Mantegazzi et al. 2013; Voisin et al. 2017) is shown in Fig. 3B. The solubility of Calcite versus SCW density, calculated according to Eq. 3, along two isotherms is shown in Fig. 3C.

**Fig. 3** Solubilities in supercritical water of three different mineralogical species as a function of density. A SiO$_2$ concentration in water as a function of SCW density at two different isotherms. Quadratic fitting extrapolated from Fournier and Potter (1982). B Solubility of NaCl as a function of SCW density (Mantegazzi et al. 2013; Voisin et al. 2017). C Solubility of Calcite versus SCW density, calculated according to Eq. 3, along two isotherms.
temperatures. In particular they analyse water silica speciation in relation to both systems, quartz–water and (orthoenstatite+forsterite)–water. At low densities, the dimer form $\text{Si}_2\text{O(OH)}_6\text{aq}$ prevails, in both systems; at increasing densities the monomer form of $\text{Si(OH)}_4\text{aq}$ prevails. According to the above authors, density variations in the highly compressibility field produce extremely rapid variations: at low pressures and 600 °C (low density), the dimers are around 85%. At about 400 MPa the percentages of both forms are equal. Above 900 MPa the percentages of both forms are equal. For speciation in the (orthoenstatite+forsterite)-water system variations in the highly compressibility field are more rapid. The monomeric form prevails in the liquid-like density field of SCW, just as in the liquid phase.

3.2 Sodium chloride

$\text{NaCl}$ and in general halide alkaline and alkaline-earth compounds are mostly ionic solids (around 73% of ionic character); their solubility correlates directly with the temperature of the aqueous liquid phase. However, in near critical and supercritical fields, the density becomes a primary factor in determining solubility (Fig. 3B).

The solute–solvent relationship in the supercritical phase is indeed different. The forms of solvation and ion pair association of halides have been studied in SCW (Cochran et al. 1992; Duan et al. 2006; Lee and Cummings 1999; Balbuena et al. 1996) also close to the critical pressure at low density (Keshri et al. 2016; Chialvo et al. 1995). The speciation between these two forms is again a function of density and the dielectric constant. Chialvo and Simonson (2003) modelled the behaviour of NaCl as electrolyte concluding that in diluted solutions it goes from weak-no dissociation ($\alpha=0$) to moderately-strong dissociation ($\alpha=1$), having a dielectric constant from 1 to 20 $\varepsilon$, respectively. In fact, at 427 °C and density $= 1$ g/cm$^3$ (Table 1), the dielectric constant equals $21 \varepsilon$; at these conditions, the formation of hydration shells around ions is plausible thanks to a dielectric field that has sufficient strength to solvate ions.

Ion pairing models describe ion associations: from the CIP (contact ion pair) configuration to SSIP (solvent separated ion pair) as a transition from real ion pairing to ions shielded by a single shell of water molecules (Fig. 4). Sakuma and Ichiki (2016), analysing the “structure of hydrated $\text{Na}^+$ and $\text{Cl}^-$ and $\text{Na}^-\text{Cl}$ ion pairs”, showed that the “hydration number increased with increasing pressure and decreasing temperatures”. This confirms the existence of a relationship between dielectric constant and temperature/pressure conditions (Sakuma et al. 2013): as the density decreases, the dielectric constant drops rapidly to its lowest value of 1.2 $\varepsilon$, with ions that are no more shielded (going beyond CIP—contact ion pair—formation, see Fig. 4) and that constitute the nucleation centres of mineral precipitation.

Walther (1986) analysed the behaviour of alkali and alkaline-earth metals in SCW and ion exchange between host rocks (mainly metapelitic mineral assemblage) and fluids (mainly $\text{H}_2\text{O}$). This author shows how the solubility increases by two orders of magnitude, from 100 to 300 MPa, with isothermal compression. Total solubility is therefore related.

![Fig. 4](image1.png)

**Fig. 4** Water structures with ionic solutes: $\text{Na}^+\text{Cl}^-$ hydration scheme. (1) CIP structure. Ions are in close contact, and only one shell of water molecules surrounds the ions couple. Low water density. (2) SSIP structure has only one hydration shell surrounding each ion but. Slightly higher water density. (3) Classic solvation: each ion has two hydration shells. Medium–high water density (modified from Chialvo et al. 1995). Going from left to right it is shown the variations in the hydration structure with increasing density.
Effectiveness of bulk solubility process is linked to the solute stability in SCW and to the solvation mechanism. As already seen in the case of SiO₂, also in NaCl (ionic solute) the solubility seems to be related to the density. At low density, the solubility is extremely low.

NaCl apparently follows the same scheme of SiO₂. In fact, Oelkers and Helgeson (1993) report formation of a polyatomic clusters at low density with solubility values approaching zero. Instead, at high density salt dissociation is complete (Fig. 4). At 400 °C and at pressure of 0.5 GPa (density = 1.040 g/cm³), Mantegazzi et al. (2013) report concentration of 3 M of NaCl, equal to 17.5% w/w. For comparison, seawater averages around 3.5% w/w and at standard conditions NaCl solubility is 6 M.

### 3.3 Calcite and carbonates

The fate of carbonates is similar to that of other inorganic solutes: solubility is correlated with SCW density. Based on experimental data for Calcite, Caciagli and Manning (2003) propose the following equation between 400 and 750 °C and 100–1600 MPa, with a mean standard deviation of 10% (Fig. 3C):

\[
\log m_{\text{CaCO}_3} = -3.95 + 0.00266T + (32.8 - 0.028)\log \rho_{\text{H}_2\text{O}} 
\]  

(3)

where \( T \) is the temperature and \( \rho_{\text{H}_2\text{O}} \) is the SCW density.

Calcite hydration process is a little more complicated than quartz and sodium chloride, since its solvation involves stoichiometric equilibria that include other molecules. Among other, CO₂ is believed to be one of the most important. Nevertheless, in an experiment, Fein and Walther (1987) measured calcite solubility in pure, decarbonated water, finding that the log of Ca molality in equilibrium with calcite equals −3.75 at 200 MPa and 500 °C (\( \rho_{\text{H}_2\text{O}} = 0.69 \text{ g/cm³} \)). Solubility, in this case, plausibly could follow the reaction:

\[
\text{CaCO}_3 + \text{OH}^- + \text{H}^+ + \text{H}_2\text{O} = \text{CaOH}^+ + \text{HCO}_3^- + \text{H}_2\text{O} 
\]  

(4)

The high grade of water dissociation yields hydroxyl and hydrogen ions that constitute major components in SCW: their high concentration is sufficient for the occurrence of reactions [4]. Therefore, calcite dissolution is possible in absence of CO₂, i.e. without the need of acid water.

Indeed, the presence of CO₂ could change calcite solubility: while up to a CO₂ molar fraction of 0.05 its solubility increases, at higher CO₂ concentrations the solubility is apparently hindered. Pan and Galli (2016) modelled the SCW and supercritical CO₂ coexistence during Na₂CO₃ dissolution at upper-mantle/lower-crust conditions. They observe that no CO₂(aq) is present in the final solution. Carbon bearing species are carbonate and bicarbonate ions. In extreme conditions, even in a CO₂ injection in SCW, the same authors find that, at 11 GPa and 727 °C, carbon dioxide becomes immediately speciated in HCO₃⁻ (80%), CO₃²⁻ and perhaps H₂CO₃.

CO₂ solubility in water is a direct function of pressure and an inverse function of temperature up to 100°. With 100° < T < 250°, and with P > above 10 MPa, the relationships between T and CO₂ solubility becomes direct. On the 250 °C isotherm, the dependence with pressure become prevalent. The increase of pressure from 140 to 160 MPa produces a solubility increase in the order of 1 mol/kg (Hangx 2005).

### 3.4 Subcritical crack growth and rock weakening

The creation of new microcracks in the dilatant region offers existing waters new rock surfaces where new interactions can begin. Classic solvation has already been illustrated in three cases of different minerals with a dedicated focus on supercritical water and density variations: this kind of relationship is surely one of the principals that begins, subordinating eventual mass transfer principally to saturation indexes. In each new or reactivated micro crack, the tip constitute a zone of weakness, even though, soon after the cracking, the stress level acting on the tip decrease immediately. Nevertheless, cracks continue to grow, even if the stress level is nominally below the critical threshold of rupture.

The real origin of the subcritical crack growth, defined as a slow propagation of a fracture, is unknown. Diverse theses have been proposed, most of which, based on experimental results, require the presence of the water. Among these, Anderson and Grew (1977 and references therein) explain the slow crack propagation with the mechanism of the stress corrosion, i.e. the cracks grow in presence of a reactive chemical environment in proximity of the crack tips that reduces the energy requirements of cracks’ growth.
Parks (1984) suggests that the fracture of a quartz crystal produces a break in the Si–O–Si bonds: roughly Si–O on one side and Si on the other. This fracture produces unbalance charges at freshly opened surface at crack tip and more specifically negative charges in O still bonded with a Si, and positive charges in the remaining Si. These “dangling” bonds are highly reactive, and prone to link counterions to achieve again electroneutrality. In the Earth crust, water is in general the first charge supplier, with its variable concentration of hydrogen and hydroxyl ions. Thus, the presence of aqueous fluids has a substantial effect on the weakening of quartz (Dunning et al. 1984), facilitating crack propagation. The cited references also suggest that this weakening effect due to chemical reaction should occur also on polycrystalline natural rocks. Michalske and Freiman (1982) give a chemical and molecular explanation of this weakening. They report that the presence of water in the crack tips is the principal mechanism of chemical corrosion stress in silica; according to their model, environmental liquid water—i.e. well below critical temperature—can react, at the crack tip, with the (stress) strained bridging Obr (Si–Obr–Si). These links develop by establishing a hydrogen bond with the bridging-silica oxygen, and through interaction between lone pairs of water’s oxygen and Si atom, forming, at the end, Silanols (Si–O–H) groups (see Fig. 5). These groups are the responsible of the weakening of the crack tip and process zone, by having a lower surface energy (e.g. Parks 1984; Kronenberg 1994). Summarising, this process facilitates crack propagation at (not quantified) low stress intensity, over ultra-low and low velocity ranges, from $10^{-9}$ to $10^{-2}$ m s$^{-1}$ (Michalske and Freiman 1982).

The model highlights two apparently secondary mechanisms but it contains two key points used by subsequent research. The first: strained bonds. In a simulation carried out by Rimsza et al. (2018), it is highlighted how the strained bonds are localised not only at the crack tip but also far from it. Some numbers. In their simulation, the crack tip

![Fig. 5 Model proposed by Michalske and Freiman. a H$_2$O molecule going toward the crack tip. b formation of a hydrogen bond between a hydrogen of H$_2$O and (lower in the figure) the oxygen of the quartz. c replacement of the hydrogen bond formed in b with a O–H bonding, creation of a bond between oxygen of the water with the (upper) silica and creation of hydrogen bonding of the (lower) hydrogen with the (upper) oxygen, formerly belonging to the same H$_2$O molecule and d disrupting of hydrogen bond and creation of two new silanols (SiOH). Redrawn and modified from Kronenberg (1994)](image-url)
radius was observed to be 0.5 nm, and the extension of the strained bonds is close to 7 nm. The second. The water molecule that establishes a bond with the oxygen bridge (Si–O_b–Si), dissociates into H^+ and OH^- in the central and final stages of this process. As reported by Kronenberg (1994) water and dissociated components are likely to penetrate quartz structure, up to 7 angstroms below the fracture surface (Mahadevan and Garofalini 2007) and subsequent local silanol formation through, in case of an entire water molecule, “dissociative chemisorption”. The role of the water in this process lowers the fracture toughness by about 25% in the entire fracture process, “either on surface or in the bulk” thus “allowing for fracture at lower strain”, (Rimsza et al. 2018).

Remarks following an experiment conducted on andesite and granite, suggest that temperature has a positive correlation with subcritical crack growth too (Nara et al. 2012).

4 The chemical role of liquid and supercritical waters in earthquake preparation process

This conceptual model has two assumptions: water is at hydrostatic pressure (understanding, below any given depth, water could be at lithostatic pressure) and only water chemistry is considered (the ionic content of water may be neglected for the purposes of a general discussion). It starts from a static situation by merging a generic earth crust profile with the water state diagram. Depth-pressure relationship is the hydrostatic pressure; temperature values are extrapolated considering two different geothermal gradients: one of 25 °C/km and the second of 40 °C/km.

The analysis of the steady state situation evidences some edges. The first is what here is defined the critical depth. Water, if present, is in its supercritical state beyond this depth. This edge separates two different ways for water to relate itself with surrounding environment. The liquid way is sufficiently known, while the supercritical has been poorly investigated in earth sciences; its behaviour is mostly inferred from laboratory experiments.

The second edge indicates the brittle ductile transition line, as reported in Fig. 6. Maximum reachable value is around the 500 °C isotherm, considering a tectonic strain rate around 10^{-14} s^{-1}, assuming the values reported in Violay et al. (2017).

Then, a dynamic system points out transformation occurring at depth before the main rupture. The opening of microcracks is the starting point of these deep transformations that translates in fluid chemistry modification, even with the separation of other

![Fig. 6 State diagram of water merged to a general crustal section. Water pressure is assumed to be hydrostatic at equilibrium. Dashed lines represent SCW density, bold polygon evidences the area where, at equilibrium, are located points with SCW prone to be subjected to the pressure cycle due to earthquake preparation process. The opening of a microcrack produces a vertical upward movement in the pressure values and so, as it is visible, a rapid lose in density. Reapplication of pressure is a downward movement, i.e. a compression where SCW acquire again high-density values. BDT is the brittle-ductile transition line (Violay et al. 2017)
chemical phases, and especially in the case of SCW, in a substantial decrease of rock resistance.

Hypocentral depths are variable. As an example, Chiarabba et al. (2003) affirm that in northern and southern Apennines (Italy), the NW-striking segments are confined within the upper 6–8 and 12–15 km of depth respectively. Present model assumes a maximum hypocentral depth of about 20 km. If water is present and assuming that it is in equilibrium with T-P conditions, then it is helpful in differentiating two distinct zones:

**Below water critical point (T < 373 °C)**

**Above water critical point (T > 373 °C)**

The critical depth is the divide between these two domains, a boundary between two different physical, chemical, and probably rheological domains, identified as the depth beyond which water is in the supercritical state. This depth is a function of the local geothermal gradient crossing the critical temperature isotherm (see Fig. 6).

In the earthquake preparation process, the opening of microcracks produces a depressurisation on the locally present free water. Subsequent pressure re-equilibration closes the pressure cycle on water. This cycle can have consequences on the solvent capacity of water, especially on freshly opened crack faces, that, through coalescence, may become a microfracture interconnected network. These water–rock interactions at seismogenic depth do play a role in host-rocks weakening that could lead to rupture. This mechanism may occur with relevant differences as a function of the water aggregation phase.

This mechanism occurs with relevant differences in relation to the critical depth and the associated aggregation phase of the water.

**4.1 Below the critical point of water: liquid phase**

Below the critical point, water compressibility is low, since, even close to subcritical conditions, the water density is close to 0.8 g cm$^{-3}$ at 250–300 °C and at relatively low pressure around 10 MPa. In liquid field, water–rock interaction is mainly governed by temperature. Few published data discuss mineral solubilities as a function of pressure in liquid water; most of these data come from low-temperatures oceanographic studies. As an example, a pressure variation from 1 to 1000 bar produces only an eightfold variation in solubility of halides and carbonates, while corresponds to an even lower variation in solubility of quartz and silicates (e.g. Millero 1982; Macdonald and North 1974).

Therefore, if there is no liquid/vapour phase transition, pressures correlate weakly with ion solubility. Pressure has instead appreciable effects in the separation of pressure sensitive fluids like gases (e.g. H$_2$, CH$_4$) and supercritical CO$_2$ (Portier and Rochelle 2005) now free to migrate elsewhere much more effectively than water (regarding the behaviour of supercritical CO$_2$-water see e.g., Bahadori et al. 2009; Pruess 2005). The removal of CO$_2$ from the liquid solution changes all aqueous equilibria, while a bi- or multiphasic system is created. Here, in addition to water, the fracture network could become occupied by scCO$_2$ that, according to Criscenti and Cygan (2012), can transport aliquot of some major ionic elements through a partition process. In some cases, H$_2$ development occurs. Leaving aside serpentinisation reactions, hydrogen formation could be related to the contact between newly pulverised saturated igneous rocks and waters (e.g. Sugisaki et al. 1983). Authors observe in laboratory experiment the formation and the quantity of formed H$_2$ in contact between pulverised rocks (peridotite > biotite > granite) with distilled water, reaching concentration close to 3% of H$_2$.

If the water in the new P–T state falls into the vapour field instead, water distillation may occur, with associated solute precipitation. The vapour phase could migrate easily and the successive increase of pressure yields again a liquid, aggressive phase. In these conditions, water can establish intensive water–rock interactions. A simulation conducted with phreeqc (Charlton and Parkhurst 2011; Parkhurst and Appelo 2013) between hot pressurised water with low ionic strength and granite, points out the low-pressure dependence in water rock interaction, and at the same time the possible secondary mineral formation, even at high temperature (300 °C), most of them are clayey minerals and/or minerals with OH groups.

**4.2 Above the critical point of water: supercritical phase**

Above the critical point of water, the pressure cycle, acting on the highly compressible SCW makes the fluid vary its chemical properties. This process may
be described in three stages. A similar scenario could be reasonably applied even to the liquid phase, if and only when the liquid water undergoes to vaporisation during the opening of microcracks. Here is as follows.

4.2.1 First stage

This stage begins at equilibrium. The net chemical exchange between the two parts in SCW–rock interaction is equal to zero. The local values of temperature and pressure could be extrapolated respectively from local geothermal gradient and from depth, with the hypothesis that the pressure is hydrostatic. Departures from hydrostatic pressure is due to the continuous tectonic load acting on the rock interested and on free water. Here starts the pressure cycle described as follows.

4.2.2 Second stage

In response to the continuing tectonic load, microcracks may open, causing the drop in fluid pressure. This decompression has consequences on \( N_{HB} \) and on density. In this stage, SCW could lose all the polar properties that normally characterise liquid water and dense SCW. So, no acid/base dissociation, no self-dissociation (eventual pH speculation does not make any sense), low dielectric value, no possibility therefore to solvate minerals. Gaseous components previously dissolved in SCW separates and a bi-multiphasic system develops, with different migration modalities. Variation of water chemistry if \( CO_2 \) is involved. In any case, all the solutes precipitates rapidly passing through ion pair association (chlorine) or dimer formation (quartz).

SWC, thanks also to its low viscosity, low density, and thanks also to the absence of surface tension, can easily migrate, adhere (i.e. wettability) and permeate tiny and freshly opened fissures that normally are a barrier for standard water to penetrate, following the geometry of the crack network.

4.2.3 Third stage

Due to continuing deformation due to constant tectonic load, the pressure of the fluids contained in the micro-fractures system begins to rise, switching back the polar attributes of the water molecules network. Due to rising \( N_{HB} \) and density, the SCW starts again to behave as an ionic solvent, and, being now strongly undersaturated, is avid and rapid in solvating minerals all along the micro-fractures system, even in new freshly opened fractures. Eventual other residual fluid phases present could be reabsorbed in the SCW. In other words, as the fluid pressure increases, minerals solubilities rise, in some cases exponentially, with increasing density (cf. Figure 3). Some chemical processes that may take place are: mineral dissolution in the newly opened surfaces, quartz and silicate permeation and weakening for increased subcritical crack growth and hydrogen penetration, and eventual acid shift in case of \( OH^- \) subtraction by secondary clayey minerals (such as illite, smectite and chlorite).

4.2.4 Rock weakening

The consequence of the described interaction between SCW (and liquid water if undergoes to vaporisation) and host rocks is the chemical contribution to a general weakening of the portion of rock interested by the microcracks and earthquake preparation process. If the cycle of pressure happens entirely during the earthquake nucleation process, this could be a key factor leading to the triggering of a main shock at a smaller stress level compared to that needed for the unaltered rock, being now the rock resistance dramatically reduced thanks to the chemical action. Summarising, the chemical contribution to the rock weakening is due to two parallel causes triggered by the cycle of pressure.

The first cause is the rock solubility. Specifically, in the case of SCW, the pressure variations could be seen as an effective tuner of solubility by varying SCW electrostatic and molecular properties. In some cases, these mineral solubility variations are exponential. In absolute terms, quartz solubility is even higher in liquid-like density of SCW than in liquid water. Here, it is arguable the meaning of the critical depth: it indicates a net border between two possible solvent and distinct behaviour in water–rock interaction. If liquid water has the possibility to weaken rock, SCW do it, effectively and even rapidly. In this respect, an experiment, carried by Takahashi and Hashida (2004), helps to better understand the divide existing in the water–rock interaction between the liquid and SCW field. They performed a triaxial shear deformation test with a granite specimen and water up to 600 °C and
150 MPa. The results show a net and rapid strength decrease as the water temperature is equal or above critical value. Optical inspection around fracture surface reveals crack density values sharply higher in supercritical water rather than in liquid one, with a net and substantial increase in permeability.

Second general effect of the cycle of pressure applies principally to quartz and silicate in general, namely the subcritical crack growth. Neglecting as a first approximation the (existing) influence of the ionic content of water, subcritical crack growth is transversal to the water aggregation state. Moreover, the high concentration of H\(^+\) and OH\(^-\) ions, due to high temperatures, could eventually speed up this process, according to the dissociative chemisorption model (Mahadevan and Garofalini 2007). New and strained silicate surfaces offer to the water and to its dissociated components reactive sites for silanol (SI–O–H) formation, a structure that weakens the superficial strata of silicates, permitting an easier crack propagation and a higher number of fracture events (Rimsza 2018).

5 L’Aquila earthquake example

As a preliminary example, it is possible to apply this model, or part of it, to the Mw 6.3 L’Aquila earthquake of 2009, April 6th. The role of the fluids in this event has been extensively ascertained and highlighted (e.g. Savage 2010 and references therein). In detail, Di Luccio et al. (2010) explain the observed Vp/Vs variations with the action of moving deep fluids, capable to vary the effective pressure acting on rocks. Thus, they assign to the fluids a primary role in the reactivation of old cracks and in the activation of new ones during main shock nucleation process. Based on a similar dataset of negative and positive variations in the velocity ratio, Lucente et al. (2010) provide an articulated picture based on dilatancy and related fluid diffusion mechanism, occurred before the main shock, with an acceleration of events just one week before the main shock and testified by the most intensive foreshock seismic activity. Chiodini et al. (2020) explain the role of these CO\(_2\)-rich fluids and their deep origin. Thanks to the CO\(_2\) isotopic signature, they demonstrated the relationship of higher deep CO\(_2\) discharge at surface for the event that struck L’Aquila. The explanation they give focuses on a thermal mechanism of CO\(_2\) release from the subduction zone into deep reservoirs in the crust. The high pressure reached by the continuous production of CO\(_2\) should push it towards the surface aquifers. During earthquakes, then, the mechanical shaking triggers the release of unstable quantities towards the surface, “such as a shaken bottle of a carbonated drink”.

The complex sequence of dilatancy and fluid diffusion offers instead a basis that may explain the mentioned cracking with the chemical action described in the present model. The involved fluids are saturated with CO\(_2\) in a carbonatic system. The following equation describes the general chemical equilibrium:

\[
\text{H}_2\text{O} + \text{CO}_2(\text{sc}) + \text{CaCO}_3 \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \tag{5}
\]

At depth, the pH of CO\(_2\) saturated water could reach values well below 4 units (Haghi et al., 2017) and, at these values, the solubility of carbonates is extremely high. The dilatancy phase breaks the equilibrium: it allowed the separation of CO\(_2\) according to the new pressure conditions. Consequently, the precipitation of CaCO\(_3\) occurs since the fluids tends to reach the new chemical equilibrium (Eq. 5 proceeds to the left side). Separated scCO\(_2\) and produced water vapour are the first phases free to migrate elsewhere, mainly for a lower viscosity than liquid water (the presumable aggregation phase of water in this event), in new created voids and come into contact with newly fractured carbonate formations.

Then, the presence of detected highly pressurised fluids occurred at least 8 days before the main event (Sugan et al. 2014), testify a (re)pressurisation of the fluids in the system. Water vapour can condense again into flowing liquid water. The mixture is now undersaturated in ions and, if it still contained adequate concentrations of reactive CO\(_2\), definitely acid. These were the perfect conditions to solubilise quickly the new calcareous surfaces, especially at the crack tips. The present model also provides a different explanation on CO\(_2\) discharge at surface. As already mentioned, deep CO\(_2\) is in supercritical state (scCO\(_2\)) and is highly compressible; its solubility in water is an inverse function of salinity, a direct function of pressure; in a minor extent it is a direct function of temperature for \(P > 15\) MPa (Spycher and Pruess 2010). Starting from an equilibrium condition of 150 °C and 60 MPa, a depressurisation of 10 MPa produces the release of about 20 g of scCO\(_2\) per
1000 g of H2O (Rochelle and Moore 2002; Spycher and Pruess 2010). Based on this simple consideration, the presented model explains fluids separation during the dilatancy phase. As soon as excess scCO2 has been released, a bi or multiphasic system may have developed with significantly amount of separated scCO2; then, due to a better buoyancy, scCO2 overwhelmed water. Once created the sufficient permeability, scCO2 could have found the route path to surface, entering in its gaseous phase at shallow depth.

Further and more detailed investigations however are needed for a complete application of present model to this case.

6 Conclusion

This work defines for the first time the chemical mechanisms that take place in the hypocentral zone during the earthquake preparation process, starting from the analyses of the modifications of water properties due to equilibria perturbation at molecular scale, and the relative consequences on surrounding rocks.

This model overcomes the general conception of other models based on the notion that water is only a physical agent (e.g. Miller 2013; Yoshida and Hasegawa 2018) by integrating them, and giving the whole phenomenon of the earthquake preparation process a wider and more complete dimension. For instance, it explains the chemical deposition in fault zones described also in Yamashita and Tsutsumi (2018), it contributes to a much broader framing of what it was observed by Heinicke et al. (2009) and, as reported in the discussion, presents a broader, working hypothesis on the long and complex preparation phase of the L’Aquila earthquake, based on the active role of the chemical action of the fluids present at depth.

The main outcomes of the present work are:

a. The opening of micro fractures triggers an almost irreversible process on the water–rock system;

b. Due to solubility product variations and to sub-critical crack growth, the rock resistance undergoes to significant modifications; this is true especially in case of supercritical water;

c. The chemical differentiation of waters occurs in the earthquake nucleation zone even with phase separation and chemical modification;

d. Thanks to its high compressibility, supercritical water responds easily to pressure variations by varying its density. The zone of interest of SCW in the present model is delimited by critical temperature line as lower limit, and BDT line as upper limit.

It seems evident that the presence of water at depth is a powerful destabilising factor. Once the micro-fracturing has begun, the chemical action of water could become of primary importance in causing further weakening of the rocks involved in the earthquake preparation process, up to the main shock. This model intends to place another brick in the study of the earthquake preparation process, by integrating physical models highlighting the important chemical role of the two kinds of Waters examined: liquid and supercritical.

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Data availability Data are obtained from published papers cited in the figure captions and from the National Institute of Standards and Technology.

Declarations

Competing interests I affirm that no competing interests exist, nor conflict of interest of any kind.

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