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**1 Explosive properties of water in volcanic and**  
**2 hydrothermal systems**

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7 **Abstract.** This paper describes, from a thermodynamic point of view,  
8 the physico-chemical conditions, under which water behaves as an explosive.  
9 This phenomenon occurs frequently in hydrothermal and volcanic systems,  
10 when water is brutally shifted from its initial equilibrium state. Water (ei-  
11 ther liquid or gas) becomes metastable or unstable, and reequilibrates by vi-  
12 olent demixing of a liquid-gas mixture. In a first step, a phenomenological  
13 approach of metastability is given in an one-component perspective, intro-  
14 ducing the notion of spinodals and delimiting the extent of metastable fields.  
15 The physical mechanisms (bubble nucleation, cavitation, spinodal decom-  
16 position), which are involved in these explosive transformations of water, are  
17 detailed in what relates to the natural eruptions topic. The specific thermo-  
18 dynamic properties ( $P$ - $v$ - $T$ - $H$ - $U$ ) of metastable water are presented by us-  
19 ing the reference Wagner and Pruss equation of state. Then, the mechani-  
20 cal work produced by the different possible physical transformations, includ-  
21 ing decompression, vaporization, isobaric heating and exsolution, involved  
22 in water explosions are quantified. The classic calculation of the energy bal-  
23 ance under the reversible assumption is here extended proposing a pathway  
24 to take irreversibility into account. This model can be used to estimate mag-  
25 nitude of volcanic impacts from scaling laws based on explosion energies.

## 1. Introduction

Magmatic, volcanic and hydrothermal systems are characterized by an explosive release of energy, which is produced essentially by the mechanical work of expansion of fluids. This explosivity is firstly caused by the exsolution of juvenile, hot and pressurized fluids, mainly composed of water (> 80% by volume) [Mills, 2000], during the magma crystallization and ascent through the crust. This feature is best visualized by the drastic increase of the volumetric fraction ( $f_v$ ) of exsolved water at near-surface conditions of the Earth (Figure 1), where  $f_v$  is computed from the mass fraction of exsolved water (wt % H<sub>2</sub>O) by:

$$\text{wt \% H}_2\text{O} = \frac{\rho_w f_v}{\rho_w f_v + \rho_m (1 - f_v)}, \quad (1)$$

with  $\rho_m$  being the magma density ( $\rho_m \simeq 2500 \text{ kg/m}^3$ ) and  $\rho_w$ , the density of the aqueous phase (in  $\text{kg/m}^3$ ) calculated by the *Wagner and Pruss* [2002] equation of state for water. As pointed out by *Burnham* [1979], more than 3 Gm<sup>3</sup> of steam can be produced from only one Gm<sup>3</sup> of magma exsolving 2 wt % of water at 100 bar. Such a fluid volume cannot be retained on a long period of time under surface, and one of the essential questions of volcanic processes is the evacuation of this excess water out of magmas. The main factor controlling the gas removal is the viscosity of magmas, giving a wide range of contrasted behaviours, from strombolian fountaining to the violent plinian explosions. The most explosive (and sometimes cataclysmic) volcanism arises at the conjunction of both factors, i.e. high water content and high magma viscosity. Figure 1 shows also that the increase of the water volume fraction is accompanied by a marked change of the magma nature, where the silicate melt is fragmented into an aerosol of ash and steam.

38 Obviously, this transition occurs when the water volume fraction overruns some threshold,  
39 which was approximated ca. 50 % by *Wohletz et al.* [1984] or 75-84 % by *Sparks* [1978].  
40 However, recent experimental and theoretical studies [*Thomas et al.*, 1994; *Zhang et al.*,  
41 1997; *Zhang*, 1999; *Spieler et al.*, 2004] have demonstrated the influence of others factors,  
42 like the depressurization rates and intensities, the melt viscosities, surface tensions or  
43 gas diffusivities on the fragmentation onset. Anyway, this catastrophic exsolution occurs  
44 either in the sommital parts of the magmatic chamber just before the eruption, or in the  
45 vent during the eruption. The rapid exsolution, decompression and blowing out of these  
46 magmatic chambers filled with fluid-rich magmas, leads to the ejection of huge amounts  
47 of gas and tephra (pumice and ash), development of pyroclastic falls, flows or surges, and  
48 finally, the collapse of a caldera.

49 The second main cause of explosive eruptions is due to the presence of cold liquid water  
50 on the Earth surface. Sudden mixings of large quantities of non-juvenile liquid water  
51 with hot materials produce violent explosions, giving rise to a large number of various  
52 explosive phenomena (hydroeruptions, [*Moyer and Swanson*, 1987]; surtseyan volcanism,  
53 [*Kokelaar*, 1986]; phreato-magmatic eruptions including hydrothermal geysering, [*Browne*  
54 *and Lawless*, 2001]). Additionally, hydrothermal eruptions are not the simple result of liq-  
55 uid water heating, but also require the incidental and sudden decompression of pressurized  
56 waters, which are close to their boiling conditions.

57 Thus, water is the main explosive agent on Earth. For this reason, the properties of wa-  
58 ter have been the subject of numerous studies, both experimental and theoretical [*Wohletz*,  
59 1983, 1986, 2002; *Zimanowski et al.*, 1991, 1995, 1997b]. In particular, the explosions  
60 of water in contact with magma are usually explained by complicated physico-chemical

61 mechanisms, usually termed "Molten-Fuel-Coolant Interactions" (MFCI) [*Wohletz*, 1983;  
62 *Theofanous*, 1995; *Zimanowski et al.*, 1997a]. Despite the abundant litterature, mainly in  
63 the volcanological, physico-chemical or industrial engineering fields, these processes are  
64 so complex that they are not well understood yet.

65 In a first part, we will show how water explosions can be described in a general the-  
66 oretical framework of fluid metastability [*Debenedetti*, 1996]. The notions of so-called  
67 spinodal curves, superheated liquids, supercooled gas and others will be introduced, and  
68 we will see how these concepts, originating from fundamental physics of fluids, can be  
69 useful to understand these eruptive phenomena. Next, the physical mechanisms involved  
70 in explosive water reactions will be detailed in what may be used by the volcanological  
71 community. Then, the five main energetical contributions involved in magma-water inter-  
72 actions, which are respectively (1) decompression, (2) vaporization, (3) liquid heating, (4)  
73 steam heating and (5) magma exsolution, will be quantified by using the reference equa-  
74 tion of state for water of *Wagner and Pruss* [2002]. The part of the magmatic thermal  
75 energy, which can be transformed into explosive kinetic energy, will be analysed. This will  
76 help us to differentiate the different types of hydrothermal and volcanic environments as a  
77 function of their explosion energy, calculated according to the one-component water case.  
78 Finally, we will show how our model can be used to estimate the intensity of volcanic  
79 explosions with the help of scaling laws.

## 2. What Makes Water an Explosive ?

80 An explosion is always the violent response of a system to a physico-chemical pertur-  
81 bation, which has left it in an energetic, metastable or unstable, state. For instance, fast  
82 thermodynamic processes (water heated at the contact of a magma, rapid depressurisation

83 of a liquid, high-speed flow of a fluid, . . . ) produce highly transient metastable states,  
84 which return towards equilibrium in a very rapid and explosive way. In other words,  
85 metastable states are temporary configurations, which are more or less distant from an  
86 equilibrium state. The more important is this distance (i.e. the metastability degree),  
87 the more explosive will be the relaxation towards equilibrium. As a consequence, the  
88 characterization of metastable states can give us some indications about the explosive  
89 feature of physico-chemical transformations.

90 This paper follows a phenomenological approach, based on classical thermodynamics  
91 and equations of state. This introduces the notion of spinodals, which are the theoretical  
92 bounds between metastability and instability.

## 2.1. A Phenomenological Approach of Metastability

The thermodynamic properties of a pure substance is described by an equation of state, which is usually formulated by means of a mathematical formulation of the Helmholtz free energy  $A$ , as a function of the temperature  $T$  and molar volume  $v$  for pure fluids:

$$A = A(T, v). \quad (2)$$

93 Any thermodynamic parameter can then be obtained by simple differentiation of the  
94  $A(T, v)$  function of adequate order [*Thiéry, 1996*].

95 Variables  $T$  and  $v$  are independent, but one important consequence of the second law  
96 of thermodynamics is that some sets of  $(T, v)$  values are not allowed. Indeed, to be at  
97 internal equilibrium, a fluid of given  $(T, v)$  must obey the following relations [*Debenedetti,*  
98 1996]:

$$\left(\frac{\partial T}{\partial S}\right)_P > 0, \quad (3)$$

where  $S$  is the entropy; and,

$$\left(-\frac{\partial P}{\partial v}\right)_T > 0. \quad (4)$$

99 Equation 3 is commonly referred to as the thermal stability criterion, and equation 4 as  
 100 the mechanical stability criterion. Thus, the  $(T, v)$  space of a pure compound is splitted  
 101 into three main regions (Figure 2):

102 1. the instability field, where neither the thermal nor the mechanical stability criteria 3  
 103 and 4 are satisfied. The incidental formation of a fluid with  $(T, v)$  properties in the  
 104 unstable field will be immediately followed by its explosive demixion into a biphasic liquid-  
 105 gas mixture by a process of spinodal decomposition ([*Debenedetti*, 2000], see Section 2.2).

106 2. the metastability field, where the fluid phase obeys the stability criteria, but appears  
 107 to be less stable than a biphasic association. Demixing of the initial fluid (either by  
 108 partial vaporization or condensation) will proceed by means of nucleation processes (see  
 109 Section 2.2). The metastable and unstable regions are separated by the spinodal curves.  
 110 The first spinodal, noted Sp(L), is the liquid spinodal, and is the limit of a metastable  
 111 (superheated) liquid; whereas the second spinodal, noted Sp(G), is the gas spinodal,  
 112 limiting the metastable (supercooled) gas field. Both spinodals meet at the critical point.

113 3. and the stability field, where the fluid is fully stable. Metastable and stable fields  
 114 are delimited by the binodal curve.

115 Metastable fields can also be depicted in a  $(P, T)$  diagram (Figure 3). The liquid spin-  
 116 odal starts from the critical point and runs to lower pressures with decreasing tempera-

117 tures (at least, up to 330 K where the liquid spinodal curve exhibits a pressure minimum,  
118 see [Imre *et al.*, 1998] for further details about the topology of the liquid spinodal curve  
119 of water). It is worth to note that the liquid spinodal curve runs through the region  
120 of negative pressures. As a matter of fact, any condensed material can indeed support  
121 negative pressures. Thus, the liquid spinodal curve indicates the highest (theoretical)  
122 tensile stresses that a liquid can bear out. This property of water (and other liquids) has  
123 been well demonstrated by experimental studies of aqueous fluid inclusions [Zheng, 1991;  
124 Zheng *et al.*, 1991; Shmulovich *et al.*, 2009]. Note that the field of negative pressure relates  
125 only to the liquid, as negative pressure for gases is a nonsense (due to pressure-density  
126 proportionality, zero gas pressure corresponds to vacuum).

127 The representation of thermodynamic properties of a fluid in the metastable region is a  
128 highly demanding task for an equation of state, firstly because of the divergence of some  
129 thermodynamic variables (for instance, the isobaric heat capacity), and secondly because  
130 of the scarcity of experimental data. The equation of state of *Wagner and Pruss* [2002]  
131 has been selected, as it is well acknowledged by the scientific community for the liability of  
132 its extrapolation in the metastable field (see [Wagner and Pruss, 2002], where its validity  
133 for superheated liquid water is fully discussed). Note however that the equation of state  
134 of *Wagner and Pruss* [2002] yields meaningless results in the unstable field, and care must  
135 be taken to avoid this domain, in particular, for the calculations of spinodals.

## 2.2. Nucleation-Growth and Spinodal Decomposition

136 The distinction between metastable and unstable states is closely linked to the type of  
137 relaxation mechanism towards equilibrium. Metastable systems re-equilibrate themselves  
138 by nucleation and phase growth, whereas unstable ones proceed to equilibrium by spin-

139 odal decomposition [*Debenedetti*, 1996, 2000]. This distinction between nucleation and  
 140 spinodal decomposition is important, as this will control many parameters, such as the  
 141 incubation time before relaxation, the final distribution of matter, the kinetic rate of the  
 142 transformation, the rate of energy release and hence its explosivity.

143 Nucleation and spinodal decomposition are both the results of fluctuations of an or-  
 144 der parameter (i.e. the fluid density for a pure system) describing the system at the  
 145 microscopic scale. Modalities of phase separation are totally different between these two  
 146 mechanisms.

147 Spinodal decomposition does not require any thermal activation energy: it is a spon-  
 148 taneous process, which occurs as soon as the system enters the unstable domain. In-  
 149 versely, nucleation is an activated process, which will take more or less time to occur in a  
 150 metastable system.

151 Nucleation is produced by a localized high-amplitude fluctuation of the density. The  
 152 growth of a small nucleus entails an energy cost as long as a critical size is not attained.  
 153 The energy barrier  $E_b$ , which has to be overcome for a critical radius  $r_c$ , can be approx-  
 154 imated by the classical nucleation theory (e.g. [*Debenedetti*, 1996]):

$$E_b = \frac{16 \pi \sigma^3}{3 (P_{\text{vap}} - P_{\text{liq}})^2}, \quad (5)$$

$$r_c = \frac{2 \sigma}{|P_{\text{vap}} - P_{\text{liq}}|}, \quad (6)$$

155 where  $\sigma$  is the surface tension between liquid and gas,  $P_{\text{vap}}$  and  $P_{\text{liq}}$  are respectively the  
 156 pressure in the gas and liquid phases. The important control parameter is  $|P_{\text{vap}} - P_{\text{liq}}|$ ,  
 157 which increases from zero at saturation conditions to large values at spinodal conditions.  
 158 Thus, nucleation is facilitated, when both  $E_b$  and  $r_c$  become sufficiently small, giving rise

159 to the process of homogeneous nucleation. Thermodynamic spinodal corresponds to nil  
160  $E_b$ . Homogeneous nucleation becomes spontaneous as soon as  $E_b$  is of the same magnitude  
161 order than thermal fluctuations: this is the kinetic spinodal limit [*Kiselev, 1999; Kiselev*  
162 *and Ely, 2001*], whose curve follows roughly, but shifted at lower temperatures and higher  
163 pressures, the theoretical liquid spinodal curve Sp(L) in a  $(P, T)$  diagram [*Shmulovich*  
164 *et al., 2009*]. At any condition between saturation and the kinetic spinodal curve, nucle-  
165 ation occurs only at some favourable sites, produced by impurities in the fluid or along  
166 solid surfaces, where the energy barrier is considerably lowered. This nucleation process  
167 is well known under the name of heterogeneous nucleation (e.g. [*Lasaga, 1998*]).

168 Conversely, spinodal decomposition is produced by low-amplitude density fluctuations  
169 between adjacent regions in the fluid: slightly more dense domains evolve towards a  
170 liquid-like density, and less dense regions evolve towards a gas-like density [*Debenedetti,*  
171 *1996, 2000*]. Because this process involves also the creation of liquid-gas interfaces (which  
172 is expensive in energy), only regions of long wavelengths (i.e. covering large areas for  
173 a minimal surface cost) will be favoured by these density evolutions at the expense of  
174 smaller domains, which will shrink away.

175 In other words, spinodal decomposition is the separation of regions, whose densities  
176 are progressively evolving towards two poles, liquid and gas, until stable conditions are  
177 reached, whereas nucleation-growth is the formation of new regions from the nucleation  
178 sites, but presenting a net density contrast with their surroundings since the beginning.

179 In the case of spinodal decomposition, phase separation occurs throughout the material,  
180 whereas phase splitting for nucleation arises only at some nucleation sites and proceeds  
181 by means of a reactive interface (either a boiling front or a condensation surface). This

182 implies slower transformation rates for nucleation-growth, as the growth of the newly  
183 nucleated phases requires longer pathways for heat and/or mass transfer. Therefore, the  
184 heat and/or mass diffusion may be critical limiting parameters in the nucleation-growth  
185 process. On the contrary, spinodal decomposition of liquids into vapours is particularly  
186 explosive, as it is accompanied by a partial vaporization and an important energy release  
187 in a very short lapse of time. Table 2 summarizes the main differences between these two  
188 fundamental kinetic processes of phase separation, which are nucleation-growth and spin-  
189 odal decomposition. It is worth to note that both mechanisms are not mutually exclusive:  
190 a reequilibration transformation of a high-disequilibrium state can start with spinodal de-  
191 composition, and then proceed further by the classical mechanism of nucleation-growth.  
192 Because the spinodal decomposition of fluids into liquid-gas mixtures is a very rapid  
193 process, it cannot be studied experimentally [*Nonnenmacher*, 1980; *Debenedetti*, 2000],  
194 except at conditions, which are very close to the critical point.

195 Very rapid changes of thermodynamic conditions are needed to initiate explosive phys-  
196 ical transformations by spontaneous nucleation or spinodal decomposition: these are  
197 treated in the next section.

### 2.3. The Explosive Physical Transformations of Water

198 Different physical transformations can lead to explosive phenomena (Figure 3): the  
199 explosion intensity can be, indeed, visualized by considering the relative positions between  
200 the spinodals and the  $P - T$  paths undergone by the fluid.

#### 2.3.1. Rapid Heating of Liquid Water

202 The fortuitous contact of liquid water with a hot surface (at the microscopic scale) is  
203 the first way to trigger an explosive boiling. It mainly relates to (1) explosive water-

204 magma interactions [*Wohletz*, 1986; *Zimanowski et al.*, 1986, 1991, 1995; *Wohletz*, 2002],  
205 and to (2) steam explosions caused by water spills onto molten metals or salts [*Reid*,  
206 1983]. To a first step, all of these processes can be approximated by isobaric heating  
207 transformations, i.e. by a horizontal line in the  $P - T$  phase diagram of Figure 3, running  
208 from the stable liquid field up to the metastable or unstable regions. Extensive laboratory  
209 investigations have demonstrated that the boiling temperature  $T_b$  of water is the main  
210 parameter controlling its explosivity [*Reid*, 1983]: indeed, most explosive boilings are  
211 obtained when  $T_b$  is, roughly, either around  $T_{hn}$  or  $T_L$  [*Reid*, 1983].  $T_{hn}$  refers to the  
212 temperature of homogeneous nucleation, or the temperature of superheating limit. A value  
213 of 577 K (304°C) is usually accepted for the temperature  $T_{hn}$  of water at one bar [*Reid*,  
214 1983].  $T_L$  is the Leidenfrost temperature [*Leidenfrost*, 1756], at which a thin and stable  
215 vapour layer forms at the interface between the hot body and liquid water. Above  $T_L$ ,  
216 this stable vapour layer film constitutes an insulating zone, which prevents any explosion  
217 [*Mills*, 1984]. However, a mechanical shock can force contact between liquid water and the  
218 hot body, and trigger a violent thermohydraulic explosion [*Zimanowski et al.*, 1991]. A  
219 precise and definite value for  $T_L$  cannot be given, as it depends on the physical properties  
220 of the hot surface, such as its thermal diffusivity, its surface roughness, its prefragmented  
221 state and others. Nevertheless,  $T_L$  is below the critical temperature  $T_c$  of water, and may  
222 be as high as the liquid spinodal temperature  $T_{sp}$  at 1 bar, ( $T_{sp} = 320.45^\circ C = 593.6$  K).  
223 Hence, explosive water boilings occur either by spontaneous homogeneous nucleation or  
224 by spinodal decomposition. In this latter case, nucleated boiling does not succeed to keep  
225 the pace to evacuate the excess heat: this results to a thermal shock and to the spinodal  
226 decomposition of the interfacial liquid water.

### 2.3.2. Liquid Decompressions

Another important cause of fluid instabilities is the rapid depressurization of a liquid, whose  $P - T$  path in Figure 3 is represented by a descending vertical line up to a final pressure  $P_f$ . But depending upon the initial liquid temperature  $T_i$ , this pressure drop can lead to two contrasted evolutions, which we will define as (1) superspinodal decomposition and (2) subspinodal decomposition. The first case is a decomposition in the subcritical region, where the  $P - T$  depressurization path cuts the kinetic liquid spinodal in a temperature range, let's say between  $250^\circ\text{C}$  ( $\simeq 0.8 T_{hn}$ ) and  $T_c$ , the critical temperature of water ( $T_c = 374^\circ\text{C}$ ). As a consequence, the liquid state goes through the metastable field, and subsequently through the unstable field. Such an evolution, which is very rapid, results finally to an explosive vaporization through spinodal decomposition or spontaneous nucleation, which we call a superspinodal decomposition.

The second case is a pressure drop of a liquid up to 1 bar, but at a temperature below  $250^\circ\text{C}$ . At the difference of the former case, the  $P - T$  decomposition path does not crosscut the liquid spinodal curve and will produce either non-explosive or moderately explosive boiling, which we refer to as a subspinodal depressurization. This last situation may be also at the origin of cavitation (see next section).

Thus, spinodals are useful to assess the explosive character of a transformation, a conclusion already inferred by engineers dealing with the failure of containers of pressurized liquids. The most serious damages occur, as a rule of thumb, when the temperature of the liquid reservoir is between  $0.9 T_c$  (i.e. roughly  $T_{sp}$ ) and  $T_c$ . Such explosions are called BLEVEs, for Boiling Liquid Expanding Vapour Explosions [*Birk and Cunningham, 1996; Casal and Salla, 2006; Salla et al., 2006; Abbasi and Abbasi, 2007*]. From this temperature

250 range, one can estimate that the violence of these explosions may be explained, at least  
251 in the very first steps, by the spinodal decomposition of superheated liquids induced by a  
252 sudden depressurization.

253 This distinction between subspinodal and superspinodal decompressions may have pro-  
254 found implications on the functioning of hydrothermal systems, as they are subjects to  
255 recurring pressure drops up to their lower external pressure  $P_{\text{ext}}$ . For continental hy-  
256 drothermal systems,  $P_{\text{ext}}$  is the atmospheric pressure, whereas for oceanic systems,  $P_{\text{ext}}$  is  
257 the pressure of the sea bottom (mainly between 100 bar and 500 bar for sea floors between  
258 1000 m and 5000 m). Superspinodal liquid depressurizations may occur in eruptions of  
259 continental high-temperature and liquid-dominated hydrothermal fields (whose tempera-  
260 tures typically exceed 250°C). The conditions of the largest known hydrothermal eruptions  
261 in New Zealand are not known precisely, but maximal explosion focal depths have been  
262 estimated up to 450 meters [*Browne and Lawless, 2001*]. This implies incipient boiling at  
263 260°C and 45 bars, i.e. favourable conditions for a nearly superspinodal depressurization  
264 against the atmospheric pressure. Phreato-magmatic eruptions produced by deep maar-  
265 diatreme systems may also be linked to superspinodal decompressions. To the contrary,  
266 subspinodal decompressions are produced by low-temperature continental hydrothermal  
267 fields (initial temperature  $T_i$  below 250°C) and oceanic hydrothermal fields (final pressure  
268  $P_f$  mostly above the spinodal pressure  $P_{\text{sp}}$ ), producing less explosive phenomena, like gey-  
269 sering and biphasic liquid-gas discharges. The contrasted behaviour between subspinodal  
270 and superspinodal systems may explain the large temperature difference between oceanic  
271 and continental hydrothermal systems. Oceanic hydrothermal fields typically discharge  
272 fluids between 300 and 400°C, whereas the temperatures of fluids in continental geothermal

273 fields are lower, mainly between 100°C and 225°C [Lee, 2001]. Both mentioned tempera-  
274 ture ranges correspond to subspinodal conditions for oceanic and continental fields. This  
275 suggests that no hydrothermal field can operate sustainedly in a superspinodal regime.

### 276 **2.3.3. Cavitation**

277 With boiling, cavitation is the other phenomenon associated to subspinodal liquid de-  
278 compression, and is a two-step process. In a first step, fast liquid decompressions or  
279 high-speed liquid flows create transient and local density perturbations. The liquid pres-  
280 sure drops below the saturation pressure or even to negative values. As a result, the liquid  
281 is stretched up to a certain point until mechanical failure and apparition of microscopic  
282 cavities in the liquid [Xiao and Heyes, 2002]. Then, in a second step, the stretched liquid  
283 relaxes to equilibrium by elastic rebound. Thus, in the  $P - T$  diagram of Figure 3, cavi-  
284 tation is represented by two vertical arrows: the first one, downward, indicates the liquid  
285 decompression up to the liquid metastable field, and the second one, upward, represents  
286 the compressive reaction towards the binodal curve. The vapour inside the cavities fol-  
287 lows a similar pressure evolution, i.e. a pressure drop followed by a compression, but with  
288 some distinctive features. Firstly, the gas pressure remains always positive. Secondly,  
289 the compression leads the gas through the metastable field of supercooled gases, and then  
290 through the high-pressure unstable domain of steam. As a consequence, gas bubbles finish  
291 up to implode.

292 The implosion of these gas cavities is not without important consequences. The elastic  
293 rebound of the surrounding liquid produces a large amount of mechanical energy, which  
294 is focused on these microscopic imploding cavities. This process is similar to a stretched  
295 string, which hits the hanging wall and transfers to it a significant energy quantity. This

296 enormous concentration of energy is responsible of a localized and very fast increase of  
297 temperatures and pressures (up to 5000 K and 1000 bar [*Suslick et al.*, 1999]), followed  
298 immediately by a very rapid cooling. This is the development field of sonoluminescence  
299 [*Frenzel and Schultes*, 1934] and sonochemistry [*Caupin and Herbert*, 2006]. Additionally,  
300 cavitation allows to explain the formation of some natural geological, but exotic materials,  
301 like C<sub>60</sub> and C<sub>70</sub> fullerenes [*Phipps Morgan et al.*, 2004] or nanodiamonds [*Ozima and*  
302 *Tatsumoto*, 1997].

303 The close environment around collapsing cavities exerts also a strong influence on their  
304 dynamics. While the implosion of isolated bubbles can be approximated by a spherically  
305 symmetrical collapse [*Rayleigh*, 1917; *Benjamin and Ellis*, 1966; *Ohl et al.*, 1999], the  
306 dynamics of bubble implosions change drastically at the proximity or contact of a solid  
307 surface: the bubble surface is deformed by an involution, which gives rise to an energetic  
308 and high-speed liquid jet hitting the solid surface [*Ohl et al.*, 1999]. This phenomenon is  
309 similar to Taylor fluid instabilities caused by the collapse of steam films between boiling  
310 liquid and a hot surface, which are known to play an important role in water-magma  
311 interactions [*Wohletz*, 1986]: as a result, the magma is distorted up to the point to be  
312 torn out and fragmented into small bulbous, mossy and nearly spherical clasts, which are  
313 typically found in fluidal peperites [*Busby-Spera and White*, 1987].

314 Cavitation takes too an important part in superspinodal liquid decompressions. *Yu and*  
315 *Venart* [1996]; *Venart et al.* [2004]; *Abbasi and Abbasi* [2007] have demonstrated the exis-  
316 tence of another type of explosive liquid decompressions, which have been called BLCBE  
317 (Boiling Liquid Compressed Bubble Explosion). These explosions are produced by the  
318 failure of a tank containing a pressurized liquid at near-critical conditions, but BLCBE

319 differs from BLEVE by the fact the container does not break off at once. Instead, in a  
320 first step, the container failure is limited to the development of a crack through which  
321 the depressurizing liquid escapes out. As a result, the initial depressurization wave in  
322 the vessel is followed by a reflected compression wave caused by the rapid expansion of  
323 the in-situ gas. The subsequent repressurization leads to coherent bubble collapse and  
324 cavitation. The implosion of the bubbles generates a shock wave, emitting a high dynamic  
325 pressure peak resulting to the final failure of the container. In this sense, BLCBE is a  
326 phenomenon relevant for describing the explosive liquid decompressions from hydrother-  
327 mal reservoirs and magmatic chambers. In the same category of events, the rarefaction  
328 wave following a meteoritic impact [*Ozima and Tatsumoto, 1997*] or a deep-lithospheric  
329 eruption (the so-called "Verneshots" of *Phipps Morgan et al. [2004]*) are analogous cav-  
330 itation situations, where a depressurization is followed by a compressive equilibration.  
331 As a consequence, cavitation can be considered as one of the fundamental processes of  
332 volcanic and hydrothermal systems.

## 2.4. Expansion of a Gas Under Pressure

333 The sudden decompression of a pressurized gas is undoubtedly an explosive phe-  
334 nomenon, whose violence is sufficient to generate shock waves. However, at first sight,  
335 this explosion type does not seem to fit our theoretical framework proposed here, where  
336 explosions result from spinodal processes. Nevertheless, one can note that the equation  
337 of state of the perfect gas ( $Pv = RT$ ) predicts that the  $(\partial P/\partial v)_T$  quantity tends to  
338 zero for high expansion degrees, indicating a begin of violation of the mechanical stability  
339 criterion (see equation 4). Moreover, the surface ( $P = 0$ ) corresponds to a thermody-  
340 namic frontier in the  $P - v - T$  space of the ideal gas, separating the forbidden domain of

341 negative pressures from the stable/metastable field of positive pressures. Thus, the limit  
342 ( $P = 0$ ) of infinite expansion shares some similarity with the liquid spinodal boundary,  
343 as it generates also a violent explosion.

### 3. The Explosive Energy of Water

344 The mechanical energy released by any substance is function of its expansivity through  
345 the classical relation, valid under reversible conditions:

$$dW = -P dv, \quad (7)$$

346 where  $dW$  is the amount of mechanical energy produced by the expansion  $dv$  of a  
347 fluid. As a result, the main sources of explosive energy are: (1) the fluid exsolution from  
348 magma by magmatic vesiculation and/or fragmentation (*Burnham* [1979]), (2) and the  
349 fluid expansion. Therefore, to quantify the energy balance of volcanism, it is necessary to  
350 differentiate precisely the explosive potential of the five energetic processes of water, which  
351 are respectively (1) liquid expansion by heating, (2) vaporization, (3) steam expansion by  
352 heating, (4) steam adiabatic decompression and (5) water exsolution from magma. We  
353 will see later that these contributions are, indeed, not involved in the same way for the  
354 different types of hydrothermal and magmatic systems. Thus, a close analysis of these  
355 different energetic sources is necessary. We have seen also that water metastability plays an  
356 important role in the explosive character of hydrothermal and volcanic eruptions. Hence,  
357 a last question to be addressed is how metastability modifies the energetic properties of  
358 water.

### 3.1. The Decompression Energy

359 Decompression up to the atmospheric pressure is the main source of mechanical energy  
360 produced by pressurized fluids. The eruption energy of hydrothermal systems (geysers)  
361 or volcanic systems comes principally from the opening and decompression of a deep fluid  
362 reservoir, which is suddenly connected to the atmosphere. It may even be proposed that  
363 this type of energy is produced during contact of lava with water under atmospheric  
364 pressure, as strong transient overpressures can be generated too by boiling of superheated  
365 waters [*Zimanowski et al.*, 1995].

366 The decompression process is so rapid that the system has not enough time to exchange  
367 heat with the exterior. Thus, to a first approximation, the decompression is considered  
368 to be adiabatic. A further simplification is to state that the decompression is reversible.  
369 This is clearly not exact (see below), but this allows to treat the decompression as an  
370 isentropic process (i.e., the entropy of the system is constant :  $dS = 0$ ).

#### 3.1.1. Reversible Conditions

372 Using the Wagner and Pruss (2002) equation of state, the classic  $T - U$  and  $T - H$   
373 diagrams (Figures 4 and 5) can be calculated to get a first estimation of the mechanical  
374 energy. They include isobaric and isentropic paths extrapolated up to the metastable  
375 fields. It can be noted that the isobars exhibit almost linear steep variations in  $T - U$  and  
376  $T - H$  diagrams, except in the critical and metastable fields, where they depart from their  
377 general trends and tend to get horizontal. This behaviour can be explained by the specific  
378 properties of fluids in the spinodal and critical fields. Indeed, the slope of an isobar in a  
379  $T - U$  diagram is inversely proportional to the isochoric heat capacity:

$$\left(\frac{\partial T}{\partial U}\right)_P = \frac{1}{c_v} \quad (8)$$

380 In the same way, the slope of an isobar in a  $T - H$  is inversely proportional to the  
381 isobaric heat capacity:

$$\left(\frac{\partial T}{\partial H}\right)_P = \frac{1}{c_P}. \quad (9)$$

382 Therefore, the horizontal slopes of isobars in  $T - U$  and  $T - H$  diagrams are caused by  
383 the divergence of isochoric and isobaric heat capacities at spinodal and critical points  
384 (e.g. [*Johnson and Norton, 1991*]). The reversible work released by an isentropic fluid  
385 expansion can be calculated from the first law of thermodynamics as a function of the  
386 internal energy:

$$dU = TdS - PdV = -PdV = \delta W_{rev}. \quad (10)$$

387 The  $\delta W_{rev}$  quantity is conventionally counted as negative, as the system does a work  
388 on its surroundings, and so the mechanical work ( $W_U$ ) is:

$$W_U = \Delta U = U_5 - U_3 < 0, \quad (11)$$

389 where (3) is the starting state of the decompression and (5) is the final state at atmo-  
390 spheric pressure. Equation 11 is valid for short-lived outbursts. For long-lasting eruptions  
391 or fluid flows, the enthalpy is more adapted to the calculation of the mechanical work (for  
392 example, the work yielded by a fluid flow in a vent above a magmatic chamber). As a  
393 result, the net mechanical work ( $W_H$ ) of the venting fluid is:

$$\begin{aligned}
W_H &= W_U + P_5 v_5 - P_3 v_3, \\
&= H_5 - H_3, \\
&= \Delta H \leq 0.
\end{aligned} \tag{12}$$

394 where  $v$  stands here for the specific volume at the subscribed point.

395 The quantity  $W_H$  gives the amount of energy, which can be converted to gravitational  
396 potential energy ( $E_p$ ), kinetic energy ( $E_c$ ) and all other forms of mechanical energy (frag-  
397 mentation, elastic deformation, shock waves, ...), noted  $E_d$ . Thus, the energetics of fluid  
398 flows and eruption phenomena can be assessed by using a modified form of Bernoulli's  
399 equation (Mastin, 1995):

$$-W_H = \Delta E_p + \Delta E_c + \Delta E_d + \text{'frictional terms'}. \tag{13}$$

400 The last term of this equation takes into account frictions between fluid and the sur-  
401 roundings. Depending upon the importance of this frictional term, two contrasted cases  
402 can be considered: isenthalpic expansions and isentropic decompressions.

### 403 3.1.2. Isenthalpic Decompressions

404 The so-called isenthalpic fluid expansions are decompressions where all potential and  
405 kinetic energies are dissipated through frictions ( $W_H = 0$ ). This situation occurs, in  
406 particular, for fluid flows in porous and tortuous media, such as aquifers. The evolution  
407 of these flows can be followed on a  $T - H$  diagram (Figure 5) along a vertical line starting  
408 from the initial point (3). In most cases, isenthalpic decompressions are accompanied by  
409 a temperature decrease of the fluid (and a temperature increase of the surroundings). The

410 amplitude of this temperature decrease can be visualized by considering the offset between  
411 isobars drawn in Figure 5. Thus, this effect will be particularly marked for supercritical  
412 steams ( $T$  roughly between 400 and 700°C) and supercooled steams. This property is  
413 notably invoked to explain, in part, the heating of the surrounding rocks along pathways  
414 followed by steam flows (Armstead, 1978) in geothermal reservoirs.

### 415 **3.1.3. Isentropic Decompressions**

416 If the frictional term of equation 13 can be neglected, the expansion can be consid-  
417 ered as a reversible isentropic process. To estimate graphically the mechanical work of  
418 decompression, isentropic expansion curves must be used. In Figures 4 and 5, several  
419 isentropic paths have been plotted. Detailed calculation examples are given for  $W_U$  and  
420  $W_H$  in Table 3 by using equations 11 and 12. The corresponding paths (Figures 4 and 5)  
421 are composed of two parts:

422 1. a first part, at high pressures and temperatures, where the pressure drop runs in the  
423 monophasic field, between initial point (3) and point (4). Point (4) marks the demixing of a  
424 new fluid phase (liquid or gas). This fluid transition can be located either on the saturation  
425 curve (L(G) or G(L) binodal branch), or anywhere along the metastable extrapolation of  
426 the isentropic path up to a spinodal point.

427 2. the second part is the decompression in the biphasic liquid-gas domain, up to the  
428 atmospheric pressure (point 5).

429 To assess the energetic potential of a pressurized water reservoir, isentropic heat capac-  
430 ities  $c_{U,S}$  or  $c_{H,S}$  can be considered:

$$c_{U,S} = \left( \frac{\partial U}{\partial T} \right)_S, \quad (14)$$

$$c_{H,S} = \left( \frac{\partial H}{\partial T} \right)_S, \quad (15)$$

431 ( $c_{U,S}$  and  $c_{H,S}$  coefficients are inversely proportional to the slope of isentropic paths,  
 432 respectively in  $T - U$  and  $T - H$  diagrams). Isentropic decompression works  $W_U$  and  $W_S$   
 433 can be calculated from these parameters by:

$$W_U = \int_3^5 c_{U,S} dT, \quad (16)$$

$$W_H = \int_3^5 c_{H,S} dT. \quad (17)$$

434 As a result, energetic pressurized systems (for a given temperature difference between  
 435 initial and final states) are characterized by elevated isentropic heat capacities. In Fig-  
 436 ures 4 and 5, it can be observed that most energetic isentropic paths are liquid-poor  
 437 steams, featuring the lowest slope in  $T - U$  and  $T - H$  diagrams ( $c_{H,S}$  well above 3 J/K).  
 438 To the opposite, systems, which have a rather low isentropic heat capacity, are super-  
 439 critical steams above 800–900 K ( $c_{H,S}$  about 1 J/K) or liquid-rich biphasic liquid-gas  
 440 mixtures ( $c_{H,S}$  also around 1 J/K). By performing a study of the energy balance of isen-  
 441 tropic decompressions of gas-liquid mixtures, similar to the one done by *Salla et al.* [2006]  
 442 on isenthalpic expansions, it can be shown that there is a considerable energy transfer  
 443 from the cooling liquid to the expanding steam. Therefore, the high energetic potential  
 444 of wet steams is due to the condensation and cooling of liquid water droplets, providing  
 445 an important energy source (up to 800 J/g of cooling liquid).

446 The relative contributions of monophasic and biphasic decompressions on the expansion  
447 work can be also analyzed in separate diagrams. Figure 6 displays the amplitude of the  
448 monophasic part  $W_{U,1}$  of the mechanical work  $W_U$  in a  $P - T$  diagram ( $W_{U,1} = U_4 - U_3$ ).  
449 The monophasic decompression is especially important for hot and pressurized steams  
450 with  $W_{U,1}$  values ranging from 200 to more than 1500 J/g. To the contrary, fluids of liquid-  
451 like densities have  $W_{U,1}$  values below 100 J/g. The influence of the initial pressure on  $W_{U,1}$   
452 is negligible for a liquid. The intensity of the decompression work  $W_{U,2}$  ( $W_{U,2} = U_5 - U_4$ )  
453 of a gas-liquid mixture is displayed in Figure 7 as a function of the saturation temperature.  
454 As stated above, this diagram confirms the high energetic potential of saturated steams.  
455 Maximum values of  $W_{U,2}$  of 655 J/g are obtained for a steam starting to condense around  
456 612 K (339°C). Coincidentally, this temperature is quite close to the superheat limit  
457 temperature ( $T_{sp} = 593.6$  K = 320.45°C) of water.

458 To take an example, steam, initially at a temperature of 1250 K (977°C) and a pressure  
459 of 1500 bar (in a reservoir at depth of 6 km), releases an energy  $W_U$  of 1000 J/g by decom-  
460 pression in the monophasic field (Figure 6). This energy amount is directly consumed to  
461 eject the fluid out of the erupting vent. From Figure 6, one reads that its saturation tem-  
462 perature is about 500 K (227°C). Therefore, the condensation will probably continue in  
463 the atmosphere, where the decompression in the biphasic domain will bring an additional  
464 energy quantity about 500 J/g. This energy source should play an important role in the  
465 dynamics of pyroclastic surges and flows. In conclusion, the steam expansion releases,  
466 theoretically, a total of 1500 J/g, a value which is to be compared with the explosive  
467 energy of gunpowder ( $\simeq 2000$  J/g) and TNT ( $\simeq 4600$  J/g). Thus, exsolved steam from a  
468 magmatic chamber can be doubtless classified as an explosive substance.

469 At this step, one question arises whether it is more appropriate to use isenthalpic or  
 470 isentropic conditions to assess the energetic intensity of an explosive process. In an isen-  
 471 thalpic process, all mechanical forms (gravitational, kinetic, . . . ) of energy are converted  
 472 to thermal energy, which is the fate of any depressurizing system after a certain amount  
 473 of time. Thus, the isenthalpic assumption is most adequate to characterize the fluid state  
 474 after complete relaxation. Conversely, in an isentropic process, the final state is fixed at  
 475 a virtual instant, where the system is charged with energy, but has not yet consumed it.  
 476 Thus, the isentropic assumption allows to calculate the amount of mechanical works.

#### 477 3.1.4. Ejecta

478 To check the validity of the assessment of decompression works by our theoretical model,  
 479 one can attempt to compare it with volcanological observations by following an approach  
 480 developed by *Mastin* [1995]. For 1 kg of water interacting with a mass  $m_r$  of pyroclasts,  
 481 the Bernoulli's equation (equation 13) can be detailed to give the decompression work  
 482  $W_H$  (in J/kg) as:

$$\begin{aligned}
 -W_H &= (1 + m_r) g (z_5 - z_3) \\
 &\quad + \frac{1}{2} (1 + m_r) (V_5^2 - V_3^2) \\
 &\quad + \text{'frictional terms'},
 \end{aligned}
 \tag{18}$$

483 where  $V_3$  and  $V_5$  are the respective fluid velocities (in m/s) at points (3) and (5),  $g$  is  
 484 the gravity constant ( $g = 9.81 \text{ m}^2/\text{s}$ ), and  $z$  is the altitude. By taking the point (3) as  
 485 the reference altitude level (i.e.  $z = 0$  for the magmatic chamber or the hydrothermal

486 reservoir), and by assuming that the fluid velocity  $V_3$  is negligible before expansion, one  
 487 obtains the general relation linking  $W_H$  to the height  $z$  and the fluid velocity  $V$ :

$$\begin{aligned}
 -W_H &\simeq 10 (1 + m_r) z + 0.5 (1 + m_r) V^2 \\
 &+ \text{'frictional terms'}.
 \end{aligned}
 \tag{19}$$

488 The last term of this equation, labeled 'frictional terms', includes all types of energy,  
 489 which are difficult to characterize, i.e. fragmentation, ductile deformation, seismic energy,  
 490 blasts . . . . To allow for this, the equation can be rewritten as:

$$-\zeta W_H \simeq 10 (1 + m_r) z + 0.5 (1 + m_r) V^2,
 \tag{20}$$

491 where  $\zeta$  is a conversion factor of  $W_H$  into kinetic and gravitational energies, varying  
 492 between 0 and 1. A value of 0.5 can be reasonably assumed for  $\zeta$ . Thus, the maximum  
 493 ballistic height  $z_{\max}$  (in m) can be estimated by:

$$\begin{aligned}
 z_{\max} &\simeq \frac{0.1}{(1+m_r)} \zeta |W_H|, \\
 &\simeq \frac{0.1}{m_r} \zeta |W_H|,
 \end{aligned}
 \tag{21}$$

494 or the maximal ejection speed (in m/s) by:

$$\begin{aligned}
 V_{\max} &\simeq \sqrt{\frac{2 \zeta |W_H|}{1+m_r}}, \\
 &\simeq \sqrt{\frac{2 \zeta |W_H|}{m_r}},
 \end{aligned}
 \tag{22}$$

495 or the mass  $m_r$  of pyroclasts (in kg) driven by the flow by:

$$\begin{aligned}
m_r &\simeq \frac{2\zeta|W_H|}{V_{\max}^2} - 1, \\
&\simeq \frac{2\zeta|W_H|}{V_{\max}^2}.
\end{aligned}
\tag{23}$$

496 Note that in all these equations 21-23,  $W_H$  must be expressed in J/kg of water.

497 Vulcanian eruptions are the best studied natural cases, and thus, allow us to compare  
498 observed data and model predictions. These eruptions are caused by the brittle failure of a  
499 lava dome overlying a pressurized gas zone, which formed either by exsolution of magmatic  
500 volatiles or rapid heating of groundwater [*Morissey and Mastin, 2000*]. Several eruptions  
501 (Arenal, Costa Rica, 1968; Ngauruhoe, New Zealand, 1975) have been the subject of  
502 measurements of ejection velocities of pyroclasts. The maximum velocities range between  
503 200 and 400 m/s. By assuming a magma temperature between 1000 and 1200 K, the  
504 decompression work  $W_H$  of steam initially at pressures below 300 bar can be estimated  
505 from Figure 6 between 1100 and 1400 J/g of water. From equation 23 and with a value  
506 of 0.5 for  $\zeta$ , the mass of pyroclasts driven by one kilogram of water can be calculated  
507 between 5.9 and 34 kilograms, i.e. a water weight fraction between 2.9 % and 14.5 % for  
508 the magma. The reversible assumption leads to somewhat overestimate the water content,  
509 although the lowest value is consistent with usual magmatic water contents.

### 510 3.1.5. Irreversible Conditions

511 Irreversibility can be taken into account by using the following general formula [*Planas-*  
512 *Cuchi et al., 2004*], which calculates the final state at point (5) by decompression from  
513 point (3):

$$\begin{aligned}
 U_5 - U_3 &= -P_{\text{ext}} (v_5 - v_3), \\
 &= -P_5 (v_5 - v_3),
 \end{aligned}
 \tag{24}$$

514 where  $P_{\text{ext}} = 1$  bar, and  $U$  is the molar internal energy. This equation is consistent with  
 515 the following formulation of *Zhang* [2000] to allow for irreversibility in volcanic eruptions:

$$H_5 - H_3 = v_3 (P_5 - P_3). \tag{25}$$

516 To solve equation 24, two distinct cases must be considered:

517 1. in the first case, the decompression leads to a stable monophasic system at point  
 518 (5). The unknown is the value of the temperature  $T_5$  with the constraint that the final  
 519 temperature  $T_5$  is above the normal boiling temperature ( $T_5 > 373$  K). Thus, the process  
 520 produces superheated steams (note here that the term "superheated" refers to a stable,  
 521 and not metastable, state of a steam at temperatures above its saturation point, as it  
 522 is the usage in the geothermics litterature). Therefore we have to numerically solve the  
 523 equation:

$$U_5(T_5, v_5) - U_3 = -P_{\text{ext}} (v_5 - v_3). \tag{26}$$

524 where  $v_5$  is the fluid molar volume at  $T_5$  and 1 bar.

525 2. in the second case, the decompression leads to a stable biphasic liquid-gas association  
 526 at  $P_{\text{ext}} = 1$  bar and  $T_5 = 373.15$  K. Equation 24 becomes:

$$f U_{\text{liq}} + (1 - f) U_{\text{vap}} - U_3 =$$

$$-P_{\text{ext}} [f v_{\text{liq}} + (1 - f) v_{\text{vap}} - v_3], \quad (27)$$

527 where  $U_{\text{liq}}$  (J/mol),  $v_{\text{liq}}$  (m<sup>3</sup>/mol),  $U_{\text{vap}}$  (J/mol) and  $v_{\text{vap}}$  (m<sup>3</sup>/mol) are all calculated at  
 528 373.15 K and 1 bar. The unknown is the value  $f$  of the mass liquid fraction in the system  
 529 and is simply calculated by:

$$f = \frac{P_{\text{ext}} (v_3 - v_{\text{vap}}) - U_{\text{vap}} + U_3}{U_{\text{liq}} - U_{\text{vap}} + P_{\text{ext}} (v_{\text{liq}} - v_{\text{vap}})}. \quad (28)$$

530 Results are given in Figure 8, which can be compared with Figure 6, where isocurves of  
 531 the decompression energy and the mass liquid fraction at the final state have been plotted  
 532 as a function of the initial pressure  $P_3$  and temperature  $T_3$ . At initial atmospheric pressures  
 533 (i.e.  $P_3 = P_{\text{ext}}$ ), the decompression work is zero, whatever the steam temperature. For  
 534 example, fumarolles have no explosive potential and cannot be exploited economically,  
 535 except for heat. However, with increasing initial pressure  $P_3$ , the mechanical work, which  
 536 can be extracted by expansion, increases drastically. As shown by the curvatures of the iso-  
 537  $W_U$  lines, there is an optimal pressure (from 31 bar at 700 K to 81 bar at 1200 K), at which  
 538 the hot steam can release a maximum mechanical work for a given initial temperature  
 539  $T_3$ . At pressures higher than 300 bars, the fluid decompression becomes less energetic  
 540 with increasing pressures, and the temperature becomes the key parameter controlling  
 541 the mechanical energy content of the fluid.

542 It can be also observed (Figure 8) that the expansion under irreversible conditions  
 543 produce final states, which are much more drier, as the result of the internal production  
 544 of entropy by irreversibility.

545 But most importantly, it can be seen that the assumption of irreversible conditions leads  
 546 to much smaller values for the decompression energy. Values range from 50 to 550 J/g  
 547 of water, and represent around one fourth to one third of corresponding energies under  
 548 reversible conditions. Up to now, reversibility has been almost always applied in the vol-  
 549 canological litterature [*Wohletz*, 1986; *Mastin*, 1995], with the notable exception of *Zhang*  
 550 [2000], but irreversibility yields probably more realistic values of the explosive energy, even  
 551 if it may be somewhat less practical to use. Indeed, the  $T - U$  and  $T - H$  diagrams cannot  
 552 be used directly for the irreversible case, except if one uses the approximation of an isen-  
 553 thalpic process. In Figure 9, the mass liquid fraction of liquid-gas mixtures obtained by  
 554 decompression up to 100°C and 1 bar of saturated liquid or steam is plotted as a function  
 555 of the initial temperature for the three possible assumptions, i.e. isentropic, isenthalpic  
 556 and irreversible cases. As expected, isenthalpic and irreversible depressurizations yield the  
 557 most dry mixtures, and the isentropic expansion gives the highest liquid fraction. But,  
 558 interestingly, it can be noted that the isenthalpic hypothesis provides a good approxima-  
 559 tion of the irreversible case, in particular for the liquid expansion. Thus, it is possible to  
 560 rely on the isenthalpic decompression model to estimate the mass liquid fraction  $f$  of the  
 561 final state at 100°C and 1 bar, by using the lever rule in the  $T - H$  diagram of Figure 5.  
 562 Then, the irreversible work (in J/g) of decompression of saturated liquid can be given by:

$$\begin{aligned}
 W_U &\simeq P_{\text{ext}} [(1 - f)v_{\text{vap}} + fv_{\text{liq}} - v_3], \\
 &\simeq P_{\text{ext}} (1 - f)v_{\text{vap}}, \\
 &\simeq 167 (1 - f).
 \end{aligned}
 \tag{29}$$

563 This expression is accurate with a relative error, which is less than 1 % below 550 K,  
564 and the maximum discrepancy does not exceed 4 % at the critical point.

### 3.2. The Vaporization Work

565 When cold water interacts with hot magma, the first event producing important me-  
566 chanical work is vaporization. For one gram of boiling liquid water, the resulting energy  
567 is given by:

$$W_{\text{vap}} = -P (v_{\text{vap}} - v_{\text{liq}})/M_{\text{H}_2\text{O}}, \quad (30)$$

568 where  $v_{\text{vap}}$  and  $v_{\text{liq}}$  are the molar volumes of saturated liquid and gas, and  $M_{\text{H}_2\text{O}}$  is the  
569 molar weight of water.

570 The amplitude of this energy is given in Figure 10 as a function of the boiling tempera-  
571 ture. Its mean value is around 150 J/g, and it reaches a maximum at 495 K (222°C) and  
572 24 bar, where almost 200 J/g can be yielded. This state corresponds to the point of max-  
573 imum enthalpy of saturated steam. It is worth to observe that this maximum is obtained  
574 at temperatures intermediate between normal boiling temperature and spinodal temper-  
575 ature. Thus, the sudden boiling of superheated water at this temperature can give 20 %  
576 more mechanical energy than normal boiling at 100°C. To the contrary, when approach-  
577 ing near critical conditions, vaporization energy decreases considerably up to zero at the  
578 critical point. It is also symptomatic to note that vapour-dominated geothermal systems,  
579 such as Larderello (Italia) or The Geysers (California), have pressure-temperature condi-  
580 tions which are close to the state of maximum enthalpy for saturated steams [*Goff and*  
581 *Janik, 2000*].

### 3.3. The Heating Work

582 Fluids expand when they are heated. As such, they exert a mechanical work on their  
 583 surroundings. Thus, water expansion by heating must be taken into account to assess  
 584 the energetic balance of water explosions. The case of isobaric heating under reversible  
 585 conditions will be considered here. In this case, the reversible work can be obtained from  
 586 a simple difference of the enthalpy and the internal energy:

$$dH - dU = P dv = -\delta W. \quad (31)$$

587 As the pressure is constant and is equal to the pressure of the surroundings ( $P = P_{\text{ext}}$ ),  
 588 this equation is also valid under irreversible conditions. The variations of the isobaric  
 589 heating work ( $H - U$ ) is given in Figure 11 as a function of the temperature. Two  
 590 contrasted behaviours can be observed. First, the heating work of liquids is practically  
 591 negligible, as demonstrated by the vertical slopes of isobars. The heating of liquid in  
 592 the metastable field delivers no mechanical work. To the opposite, steams can provide a  
 593 significant contribution. Isobaric heating curves show a linear trend in the steam field. At  
 594 low pressures ( $P \leq 10$  bar), steam behaves as a perfect gas, and the isobaric expansion  
 595 work is given by:

$$-W = \Delta(H - U) \simeq R \Delta T, \quad (32)$$

596 where  $R$  is the constant of ideal gas for water ( $R = 8.31/18 = 0.4617$  J/g/K) and  $\Delta T$  is  
 597 the temperature increase. At higher pressures, the slopes of isobars decrease, indicating  
 598 a higher mechanical energetic potential. For example, at 1000 bar, steam yields almost

599 twice as more expansion work than under atmospheric pressure for the same temperature  
600 increase. Note also that the isobars in Figure 11 include the expansion work produced by  
601 vaporization. Thus, as seen in the preceding section, one can recognize in Figure 11 the  
602 peak of expansion work released by the vaporization of water at 222°C and 24 bar. Another  
603 remarkable property of water is the very high potential of the mechanical expansion work  
604 in the critical and the spinodal field of supercooled gases, as illustrated by the nearly  
605 horizontal slopes of isobars.

606 To summarize, contact of cold liquid water with a hot body, like a basaltic flow, can  
607 produce a mechanical work up to 600 J/g. As a result, vaporization and steam isobaric  
608 heatings represent also significant energetic contributions of a water explosion.

### 3.4. The Exsolution Work

609 The exsolution work of water from magmas is another important source of energy, which  
610 must be taken into account in magmatic systems. Indeed, the exsolution is accompanied  
611 by a net volume increase from the partial molar volume  $\bar{v}_{\text{H}_2\text{O}}$  of water to the molar volume  
612  $v$  of steam under the  $(P, T)$  exsolution conditions. Experimental data indicate that the  
613 partial molar volume  $\bar{v}_{\text{H}_2\text{O}}$  in hydrous silicate glasses is around  $12 \pm 0.5 \text{ cm}^3/\text{mol}$  at room  
614 temperature [Richet *et al.*, 2000; Richet and Polian, 1998]. With a partial molar thermal  
615 expansion coefficient of  $\text{H}_2\text{O}$  about  $4 \times 10^{-5}$  [Richet *et al.*, 2000], a temperature increase  
616 of 1000 K leads only to an augmentation of 4 % of  $\bar{v}_{\text{H}_2\text{O}}$ , i.e.  $0.5 \text{ cm}^3/\text{mol}$ . Inversely, a  
617 pressure increase leads to a small decrease of  $\bar{v}_{\text{H}_2\text{O}}$ . Thus, we have retained a mean value  
618 of  $12 \text{ cm}^3/\text{mol}$  for  $\bar{v}_{\text{H}_2\text{O}}$  for the ranges of magmatic temperatures and pressures considered  
619 here ( $900 \text{ K} < T < 1600 \text{ K}$  and  $1 \text{ bar} < P < 3000 \text{ bar}$ ).

620 To determine the exsolution work, the first idea would be to apply the same rigorous  
 621 algorithms described in section 3.1.1 for a reversible process or section 3.1.5 for an ir-  
 622 reversible one. However, no equation of state has been yet developed to describe the  
 623 energetic properties of hydrous magmas, neither for its internal energy or its enthalpy.  
 624 Thus, the trade-off is to focus only on the isothermal and isobaric exsolution work  $W_{\text{ex}}$   
 625 under the pressure-temperature conditions  $(P_3, T_3)$  in the magmatic chamber or at the  
 626 fragmentation level in the volcanic conduit:

$$W_{\text{ex}} = -P_3 (v_{\text{vap}} - \bar{v}_{\text{H}_2\text{O}}), \quad (33)$$

627 where  $v_{\text{vap}}$  is the molar volume of steam calculated by the Wagner and Pruss equation of  
 628 state [*Wagner and Pruss, 2002*] at  $(P_3, T_3)$  conditions. Values of the exsolution work are  
 629 given in Figure 12. They range between 250 and 700 J/g of exsolved water. This represents  
 630 a notable energetic contribution of magmatic systems (almost the double of the steam  
 631 expansion work for a basaltic magma). The exsolution energies show rather a stronger  
 632 dependence with respect to the temperature than to the pressure, except at pressures  
 633 below 500 bar. The bulk explosion energy of a magmatic eruption is then estimated  
 634 by the sum of  $W_{\text{ex}}$  and the expansion work  $W_U$ , calculated either under the reversible  
 635 assumption (section 3.1.1, equation 11) or under the irreversible hypothesis (section 3.1.5,  
 636 equation 24). For instance, a basaltic lava exsolving 1 weight percent of water at the earth  
 637 surface produces only an exsolution energy of 5.5 J/g of magma at 1200 K (i.e. 550 J/g  
 638 of water from Figure 12) and no steam expansion work at all (Figure 8). The same  
 639 magma, exsolving in a magmatic chamber at a pressure of 500 bar generates 500 J/g of  
 640 exsolved water and 420 J/g of water by irreversible decompression against the atmospheric

641 pressure, that is 920 J/g of water or 9.2 J/g of magma and per weight percent of exsolved  
642 water. Our model can also be applied to the 18 May 1980 eruption of the Mount St-  
643 Helens by using the parameters of *Zhang* [2000]:  $T_3 = 1200$  K (927°C),  $P_3 = 2200$  bar  
644 and a weight percent of exsolved water of 3.7 %. By assuming that the melt is entirely  
645 expelled by exsolving water, we estimate the mass of pyroclasts  $m_r = (1000 - 37)/37 = 26$   
646 kg for one kg of steam. From Figure 8, the irreversible decompression work is found to  
647 amount to 320 J/g of exsolved water, whereas from Figure 12, the exsolution work ranges  
648 between 420 J/g of exsolved water (exsolution at  $(P_3, T_3)$ ) and 550 J/g of exsolved water  
649 (exsolution under the atmospheric pressure). This gives us a total mechanical work  $W$   
650 between 740 and 870 J/g of exsolved water. From equation 22, we calculate a maximal  
651 ejection speed  $V_{\max}$  between 165 m/s and 180 m/s by assuming an energy conversion  
652 factor  $\zeta$  of 0.5. These values are in agreement with estimations of 100-110 m/s of the  
653 choked exit velocity [*Kieffer*, 1981] or with measurements of 150 m/s for the velocity of  
654 the lateral explosion cloud [*Friedman et al.*, 1981; *Voight*, 1981].

### 3.5. The Explosion Power

655 Up to now, we have discussed about the water explosivity in terms of energy quantities.  
656 However, what makes a good explosive is not the amount of work involved, but the  
657 production rate of work per time unit, in other words, its power or, equivalently, its yield  
658 expressed in mass of TNT. The explosivity of water is due to a physical transformation,  
659 the rate of which is a function of its metastability degree. The duration of explosive  
660 reactions between water and magma is on the order of the millisecond [*Zimanowski et al.*,  
661 1991, 1995], thus an explosive vaporization of 500-1000 J/g represents a power of 500 kW

662 to 1 MW/g of water. The magnitude of this phenomenon is 3 to 4 orders higher than  
663 usual boiling conditions.

#### 4. A Typology of Hydrothermal and Volcanic Systems

664 The preceding section have analyzed the different energetic contributions, i.e. fluid  
665 expansion accompanied or not by vaporization/condensation processes, isobaric boiling,  
666 and magmatic exsolution, and their explosive potentials have been discussed. A synthe-  
667 sis of their relative contributions in hydrothermal and volcanic systems can be done in  
668 a pressure-enthalpy diagram (Figure 13). The different cases are produced by the in-  
669 teractions in various proportions of (1) meteoric, superficial and connate waters, whose  
670  $P - T$  conditions are close to the mean geothermal gradient (left part), and (2) ascend-  
671 ing magmas in the upper part of the crust, either intruding or extruding, (right part).  
672 Energy estimations given below are based on values calculated under the irreversibility  
673 assumption.

674 1. First, one can consider liquid-dominated geothermal systems, (*A* in Figure 13). The  
675 boiling must be triggered by a depressurization of the geothermal reservoir [*Armstead*,  
676 1978]. Thus, the energy source comes mainly from the liquid boiling and steam expansion,  
677 well below 100 J/g of H<sub>2</sub>O (see equation 29 and Figure 7). Moreover, their explosive  
678 potential is weak and is mainly represented by geysers (subspinodal decompressions).

679 2. Next (*B* in Figure 13), these are supercritical or slightly subcritical fluids, typically  
680 found in the lithocaps of magmatic chambers [*Norton and Dutrow*, 2001], or in deep  
681 geothermal systems (black smokers of oceanic ridges). Sudden pressure drops on such  
682 systems up to atmospheric conditions are expected to lead to superspinodal decompres-  
683 sions and produce explosions of high power (for instance, see the isentropic decompression

684 curve labeled 700 K, which intersects the liquid spinodal curve in Figure 13). Such events  
685 would involve a mechanical energy of 150–200 J/g of H<sub>2</sub>O (Figure 8).

686 3. Then, vapour-dominated geothermal systems (*C* in Figure 13) produce mechanical  
687 energy by expansion of gaseous fluids, below 150 J/g of H<sub>2</sub>O (Figure 7). Well-known  
688 examples include the geothermal fields of Larderello (Italia) or The Geysers (California).  
689 The deep parts and the porous spaces of these geothermal fields contain saturated waters  
690 in larger proportions than steam [*Goff and Janik, 2000*]. Steam migrates upwards in the  
691 fractures by isenthalpic boiling, but the condensing liquid separates and percolates deeper.  
692 As a consequence, steam evolves progressively towards the state of maximum enthalpy.

693 4. In the field labeled *D* are found fluids exsolved by magmas during their cooling and  
694 crystallization in a magmatic chamber, a few kilometers below the surface. These are  
695 volatile-rich magmas, as well as hot and pressurized fluids. The mechanical energy of of  
696 vulcanian and plinian volcanisms is produced by magmatic exsolution (450–600 J/g of  
697 H<sub>2</sub>O) and steam expansion (from 200 J/g to 400 J/g of H<sub>2</sub>O, Figure 8).

698 5. And finally, liquid waters (*E*) which are suddenly heated by contact with hot mag-  
699 matic lavas at Earth surface. This includes surtseyan volcanism and superficial phreato-  
700 magmatism. The mechanical work is mainly produced by heating, and amounts to levels  
701 between 200 and 600 J/g of H<sub>2</sub>O (Figure 11). Moreover, explosive boiling of water can  
702 create transient overpressures, probably of several ten bars [*Zimanowski et al., 1995*].  
703 Thus, the irreversible decompression of these fluids will give an additional energy amount  
704 between 100-300 J/g (Figure 8).

705 Note that the bulk energy released by phreato-magmatism can be as high as in plinian  
706 volcanism. However, a correct assessment of the energy of a phreato-magmatic explosion

707 requires a global analysis of the energy balance, as carried out by *Wohletz* [1986], that is  
 708 based on the determination of the interactive water–magma mass ratio.

## 5. Geophysical Application: Estimation of Volcanic Impacts

In the same way than the thermodynamic models of *Wohletz* [1986, 2002] and *Mastin* [1995], our model can be applied to case studies of volcanic and hydrothermal eruptions. Volcanic impacts can be approximated from a few number of scaling laws, using the explosion yield, expressed in tons of TNT. For instance, it is possible to estimate the overpressure of the blast [*Kingery and Pannill*, 1964; *Taniguchi and Suzuki-Kamata*, 1993], the diameter of the crater [*Nordyke*, 1962; *Wohletz and Heiken*, 1992; *Goto et al.*, 2001] or the height of the explosion cloud [*Ohba et al.*, 2002]. These similarity rules are mostly based on a cubic root formulation:

$$R = R_0 W^{1/3}, \quad (34)$$

709 where  $R$  is the distance from the explosion center, at which an event of given intensity is  
 710 observed;  $R_0$  is a scaling parameter and  $W$  is the explosion energy. The scaling parameter  
 711  $R_0$  is usually derived from correlations established from impact studies of explosions of  
 712 energy  $W_0$  (either chemical explosives [*Van den Berg and Lannoy*, 1993] or nuclear bombs).  
 713 In general, these methods must be used with caution [*Browne and Lawless*, 2001], and,  
 714 in particular, their application must take care of specified validity conditions (explosive  
 715 type, site geometry, confinement, explosion depth and others ...).

716 One application example can be made on the study of *Ohba et al.* [2007] about a small  
 717 phreatic eruption on the flank of a dacite lava dome of Akita Yakeyama, northern Honshu,  
 718 Japan, which occurred in 1997 and lasted for 70 minutes. The source of eruption was a

719 hot aquifer, situated at about 1000 m of depth at a temperature ca. 300–350°C and a  
720 pressure between 110 and 240 bar. The explosions were triggered by initial mud effusions  
721 from the overlying plumbing system, which released the pressure in the deep reservoir.  
722 Therefore, the explosions extract their energy from the boiling and steam expansion.  
723 The bulk volume of muddy materials involved in the eruption was estimated around  
724 1000 m<sup>3</sup> with an initial water contents of 18–20 wt.%, a rock density of 2400 kg/m<sup>3</sup> and a  
725 water density between 580 and 720 kg/m<sup>3</sup>. From these parameters, we can estimate the  
726 mass of explosive liquid water between 300 and 320 tons. From Figure 7, the explosion  
727 energy can be estimated between 242 and 370 J/g of H<sub>2</sub>O under the classical reversibility  
728 hypothesis, and between 68 and 93 J/g of H<sub>2</sub>O by assuming irreversibility. This yields a  
729 bulk explosive work between 72 and 120 GJ for a reversible process, which is somewhat  
730 below the estimations of *Ohba et al.* [2007] between 100 and 200 GJ by using the method  
731 of *Mastin* [1995]. The irreversibility hypothesis gives an estimate between 20 and 28 GJ.  
732 *Ohba et al.* [2007] used also similarity rules to estimate the energy of discrete explosions  
733 from the size of one of the craters [*Nordyke*, 1962; *Goto et al.*, 2001] and from the height of  
734 the observed clouds [*Ohba et al.*, 2002]. The energy of the largest explosions was estimated  
735 between 3 and 5 GJ by *Ohba et al.* [2007]. Thus, our estimates of the bulk explosive energy  
736 remain consistent with the similarity models used by *Ohba et al.* [2007]. Figure 8 can also  
737 be used to evaluate the mass of vapour produced by the eruption. One obtains mass  
738 fractions of steam, between 32 and 41 weight % for an isentropic process, and between 41  
739 and 54 weight % for an irreversible one. Both estimates are coherent with the muddiness  
740 of air-fall deposits. From Figure 13, one can note that the aquifer of the Akita Yakeyama  
741 volcano is just near or inside the shaded area of the explosive field of the  $H - P$  diagram.

742 This fact is well confirmed by the explosive nature of this hydrothermal system, which  
743 contrasts markedly from geothermal ones of lower temperatures. As noted by *Ohba et al.*  
744 [2007], the craters are produced by the shallow explosions of the ascending and bubbling  
745 muds at depths of 6-10 m, corresponding to near atmospheric pressures ca 1–2 bar. By  
746 referring to the  $P - T$  diagram of Figure 4, it can be noticed that the irreversible and  
747 adiabatic (and nearly isothermal) decompression path of these fluids at initial 300–350°C  
748 runs near the liquid spinodal curve  $Sp(L)$  at these surficial levels. Hence, it is suggested  
749 to associate the explosion focus to a "spinodal" zone, where the metastable bubbly muds  
750 reequilibrate violently by intensive spontaneous bubble nucleations and expansions. This  
751 conclusion could be well justified by the muddy nature of these fluids, featuring probably  
752 important concentration gradients and high viscosities, which delay their reequilibration  
753 with respect to external changes. In the classification of *Zhang* [2000], such a system tends  
754 to a "dynamically completely irreversible" behaviour, which is the trademark of explosive  
755 systems.

## 6. Conclusion

756 Rapid physical transformations (mainly magma exsolution, steam decompression or  
757 heating) are the causes of strong water instabilities, which lead to the explosive mani-  
758 festations featured by hydrothermal and magmatic systems. These explosive properties  
759 of water have been treated here from a macroscopic point of view by using basic and  
760 fundamental concepts (yet rarely used in the volcanological litterature), such as metasta-  
761 bility and spinodals. This approach can be fruitful to predict the explosive character of a  
762 transformation, here based on an one-component perspective. As a result, this allows us  
763 to differentiate superspinodal transformations, which are highly explosive (e.g. BLEVE),

764 and subspinodal ones, which are non or moderately explosive (e.g. cavitation or geysers-  
765 ing). The adopted phenomenological point of view can be linked to the more common  
766 kinetic approach, as the physical mechanism of equilibrium relaxation differ also between  
767 metastable systems (nucleation-growth process) and unstable ones (spinodal decomposi-  
768 tion).

769 The specific energetic properties of water have been presented both in the metastable  
770 and stable domains with the help of the Wagner and Pruss equation of state [*Wagner and*  
771 *Pruss*, 2002]. The mechanical work of the different possible physical transformations, in-  
772 cluding decompression, boiling, isobaric heating and magma exsolution has been assessed  
773 both under the reversibility and irreversibility assumptions. Up to now, the reversibility  
774 hypothesis has been almost always used for quantifying the energy balance of eruptions.  
775 Here is proposed a pathway to do calculations under the irreversible assumption which  
776 results in more realistic estimates. Then, a classification of the hydrothermal and vol-  
777 canic systems has been proposed by taking into account their energetic balance and their  
778 explosivity. Finally, we show how the model can be used in conjunction with empirical  
779 scaling laws to predict potential impacts of volcanic eruptions.

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786 programs used in this work can be found at the following address: [http://wwwobs.](http://wwwobs.univ-bpclermont.fr/lmv/pperm/thiery_r/index.html)  
787 [univ-bpclermont.fr/lmv/pperm/thiery\\_r/index.html](http://wwwobs.univ-bpclermont.fr/lmv/pperm/thiery_r/index.html).

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**Figure 1.** Water volume fraction ( $f_v$ ) in a mixture of melt, crystals and water as a function of the pressure  $P$  and temperature  $T$ , and for a water mass fraction of 5 % (A) and 15 % (B). A value of  $2500 \text{ kg/m}^3$  has been chosen for the density of the melt and solids. The density of water is calculated with the equation of state of *Wagner and Pruss* [2002]). Lines are iso- $f_v$  curves. In figure A, the corresponding density of the aqueous phase is indicated between parentheses in  $\text{kg/m}^3$ .

**Figure 2.** The stable, metastable and unstable fields of water projected in the  $T-v$  space. The full lines separating the stable and metastable regions are the binodal curves: the first branch, noted L(G), refers to the saturated liquid water; whereas the other one, noted G(L), refers to the saturated steam. Both branches join to the critical point (noted CP). The dashed curves are the two spinodal curves, which start from the critical point and delimit the unstable field from the metastable region. The first one, noted Sp(L), is the liquid spinodal curve; and the second one, noted Sp(G), is the gas spinodal curve.

**Figure 3.**  $P-T$  diagram illustrating the different processes generating fluid instability. Solid line: the saturation curve (Sat.). Dotted lines: the liquid spinodal curve (Sp(L)) and the gas spinodal curve (Sp(G)). These three curves meet at the critical point (CP).

**Figure 4.**  $T - U$  diagram used for estimating the mechanical work produced by isentropic expansions. This diagram includes several types of curves: (1) isobars (full thin lines), calculated at 1, 10, 50, 100, 200, 300 500 and 1000 bar; (2) isentropic decompression curves (dashed lines) for a monophasic system; and (3) isentropic decompression curves (dashed lines) for a biphasic system. Isentropic curves are labeled by their temperature at 1000 bar. Other elements of the diagram are the binodals (thick solid lines) L(G) and G(L); and the spinodals (dotted curves) Sp(L) and Sp(G).

**Figure 5.**  $T - H$  diagram used for estimating isobaric heat transfer and mechanical work produced by isenthalpic or isentropic fluid circulations. This diagram includes several types of curves: (1) isobars (full thin lines), calculated at 1, 10, 50, 100, 200, 300, 500 and 1000 bar; (2) isentropic decompression curves (dashed lines) for a monophasic system; and (3) isentropic decompression curves (dashed lines) for a biphasic system. Isentropic curves are labeled by their temperature at 1000 bar. Other elements of the diagram are the binodals (thick solid lines) L(G) and G(L); and the spinodals (dotted curves) Sp(L) and Sp(G).

**Figure 6.**  $P - T$  diagram showing the mechanical energy released by the reversible isentropic expansion of hot steam (in J/g of water) as a function of the initial pressure  $P$  and temperature  $T$  in the magmatic chamber. Thick solid lines: total work ( $W_U = U_3 - U_5$ ) produced in the monophasic and biphasic fields. Thick dashed lines: mechanical work ( $W_U = U_3 - U_4$ ) produced in the monophasic region. Dotted lines: isotherms of the condensation temperature (in K) of the steam at 1 bar. Below the isotherm 373 K, both curves of monophasic and total works are coincident.

**Figure 7.** The expansion work (J/g of water) of a liquid-gas mixture against atmospheric pressure as a function of the initial saturation temperature. The full line indicates energies calculated for an isentropic decompression process, whereas the dashed curve is calculated for an irreversible adiabatic expansion. L(G), G(L) and CP represent respectively expansion works calculated for a saturated liquid, a saturated steam and a critical fluid.

**Figure 8.**  $P - T$  diagram showing the mechanical work (full solid lines, in J/g of water) released by the irreversible adiabatic expansion of hot and pressurized steam as a function of the initial  $P - T$  conditions. Dashed lines indicate the liquid fraction (in mass percentage) of the gas-liquid mixture at a final state of 1 bar and 100°C. The field to the right of the 0% curve indicates the generation of superheated steams at 1 bar (i.e. with a final temperature above 100°C).

**Figure 9.** The mass liquid fraction of the liquid-gas mixture at 100°C and 1 bar produced by the depressurization of a saturated liquid (full curve) or saturated steam (dashed curve), as calculated by three types of decompression processes, i.e. isentropic, isenthalpic and irreversible expansions.

**Figure 10.** The mechanical work (in J/g of water) produced by liquid vaporization, as a function of the boiling temperature.

**Figure 11.**  $T - W$  diagram to calculate the work ( $W = H - U$ , in J/g of water) produced by fluid isobaric expansion as a function of the initial and final temperatures. For example, to calculate the expansion work done by heating the fluid from point A ( $T_A = 694$  K) to point B ( $T_B = 975$  K) at constant pressure (here 1 bar), one makes the difference  $W_B - W_A$  ( $= 450 - 320 = 130$  J/g). Dotted lines are projections of the spinodal curves Sp(L) and Sp(G). Full thick lines are projections of the binodal curves L(G) and G(L). Thin solid lines are the isobars calculated at pressures of 1, 10, 50, 100, 200, 300, 500 and 1000 bar.

**Figure 12.**  $P - T$  diagram showing the work produced by the isobaric and isothermal exsolution of water from magma (in J/g of exsolved water) at fixed pressure  $P$  and temperature  $T$ .

**Figure 13.**  $P - H$  diagram. Thick solid curves: binodal L(G) and G(L) curves. Thick dotted curves: spinodal Sp(L) and Sp(G) curves. Thin dashed curves: isotherms calculated at  $T = 200, 300, 350, 374$  (critical isotherm), 390, 500, 750, 1000 and 1227°C. Thin solid lines: isentropic expansion curves labeled by the initial fluid temperatures at 1000 bar. Majuscule letters refer respectively to: A: Liquid-dominated geothermal systems of low enthalpy. B: High-pressure hydrothermal systems of medium enthalpy. C: Vapour-dominated geothermal systems of high enthalpy. D: Exsolved magmatic, hot and pressurized, steams of vulcanian and plinian volcanic systems. E: Hot and low-pressure steams produced by superficial phreato-magmatism.

**Table 1.** List of symbols.

Symbol	Description
$T$	temperature
$P$	pressure
$v$	molar volume, m <sup>3</sup> /mol
$A$	Helmholtz free energy
$H$	enthalpy
$U$	internal energy
$S$	entropy
$W$	mechanical work
$\rho$	density (kg/m <sup>3</sup> )
$M_{\text{H}_2\text{O}}$	molar weight of water, 0.018 kg/mol
$f$	mass (or molar) liquid fraction in a biphasic liquid-gas mixture
$f_v$	volume liquid fraction in a biphasic liquid-gas mixture
$T_i, P_i$	initial temperature and pressure
$T_f, P_f$	final temperature and pressure
$T_c$	water critical temperature, 374°C, 647.096 K
$T_{\text{sat}}$	saturation temperature, 100°C, 373.15 K at 1 bar
$T_{\text{sp}}$	liquid spinodal temperature at 1 bar, 320.45°C , 593.6 K
$T_{hm}$	spontaneous homogeneous nucleation temperature, 304°C, 577 K at 1 bar
$T_L$	Leidenfrost temperature
$c_v, c_P$	isochoric and isobaric heat capacity, J/kg/K
$\zeta$	conversion factor of the mechanical energy into kinetic and potential energy ( $0 \leq \zeta \leq 1$ )
$c_{U,S}, c_{H,S}$	isentropic heat capacities, J/kg/K
$m_r$	pyroclasts mass driven by one kg of water
$V$	flow velocity of ejected water and pyroclasts, m/s
$\bar{v}_{\text{H}_2\text{O}}$	partial molar volume of H <sub>2</sub> O in silicate melts

**Table 2.** Comparative summary of the two fundamental kinetics, nucleation-growth and spinodal decomposition, of first-order phase transitions for an initial fluid. Note that the explosivity property is relevant only for the boiling of a liquid.

Main Characteristics		Nucleation-Growth	Spinodal Decomposition
Starting state		Metastable	Unstable
Process nature		Activated	Spontaneous
<i>Initial density fluctuations</i>			
	Localisation	At nucleation sites	Everywhere
	Amplitude	High	Low
	Wavelength	Short	Long
Final spatial biphasic pattern		Well separated liquid and gas	Imbricated biphasic association
Reactive zone		Boiling front	Everywhere
Mean diffusion length of heat and/or mass transfer		Large	Small
Transformation rate		Low to high	Very high
Explosivity		Low to high	Very high

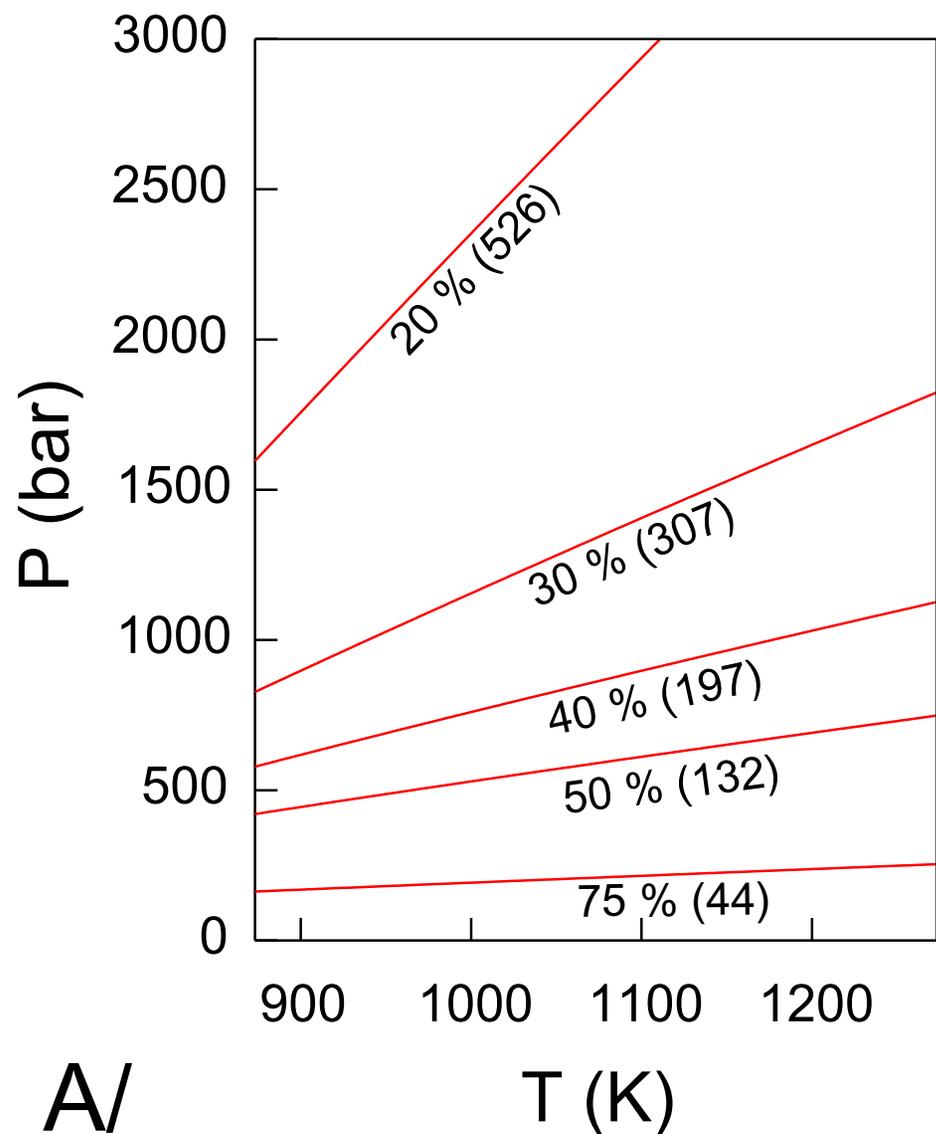
**Table 3.** Calculation example of the mechanical energy released by a fluid isentropic decompression (\*: calculated on the gas branch of the saturation curve), either in the case of a transient process, or a flow process.

State	Transient Process	Flow Process
Point 3 (900 K, 1000 bar)	$U_3 = 2711 \text{ J/g}$	$H_3 = 3003 \text{ J/g}$
Point 4* (615 K, 149 bar)	$U_4 = 2465 \text{ J/g}$	$H_4 = 2615 \text{ J/g}$
Point 5 (373.15 K, 1 bar)	$U_5 = 1799 \text{ J/g}$	$H_5 = 1911 \text{ J/g}$
% of liquid at point 5	34 %	34 %
Mechanical energy	$W_U = 912 \text{ J/g}$	$W_H = 1092 \text{ J/g}$

**Table 4.** Classification of the different hydrothermal and volcanic system types as a function of their nature, environment, energy source, energy amplitude, and explosivity. <sup>1</sup>: these values are calculated by assuming an equal contribution of (1) magma exsolution and decompression, and (2) liquid boiling and steam heating.

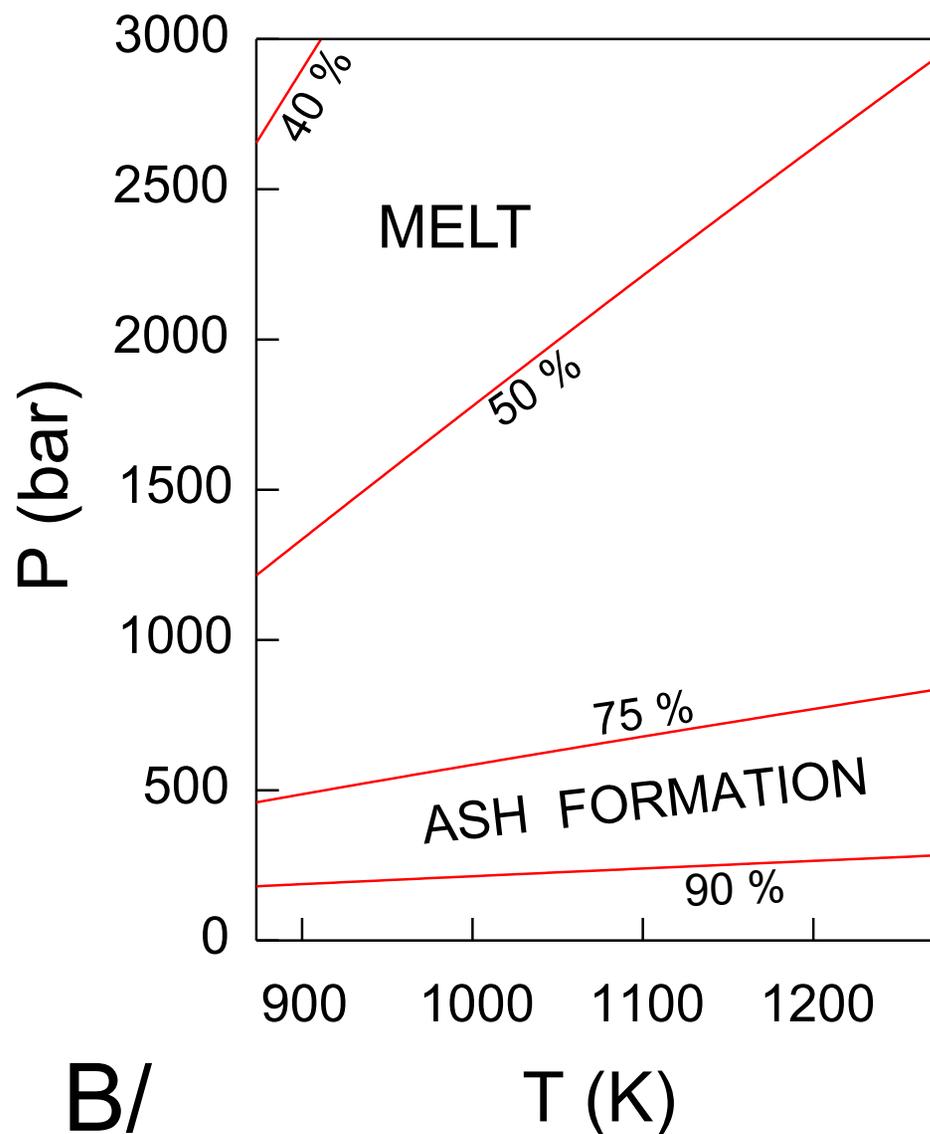
Type	Fluid nature	Environment	Energy source	Energy (J/g H <sub>2</sub> O)	Explosivity
A	Liquid	Liquid-dominated geothermal systems	Decompression	0–100	Weak
B	Super-critical	Deep hydrothermal systems	Decompression	150–200	Low to high
C	Steam	Vapour-dominated geothermal systems	Decompression	100–150	Weak
D	Steam	Vulcanian and Plinian volcanism	Exsolution and decompression TOTAL	450–600 200–400 650–1000	High
E	Liquid	Surtseyan volcanism, superficial phreato-magmatism	Boiling and decompression TOTAL <sup>1</sup>	200–600 100–300 150–450	High
E+D	Liquid and steam	Phreato-plinian volcanism	Exsolution, decompression and boiling TOTAL <sup>1</sup>	450–600 200–400 200–600 425–800	Very high

5 wt % H<sub>2</sub>O



A/

15 wt % H<sub>2</sub>O



B/

