Hydrothermal fluid circulation and its effect on caldera unrest

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This paper focuses on the role that hydrothermal systems may play in caldera unrest. Changes in the fluid chemistry, temperature, and discharge rate of hydrothermal systems are commonly detected at the surface during volcanic unrest, as hydrothermal fluids adjust to changing subsurface conditions. Geochemical monitoring is carried out to observe the evolving system conditions. Circulating fluids can also generate signals that affect geophysical parameters monitored at the surface. Effective hazard evaluation requires a proper understanding of unrest phenomena and correct interpretation of their causes. Physical modeling of fluid circulation allows quantification of the evolution of a hydrothermal system, and hence evaluation of the potential role of hydrothermal fluids during caldera unrest. Modeling results can be compared with monitoring data, and then contribute to the interpretation of the recent caldera evolution. This paper: 1) describes the main features of hydrothermal systems; 2) briefly reviews numerical modeling of heat and fluid flow through porous media; 3) highlight the effects of hydrothermal fluids on unrest processes; and 4) describes some model applications to the Phlegrean Fields caldera. Simultaneous modeling of different independent parameters has proved to be a powerful tool for understanding caldera unrest. The results highlight the importance of comprehensive conceptual models that incorporate all the available geochemical and geophysical information, and they also stress the need for high-quality, multi-parameter monitoring and modeling of volcanic activity.

Keywords: hydrothermal circulation, modeling, volcano monitoring, unrest, gas composition, gravity changes

1.Introduction

Many active calderas are densely populated and thus require effective evaluation of volcanic hazards. However, the quantification of volcanic hazards in active calderas is a difficult task. This is because a large variety of eruptive styles and intensities are possible and in addition the opening of new vents can potentially affect wide areas, but the number and location of these is uncertain. To add to this complexity, non-eruptive unrest is typical of caldera volcanic systems (Newhall and Dzurisin, 1988; Hon and Pallister, 1995, Cole et al., 2005). Unrest crises commonly involve ground deformation, gravity changes, seismic activity, in addition to changes in composition, temperature, or discharge rate of hydrothermal fluids, regardless of the eruptive or non-eruptive nature of the crisis. However, eruptions may occur at calderas without significant warning. Unrest episodes have been recorded at Long Valley since 1980 (Sorey et al., 2003, and references therein), and at Phlegrean Fields since 1969 (Troise et al. 2007, this volume) without major consequences during the following twenty years. For example, at Rabaul (New Guinea) an important unrest phase in 1983-85 (McKee et al., 1984; 1985; Mori et al., 1989) was followed by a relatively quiet period, whereas there was limited warning preceded the onset of the 1994 eruption (Smithsonian Institution-GVN). Similar pattern of unrest may lead to very different eruptive and non-eruptive scenarios; therefore the identification of possible precursors of eruptive activity is difficult. Unrest phenomena may occur as magma stored at depth approaches eruptive conditions i.e. the ascent or intrusion of magma at shallow crustal levels modifies the local stress field, affects temperature gradients, and is accompanied by exsolution of magmatic volatiles. These processes are known to trigger typical unrest phenomena that we can monitor at the surface, such as seismicity, ground deformation, or changes in geochemical and other geophysical parameters. During a volcanic crisis the mitigation measures may involve partial or total evacuation of the population, especially if a large explosive eruption is expected. In these cases crisis management decisions rely to some extent on monitoring parameters likely to signal the onset of eruptive activity, but in the case of calderas chances of a false alarm are very high. The occurrence of non-eruptive unrest crises, observed at several calderas in the world, implies that the relationship between the magmatic system and unrest phenomena may not be straightforward and that unrest crises are not necessarily synchronous with magma ascent and evolution. Discrimination between eruptive and non-eruptive crises is often possible only right before the onset of an eruption, and evacuation may require significant time, depending on the number of people and on the region involved. More research is needed to completely understand volcanic unrest, and to provide tools for the early recognition of eruptive crises.

A common characteristic of active calderas is the presence of hydrothermal systems, which can play an important role during unrest crises. The presence of a hydrothermal system may affect the eruptive style of a volcano, favoring the occurrence of phreatic or phreatomagmatic events, but it also controls heat and fluid transport within the volcanic edifice during both quiescent and unrest periods. A hydrothermal system represents the complex interface between the magma chamber and the surface. Geochemical or geophysical signals originating at the magma chamber level can be distorted, magnified or reduced by the presence of hydrothermal fluids. Hydrothermal systems may themselves generate additional measurable signals in response to changing conditions.

Physical modeling of hydrothermal systems is an important tool for studying the role of hydrothermal fluids during caldera unrest. Once an appropriate conceptual model is identified, physical modeling of heat and fluid circulation in the caldera then allows the quantification of relevant geochemical and geophysical signals generated by the hydrothermal system. This is a first step toward identifying the relationship between magmatic and hydrothermal systems, and hence toward the interpretation of volcanic unrest at calderas.

This paper focuses on illustrating the role of hydrothermal systems during caldera unrest. After describing the main features of hydrothermal circulation (see section 2), section 3 focuses on the governing equations and physical models which describe fluid circulation through porous media. The role of hydrothermal fluids during volcanic unrest is reviewed in section 4, while the final section describes results from numerical modeling of hydrothermal fluid circulation at Solfatara (Phlegrean Fields caldera, Italy).

2. The hydrothermal fluid circulation

Hydrothermal fluid circulation develops where a thermal anomaly heats pore fluids (i.e.: groundwater, meteoric water or seawater). In volcanic areas, the heat source is commonly a shallow magma reservoir which releases not only heat but also exsolved magmatic gases, such as water, carbon dioxide, and sulfur compounds, with minor HCI and HF. Hydrothermal features detectable at the surface depend on several parameters which include the size and geometry of the magmatic source, the properties of fluid components, and the characteristics of subsurface rocks. Calderas are commonly characterized by wide heat anomalies and host larger and longer-lived hydrothermal system than stratovolcanoes.

Although magmatic volatiles are commonly identified in hydrothermal systems, mechanisms of fluid transfer from the magma chamber to the surroundings are not completely understood. It is generally assumed that a transition zone exists between the molten magma and the brittle host rock, where partially molten rock acts as a ductile medium deforming plastically, and heat is mainly transferred by conduction. Across this transition zone, porosity tends to vanish, because of high temperatures (favouring a ductile rock behavior), lithostatic pressures, and abundant mineral deposition at temperatures in excess of 350-400°C (Fournier, 1987). However, petrological studies of contact metamorphism provide clear evidence of fluid transfer across this transition region. Upward and outward fluid migration from cooling plutons has been shown to occur at temperatures in excess of 500°C and pressures up to 220 MPa, preferentially along bedding or lithological contacts (Ferry et al., 2002; Buick and Cartwright, 2002). The presence of fluids, and of considerable mass transport via fluid phases, is known to take place through the deep crust, at depths greater than 15 km and under granulite facies conditions (Ague, 2003). Hydrofracturing may occur through the transition zone as pressure of exsolved volatiles increases above the tensile strength of the surrounding rocks (Tait et al., 1989; Jamveit et al., 1997). This may lead to transient high flux across the transition region, lasting as long as the source is capable of sustaining it. Metamorphic devolatilization reactions can also intervene and reduce the total solid volume, generating secondary porosity (Jamveit et al., 1997).

Once hot magmatic gases escape the magma chamber buoyancy forces prompt natural convection, provided that rock permeability is high enough (Ingebritsen and Sanford, 1998). Hot fluids then propagate through pores and/or fractures, interact with shallow groundwater and eventually reach the surface generating fumaroles, hot springs, or geysers. Hydrothermal circulation depends on fluid properties which, in turn, change as a function of system conditions. Hydrothermal systems encompass a wide range of physical conditions, spanning from almost magmatic to surface settings. As a consequence hydrothermal fluids may exist as single-phase, two-phases or supercritical fluids depending on their pressure and temperature. Physical and transport properties may change accordingly, favoring or hindering fluid motion and heat transport. If gas and liquid coexist, the mobility of each phase is reduced by the presence of the other. In this case, the gas phase tends to occupy larger pores and fractures, whereas liquid water is preferentially held into smaller pores, due to capillary pressure and surface effects (Corey et al., 1956; Elder, 1981). Above the critical point (374.15°C and 22 MPa for pure water) gas and liquid phases become indistinguishable and the resulting supercritical fluid is characterized by very high compressibility, thermal expansion, and heat capacity, and by low viscosity. Strong buoyancy forces and low viscous resistance favours fluid motion and greatly enhances convective heat transport as the critical transition is approached. High pore pressure is easily generated across the critical transition and, in general, the entire hydrothermal circulation is affected (Elder, 1981; Norton, 1984). The composition of circulating fluids, as well as the presence and nature of dissolved salts, also affect fluid properties and modify the temperature and pressure (and hence depth) at which phase transitions occur (Elder, 1981; Bishoff and Pitzer, 1984; Bishoff et al., 1986; Pitzer and Pabalan, 1986; Bishoff, 1991). Highly saline fluids (or brine) are known to evolve from crystallizing magma bodies, together with exsolved volatiles (Fournier, 1987). Denser brine tends to concentrate in the deeper region of hydrothermal systems and separate from the dilute gas phase that rises buoyantly. Double diffusive effects, driven by temperature, density, and salinity gradients, may develop between the dense and dilute convective systems (Elder, 1981; Bishoff and Pitzer, 1984; Bishoff et al., 1986; Pitzer and Pabalan, 1986; Fournier, 1987; Bishoff, 1991). At shallower depths density differences

may drive separation of hot rising gases from the denser liquid phase. As a result hot acid-sulfate springs and fumaroles, fed by CO₂- and H₂S-rich gases, tend to dominate at higher elevation, whereas neutralchloride waters will dominate at greater depths within the volcanic edifice and feed springs at lower elevation and at the periphery of the main upflow region (White et al., 1971; Ingebritsen and Sorey, 1988). Such zonation of discharge features may not exist in wide calderas, which are commonly characterized by a rather flat ground surface (Ingebritsen and Sanford, 1998; Goff and Janik, 2000).

Rock properties also greatly affect the onset and evolution of fluid circulation. Rock permeability expresses the resistance offered by a porous medium to fluid flow. It depends on lithology, varying by several orders of magnitude among different rock types. It also varies with the degree of rock fracturing or alteration. Within the same rock formation permeability may change at different locations and can be anisotropic. Stratigraphic discontinuities, faults, or fractures may act as preferred channelways for fluid propagation, focusing the flow along preferential directions (Ingebritsen and Sanford, 1998). Where fractures are present fluid flow can be relatively fast, and thermal disequilibrium between rock and fluid may exist. If more than one phase is present fractures can also affect phase distribution, as the liquid phase is preferentially held into the smaller pores while gas occupies the fractures (Helmig, 1997). Rock permeability tends to decrease with depth as higher confining pressure, diagenetic and metamorphic processes reduce pore size (Ingebritsen and Sanford, 1998).

Rock permeability can be modified via several processes and at different spatial scales, and this affects the fluid flow pattern through time. Some of these processes are intimately associated with chemical and physical interactions between fluids and host rocks: dissolution or precipitation of mineral phases changes pore size and connectivity, whilst modifying fluid composition and properties (Norton and Knight, 1977; Fournier, 1987; Verma and Pruess, 1988; Ingebritsen and Sanford, 1998). Permeability may also increase in response to hydro-fracturing induced by high pore pressure (Norton and Knight 1977; Burnham, 1985; Gudmundsson et al., 2002). As rock permeability within the hydrothermal system changes through time, surface features associated with fluid circulation change accordingly as the system adjusts to new flow rates and directions.

3. Modeling of hydrothermal fluid circulation

Physical modeling of fluid flow problems is based on the solution of the fundamental equations that govern fluid motion. However, in the case of porous media flow the classical approaches of fluid mechanics, such as those based on the solution of the Navier-Stokes equations, are not immediately applicable as the details of the microscopic pore geometry are not known and flow variables and parameters cannot be defined everywhere. In this case, it is necessary to work on a macroscopic scale, where each quantity is defined as an average over an appropriate volume of material (representative elementary volume). Within this volume it is possible to neglect the details of local variations and to assume that averaged quantities are representative of the overall macroscopic behavior over that volume. The macroscopic approach to porous media flow is based on Darcy's law, an empirical equation derived experimentally in 1856, which describes the steady flow of liquid water through a vertical column of sand. Darcy's law relates the specific water discharge (also known as filtration or Darcy velocity) to the pressure gradients across the sand's column through a coefficient known as hydraulic conductivity [m/s], which depends on both fluid and rock properties. Darcy's law has been tested over a wide range of conditions and in most cases theoretical results are

consistent with experimental data. Exceptions are found under extreme conditions, in case of very high (or very low) flow velocity when inertial (or interfacial) forces, that are neglected in the empirical formulation, become relevant. These extreme conditions are very rare in natural systems and Darcy's law has been successfully used to set up the water mass balance equation in countless hydrological applications. Detailed discussion of Darcy's law, its limitations and its derivation from the Navier-Stokes equation can be found in de Marsily (1986), Dullien (1992), Helmig (1997), Ingebritsen and Sanford (1998). Here we shall only briefly overview some of its basic aspects, following Helmig (1997).

Hydrothermal fluid circulation requires a slightly more complex formulation than common groundwater problems. Complexities mostly arise from the wide range of temperatures characterizing hydrothermal systems, where water can exist as a liquid, a gas, a two-phase mixture or a supercritical fluid. Liquid water and steam are characterized by very different thermal and transport properties, and as the fluid propagates through different regions its properties may change considerably, affecting fluid motion. At the same time fluid flow contributes significantly to heat transport, affecting temperature distribution. Physical models of hydrothermal circulation therefore need to solve the fully coupled equations of both mass and energy balance.

For multi-phase flow problems, Darcy's law can be rewritten to explicitly state the dependence of the filtration velocity, \mathbf{u}_{β} [m/s], on fluid properties:

$$\mathbf{u}_{\beta} = -\mathbf{k} \frac{k_{\beta}}{\mu_{\beta}} (\nabla p_{\beta} + \rho_{\beta} \mathbf{g})$$
(1)

where **k** is the intrinsic rock permeability [m²] and expresses the resistance opposed by porous media to fluid flow along different directions. It depends on rock porosity and pore connectivity. k_{β} is the relative permeability of phase β ; it expresses the interference between phases and it ranges from 0 to 1 as a function of gas saturation. μ_{β} is viscosity [Pa s], p_{β} is pressure [Pa] (accounting for the effects of capillary force), and ρ_{β} is density [kg/m³] (where subscript β refers to fluid phase). **g** is the gravitational acceleration [m/s²]

Based on the above multi-phase version of Darcy's law, the mass balance equation for phase β can be written in differential form as:

$$\frac{\partial \left(S_{\beta} \phi \rho_{\beta} \right)}{\partial t} + \nabla \left(\rho_{\beta} \mathbf{u}_{\beta} \right) - \rho_{\beta} q_{\beta} = 0 \quad (2)$$

where S_{β} is phase saturation (volumetric fraction occupied by phase β), ϕ is rock porosity and q_{β} is a sink or source (if negative) of phase β . Equation (2) is nonlinear due to the nonlinear relations linking phase saturation, capillary pressure and relative permeability (Helmig, 1997). If more than one component is present (i.e. volcanic gases, such as carbon dioxide, or dissolved solid phases), equation (2) is

appropriately modified, expressing the fluid mass per unit volume as $\rho_{B} X_{B}^{\kappa}$, where X_{B}^{κ} represents the

mass fraction of component κ in phase β . As mentioned above, fluid properties that explicitly appear in the mass and energy balance equations may change significantly within hydrothermal systems. As a consequence, modeling of hydrothermal fluid circulation also requires the definition of appropriate equations of state which describe fluid properties at the conditions of interest. In some case it is possible to approximate the behavior of fluid properties as linear function of pressure and temperature. In other cases this is not feasible and more accurate nonlinear equations of state are required, increasing the complexity of the numerical problem.

The energy balance equation (for phase β) is written assuming local thermal equilibrium between solid rock and fluid. It accounts for heat transport by fluid convection and by conduction through the porous matrix:

$$(1-\phi)\rho_{R}c_{R}\frac{\partial T}{\partial t}+\phi\sum_{\beta}\frac{\partial (U_{\beta}\rho_{\beta}S_{\beta})}{\partial t}+\nabla\times\left(\sum_{\beta}\mathbf{u}_{\beta}\rho_{\beta}h_{\beta}\frac{1}{\dot{f}}+\nabla\times\left(\lambda_{R}\nabla T\right)-q_{E}=0$$
(3)

where ρ_R is rock density[kg/m³] (subscript R refers to rock properties), c_R is specific heat of the rock [J/Kg °K], T is temperature [°K], U_β and h_β are the internal energy and enthalpy of phase β , respectively;, λ_R is rock thermal conductivity [W/m°K] (which depends not only on the rock, but also on thermal properties of the permeating fluid and on its saturation), and q_E represents any energy sink or source within the system.

Due to the difficulty in the simultaneous solution of these highly non-linear and fully coupled equations, early models were limited to simple systems (often isothermal) with a single-phase fluid of constant properties flowing through a homogeneous porous medium (Elder, 1967a; 1967b). Better computational capabilities and improved numerical techniques have since allowed solution of the coupled energy and mass transport equations. Pioneering studies focused on hydrothermal fluid circulation nearby cooling plutons (Cathles, 1977; Norton and Knight, 1977; Delaney, 1982), and considered fluid density to be constant everywhere except in the evaluation of buoyancy forces (Boussinesq approximation). Subsequent improvement in numerical models has been supported by the geothermal industry. A detailed overview of geothermal reservoir modeling and its development through time is given by Pruess (1990) and O'Sullivan et al. (2001). Modeling of heat and fluid flow through porous media is now a well-developed and highly sophisticated research field. At present geothermal simulators include realistic descriptions of fluid properties and account for phase transitions and associated latent heat effects (Pruess, 1990; 1991; Hayba and Ingebritsen, 1997). Different features may characterize specific models, features such as the presence of additional fluid components (non-condensable gases, or dissolved salt) or sophisticated rock descriptions, including heterogeneous, anisotropic, or time-dependent rock properties. Different strategies have been used to describe flow through fractures: considering a single, fracture-dominated continuum, accounting for discrete fracture networks, defining an equivalent (fracture and matrix) continuum, or through a dual porosity approach in which fracture and matrix are considered separately (Evans et al., 2001). More recent advances involve coupling of either non-isothermal fluid flow and chemical reactions (Xu and Pruess, 2001; Xu et al., 2001; Kiryukhin, et al., 2004), or hydrothermal circulation and deformation of the porous medium (Rutqvist et al., 2002). These modeling techniques are now widely applied to a variety of problems that involve underground flows ranging from site testing for nuclear waste storage, to mining engineering,

environmental restoration, vadose zone hydrology, and more recently for investigating carbon dioxide sequestration (O'Sullivan et al., 2001).

Despite such development, applications to volcanological problems are not common. Volcanological applications face the complexity of volcanic settings and involve extreme and highly transient physical conditions, as well as the lack of appropriate modeling-oriented data sets required to constrain subsurface properties and conditions. Surface measurements of geochemical and geophysical parameters are usually carried out as a part of surveillance programs, but do not necessarily involve the definition of hydraulic properties of subsurface rocks. Although these surface data can be integrated with subsurface data from the few sparse deep drill holes, large uncertainties commonly remain in the definition of the conceptual model. In spite of these difficulties, numerical modeling has been performed to study hydrothermal fluid circulation in volcanic areas (Ingebritsen and Sorey, 1985; 1988; Bonafede, 1991; Ingebritsen and Rojstaczer, 1993; 1996; Todesco, 1995; 1997; Gaeta et al., 1998; 2003; Kissling, 1999; Hurwitz et al., 2002; 2003; Chiodini et al., 2003; Todesco et al., 2003a; 2003b; Reid, 2004; Todesco et al., 2004; Todesco and Berrino, 2005; Villemant et al., 2005). Early studies mostly focused on the description of the natural state and were aimed at the study of some theoretical aspects of fluid flow in volcanic regions. When long-term, high-guality data sets are available it is possible to set up reliable conceptual models for the evolution of the entire volcanic system. This in turn allows implementation of more sophisticated numerical models designed to elucidate site-specific features and details of case histories. When sophisticated modeling tools and highquality data are both available, the ideal condition of being able to compare and constrain modeling results with observations becomes possible.

4. Hydrothermal systems and volcano monitoring

Hydrothermal fluid circulation plays a significant role during both eruptive and non-eruptive unrest events. Volcanic monitoring around the world commonly records changes in geochemical and geophysical parameters, many of which can be directly or indirectly related to the activity of hydrothermal fluids. In some cases these changes result from the evolution of the magmatic system at depth. In other cases the observed variations only reflect the natural evolution of the hydrothermal system or its reaction to external controls, such as tectonic events. Physical models of hydrothermal fluid circulation allow the simulation of unrest phenomena related to the hydrothermal system, and elucidates what controls observed changes in the system.

4.1 Geochemical monitoring

Surveillance programs on active volcanoes commonly involve geochemical monitoring of hot springs, fumaroles and thermal waters. Hydrothermal fluids reveal important information about subsurface conditions, and unrest phenomena are often accompanied by changes in the temperature, composition and discharge rates of hydrothermal waters (Newhall et al., 2001).

Geochemical monitoring is based on the concept that volcanic gas emissions are fed by magma degassing and thus reflects to some extent the conditions under which degassing takes place. The composition of gases exsolving from a magma chamber will depend on magma composition, the solubility of different gas components, and on the depth and temperature of the magma reservoir. Less soluble gases, such as nitrogen or carbon dioxide, exsolve first and as degassing proceeds more soluble species (such as sulfur

compounds, water, or halogens) will be progressively released. The ratio of less soluble to soluble components is therefore expected to change through time, as magma looses its volatiles (Carrol and Webster, 1994; Delmelle and Stix, 2000). Departure from the expected trends may indicate a change in the magmatic source, for example by the arrival of a new, gas-rich magma batch, or by the ascent of the degassing magma to shallower depths. An increase in gas flow rate is also expected if a larger amount of magma is available. Discharge rate at hot springs increased dramatically before eruptions at Sakurajima (Japan) in 1914, and at Monte Nuovo (Phlegrean Fields, Italy) in 1538 (Newhall and Dzurisin, 1988). Conversely, the Mount Usu (Japan) eruption in 2000 was preceded by an increase in carbon dioxide degassing within the summit caldera (Hernandez et al., 2001). Major diffuse degassing of carbon dioxide, killing trees in Mammoth Mountain area, was also observed during unrest at Long Valley caldera, California (Prinbow et al., 2003; Bergfeld et al., 2006). Seismicity and ground deformation have been recorded there since 1980, and this has been accompanied by a recorded increase of well fluid pressure and by a higher flow rate of magmatic gases (Sorey et al., 2003, and ref. therein). The interpretation of monitoring data is, however, not always straightforward. Volcanic gas emissions do not simply reflect the process of magma degassing. As magmatic gases rise toward the surface they are affected by cooling, decompression, oxidation, and reactions with host rock and groundwaters. Fluids sampled at the surface result from complex interactions between the deep, magmatic contributions and shallower components of the hydrothermal system. As hot fluids interact with shallow water bodies, heat exchange, phase transition, and chemical reactions may take place: ascending fluids may gain or loose water vapor, depending on whether condensation or evaporation prevails. In addition, reactive and soluble components, such as sulfur dioxide or halogens, may be lost in groundwaters and appear substantially depleted in volcanic gas emissions. Sulfur compounds are particularly sensitive to secondary processes and redox conditions, which ultimately control the SO₂/H₂S ratio; deposition (or revolatilization) of elemental sulfur may also occur upon cooling (heating) (Giggenbach, 1996; Delmelle and Stix, 2000; Symonds et al., 2001; Oppenheimer, 2003, and references therein). Surface hydrothermal features will therefore depend on the relative proportion of magmatic volatiles with respect to shallower fluids, and on whether or not thermal and chemical equilibrium among different components has been achieved. This in turn may depend on rock permeability, which controls fluid mobility and determines the extent and duration of the interaction between different fluid components. Temperature, discharge rate and composition of surface hydrothermal features may change as any element of these complex systems changes, either at the magma chamber level, in the groundwater system or in rocks hosting them both. As a consequence, interpretation of geochemical data can be highly controversial. Sophisticated theoretical tools are needed to estimate the conditions at which chemical equilibrium was attained, or to quantify the departure from such equilibrium conditions (Giggenbach, 1996; Chiodini and Marini, 1998; Oppenheimer, 2003).

4.2 Geophysical monitoring

The role of hydrothermal fluids in volcanic surveillance goes beyond the information we can obtain through geochemistry. The presence of hot fluids alters rock properties and affects the response of the entire volcanic edifice to thermal and mechanical changes. Seismic wave velocity is known to depend on the presence of pore fluids, and different degrees of seismic attenuation are expected in gas- and liquid-dominated regions. Anisotropy associated with fluid-filled microcracks is known to generate shear wave splitting. Shear wave splitting parameters (polarization and time delay between split waves) change with stress distribution, and these are increasingly adopted as a tool in volcano monitoring (Miller and Savage,

2001; Crampin and Chastin, 2003; Bianco et al., 2004). Although volcanological applications mostly focus on stress changes induced by magma intrusion, changes in polarization of the faster split shear wave may also arise as a consequence of increased pore pressure, as observed during injections in hot, dry-rock geothermal reservoirs or in oil fields (Cramping and Booth, 1989;Angerer et al., 2002; Crampin and Chastin, 2003).

Hydrothermal fluids can also trigger shallow seismicity. Elevated pore pressure reduces the effective normal stress, favouring focused stress release. Where rocks are close to failure pore pressure perturbations may drive seismicity, even in non-volcanic areas (Shapiro et al., 2003; Miller et al., 2004). Microseismicity is commonly observed at geothermal fields during fluid injection in boreholes (Maillot et al., 1999). In volcanic areas, hydrothermal fluids can trigger, or participate to the generation of, long- and very-long-period seismic events and volcanic tremor (Newhall and Dzurisin, 1988; Chouet, 1996;Hellweg, 2000; Konstantinou and Schlindwein, 2002; Bianco et al., 2004; De Angelis and McNutt, 2005). Banded tremor correlated with hydrothermal and geyser activity has been observed at Yellowstone and at other locations (Newhall and Dzurisin, 1988, and ref. therein). Pressurization of hydrothermal fluids, possibly associated with shallow magma intrusion, has been invoked as a possible source for LP seismic events and volcanic tremor at Redoubt, Alaska (Chouet, 1996); Aso volcano, Japan (Kaneshima et al., 1996; Yamamoto et al., 1999; Kawakatsu et al., 2000); Phlegrean Fields, Italy (Bianco et al., 2004), Rabaul (Gudmundsson et al., 2004); and at Mt. Spurr, Alaksa (De Angelis and McNutt, 2005). A connection between seismic swarms and long term pulsating degassing of a shallow magma body was also proposed for La Soufrière, Guadaloupe, Lesser Antilles (Villemant et al., 2005). At Long Valley, California, the ascent of deep, CO₂-rich fluids (later responsible for tree-killing diffuse degassing) was recently indicated as the possible trigger for the long seismic swarm recorded in 1989 (Hill and Prejean, 2005). Evidence of hydro-fracturing, associated with the ascent of hydrothermal fluids, was also recognized in the focal mechanism of small micro-earthquakes recorded in 1997 (Foulger et al., 2004).

Hydrothermal fluids also generate a variety of geophysical signals that can be detected at the surface. This is well known in the geothermal industry, where such signals are collected to monitor reservoir properties during exploitation. Circulating fluids induce changes in electrical potential as they move with respect to the host rock (electro-kinetic effect). Thermo-electric and electro-chemical effects are also known to arise from thermal and chemical gradients (Zlotnicki and Nishida, 2003). Self-potential (SP) anomalies are commonly identified upon fluid injection or production in geothermal reservoirs (Darnet et al., 2004). In active volcanic systems anomalies up to several hundreds of mV are commonly associated with thermal and hydrothermal features, and their temporal evolution is known to reflect the evolution of the volcanic system (Zlotnicki and Nishida, 2003).

Phase transition or displacement of liquid water can occur within the hydrothermal system and modify the subsurface density distribution. The resulting gravity change can be detected at the surface by accurate microgravity measurements. Gravity changes are recorded in geothermal fields to monitor reservoir properties during fluid production and to constrain numerical modeling of reservoir exploitation (Hunt and Kissling, 1994; Nortquist et al., 2004). Gravity changes are also commonly observed in active calderas during episodes of ground deformation (Brown et al., 1991; Berrino et al., 1992; Rymer, 1994; Murray et al., 2000; Battaglia et al., 2003; Battaglia and Segall, 2004; Gottsmann and Battaglia, 2007 - this volume). Even

though such changes are also caused by ground displacement, in some cases they can be ascribed to the motion of aqueous fluids (Berrino et al, 1992; Gottsmann and Rymer, 2002; Gottsmann et al., 2003; Todesco and Berrino, 2005).

To some extent, hydrothermal fluids can also drive ground deformation. Coupling of thermal gradients, fluid flows, and mechanical deformation of rocks have been widely recognized, and complex thermo-hydromechanical (THM) interactions are known to occur in many geological contexts and applications (Tsang, 1999). Prolonged fluid extraction at the Wairakei geothermal field, New Zealand, was shown to have caused up to 14 m of ground subsidence, over almost 40 years of production (1950-1997) (Allis, 2000). Localized subsidence as a consequence of fluid production was also recorded in Long Valley near the Casa Diablo power plants (Howle et al., 2003). Similarly, ground uplift may follow pore pressure increase and rock thermal expansion, associated with the circulation of hot fluids. This mechanism is particularly suited to explain ground deformation during non-eruptive unrest, when ground uplift is followed by a subsidence phase that cannot be ascribed to magma withdrawal. If uplift is generated by an increase in pore pressure, subsidence may occur as fluids propagate and eventually discharge at the surface and gradually dissipate the initial overpressure. In the case of Phlegrean Fields caldera, a long scientific tradition has suggested the involvement of hydrothermal fluids in the two recent episodes of non-eruptive unrest, each of which was accompanied by remarkable ground uplift (bradyseism) (Olivieri del Castillo and Quagliariello, 1969; Casertano et al., 1976, Bonafede, 1991, Gaeta et al., 1998; Orsi et al., 1999; De Natale et al., 2001; Castagnolo et al., 2001). Recent findings substantiate the concept and emphasize the role of hydrothermal system during recent unrest events (Chiodini et al., 2003; Todesco et al., 2004; Todesco and Berrino, 2005; Battaglia et al., 2006).

5. An example of assessing the role of hydrothermal processes during unrest: Solfatara (Phlegrean Fields caldera, Italy)

The Phlegrean Fields caldera (Figure 1) represents an optimal site for modeling hydrothermal fluid circulation. Volcanic surveillance was started here in the early 1980's and long data series are now available to describe the caldera's recent evolution. The last major unrest took place between 1982 and 1984 and involved seismic activity, ground deformation (with ground uplift up to 1.8 m), positive gravity residuals and significant changes in the composition of gases discharged at Solfatara crater. A slow subsidence begun in 1985, periodically interrupted by minor uplift (few cm each), accompanied by significant changes in gas composition and occasional minor seismic activity (see Troise et al., 2007 - this volume, and references therein). As mentioned above, several authors highlight the role of hydrothermal fluid circulation in governing the recent evolution of the Phlegrean Fields caldera (Bonafede, 1991, Gaeta et al., 1998; Orsi et al., 1999; De Natale et al., 2001; Castagnolo et al., 2001). Recent new analyses of deformation and gravity data confirm the role of hydrothermal fluids in generating uplift (at least partially) and subsidence observed since the last unrest crisis (Gottsmann et al., 2003; Battaglia et al., 2006; Gottsmann et al., 2006).

Physical modeling of heat and fluid flow is a useful tool to quantify the effects of hydrothermal fluid circulation. The simulations presented below describe fluid circulation within the shallow hydrothermal system that feeds surface discharges at the Solfatara crater (Todesco et al., 2003a; 2003b; Chiodini et al., 2003; Todesco et al., 2004; Todesco and Berrino, 2005). The role of new magmatic intrusions in the recent

unrest crises is not explicitly accounted for, but it is represented in terms of variable magmatic degassing and by the emplacement of a deep source of hot fluids. Simulations were performed with the TOUGH2 geothermal simulator (Pruess, 1991; Pruess et al., 1999). The model describes the coupled heat and fluid flow through porous media for a multi-phase, multi-component system. Phase transitions (gas-liquid) and associated latent heat effects are fully accounted for. Water and carbon dioxide are the two fluid components considered in the model. Details on model formulation and solution techniques can be found in Pruess et al. (1999). Shallow hydrothermal circulation at Solfatara is simulated on a uniform, 2-dimensional, axisymmetric domain (Figure 2a). A source of hot (350°C) water and carbon dioxide is placed at the bottom (near the symmetry axis) to represent magmatic degassing. Discharge of these hot fluids generates a wide two-phase plume, within which a shallow dry-gas region forms (Figure 2b, Todesco et al., 2003a). Existence and conditions of such single-phase gas region are in good agreement with geochemical data, postulating that fumaroles are fed by a super-heated vapor zone (Chiodini and Marini, 1998).

Using these initial system conditions the model can be applied to study the recent evolution at Solfatara. Simulations were carried out under the assumption that observed compositional changes were driven by periods of increased magmatic degassing. Unrest crises are therefore simulated as periods of higher gas flow rate and CO₂ content at the deep source (Chiodini et al., 2003). The model describes the fluid composition and properties throughout the simulation, allowing comparison of modeling results with available geochemical and geophysical data. The composition of the single-phase gas region is taken as representative of fumarolic gases, and is compared with observed gas composition. Appropriate number, timing, and duration of each unrest period allows successful matching with the observed compositional variation (Figure 3). If magmatic degassing increases, pore pressure and fluid temperature are also expected to increase. Mechanical effects associated with such changes can be evaluated based on the calculated pressure and temperature distribution. Coupling between TOUGH2 and FLAC3D, a commercial code for rock mechanics (Itasca, 1997), was performed to study thermo-hydro-mechanical problems (Rutqvist et al., 2002). Taking advantage of this methodology, simulations were carried out to model the deformation arising from increased magmatic degassing, under the assumption of pure elastic behavior (Todesco et al., 2003b; 2004). Results from coupled simulations showed how increased magmatic degassing can drive significant amounts of rock deformation (Figure 4). Rapid uplift was calculated during the 2-year long unrest period. Afterwards, a slower and longer subsidence takes place as the magmatic contribution is strongly reduced. Even though the model only describes a very shallow portion of the entire volcanic system, therefore neglecting deformation arising from deeper contributions, the bell-shape form of the uplifted region, temporal evolution of ground deformation and even the delay of compositional changes with respect to ground displacement are all consistent with the available observations (Todesco et al., 2003b; 2004). Alternating unrest and quiescent periods also drives significant changes in fluid density, arising from variable fluid composition and phase distribution. Subsurface density changes then affect the value of gravity that can be recorded at the surface. Based on modeling results the gravity changes arising from the simulated unrest periods were calculated (Todesco and Berrino, 2005). Each unrest period causes a sudden and short-lasting gravity increase, associated with the stronger degassing rate. As the newly injected fluids rise toward the surface, the two-phase plume widens and the average gas fraction increases. The overall effect of subsequent unrest crises is therefore to progressively reduce the value of gravity at the surface (Figure 5). Todesco and Berrino (2005) showed that this effect explains the discrepancy between gravity data measured at Solfatara and those recorded at nearby stations, where hydrothermal fluids do not reach the surface. In this case, it was possible to compare modeling results with both geochemical and geophysical data. A good match with both data sets was obtained by progressively refining the model's initial and boundary conditions. These conditions correspond to an initially hotter system (which indeed had already experienced another important unrest crisis in 1969) and to shorter (but slightly stronger) unrest crises, characterized by a higher CO₂/H₂O ratio with respect to previous simulations (Todesco and Berrino, 2005). This new characterization of magmatic degassing is in good agreement with recent refinements of the geochemical model (Chiodini, personal communication).

The opportunity to compare modeling results with two sets of independent parameters represented a valuable chance to constrain modeling results in a field, such as Volcanology, where model calibration and validation are usually impossible to carry out. Simulation of two different parameters can also be used to improve our understanding of system evolution based on monitoring data. Parametric studies can be carried out to show the different effects of selected source properties (i.e., fluid composition, gas flow rate) on fumarole composition and gravity data. The model can then be used to define different scenarios and to establish a reference framework for the interpretation of monitoring data.

6. Discussion and conclusions

Hydrothermal fluid circulation is a very special feature of active volcanic systems. By controlling the transport of heat and fluids from the magma reservoir to the surface, hydrothermal fluids play a significant role in the evolution of volcanic centers. Circulating fluids affect rock properties, generate various types of geochemical and geophysical signals, and can trigger shallow seismicity and ground deformation. Pore pressure build-up, followed by intense degassing, may explain uplift and subsidence cycles observed during non-eruptive unrest at many calderas in the world. Repeated crises, accompanied by ground deformation and by widespread hydrothermal alteration, can progressively weaken rocks strength and, on the long term, this can be one of the many features favouring a renewal of the eruptive activity. Hydrothermal systems therefore represent an important key to understanding volcanic unrest. Physical modeling of hydrothermal fluid circulation is a powerful tool to study the evolution of hydrothermal systems, and to quantify their effects on selected geochemical and geophysical parameters. Volcanic surveillance collects geochemical and geophysical data, whose evolution depends on the complex interactions between the magmatic source, hot circulating fluids and the host rocks through which they circulate. It is impossible to fully assess all these interactions, but the interpretation of monitoring data should account for this complexity. Results from numerical modeling of hydrothermal circulation are promising, but the complexity of the natural systems demand further improvement to achieve satisfactory results, beyond the theoretical study. A fully multidisciplinary approach is required to improve and further connect conceptual models, numerical models, and monitoring data. We need robust conceptual models capable of describing caldera evolution in all its geochemical and geophysical aspects that consistently incorporate all available information.

Several aspects need to be further investigated to fully understand the role of fluids in unrest crises. Mechanisms controlling magma degassing and the transport of heat and fluid from the magma chamber to the hydrothermal system are still poorly constrained. Pulsating degassing, alternating phases of higher and lower gas flow rates, seems to be a common behavior, but we lack a coherent explanation for it. A better characterization of magmatic degassing could greatly improve our description of hydrothermal circulation, and provide further insights on the functioning and ultimate meaning of non-eruptive unrest crises.

Subsurface rock properties are usually poorly defined - few measurements may be available on thermal and acoustic properties of subsurface rocks, but information on hydraulic properties is usually missing. Data used to set up numerical models are commonly taken from the literature and are hardly representative of the natural system. Changes of rock properties through time, or with changing system conditions, are also poorly constrained and generally are not accounted for in models applied to volcanological problems. Nevertheless, these changes could play an important role during unrest crises and their effects on fluid flow pattern, and on pressure and temperature distribution, should be assessed. More data are available on hydrothermal alteration and, in general, on chemical reactions taking place during fluid circulation. However, modeling of volcanic unrest has not yet included their description, and does not take into account their effects on fluid circulation. Further work is needed on these coupled processes, including thermal, chemical and mechanical effects and their feedback on fluid circulation. Development of numerical models should also include a better description of fluid properties through the transition from subcritical to supercritical temperatures, and under the extreme conditions that characterize active volcanic systems. Implementation of inverse modeling, directly incorporating data from monitoring networks, would greatly improve our ability to interpret signals gathered during unrest and could contribute to volcanic hazard assessment.

Another important aspect to be considered in future research is the connection between models and observations. This should be improved to ensure at least some degree of model calibration. Therefore it is necessary that models describe parameters that can be measured in the natural system. We cannot access hydrothermal system at depths and consequently we cannot compare simulated flow variables to direct measurements of pressure or phase saturation. We need to convert modeling results into a larger number of observables, such as gravity changes, which can be actually compared with available data. Preliminary successful results are encouraging, but the comparison between observation and modeling results should be performed over a larger number of physical and chemical data. Coordinated monitoring campaigns are necessary to provide simultaneous measurements of different geochemical and geophysical parameters. Simultaneous matching of independent data sets is an effective way to validate modeling results. Monitoring data and modeling results should freely circulate inside the scientific community to ensure a continuous positive feedback, with prompt updating of the conceptual model, progressive refinement of model calibration, and rational optimization of monitoring activities.

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Figures



Figure 1. The Phlegrean Fields caldera and the Solfatara crater, where fumaroles and diffuse degassing are concentrated. Locations of two gravity stations (Solfatara and Serapeo) are also shown (modified after Todesco and Berrino, 2005).



Figure 2a. Computational domain, boundary conditions and rock properties utilized in numerical simulations of hydrothermal fluid flow. The star indicates the position of a deep source of fluids, discharging a mixture of water and carbon dioxide at 350°C (modified after Todesco and Berrrino, 2005).



Figure 2b. Temperature (°C, solid line) and volumetric gas fraction (shades) obtained after a prolonged injection of hot gases at the deep source, and applied as initial conditions in the simulations thereafter (modified after Chiodini et al., 2003). The shallow gas-dominated region (dark gray) corresponds to the superheated vapor region that, according to the geochemical model (Chiodini and Marini, 1998), feeds the fumaroles.



Figure 3. Comparison between the CO_2/H_2O molar ratio observed at Solfatara fumaroles (dots) and gas composition simulated by the model (solid line). Shaded bars represent the simulated periods of system unrest, characterized by higher gas flow rate and CO_2 content at the deep source (modified after Chiodini et al., 2003).



Figure 4. Distribution of (a) pore pressure (MPa) and (b) temperature (°C) distribution at the end of a 2-year long unrest crisis. The corresponding ground uplift (m), resulting from heating and pressurization, is shown in (c). The distribution of vertical ground displacement over the computational domain is shown in (d). Rock deformation is calculated assuming elastic behavior, and low values of elastic properties due to high temperatures. Bulk modulus = 5GPa; shear modulus = 2 GPa (modified afer Todesco et al., 2003b; 2004).



Figure 5. Temporal variations of gravity residuals observed at Solfatara (diamonds) and Serapeo (squares). The difference between the values recorded at the two stations (dots) is compared with calculated gravity change (solid line) arising from the temporal variation of fluid density. The good correspondence confirms that anomalous gravity residuals at Solfatara are associated with the hot plume of hydrothermal fluids (modified after Todesco and Berrino, 2005).

References

Ague, J.J., 2003. Fluid flow in the deep crust. In: Rudnick, R. L. (Ed.), The Crust, Vol. 3. Holland, H.D., Turekian, K.K. (Eds.) Treatise on Geochemistry, Elsevier-Pergamon, Oxford.

Allis, R.G., 2000. Review of subsidence at Wairakei field, New Zealand. Geothermics 29, 455-478.

Angerer, E., Crampin, S., Li, X.-Y., Davis T.L., 2002. Processing, modeling and predicting time-lapse effects of overpressured fluid-injection in a fractured reservoir. Geophys. J. Int. 149, 267-280.

Battaglia, M., Segall, P., 2004. The interpretation of gravity changes and crustal deformation in active volcanic areas. Pure App. Geophys. 161, 1453-1467.

Battaglia, M., Segall, P., Roberts, C., 2003. The mechanics of unrest at Long Valley caldera, California. 2. Constraining the nature of the source using geodetic and micro-gravity data. J. Volcanol. Geotherm. Res. 127, 219-245.

Battaglia et al., this volume?

Battaglia, M., Troise, C., Obrizzo, F., Pingue, F., De Natale, G., 2006. Evidence for fluid migration as the source of deformation atCampi Flegrei caldera (Italy). Geophys. Res. Lett. 33, L01307, doi: 10.1029/2005GL024904.

Bergfeld, D., Evans, W.C., Howle, J.F., Farrar, C.D., 2006. Carbon dioxide emissions from vegetation-kill zones around the resurgent dome of Long Valley caldera, eastern California, USA. J. Volcanol. Geotherm. Res. 152, 140-156.

Berrino, G., Rymer, H., Brown, G.C., Corrado, G., 1992. Gravity-height correlations for unrest at calderas. J. Volcanol. Geotherm. Res. 53, 11-26.

Bianco, F., Del Pezzo, E., Saccorotti, G., Ventura, G., 2004. The role of hydrothermal fluids in triggering the July-August 2000 seismic swarm at Campi Flegrei, Italy: evidence from seismological and mesostructural data. J. Volcanol. Geotherm. Res. 133, 229-246.

Bishoff, J.L., 1991. Densities of liquids and vapors in boiling NaCl-H₂O solutions; a PVTX summary from 300° to 500° C. Am. J. Sci. 291, 309-338.

Bishoff, J.L., Pitzer, K.S., 1984. Phase relations and adiabats in boiling seafloor geothermal systems. Earth Plan. Sci. Lett. 75, 327-338.

Bishoff, J.L., Rosenbauer, R.J., Pitzer, K.S., 1986. The system NaCl-H₂O: relations of vapor –liquid near the critical temperature of water and of vapor-liquid-halite from 300° to 500°C. Geochim. Cosmochim. Acta 50, 1427-1444.

Blong, R.J., McKee, C.O., 1995. The Rabaul eruption, 1994 - destruction of a town. Macquarie University, Natural Hazards Research Centre Report.

Bonafede, M., 1991. Hot fluid migration, an efficient source of ground deformation, application to the 1982-1985 crisis at Campi Flegrei-Italy. J. Volcanol. Geotherm. Res. 48, 187-198.

Bowers, T.S., Hegelson, H.C., 1983a. Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system H_2O-CO_2 -NaCl on phase relations in geologic systems: equation of state for H_2O-CO_2 -NaCl fluids at high pressure and temperatures. Geochim. Cosmochim. Acta 47, 1247-1275.

Bowers, T.S., Hegelson, H.C., 1983b. Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system H_2O-CO_2 -NaCl on phase relations in geologic systems: metamorphic equilibria at high pressure and temperatures. Am. Mineral. 68, 1059-1075.

Brown, G.C., Rymer, H., Stevenson, D., 1991. Volcano monitoring by microgravity and energy budget analysis. J. Geol. Soc. London 148, 585-593.

Buick, I.S., Cartwright, I., 2002. Fractured-controlled fluid flow and metasomatism in the contact aureole of the Marulan Batholith (New South Wales, Australia). Contrib. Mineral. Petrol. 143 (6), 733-749.

Burnham, J. K., 1985. Energy release in subvolcanic environments : Implication for breccia formations. Econ. Geol. 80, 1515-1522.

Cathles, L.M., 1977. An analysis of the cooling of intrusives by ground-water convection which includes boiling. Economic Geol. 72, 804-826.

Carroll, M.R., Webster, J.D., 1994. Solubilities of sulfur, noble gases, nitrogen, chlorine and fluorine in magmas. In: Carroll, M.R., Halloway, J.R. (Eds.), Volatiles in Magmas, Rev. Mineral. 30, 231-279.

Casertano, L., Olivieri del Castillo, A., Quagliariello, M.T., 1976. Hydrodynamics and geodynamics in the Phlegrean Fields area of Italy. Nature 264, 154-161.

Castagnolo, D., Gaeta, F.S., De Natale, G., Peluso, F., Mastrolorenzo, G., Troise, C., Pingue, F., Mita D.G., 2001. Campi Flegrei unrest episodes and possibile evolution towards critical phenomena. J. Volcanol. Geotherm. Res. 109, 13-30.

Chiodini, G., Marini, L., 1998. Hydrothermal gas equilibria: the H₂O-H₂-CO₂-CO-CH₄ system. Geochim. Cosmochim. Acta 62, 2673-2687.

Chiodini, G., Frondini, F., Cardellini, C., Granieri, D., Marini, L., Ventura, G., 2001. CO₂ degassing and energy release at Solfatara Volcano, Campi Flegrei, Italy. J. Geophys. Res. 106, 16213-16221.

Chiodini, G., Todesco, M., Caliro, S., Del Gaudio, C., Macedonio, G., Russo, M., 2003. Magma degassing as a trigger of bradyseismic events: The case of Phlegrean Fields (Italy). Geophys. Res. Lett. 30 (8), 1434-1437.

Chouet, B.A., 1996. New methods and future trends in seismological volcano monitoring. In: Scarpa, R., Tilling, R.I. (Eds.), Monitoring and mitigation of volcano hazard. Springer Verlag, Berlin-Heidelberg.

Cole, J.W., Milner, D.M., Spinks, K.D., 2005. Caldera and caldera structures: a review. Earth-Science Review 69, 1-26.

Corey, A.T., Rathjens, C.H., Henderson, J.H., Wyllie, M.R., 1956. Three-phase relative permeability. Trans. AIME 207, 349-351.

Crampin, S., Booth, D.C., 1989. Shear-wave splitting showing hydraulic dilatation of pre-existing joints in granite. Sci. Drilling 1, 21-26.

Crampin, S., Chastin, S., 2003. A review of shear wave splitting the crack-critical crust. Geophys. J. Int. 155, 221-240.

Darnet, M., Maineult, A., Marquis, G., 2004. On the origin of self-potential (SP) anomalies induced by water injections into geothermal reservoirs. Geophys. Res. Lett. 31, L19609, doi:10.1029/2004GL020922.

De Angelis, S., McNutt, S.R., 2005. Degassing and hydrothermal activity at Mt Spurr, Alaska, during the summer 2004 inferred from complex frequencies of long-period events. Geophys. Res. Lett. 32, L12312, doi:10.1029/2005GL022618.

Delaney, P. T., 1982. Rapid intrusion of. magma into wet rock: groundwater ... and stress evolution in cooling pluton. environments. Am. J. Sci. 281, 35-68.

Delmelle, P., Stix, J., 2000. Volcanic gases. In: Sigurdsson, H., Houghton, B., McNutt, S. R., Rymer, H., Stix, J. (Eds), Encyclopedia of volcanoes. Academic Press, San Diego.

de Marisly, G. (1986) Quantitative hydrogeology. Groundwater hydrology for Engineers. Academic Press Inc., San Diego, California, 440 pp.

De Natale, G., Pingue, F., Allard, P., Zollo, A., 1991. Geophysical and Geochemical Modeling of the 1982– 1984 Unrest Phenomena at Campi Flegrei Caldera (Southern Italy). J. Volcanol. Geotherm. Res. 48, 199– 222.

De Natale, G., Troise, C., Pingue, F., 2001. A mechanical fluid-dynamical model for ground movements at Campi Flegrei caldera. J. Geodyn. 32, 487-571.

Dullien, F.A.L., 1992. Porous Media. Fluid transport and pore structure. Academic Press, San Diego, CA, 574 pp.

Elder, J.W., 1967a. Steady free convection in a porous medium heated from below. J. Fluid Mechan. 27, 29-48.

Elder, J.W., 1967b. Transient convection in a porous medium. J. Fluid Mechan. 27, 609-623.

Elder, J.W., 1981. Geothermal systems. Academic Press, New York.

Evans, D.D., Rasmussen, T.C., Nicholson, T.J., 2001. Flow and transport through unsaturated fractured rock: an overview. In: Evans, D.D., Rasmussen, T.C., Nicholson, T.J. (Eds.), Flow and transport through unsaturated fractured rock. Geophys. Monograph 42, AGU, Washington, DC.

Ferry, J.M., Wing, B.A., Penniston-Dorland, S.C., Rumble, III D., 2002. The direction of fluid flow during contact metamorphism of siliceous carbonate rocks: new data for the Monzoni and Predazzo aureoles, northern Italy, and a global review. Contrib. Mineral. Petrol. 142, 679-699.

Foulger, G.R, Julian, B.R., Hill, D.P., Pitt, A.M., Malin, P., Shalev, E., 2004. Non-double-couple microearthquakes at Long Valley Caldera provide evidence for hydraulic fracturing. J. Volcanol. Geotherm. Res. 132, 45-71.

Fournier, R.O., 1987. Conceptual model of brine evolution in magmatic hydrothermal systems. In: Decker R.W., Wright, T.L. and Stauffer, P.H. (Eds), Volcanism in Hawaii, USGS.

Gaeta, F.S., De Natale, G., Peluso, F., Mastrolorenzo, G., Castagnolo, D., Troise, C., Pingue, F., Mita, D.G., Rossano, S., 1998. Genesis and evolution of unrest episodes at Campi Flegrei caldera: the role of thermal-fluid-dynamical processes in the geothermal system. J. Geophys. Res. 103 (B9), 20921-20933.

Gaeta, F.S., Peluso, F., Arienzo, I., Castagnolo, D., De Natale, G., Milano, G., Albanese, C., Mita, D., 2003. A physical appraisal of a new aspect of bradyseism: the miniuplifts. J. Geophys. Res. 108 (B8), 2363, doi: 10.1029/2002JB001913.

Giggenbach, W.F., 1996. Chemical composition of volcanic gases. In: Scarpa, R., Tilling, R.I. (Eds.), Monitoring and Mitigation of Volcanic Hazards, Springer Verlag, Berlin-Heidelberg.

Goff, F., Janik, C.J., 2000. Geothermal systems. In: Sigurdsson, H., Houghton, B., McNutt, S. R., Rymer, H., Stix, J. (Eds.), Encyclopedia of volcanoes. Academic Press, San Diego.

Gottsmann, J., Rymer, H., 2002. Deflation during caldera unrest; constraints on subsurface processes and eruption prediction from gravity-height data. Bull. Volcanol. 64, 338-348.

Gottsmann, J., Berrino, G., Rymer, H., Williams-Jones, G., 2003. Hazard assessment during caldera unrest at the Campi Flegrei, Italy: a contribution from gravity-height gradients. Earth Plan. Sci. Lett. 211, 295-309.

Gottsmann, J., Rymer, H., Berrino, G., 2006. Caldera unrest at the Campi Flegrei: a critical evaluation of source parameters from geodetic data inversion. J. Volcanol.Geotherm.Res. 150, 132-145.

Gottsmann, J., Battaglia, M., 2007. Deciphering causes of unrest at explosive collapse calderas: Recent advances and future challenges of joint time-lapse gravimetric and ground deformation studies. – this issue.

Gudmundsson, A., FJeldskaar, I., Brenner, S. L., 2002. Propagation pathways and fluid transport of hydrofractures in jointed and layered rocks in geothermal fields. J. Volcanol. Geotherm. Res. 116, 257-278.

Gudmundsson, O., Finlayson, D., Itikarai, I., Nishimura, Y., Johnson, W., 2004. Seismic attenuation at Rabaul volcano, Papua New Guinea. J. Volcanol. Geotherm. Res. 130, 77-92.

Hayba, D.O., Ingebritsen, S.E., 1997. Multiphase groundwater flow near cooling plutons. J. Geophys. Res. 102, 12,235-12,252.

Helmig, R., 1997. Multiphase flow and transport processes in the subsurface. A contribution to the modeling of hydrosystems. Springer-Verlag, Berlin.

Hellweg, M., 2000. Physical models for the source of Lascar's harmonic tremor, J. Volc. Geoth. Res. 101, 183-198.

Hernández, P.A., Notsu, K., Salazar, J.M., Mori, T., Natale, G., Okada, H., Virgili, G., Shimoike, Y., Sato, M., Pérez, N.M., 2001. Carbon dioxide degassing by advective flow from Usu Volcano, Japan. Science 292, 83-86.

Hill, D. P., Prejean, S., 2005. Magmatic unrest beneath Mammoth Mountain, California. J Volc Geotherm Res 146, 257-283.

Hon, K., Pallister, J., 1995. Wrestling with restless calderas and fighting floods of lava. Nature 376, 554-555.

Howle, J.F., Langbein, J.O., Farrar, C.D., Wilkinson, S.K., 2003. Deformation near the Casa Diablo geothermal well field and related processes Long Valley caldera, Eastern California, 1993-2000. J. Volcanol. Geotherm. Res. 127, 365-390.

Hunt, T.M., Kissling, W. M., 1994. Determination of reservoir properties at Wairakei geothermal field using gravity changes measurements. J. Volcanol. Geotherm. Res. 63 129-143.

Hurwitz, S., Ingebritsen, S.E., Sorey, M.L., 2002. Episodic thermal perturbations associated with groundwater flow: An example from Kilauea Volcano, Hawaii. J. Geophys. Res. 107, (B11), 2297, doi: 10.1029/2001JB001654.

Hurwitz, S., Kipp, K.L., Ingebritsen, S.E., Reid, M.E., 2003. Groundwater flow, heat transport, and watertable position within volcanic edifices: Implications for volcanic processes in the Cascade Range. J. Geophys. Res. 108 (B12), 2557, doi:10.1029/2003JB002565.

Ingebritsen, S.E., Rojstaczer, S.A., 1993. Controls on geyser periodicity. Science, 262, 889-892.

Ingebritsen, S.E., Rojstaczer, S.A., 1996. Geyser periodicity and the response of geysers to deformation. J. Geophys. Res. 101, 21,891-21,905.

Ingebritsen, S.E., Sorey, M.L., 1985. A quantitative analysis of the Lassen hydrothermal system, north-central California. Water Res. Res. 21, 853-868.

Ingebritsen, S.E., Sorey, M.L., 1988. Vapor-dominated zones within hydrothermal systems: Evolution and natural state. J. Geophys. Res. 93, 13, 635-13, 655.

Ingebritsen, S.E., Sanford, W.E., 1998. Groundwater in geologic processes. Cambridge University Press, New York.

Itasca Consulting Group Inc., 1997. FLAC3D Manual: Fast Lagrangian Analysis of Continua in 3 dimensions —Version 2.0. Itasca Consulting Group Inc., Minnesota, USA.

Jamtveit, B., Grorud, H.F., Ragnarsdottir, K.V., 1997. Flow and transport during contact metamorphism and hydrothermal activity: An example from the Oslo rift. In: Jamtveit, B., Yardley, B.W.D. (Eds.), Fluid flow and transport in rocks: Mechanisms and effects. Chapman and Hall, London.

Kaneshima S., Kawakatsu, H., Matsubayashi, M., Sudo, S., Tsutsui, T., Ohminato, T., Ito, H., Uhira, K., Yamasato, H., Oikawa, J., Takeo, M., Iidaka, T., 1996. Mechanism of phreatic eruptions at Aso volcano inferred from near-field broadband seismic observations. Science 273, 642-645.

Kawakatsu, H., Kaneshima, S., Matsubayashi, H., Ohminato, T., Sudo, Y., Tsutsui, T., Uhira, K., Yamasato, H., Ito, H., Legrand, D., 2000. Aso94: Aso seismic observation with broadband instruments. J. Volcanol. Geotherm. Res. 101, 129-154.

Kiryukhin, A., Xu, T., Pruess, K., Apps, J., Slovtsov, I., 2004. Thermal-hydrodynamic-chemical (THC) modeling based on geothermal field data. Geothermics 33(3), 349-381.

Kissling, W., 1999. Modeling of cooling plutons in the Taupo volcanic zone, New Zealand. Proc. Twenty-Fourth Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California, January 25-27.

Konstantinou, K.I., Schlindwein, V., 2002. Nature, wavefield properties and source mechanism of volcanic tremor: a review. J. Volcanol. Geotherm. Res, 119, 161-187.

Maillot, B., S. Nielsen, Main, I., 1999. Numerical simulation of seismicity due to fluid injection in a brittle poro-elastic medium. Geophys. J. Int. 139, 263-272.

McKee, C.O., Lowenstein, P.L., De Saint Ours, P., Talai, B., Itikarai, I., Mori, J.J., 1984. Seismic and ground deformation crisis at Rabaul Caldera: prelude to an eruption? Bull. Volcanol. 47, 397-411.

McKee, C.O., Johnston, R.W., Lowenstein, P.L., Riley, S.J., Blong, R.J., De Saint Ours, P., Talai, B., 1985. Rabaul Caldera, Papua New Guinea: volcanic hazards, surveillance, and eruption contingency planning. J. Volcanol. Geotherm. Res. 23, 195-237.

Miller, S.A., Collettini, C., Chiaraluce, L., Cocco, M., Barchi, M., Boris, J., Kraus, P., 2004. Aftershock driven by a high-pressure CO₂ source at depth. Nature 427, 724-727.

Miller, V., Savage, M., 2001. Changes in seismic anisotropy after volcanic eruptions: evidence from Mount Ruapehu. Science 293, 2231-2233.

Mori, J., McKee, C.O., Itikarai, I., Lowenstein, P.L., De Saint Ours, P., Talai, B., 1989. Earthquake of the Rabaul seismo-deformational crisis September 1983 to July 1985: seismicity on a caldera ring fault. In: Latter, J.H. (Ed.), Volcanic Hazards. IAVCEI Proc. Volcanol., 1.

Murray, J.B., Rymer, H., Locke, C.A., 2000. Ground deformation, gravity, and magnetics. In: Sigurdsson, H., Houghton, B., McNutt, S. R., Rymer, H., Stix, J. (Eds), Encyclopedia of volcanoes. Academic Press, San Diego.

Newhall, C.G., Dzurisin, D., 1988. Historical unrest at large calderas of the world. USGS Bulletin 1855, 1108.

Newhall, G.G., Albano, S.E., Matsumoto, N., Sandoval, T., 2001. Roles of groundwater in volcanic unrest. J.Geol. Soc. Phil. 56, 69-84.

Norton, D.L., 1984. Theory of hydrothermal systems. Ann. Rev. Earth Plan. Sci. 12, 155-177.

Norton, D.L., Knight, J., 1977. Transport phenomena in hydrothermal system: cooling plutons. Am. J. Sci. 277, 937-981.

Nortquist, G., Protacio, J.A.P., Acuña, J.A., 2004. Precision gravity monitoring of the Bulalo geothermal field, Philippines: independent checks and constraints on numerical simulation. Geothermics 33, 37-56.

Olivieri del Castillo, A., Quagliariello, M.T., 1969. Sulla genesi del bradisismo flegreo. Atti Associazione Geofisica Italiana, 18mo Congresso, Naples, pp.557-594.

Oppenheimer, C., 2003. Volcanic degassing. In: Rudnick, R. L. (Ed.), The Crust, Vol. 3. Holland, H.D., Turekian, K.K. (Eds.) Treatise on Geochemistry, Elsevier-Pergamon, Oxford.

O'Sullivan, M.J., Pruess, K., Lippmann, M.J., 2001. The state of the art of geothermal reservoir simulation. Geothermics 30, 395-429.

Orsi G., Petrazzuoli, S.M., Wohletz, K., 1999. Mechanical and thermo-fluid behaviour during unrest at the Campi Flegrei caldera (Italy). J. Volcanol. Geotherm. Res. 91, 453-470.

Pitzer, K.S., Pabalan, R.T., 1986. Thermodynamics of NaCl in steam. Geochim. Cosmochim. Acta 50, 1445-1454.

Pribnow, D.F.C., Schütze, C., Hurter, S.J., Flechsig, C., Sass, J. H., 2003. Fluid flow in the resurgent dome of Long Valley Caldera: implications from thermal data and deep electrical sounding. J. Volcanol. Geotherm. Res. 127, 329-345.

Pruess, K., 1990. Modeling of geothermal reservoirs: fundamental processes, computer simulation and field applications. Geothermics 19, 3-15.

Pruess, K., 1991. TOUGH2 – A General Purpose Numerical Simulator for Multiphase Fluid and Heat Flow. Report LBL 29400, Lawrence Berkeley National Laboratory, Berkeley, CA, USA.

Pruess, K., Oldenburg, C.M., Moridis, G., 1999. TOUGH2 User's Guide, Version 2.0. Lawrence Berkeley National Laboratory Report LBNL-43134, Berkeley, California.

Reid, M.E., 2004. Massive collapse of volcano edifices triggered by hydrothermal pressurization. Geology 32, 373-376.

Rutqvist, J., Wu, Y.-S., Tsang, C.-F., Bodvarsson, G., 2002. A modeling approach for analysis of coupled multiphase fluid flow, heat transfer, and deformation in fractured porous rock. Int. J. Rock Mechan. 39, 429-442.

Rymer H., 1994. Microgravity change as a precursor to volcanic activity. J. Volcanol. Geotherm. Res. 61, 311-328.

Shapiro, S.A., Patzig, R., Rothert, E., Rindschwentner, J., 2003. Triggering of seismicity by pore-pressure perturbations: permeability related signature of the phenomenon. Pure Appl. Geophys. 160, 1051-1066.

Smithsonian Institution-GVN, 1990- [Monthly event reports]. Bull. Global Volc. Network, 15-30

Sorey, M.L., McConnel, V.S., Roeloffs, E., 2003. Summary of recent research in Long Valley Caldera, California. J. Volcanol. Geotherm. Res. 127: 165-173.

Sudo Y., Ono, H., Hurst, A.W., Tsutsui, T., Mori, T., Nakaboh, M., Matsumoto, Y., Sako, M., Yoshikawa, S., Tanaka M., Kobayashi, Y., Hashimoto, T., Hoka, T., Yamada, T., Masuda, H., and Kikuchi, S., 1998. Seismic activity and ground deformation associated with the 1995 phreatic eruption of Kuju volcano, Kyusgu, Japan. J. Volcanol. Geotherm. Res. 81, 245-267.

Symonds, R. B., Gerlach, T.M., Reed, M.H., 2001. Magmatic gas scrubbing: implications for volcano monitoring. J. Volcanol. Geotherm. Res. 108, 303-341.

Tait, S., Jaupart, C., Vergniolle, S., 1989. Pressure, gas content and eruption periodicity of a shallow, crystallising magma chamber. Earth Plan. Sci. Lett. 92 (1), 107-123.

Todesco, M., 1995. Modeling of the geothermal activity at Vulcano (Aeolian Islands, Italy). Proc. of the World Geothermal Congress '95., 2, 1309-1314. Int. Geotherm. Ass., Firenze.

Todesco, M., 1997. Origin of fumarolic fluids at Vulcano (Italy). Insights from isotope data and numerical modeling of hydrothermal circulation. J. Volcanol. Geotherm. Res. 79, 63-85.

Todesco, M., Berrino, G., 2005. Modeling hydrothermal fluid circulation and gravity signals at the Phlegraean Fields caldera. Earth Plan. Sci. Lett. 240, 328-338.

Todesco, M., Chiodini, G., Macedonio, G., 2003a. Monitoring and modeling hydrothermal fluid emission at La Solfatara (Phlegrean Fields, Italy). J. Volcanol. Geotherm. Res. 125, 57-79.

Todesco, M., Rutqvist, J., Pruess, K., Oldenburg, C.M., 2003b. Multi-phase fluid circulation and ground deformation: a new perspective on bradyseismic activity at the Phlegrean Fields (Italy). Proc. Twenty-Eight Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA, SGP-TR-173.

Todesco, M., Rutqvist, J., Chiodini, G., Pruess, K., Oldenburg, C.M., 2004. Modeling of recent volcanic episodes at Phlegrean Fields (Italy): geochemical variations and ground deformation. Geothermics 33 (4), 531-547.Troise, C. De Natale, G., Pingue, F., Tammaro, U., De Martino, P., Obrizzo, F., Boschi, E., 2007. A new uplift episode at Campi Flegrei caldera (Southern Italy): implications for unrest interpretation and eruption hazard evaluation, this volume.

Truesdell, A.H., White, D.E., 1973. Production of superheated steam from vapor dominated geothermal reservoirs. Geothermics 2, 154-173.

Tsang, C.-F., 1999. Linking thermal, hydrological, and mechanical processes in fractured rocks. Ann. Rev. Earth Plan. Sci. 27, 359-384.

Verma, A., Pruess, K., 1988. Thermohydrological conditions and silica redistribution near high-level nuclear waste emplaced in saturated geological formations. J. Geophys. Res. 93, 1159-1173.

Villemant, B., Hammouya, G., Michel, A., Semet, M.P., Komorowski, J.C., Boudon, G., Cheminée, J.L., 2005. The memory of volcanic waters : shallow magma degassing revealed by halogen monitoring in thermal springs of La Soufrière volcano (Guadeloupe, Lesser Antilles). Earth Plan. Sci. Lett. 237, 710-728.

White, D.E., Muffler, L.J.P., Truessdell, H.A., 1971. Vapor-dominated hydrothermal systems compared with hot water systems. Econ. Geol. 66, 75-97.

Xu, T., Pruess, K., 2001. Modeling multiphase non-isothermal fluid flow and reactive geochemical transport in variably saturated fractured rocks: 1. Methodology. Am. J. Sci. 301, 16-33.

Xu, T., Sonnenthal, E., Spycher, N., Pruess, K., Brimhall, G., Apps, J., 2001. Modeling multiphase nonisothermal fluid flow and reactive geochemical transport in variably saturated fractured rocks: 2. Applications to supergene copper enrichment and hydrothermal flows. Am. J. Sci. 301, 34-59. Yamamoto, M., Kawakatsu, H., Kaneshima, S., Mori, T., Tutui, T., Sudo, Y., Morita, Y., 1999. Detection of a crak-like conduit beneath the active crater at Aso volcano, Japan. Geophys. Res. Lett. 26, 3577-3680.

Zlotnicki, J., Nishida, Y., 2003. Review on morphological insights of self-potential anomalies on volcanoes. Survey in Geophysics 24, 291-338.