

Geological Assessment of Castelnovo (Italy) Demonstration Site for CO₂ Reinjection in Deep Geothermal Reservoir. H2020 GECO Project

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ABSTRACT

The EU H2020 GECO project is primarily aimed to set-up technologies to lower emissions from geothermal power generation by capturing them for either reuse or storage, to turn captured emissions in to commercial products and demonstrate the technical and economic feasibility of the injection method. To achieve this goal a site specific characterization and modelling of geology and geochemistry of the geothermal reservoir are in progress for optimization of the injection experiments at four distinct geothermal systems throughout Europe are in progress.

The Italian GECO demonstration site is Castelnovo, which is located in the northeaster side of the Larderello geothermal area and where Graziella Green Power and Storengy are planning to exploit a deep seated high temperature resource for power production with the scope of no non condensable gases (NCGs), release in atmosphere. The geothermal fluid will be extracted from 2 production wells and then it will be reinjected in the reservoir by mean of 1 reinjection well. A Zero emissions ORC power plant will produce 5MWe.

For the geological assessment of Castelnovo site an integrated methodology was designed and is applied to obtain the most reliable and accurate assessment of the site. The geological, reservoir and chemical reactive modelling are performed using field or labs data and observations (i.e., geology, geophysics, geochemistry surveys). Moreover, we adopted a double scale approach where regional, and larger, model was built to provide constraints to local, smaller and detailed, models. At regional scale a geological model including the main structures of the area is modelled to create the geometries needed to local models. At locale scale, firstly the thermal steady state of the rock volume and secondly the reinjection simulations on reservoir and fluids-rocks interaction during the reinjection are numerically computed.

1. INTRODUCTION

The GECO project, funded in the framework of Horizon 2020 EU program, has the overall aim to generate viable, safe and cost-effective technologies for cleaning geothermal power plant exhaust gases to be applied widely at European and global scale. The GECO partners are committed to characterise 4 different demonstration sites located in Germany, Iceland, Italy and Turkey providing a pre-feasibility assessment of the baseline reservoir conditions and to demonstrate the feasibility of the re-injection (including NCGs) of geothermal fluids and the development of efficient and environmentally safe and economic viable methods to reduce the geothermal emissions.

The rationale of GECO project largely relays on a successful technology recently tested in Iceland at pilot scale, where the gas emissions (mostly steam and CO₂) from geothermal power plant were condensed and re-injected in the geothermal reservoir, or turned into commercial products.

The Italian demonstration site is named Castelnovo and is located a few kilometres northeast of the Larderello geothermal area (see Fig.1) where a deep, steam dominated reservoir with about 8% of expected NCGs mainly CO₂ (98%) and H₂S (1,8%) is hosted mainly in the metamorphic units and is characterised by temperature ranging between 300° and 350°C and pressure up to 70 bar at depths of 3,5 and 4,5 km (Barelli et al. 2000, Batini et al., 2002, Bertini et al., 2006, Romagnoli et al., 2010).

In the Castelnovo site, Graziella Green Power (GGP) and Storengy (Storengy) are planning to exploit a deep seated (> 3 km) high temperature (>250 °C) resource for power generation, without releasing into atmosphere any of the expected NCGs. This demonstration project is a test case for other projects where NCGs content of geothermal fluids is high and emission is a critical issue. Castelnovo Pilot Project foresees the drilling of 3 wells (i.e., 2 production and 1 reinjection) and the realization a 5 MWe Zero Emission power plant. The power plant design includes an ORC (Organic Rankine Cycle) and closed loop system for avoiding the emissions of NCGs from geothermal fluids, so that the whole amount of the same fluid will be available for reinjection.

This paper describes the methodological approach on going for the Italian GECO demonstration site to define the baseline reservoir conditions able to support the re-injection of geothermal fluids. In the following sections the methodology, the geological, geophysical and geochemical data collection and acquisition and the modelling activities beside some preliminary results are described.

2. METHODOLOGY

The assessment was conducted in a team work gathering colleagues from different project partners. To this aim, data and knowledge acquisition, modelling and validation tasks are carried out in an iterative loop. Once new data or knowledge become available, it is input in a new loop until the updated models are double checked by the involved partners. To facilitate this process monthly in person meetings were organised to allow the best communication and data integration among the scientists, moreover foreign colleagues were invited to join virtually the meetings. In these occasions the scientists could compare, discuss and adapt their own interpretations for a mutual result. With this strategy a more robust and reliable interpretation is guaranteed to have better comprehension of the underground of the study area.

For the assessment of the Castelnuovo site a geological, geophysical and geochemical integrated approach is proposed. To this aim, different scales and typologies of modelling are ongoing. The area of modelling is about 25 km x 37 km, which includes the main geological regional structures. A first level of modelling is producing a geological regional model, where existing data and information from structural geology, geophysical and geochemical field works are embedded. The geometries from geological regional model is acting as input and boundary conditions for the reservoir modelling (spacing of about 12 km x 16 km). The reservoir modelling is the second level of modelling, i.e. local model, and is carried out to assess the thermal steady state of the underground and the exploitation scenario accounting for injection and production (see Fig.1). Moreover, at reservoir scale, geochemical modelling of the gas-water-rock interaction during the exploitation is ongoing to predict the fate of reinjected fluids at depth. Laboratory experiments will also provide some constrains on the fluid-rock geochemical reactions expected in the reservoir as consequence of re-injection. In addition, based on the poro-elasticity model, the setting of fully coupled thermo-hydro-mechanical models is furthermore ongoing to evaluate the stress-strain relationship under injection conditions.

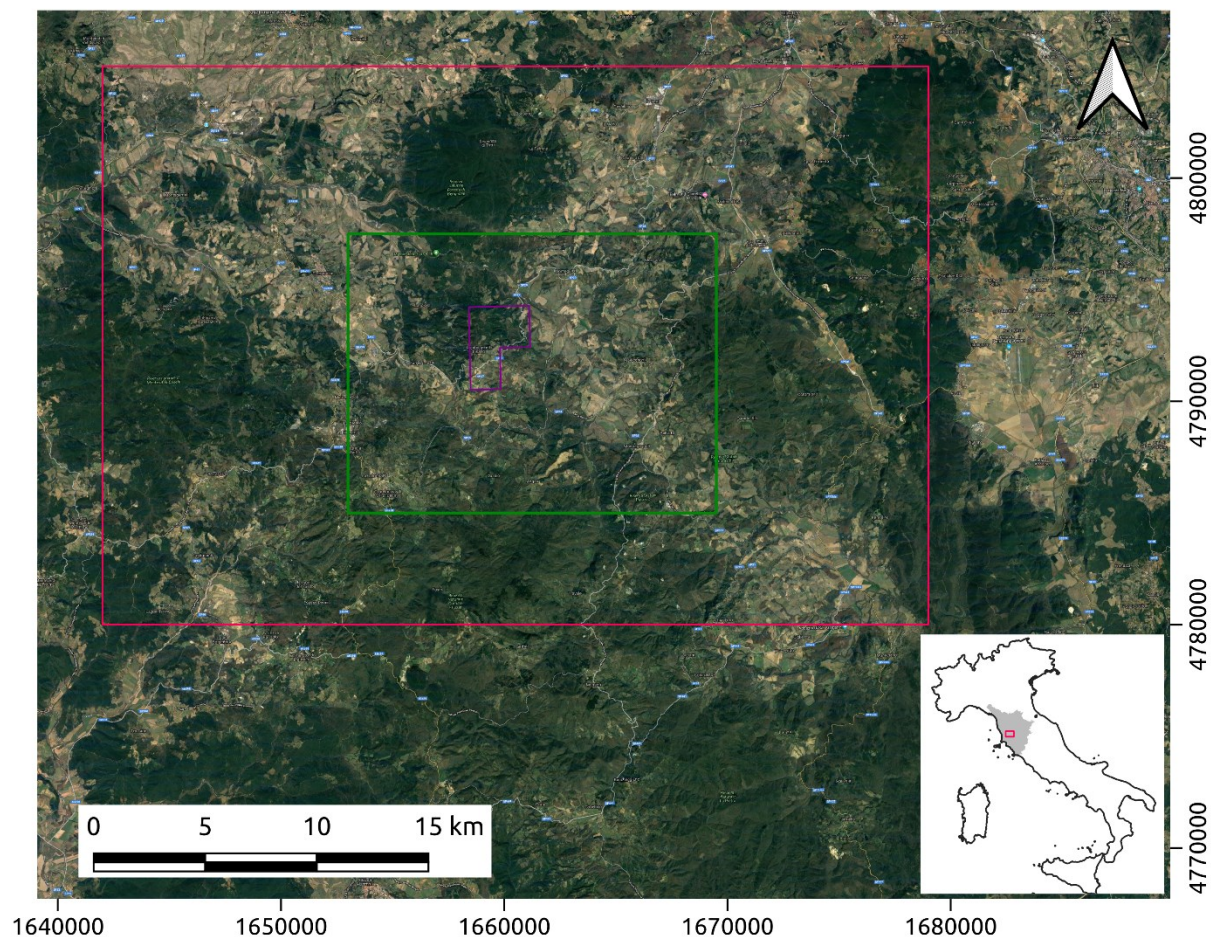


Figure 1: Location of the Castelnuovo GECO Italian site. Red and green boundary shows the regional and local model limits respectively. The magenta border is the Castelnuovo research permit, nowadays under review by the Italian Ministry in charge.

3. GEOLOGICAL SETTING

3.1 Existing data and new acquisition

The study region is located in the hinterland side of the Northern Apennines fold-and-thrust belt. Its geological and structural setting is characterized by polyphase tectonics. During Oligocene-Early Miocene, the Adria microplate of African pertinence, collided with the European Corsica-Sardinia Massif (Boccaletti et al., 1971), determining HP/LT metamorphism and eastwards stacking of tectonic units, deriving from the oceanic and continental paleogeographic domains of the Northern Apennines (Molli, 2008). From the top, the units are (Carmignani et al., 1994): (a) the Ligurian Units, derived from the Ligurian-Piedmont Domain, and consisting of remnants of Jurassic oceanic crust and its late Jurassic-Cretaceous, mainly clayey, sedimentary cover; (b) the Sub-Ligurian Units (Sub-Ligurian Domain), made up of Cretaceous-Oligocene turbidites; (c) the Tuscan Nappe (from the Tuscan Domain), made up of, from the bottom upwards: the Late Triassic evaporite, Early Jurassic-Early Cretaceous carbonatic succession, Early Cretaceous-Oligocene argillaceous sequence and, finally of a Late Oligocene-Early Miocene arenaceous flysch. The basement of the Tuscan Domain is consisting of metamorphic rocks, Late Carboniferous-Tertiary quartzite and phyllites (Verrucano Group) and older Palaeozoic phyllites. During collision, duplex structures involved the Tuscan Nappe, the Verrucano Group and, partially, the Palaeozoic phyllites. Subsequent continental extension affected such an over-thickened orogen, producing crustal thinning and tectonic delamination, as it is the case of the direct juxtaposition of the Ligurian Units, the uppermost tectonic units of the tectonic pile (Ligurian Units), onto deeper rock units, typically the Triassic Burano Fm. and/or the underlying metamorphic rocks. Such an extensional phase process began during Early-Middle Miocene (Carmignani et al., 1994). In another model, a moderate phase of continental shortening interrupted extension during Late Miocene (Bonini et al., 2014). The most recent evolution of the study region (approximately Late Pliocene-Quaternary) is mostly related to high-angle normal faults and transfer faults, which could have also controlled the emplacement of subsurface plutons in the inner zone of the Northern Apennines, including the buried Larderello pluton (e.g., Brogi et al., 2005; Dini et al., 2008; Sani et al., 2016).

3.2 Preliminary results

The new geological and structural analysis carried out in the study region has revealed the occurrence of NE-ENE-striking shear zones mainly made up of strike- to oblique slip fault-segments, controlling the deformation pattern. These shear zones display variable width and length, interacting with the NW-SE striking normal faults and antiforms, the latter representing potential traps for geothermal fluids. The flow of geothermal fluids would exploit the secondary permeability of antiforms, normal faults and NE-striking shear zones, so that the 3D fluid flow pattern would thus result from interactions among these structural elements.

4. GEOPHYSICAL INSIGHTS

4.1 Existing data and new acquisition

The Larderello field, in development for power production since 1913, has been explored for decades by several geophysical techniques. Of the enormous amount of acquired data only a small part is publicly available, coming from scientific projects or published in scientific article.

General insights on the subsurface characteristics of the Larderello field come from the interpretation of 2D-3D reflection seismic surveys available in literature (e.g. Casini et al., 2010; Cameli et al., 2000). The main features are constituted by two seismic markers named “H” and “K” horizons. The H-horizon is a discontinuous high-amplitude reflector and represents the current mining target, corresponding to highly productive intervals (Bertini et al., 2006). The K-horizon is series of a high-amplitude and locally bright-spot-type reflectors, whose origin is highly debated in literature (see De Franco et al., 2019 and references therein): mineralogical or rheological transitions, natural hydrofracturing, thermometamorphic aureola at the top of a Quaternary granitic intrusion and presence of fluids at supercritical conditions. The occurrence of shallow still molten igneous intrusions, acting as heat source of the system, is supported by several geophysical data and thermal numerical models (see Santilano et al., 2015 for a review).

The electrical resistivity is a key parameter in the exploration of geothermal systems. With regard to the Larderello field, the interpretation of the resistivity distribution is not trivial due to the vapour state of the geothermal fluids and the lithology of the reservoir, which should result as highly resistive whereas in practice large low resistivity anomalies were detected by magnetotelluric (MT) studies at the depth of reservoir and at deeper levels (e.g. Manzella 2004). In the latter case molten intrusion can be inferred, and the low resistivity anomalies in the reservoir have been referred to different processes, i.e. mineralogical alteration of the rocks and the occurrence of residual fluids in a liquid phase not involved in the hydrothermal circulation but stored in micro-pores (Manzella et al., 2010).

The Castelnuovo pilot site is located close to the northern limit of the currently developed field; this area was not covered by any detailed geophysical survey. The preliminary geophysical dataset used in the frame of this study is composed of wide magnetotelluric and gravimetric surveys acquired by the operator GGP in the adjacent research permit named “Mensano” and the magnetotelluric dataset of CNR obtained by various research projects. The complete magnetotelluric dataset for the Larderello geothermal area counts over 200 MT soundings covering the areas of Travale-Radicondoli, Lago Boracifero and Mensano.

In order to include the area of interest (Castelnuovo permit) in the magnetotelluric modelling, a further MT survey is planned in the frame of the GECO Project by the geophysical group of CNR. At the moment, the early stages of the MT survey have been completed, and included the logistic scouting and selection of the remote reference site. The latter is strategic, since it is well known that the area is affected by an electromagnetic noise due to electrified railways that produce a near-field effect and affects the low frequency band of MT soundings (Larsen et al., 1996). For this project we selected a site close to the Travale field, that ensures an efficient remote-reference processing and an easy logistic with respect to the remote Mediterranean islands used in previous MT surveys by CNR. A first MT sounding was measured in the permit showing a very good signal to noise ratio in the area.

4.2 Preliminary results

A preliminary integrated interpretation of the available geophysical dataset was provided in the frame of the GECO Project in order to support the numerical modelling activity (see next sections). With this purpose we analysed the results coming from previous MT survey provided by the industrial operator GGP and carried out in the Mensano permit adjacent to the Castelnuovo pilot site. The dataset counts 125 MT soundings with a variable quality data, mainly reliable in the frequency range of 1000-0.01 Hz. A 3D inversion model was computed by Western Geco using the code from Mackie et Madden, 1993. The dimension of the full mesh is 250 km x 253 km x 65 km whereas the core of the model is about 22 km x 19 km. The resulting model showed a RMS of 1.94. The 3D resistivity model was imported in Petrel environment for an integrated interpretation with wells stratigraphy and other geological and geophysical data.

Generally speaking, the resistivity of the impermeable cover of the geothermal system (in our case post orogen Neogene deposits, Ligurian units and Sub-Ligurian Units, argillaceous sequences and arenaceous flysch of the Toscana nappe) is expected very low due to lithology. The Tuscan Nappe shows locally very low resistivity although limestone and evaporites hosting steam circulation are expected to be high resistive. This response is common in the Larderello field. An important contribution of the MT data is the reconstruction of the top of metamorphic units, which is clearly defined due to the high resistivity contrast between the metamorphic basement and the overlying rocks. The wells available in the area confirm this interpretation. From a tectonic point of view, the data define two main strike directions. The principal strike direction is NW-SE, in agreement with the main “apenninic” tectonic structures. In proximity of the pilot site, a very low resistivity anomaly (about 10 ohm*m) occurs with a strike direction NE-SW and comprise part of the crystalline basement. The Bouguer anomaly, resulting from the gravimetric survey, also depicts this structure. The geometry of this anomaly, which could represent a preferential fluid pathway, will be tested and refined with the acquisition of new data in the pilot site area.

5. NATURAL CO₂ EMISSIONS

5.1 New acquisition

During April 2019, in the area of Montecastelli, a first survey on diffuse CO₂ flux have been carried out, and about 600 measurements were performed by means of the accumulation chamber method. In figure 2 the location of measurements sites has been reported.

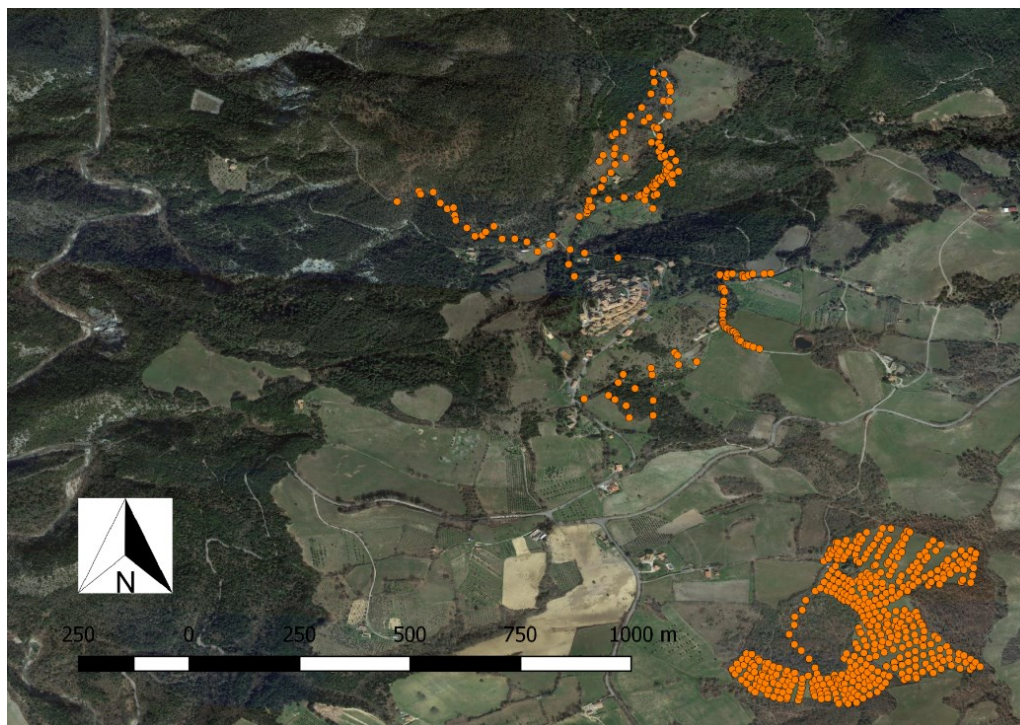


Figure 2: Location of CO₂ measurements sites

The main goals were to study the spatial distribution of CO₂ diffused from the soil, identify potential soil gas anomalies and quantify the total CO₂ emissions through soil in an area. The results will also be used in the future as a baseline observation to quantify the effects of fluid production on diffuse degassing when the area have been taken into exploitation.

5.1 Method of data processing

Following the procedure of Chiodini et al. (1998), and already applied in several works elsewhere (e.g., Cardellini, 2003a; 2003b; Frondini et al., 2004; Nolasco et al., 2008; Raco et al., 2010), a first statistical analysis aimed at evaluating the statistical distribution of the data set was carried out. Two different software codes, ProUCL and Statistica 7, were used to investigate the frequency distribution of CO₂ fluxes. These software codes were also employed to evaluate the main statistical parameters of the measured gas and to process the data in order to build histograms, box plots and quantile-quantile plots (Q-Q plots).

CO₂ flux data were partitioned following the approach of Sinclair (1974, 1991). Main statistical parameters were computed for each individual population, including the Arithmetic Mean of Raw Data (AMRD) and the 95% confidence interval of the mean, which

was obtained using the Sichel's t-estimator (Sichel, 1966, Davis, 1977). For each individual population and for the whole dataset, the total diffuse CO₂ output from soil was then estimated by multiplying the AMRD times the pertinent surface area.

Results of partitioning were also used to evaluate the local background threshold of soil CO₂ fluxes. This evaluation was performed by means of the ProUCL software code, following the indication of US-EPA, that is assuming the 95% Upper Tolerance Limit (UTL) of the second higher statistical population as robust indicator of the local background threshold of soil CO₂ fluxes. This value is the maximum soil CO₂ flux expected for bacterial activity in the rhizosphere and soil respiration. Measures exceeding this threshold, that cannot be explained by biogenic soil emissions, were considered as the product of other, presumably deep, resources including geothermal degassing.

Both Box-Whisker plots and an analytical process based on the Central Limit Theorem (Sigh, 1993; Sigh et al., 1997) were used to individuate potential outliers. Potential outliers and values lower than the instrumental detection limit (DL, equal to 0.002 mol m⁻² d⁻¹) were eliminated from the original data set in the data elaboration finalized to the evaluation of total diffuse CO₂ output from soil. In contrast, potential outliers and values below DL were assumed equal to DL/2 and included in the geostatistical data elaboration.

Concerning the geostatistical data processing, data were processed using the ISATIS software package that allows the realization of both the experimental variogram and the variogram model. A "cross-validation" test was performed to evaluate the goodness of the selected variogram model (Devijver et al., 1982). The variogram model was used to build iso-flux maps by means of kriging interpolator (Krige, 1951; Matheron, 1962, 1965, 1969, 1970; Matheron and Monget, 1969; David, 1977; Clark, 1979; Chauvet, 1982; Chauvet and Galli, 1982, Armstrong, 1984a, 1984b; Davis, 1986; Chauvet, 1991, 1993; Wackernagel, 1995).

5.2 Preliminary results

Preliminary results of this work indicate the CO₂ background level of the investigated area ranging about 1.7 mol m⁻² d⁻¹, while the total output is about 77000 Kg/day (81000 ÷ 75000) corresponding to a specific flux of 300 g/day. Anomalous CO₂ flux have been found in the North-East zone. The two sources contributing to the diffuse CO₂ flux from soil are:

- (1) the shallow soil source, producing biogenic CO₂, and
- (2) the deep sources, probably due to degassing geothermal reservoirs, from where CO₂ upraises towards the surface along fractures and faults.

6. LAB EXPERIMENTS

To build-up reliable geochemical models used to forecast the fate of reinjected fluids, which would be pumped underground in deep geological reservoirs, several kinds of data are needed (i.e. chemical and mineralogical composition, porosity, specific surface reactions of the host rocks). Also, the output of geochemical models can be compared with those data derived from batch reactor experimental runs that are useful for identifying key mechanisms, such as the stability of certain minerals and the formation of new mineral phases under specific condition, which play a pivotal role in the fluid-rock interaction processes. These runs are presently representing the easiest way to gather experimental data to be compared to scenarios provided by geochemical models.

Thus, a set of batch reactor experiments has been conducted to evaluate the stability of mineral phases present in the inferred host rocks, i.e. the "Filladi di Boccheggiano, FB", metamorphic phyllites of Paleozoic age mainly made up of quartz, Fe-chlorite, muscovite and trace of paragonite and pyrite (Franceschelli, 1980; Gianelli & Rossini, 1991) under a range of P-T conditions expected while reinjecting fluids in the geothermal reservoir of Castelnuovo (Fig. 3). X-ray powder diffractions and electron microprobe analyses performed for this work on FB samples confirmed the former paragenesis reported in the literature plus the presence of small amounts of Na-plagioclase and K-feldspar. Moreover, these analyses highlighted that muscovite is actually phengite, a variety of dioctahedral K-mica that, with respect to muscovite, contains also small amounts of Fe-Mg and is more prone to be chemically altered. Powders (size 63<Ø<125 µm) of FB samples undergo to a 5-day long experiments in a PARR 5500 HP stirred reactor (25 ml of total volume) with a pure CO₂ or CO₂-H₂S mixture (98% and 2% by vol., respectively) gas phase and a salts-free Milli-Q® water, while the adopted P and T values ranges from 45 to 90 bar of total pressure (H₂O+CO₂+H₂S) and from 90 to 200 °C. Solid to liquid mass ratio is set to be 1:5. Liquids resulting from the experiments are cooled down to 40 °C, filtered at 0.45 µm mesh size and analysed for major cation and anion species contents via acidimetric titration and ionic liquid chromatography.

Preliminary results of the experiments indicate that FB are relatively poorly reactive under the P-T conditions investigated. Indeed, the major constituents of the ions in the liquid examined, i.e. carbon and sulphur species (HCO₃⁻ up to 600 mg/L, SO₄²⁻ up to 140 mg/L), derives from the dissolution of the gas phase into the liquid and from the oxidation of H₂S or sulphur-bearing minerals such as pyrite. Concerning the cations, the most abundant species are the K⁺ and Na⁺ (up to 71 and 53 mg/L, respectively) that likely indicates phengite and Na-plagioclase to be the most reactive among the FB minerals and responsible for the presence of these ions in solution. Instead, Ca²⁺ and Mg²⁺ were found to be as low as <25 mg/L, the magnesium presence being possibly related to both chlorite and phengite alteration. It is worthy noticing that, as expected, the highest Na⁺-K⁺ contents correspond to the highest temperature experiments (150 and 200 °C), when increased rates of chemical alteration and leaching of the solid is expected. No data concerning Fe contents in the analysed liquids are presently available.

Laboratory experiments and analyses are still in progress and will include a recognition and a quantitative assessment of the mineral phases abundance in the solid material recovered after the fluid-rock reactions occurred in the batch reactor. Analyses to determine the contents of Fe, Al and trace elements that dissolved into the liquid phase during the experiments are scheduled for the future. Furthermore, experimental runs with small rock cylinders (instead of powders), will be performed to better simulate precipitation and dissolution processes on the rock surfaces. The final scope is providing an exhaustive dataset to be employed for comparison and tuning of the geochemical models.

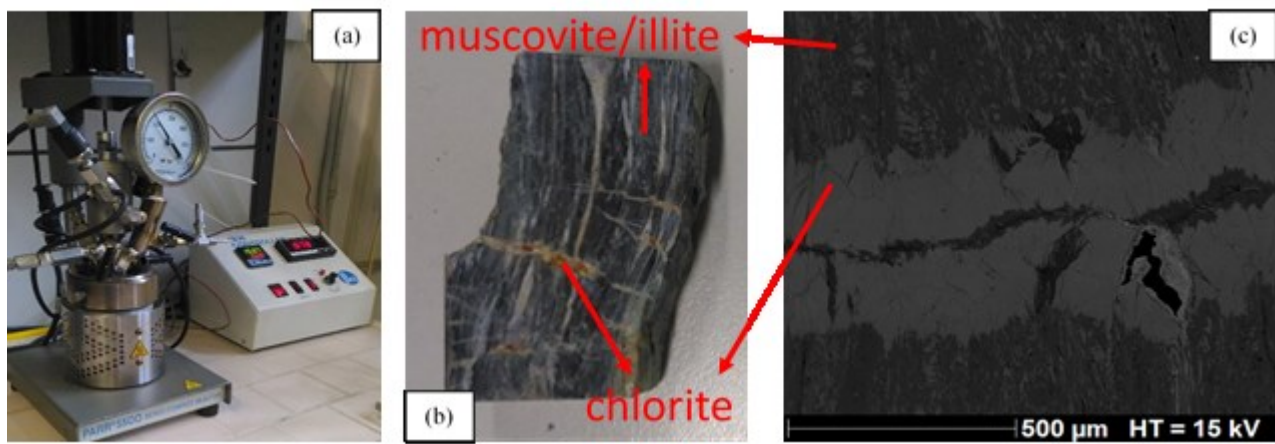


Figure 3: (a) batch reactor PARR 5500 HP during an experimental run, (b) sample of FB rock, (c) back scattered electron image of FB sample: phengite cut by a chlorite + quartz vein.

7. MODELLING APPROACH

7.1 Regional models

7.1.1 Geological model construction

The geological model is built in the 3D GeoModeller package⁽¹⁾. To construct the geometry of the 3D geomodels an interpolation of data is performed by using a co-kriging geostatistical method. The 3D points that define the geological interface and the 3D vectors showing the dip of the same interface are used at the same time (Lajaunie et al., 1997). The geological interfaces are represented as isovalues of a 3D scalar potential obtained with the interpolation of the points above mentioned. The chronological and topological relations among the geological formations are represented by a geological pile, which allows the gradual or erosion management of the geological boundaries. To automatically compute how the faults affect the formations, links between faults and formations are set-up. Moreover, the faults are combined each other on the basis of their relation to describe the existing faults network (Calcagno et al. 2008).

The main reference of the geomodels is the draft version of the geological map of the Castelnuovo site and its surroundings that is under development in this period by the geologists and the many deep boreholes drilled in the past by ENEL for geothermal exploration and utilization that are stored in the Italian National Geothermal Database (Trumpy and Manzella 2017). The draft geological map is built considering the field works already performed, the most updated version of the Tuscan region geological map at 1: 10.000 scale as well as the known information from literature. The map includes the principal structures existing in the regional area of modelling. Beside the geomap we are using the information of about 70 deep boreholes extracted from the Italian National Geothermal Database where per each borehole the coordinates, the elevation, the depth and the litho-stratigraphic data were inserted in the 3D geomodel and used to constrain geological information. A Digital Elevation Model (DEM) is also added to the model. Geological cross-sections, shallow boreholes and existing geological deep surfaces from literature are also considered to control the geomodel.

The geomodel at regional scale (37 km x 25 km x 10.2 km, i.e. down to 9 km below sea level) presents eight geological bodies reported in Table 1.

The draft geological map was firstly georeferenced in Geomodeller in order to trace the network of the faults to be used in the geomodel. The faults are then edited on the base of their relations, characterised in terms of lying and influence distances and geological bodies affecting. Some complementary cross sections are drawn to ensure a coherent interpretation, for instance in terms of geological formations thickness. Fig. 4 represents the preliminary geomodel at the regional scale.

The geometries of the preliminary geomodel of the Castelnuovo GECO Italian site were then used as input geological constrain for reservoir models.

Table 4: Description of the modelled group of formations.

Modelled geological bodies	Litho - Stratigraphy references	Age
Impermeable cover	Neogene-Quaternary continental, marine, lacustrine deposits	Middle Miocene - Holocene
	Ligurian and Sub-Ligurian units	Middle Jurassic - Oligocene
	Tuscan Nappe: siliceous and terrigenous succession (Diaspri Fm, Maiolica Fm, Scaglia Toscana Fm, and Macigno Fm (Tuscan Nappe))	Malm – Eearly Miocene (Aquitanian)
Carbonate Unit	Tuscan Nappe: carbonate succession (Calcare a Rhaetavacula contorta Fm, Calcare massiccio, Calcare rosso ammonitico Fm, Calcare selcifero Fm, Marne a Posidonia Fm)	Rhaetian – Dogger
Evaporites	Tuscan Nappe: evaporite succession (Burano Fm)	Norian-Rahetian
Tectonic wedge mainly composed by the Verrucano Group	Tuscan Units: Tectonic wedge made up of quartitic metaconglomerate, metasandstone, metasiltstone and phyllite (Verrucano); discontinuous slices of metacarbonate and evaporite levels are also present	Carboniferous-Late Trias
Tectonic wedge mainly composed by Palaeozoic phyllite	Tuscan Units: Tectonic wedge made up of phyllite, metasandstone and metacarbonate (Quartzitic-phyllite Group); discontinuous slices of evaporite levels are also present	Ordovician-Silurian and Triassic ?
Micaschists	Tuscan Units: Micaschist, quartzite and phyllite	Pre-Carbonifereous
Gneiss	Tuscan Units: Gneiss	Pre-Carbonifereous
Magmatic intrusion	Magmatic bodies, mainly felsic	Pliocene-Quaternary

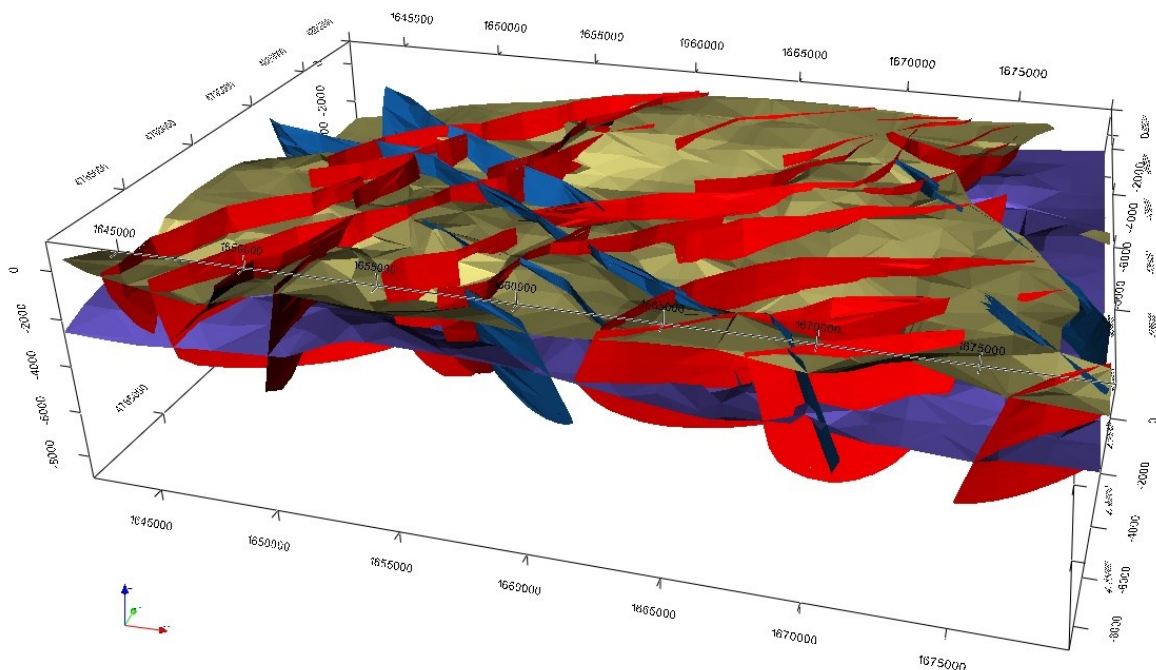


Figure 4: 3D view of the preliminary regional geolmodel. In blue the high angle normal faults (average trend NW-SE), in red the transfer faults (average trend NE-SW). In yellow and violet the preliminary representation of the bottom of the impermeable cover and Paleozoic phyllites respectively.

7.2 Local models

7.2.1 Reservoir model

The geothermal industry has a thriving research sector, which has developed several software codes for modelling purposes. Some of these codes have become widely used within the industry and are commercially available. Typically, these codes have a long history, though their designs rooted in the 1980s. Very few of these codes focus on the flexibility and robustness required by the geothermal industry, nor they attempt to integrate models from different disciplines. Limitations in the existing numerical, geophysical and chemical modelling tools have challenged the geothermal industry and research community for the last decades. Efforts are spent attempting to overcome these limitations in order to address current day issues.

TOUGH2 (Pruess, 2003) has been a success story for the geothermal modelling community and has been widely adopted for geothermal reservoir modelling and many other applications. This success is due to a combination of factors including availability at a relatively low cost with full access to source code and design decisions that allowed limited extensions to the code.

In this study, the reservoir model starts with the simulation of the steady state 3D numerical model, that is obtained using the TOUGH2 V.2.1 (Pruess et al. 2012) numerical reservoir simulator extended for handling the properties of CO₂ and water in a wide range of temperature and pressure conditions by means of ECO2H EOS (Pan et al., 2015). The model handling of the geological layers and grid refining is managed by using the Petrasim pre- and post-processing software package. These extensions were needed to overcome the limit of the previous water-CO₂ models, not fully able to handle the properties of CO₂ and water-CO₂ mixture in the range 20-300°C, 1-200 bar needed for a model that simultaneously include the production of the geothermal fluids (a mixture with 8%w/w of CO₂) from a high temperature reservoir and the injection of the cold fluid with a compressed NCG phase (CO₂).

7.2.2 Chemical reactive model

A numerical model is performed to forecast the short-and long-term geochemical impact of CO₂ total re-injection in the system. The model was carried out in different stages. On the basis of the mineralogical composition of rock-analogues, a geochemical gas-water-rock interaction model could be set up using PHREEQC (<https://www.usgs.gov/software/phreeqc-version-3> , Parkhurst & Appelo 1999), with the thermodynamic database Thermodden (<http://thermodden.brgm.fr/> , Blanc 2017, Blanc et al., 2015). Kinetically-controlled reactions can be modeled through the transition state theory (Lasaga, 1984; Steefel and Lasaga, 1994) where the temperature dependence of the reaction rate constant is expressed by the Arrhenius equation. A useful compilation of reaction constant used as a reference is Palandri & Kharaka, 2004. However, the main source of inaccuracy and a parameter that need to be calibrated is the specific reactive surface area. In this work, a first evaluation of it is done by using the pore surface area proportionally parted according to mineral abundancy, that is generally better than geometrical area.

The rock of interest, that make up the reservoir, is “Filladi di Boccheggiano, FB formation”, investigated by experimental method. The different stage of modelling deal first with a calibration done by comparing the model prediction with the laboratory experimental results (see section 6), and then the model could be directly transferred to TOUGHREACT since the Thermodden database is available in TOUGHREACT formalism too, in order to perform a predictive model of any problem that may arise during the total fluid re-injection.

7.2.3 Hydro-thermo-mechanical model

Subsurface temperature distribution will be evaluated both at natural conditions and coupled with the injection experiments. As the thermal field, the stress field and the hydrological field form a complex system, fully coupled Thermo-Hydro-Mechanical (THM) models will be solved based on the Biot's poroelasticity theory. The ongoing modelling activity focus on the setting of a 2D axial symmetric benchmark model describing the linked interaction between fluids flow and deformation in porous media surrounding the well. A point source/sink is defined in order to model the injection/production borehole. Further improvements will focus on the definition of the physical problem within a 3D framework including the modelled geometries and characterizing the rocks by geotechnical experiments on selected lithologies.

8. CONCLUSIONS

The preliminary results of the different kind of modelling are used in the project as base to demonstrate the feasibility of the geothermal fluids reinjection. Moreover, this integrated approach allows a better understanding of the reservoir baseline conditions at site level by combining complementary knowledge.

The preliminary geomodel at regional scale guarantees a wider view of the geological structures affecting the local area which is of interest of the more detailed reservoir and reactive chemical models. Moreover, it provides the geological geometries for the local models. Coherently with the adopted methodology once the data acquisition will produce final outcomes, they will be used to update the preliminary model to make the geomodel more robust.

3D numerical simulations of reactive transport of CO₂-rich fluids into a geothermal prospect in central Italy were performed at different scales to evaluate: i) the geochemical evolution at the reservoir–gas cap interface, ii) the porosity and permeability variations around production and re-injection wells, and iii) the CO₂ path from the injection well throughout the geological structure, that will differ from the reinjected liquid phase.

By coupling geochemical reactions and fluid flow processes, the dissolution of host rock close to the injection zone, and the precipitation of secondary minerals at the boundary between the acidic and neutral zone, where less acidic conditions prevail, were hypothesized, even though very low due to the low reactivity of the host rock.

The methodology used in the Castelnovo site can be easily exported to different plays and context and even for different purpose where natural reservoir behaviour has to be investigated.

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FOOTNOTE

⁽¹⁾ 3D GeoModeller is a commercial software developed by BRGM and Intrepid Geophysics. For further information, please refer to Calcagno et al. (2008) and Guillen et al. (2008), and visit: <https://www.geomodeller.com>.

REFERENCES

- Armstrong, M., Problems with universal Kriging. *Math. Geol.*, (1984a), 16(1): 101-108.
- Armstrong, M., Problems with universal Kriging. *Math. Geol.*, (1984b), 16(3): 305-316.
- Barelli, A., Bertini, G., Buonasorte, G., Cappetti, G. and Fiordelisi, A. Recent deep exploration results at the margins of the Larderello-Travale geothermal system, *Proceedings of the World Geothermal Congress 2000 –Japan*, (2000), pp 965-970.
- Batini, F., Bertani, R., Ciulli, A., Fiordelisi, A., Valenti, P. Geophysical well logging: A contribution to the fractures characterization. *Proceedings, Twenty-Seventh Workshop on Geothermal Reservoir Engineering Stanford University*, Stanford, California, January 28-30, SGP-TR-171 (2002).
- Bertini, G., Casini, M., Gianelli, G. and Pandeli, E. Geological structure of a long-living geothermal system, Larderello, Italy. *Terra Nova*, 18, (2006) 163-169. doi:10.1111/j.1365-3121.2006.00676.x.
- Blanc, P. Thermodem : Update for the 2017 version, Final Report BRGM/RP-66811-FR May, (2017).
- Blanc, P., Vieillard, P., Gailhanou, H., Gaboreau, S., Gaucher, É., Fialips, C.I., Madé, B., Giffaut, E. A generalized model for predicting the thermodynamic properties of clay minerals. *American Journal of Science*, (2015), v. 315, p. 734-780.
- Boccaletti, M., Elter, P., Guazzone, G.J.P.: Plate tectonic models for the development of the western Alps and Northern Apennines. *Nature* 234, (1971), 108–111
- Bonini, M., Sani, F., Stucchi, E.M., Moratti, G., Benvenuti, M., Menanno, G., Tanini, C. Late Miocene shortening of the Northern Apennines back-arc. *J. Geodyn.*, (2014), 74, 1–31.
- Brogi, A., Lazzarotto, A., Liotta, D., CROP 18 Working Group, 2005. Structural features of southern Tuscany and geological interpretation of the CROP 18 Seismic Reflection Survey (Italy). In: Brogi, A., Lazzarotto, A., Liotta, D. (Eds.), *Results of the CROP 18 Project. Bollettino della Società Geologica Italiana, Spec. 3.*, (2005), pp. 213-236.
- Calcagno, P., Courrioux, G., Guillen, A., and Chilès, J. P.: Geological modelling from field data and geological knowledge, Part I – Modelling method coupling 3-D potential-field interpolation and geological rules, *Phys. Earth Planet. Int.*, (2008), 171, 147–157.
- Cameli, G.M., Ceccarelli, A., Dini, I., Mazzotti, A.: Contribution of the seismic reflection method to the location of deep fractured levels in the geothermal fields of southern Tuscany (central Italy). *Proceedings of the World Geothermal Congress 2000 – Japan*, (2000), 1025-1029.
- Cardellini, C., Chiodini, G., Frondini, F., Application of stochastic simulation to CO₂ flux from soil. Mapping and quantification of gas release. *J. Geophys. Res.-Sol. Earth*, (2003a), 108: 2425
- Cardellini, C., Chiodini, G., Frondini, F., Granieri, D., Lewicki, J., Peruzzi, L., Accumulation chamber measurements of methane fluxes: application to volcanic-geothermal areas and landfills. *Applied Geochemistry*, (2003b), vol. 18:45-54
- Carmignani, L., Decandia, F.A., Disperati, L., Fantozzi, P.L., Lazzarotto, A., Liotta, D., Meccheri, M.: Tertiary extensional tectonics in Tuscany (northern Apennines, Italy). *Tectonophysics*, (1994), 238, 295-315.
- Casini, M., Ciuffi, S., Fiordelisi, A., Mazzotti, A., Stucchi, E.: Results of a 3D Seismic Survey at Travale geothermal field (Italy). *Geothermics*, (2010), 394–12.
- Chauvet, P., Aide mémoire de géostatistique linéaire, *Chaiers de Géostatistique*, (1991), Fascicule 2. Ecole des Mines de Paris, Fontainebleau, 210 pagg.
- Chauvet, P., Processing data with a spatial support: geostatistics and its method, *Chaiers de Géostatistique*, (1993), Facicule n. 4, Ecole des Mines de Paris, Fontainebleau, 57 pagg.
- Chauvet, P., The variogram cloud, Johnson TB & Barnes RJ (Ed.), 17th APCOM, Society of Mining Engineers, New York, 757 – 764, (1982).
- Chauvet, P., Galli, A. Universal Kriging, Publication n. C – 96, (1982), Centre de Géostatistique, Ecole des Mines de Paris, Fontainebleau.
- Chiodini, G., Cioni, R., Guidi, M., Marini, L., Raco, B. Soil CO₂ flux measurements in volcanic and geothermal areas. *Applied Geochemistry*, (1998), 13, 543-552.
- Clark, I., *Practical Geostatistics*, (1979), Department of Mineral Resources Engineering, Royal School of Mines, Imperial College of Science and Technology, London, 129p.
- David, M., *Geostatistical ore reserve estimation (Developments in geomathematics 2)*, (1977), Elsevier, New York, pp 363.
- Davis, J.C., *Statistics and Data Analysis in Geology*, (1986), John Wiley & Sons, Inc. Second Edition, New York, 646 pp.

- De Franco, R., Petracchini, L., Scrocca, D., Caielli, G., Montegrossi, G., Santilano, A., Manzella, A.: Synthetic Seismic Reflection Modelling in a Supercritical Geothermal System: An Image of the K-Horizon in the Larderello Field (Italy), *Geofluids*, (2019), Article ID 8492453, 21 pages – DOI: <https://doi.org/10.1155/2019/8492453>.
- Dini, A., Westerman, D.S., Innocenti, F., Rocchi, S.: Magma emplacement in a transfer zone: the Miocene mafic Orano dyke swarm of Elba Island, Tuscany, Italy. *Geological Society London Special Publications*, (2008), 302, 131–148.
- Franceschelli, M. Lineamenti geologico-petrografici delle formazioni metamorfiche paleozoiche affioranti nell'area di Boccheggiano (Toscana Meridionale). *Atti Soc. Tosc. Sci. Nat., Mem., Serie A*, (1980), 87, 65-92.
- Fronzoni, F., Chiodini, G., Caliro, S., Cardellini, C., Granieri, D., Ventura, G. Diffuse CO₂ Degassing at Vesuvio, Italy. *Bull Volcanol*, (2004), 66:642–651
- Giannelli, G., and Rossini, G. Analisi dei dati geochimici della Formazione di Boccheggiano e suo confronto con altre unità triassiche e paleozoiche toscane. *Atti Soc. Tosc. Sci. Nat., Mem., Serie A*, (1991), 98, 287-306.
- Krige D.G., A statistical approach to some basic mine valuation problems on the Witwatersrand. *J. Chem. Metall. Min. Soc. S. Afr.*, (1951), 52:119-139
- Lajaunie, C., Courrioux, G., and Manuel, L.: Foliation fields and 3-D cartography in geology; principles of a method based on potential interpolation, *Mathemat. Geol.*, (1997), 29, 571–584.
- Larsen, J. C., Mackie, R. L., Manzella, A., Fiordelisi, A., Rieven, S.: Robust smooth magnetotelluric transfer functions. *Geophys. J. Int.*, (1996), 124, 801-819.
- Lasaga, A.C. Chemical kinetics of water–rock interactions. *Journal of Geophysical Research*, (1984), 89, 4009–4025.
- Mackie, R.L. and Madden, T.R.. Three-dimensional magnetotelluric inversion using conjugate gradients. *Geophysical Journal International*, (1993), 115 (1), 215-229.
- Manzella, A.: Resistivity and heterogeneity of Earth crust in an active tectonic region, Southern Tuscany (Italy). *Annals of Geophysics*, (2004), 47 (1), 107-118.
- Manzella, A., Ungarelli, C., Ruggieri, G., Giolito, C., Fiordelisi, A.: Electrical resistivity at the Travale geothermal field (Italy). *Proceedings of the World Geothermal Congress 2010, Bali, Indonesia* (2010).
- Matheron, G., *Traité de géostatistique appliquée*, (1962), Mémoire du BRGM 14, Ecole des Mines de Paris, Fontainebleau.
- Matheron, G., *Les variables régionalisées et leur estimation: une application de la théorie des fonctions aléatoires aux sciences de la nature*, (1965), Paris, Masson. 306 p.
- Matheron, G., *Le krigeage universel*, (1969), Les cahiers du CMM de Fontainebleau, Fasc. 1, Ecole des Mines de Paris.
- Matheron, G., *The theory of regionalized variables and its applications*, (1970), Fascicule n. 5, Les Cahiers du Centre De Morphologie Mathématique, Ecole des Mines de Paris, Fontainebleau, 211.
- Matheron, G., Monget J.M., *Théorie des variables régionalisées*, (1969) C-46, Ecole des Mines de Paris.
- Molli, G. Northern Apennine-Corsica orogenic system: an updated overview. *Geological Society London Special Publications*, (2008), 298, 413–442.
- Nolasco, D., Lima, N. L., Hernández, P. A. and Pérez, N. M., Non-Controlled Biogenic Emissions to the Atmosphere from Lazareto Landfill, Tenerife, Canary Islands. *Env. Sci. Pollut. Res.* (2008), 15 (1): 51 – 60.
- Palandri, J.L., Kharaka, Y.K., A compilation of rate parameters of water–mineral interaction kinetics for application to geochemical modelling, (2004), U.S. Geological Survey Open File Report 2004–1068, p. 74
- Pan, L., Spycher, N., Doughty, C., Pruess, K. ECO2N V2.0: A TOUGH2 Fluid Property Module for Mixtures of Water, NaCl, and CO₂, (2015), LBNL-6930E.
- Parkhurst, D.L., Appelo, C.A.J. User's guide to PHREEQC (version 2)-A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations, (1999), U.S. Geological Survey Water-Resources Investigations Report 99–4259, p. 312.
- Pruess K. The TOUGH Codes - A Family of Simulation Tools for Multiphase Flow and Transport Processes in Permeable Media. Earth Sciences Division, Lawrence Berkeley National Laboratory University of California, Berkeley, CA 94720 (2003).
- Pruess, K., Oldenburg, C., Moridis, G. TOUGH2 USER'S GUIDE, VERSION 2, Earth Sciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, LBNL-43134 (2012).
- Raco, B., Battaglini, R., Lelli, M. Gas emission into the atmosphere from controlled landfills: an example from Legoli landfill (Tuscany, Italy) *Environ Sci Pollut Res* (2010) 17:1197–1206 DOI 10.1007/s11356-010-0294-2.
- Romagnoli, P., Arias, A., Barelli, A., Cei, M., Casini, M. An updated numerical model of the Larderello-Travale geothermal system, Italy. *Geothermics*, (2010), 39,4, 292-313.
- Sani, F., Bonini, M., Montanari, D., Moratti, G., Corti, G., Del Ventisette, C. The structural evolution of the Radicondoli–Volterra Basin (southern Tuscany, Italy): Relationships with magmatism and geothermal implications. *Geothermics*, (2016), 59, 38–55. <http://dx.doi.org/10.1016/j.geothermics.2015.10.008>.

- Santilano, A., Manzella, A., Gianelli, G., Donato, A., Gola, G., Nardini, I., Trumpy, E., Botteghi, S. Convective, intrusive geothermal plays: what about tectonics?. *Geoth. Energ. Sci.*, (2015), 3, 51–59. www.geoth-energy-sci.net/3/51/2015/doi:10.5194/gtes-3-51-2015.
- Sichel, H.S., The estimation of means and associated confidence limits for small samples for lognormal population, (1966), Proc. 1966 Symp. South African Institute of Mining and Metallurgy
- Sinclair, A.J., Selection of threshold values in geochemical data using probability graphs. *Journal of Geochemical Explorat.*, (1974), 3:129 – 149.
- Sinclair, A.J., A fundamental approach to threshold estimation in exploration geochemistry: probability plots revisited. *Journal of Geochemical Explorat.*, (1991), 41:1 – 22.
- Singh, A., Omnibus Robust Procedures for Assessment of Multivariate Normality and Detection Of Multivariate Outliers, (1993), In *Multivariate Environmental Statistics*, Patil G.P. and Rao, C.R., Editors, pp. 445-488. Elsevier science Publishers
- Singh A., Singh A. K., Engelhardt M., The Lognormal Distribution in Environmental Applications, (1997), Technology Support Center Issue, EPA/600/S-97/006
- Steefel, C.I., Lasaga, A.C. A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. *American Journal of Science*, (1994), 294, 529–592
- Trumpy, E. and Manzella, A. Geothopica and the interactive analysis and visualization of the updated Italian National Geothermal Database. *International Journal of Applied Earth Observation and Geoinformation*, (2017), 54:28-37. DOI: 10.1016/j.jag.2016.09.004
- Wackernagel, H., *Multivariate geostatistics*, (1995), Springer – Verlag, Berlin, 256p