Interaction of B-rich supercritical magmatic fluids with granite: first report of dumortierite in a geothermal field, Larderello, Italy

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ABSTRACT

In a peraluminous two-mica monzogranite cored at 4.5 km depth in well Radicondoli 29, dumortierite occurs together with andalusite, Li-rich tourmaline, fluorite and fluorapatite. The average composition is SiO_2: 30.9, Al_2O_3: 58.6, FeO: 0.44, MgO: 0.47, CaO: 0.02, F: 0.15. Dumortierite crystallized from supercritical magmatic fluids at T =520-620°C, P = 100 ± 30 MPa. Synthetic fluid inclusions yielded T = 510 ± 10 MPa, P = 42 ± 3 MPa at 2.9 km depth in well Venelle 2. Al data suggest present day T = 450-550°C, P = 40-80 MPa. The supercritical magmatic fluids were hypersaline brines with ~ 30 wt % LiCl and up to 2.4 wt % F, extreme contents that can be found only in pegmatites, aplites and leucogranites. Larderello granites derived from partial melting of a lower crust made up of interlayered metasediments and amphibolites. Extensive melting took place in the lower crust during the last 10 Ma owing to extensional tectonics, lithosphere thinning, roll back or break down of the west merging Adria plate and swelling of the asthenosphere below the western side of the Apennines.

Keywords: boron, dumortierite, supercritical magmatic fluids, granite, geothermal field, larderello.

1 DUMORTIERITE FROM SAMPLE RAD 29-4548

Dumortierite, an orthorhombic pseudohexagonal borosilicate, was discovered in well Radicondoli 29 at 4,548 m depth (all depth values are below ground level), in the Larderello geothermal field (see Fig. 1 for location). It is the first report in the world in a geothermal field. Dumortierite is the most abundant B-bearing mineral after tourmaline and frequently occurs together with tourmaline and andalusite in pegmatites, aplites, leucogranites, Al-rich metamorphic and metasomatic rocks and in high temperature hydrothermal systems. The mineral, whose formula is $AlAl_6BSi_3O_{18}$, shows variable contents of Fe, Mg, Ti. As, Sb, P, Zn. The sample Rad 29-4548 is a porphyritic, hypidiomorphic two-mica peraluminous monzogranite made up of quartz, orthoclase, oligoclase to andesine plagioclase, biotite, muscovite and cordierite. Quartz crystals, rounded, with embayments, occur as graphic quartz in poikilitic orthoclase. Accessory minerals are tourmaline, dumortierite, fluorite, fluorapatite, zircon and ilmenite. Fluorite occurs as colourless to pale violet blades in cavities and along fractures and cleavages of plagioclase crystals. Dumortierite forms scattered interstitial crystals, it appears as squat prisms with pleochroism: X,

reddish brown to violet; Y and Z, pale green (Fig.2a) and fibrous crystals, often altered in chlorite and sericite, with pleochroism X, greenish blue, Y, Z, pale yellow (Fig. 2b).

The average composition in wt % is SiO_2: 30.9, Al_2O_3: 58.6, FeO: 0.44, MgO: 0.47, CaO: 0.02, F: 0.15. Noteworthy are the complete lack of TiO_2, likely due to its low content in the host rock (0.14 wt %) and the high F content largely exceeding normal values generally <0.05 and rarely in the range 73.78°C/100 0.05-0.10 wt %.

2 GEODYNAMIC AND GEOCHRONOLOGIC FRAMEWORK

During the collision between Adria and Corsica-Sardinia microplates the eastward roll back of the subducting and west merging Adria plate during the last 10 Ma (MONGELLI *et al.*, 1998) caused thinning of the Tuscan lithosphere, widespread decompression melting in the mantle and swelling of the asthenosphere below the western side of the Northern Apennines. The underplating of mafic magmas induced partial melting of a lower crust made up of interlayered metasediments and amphibolites giving origin to the peraluminous two mica granites of the Tuscan Magmatic Province (TMP). The prevailing metasedimentary nature of the source rocks at depth in the lower crust is indicated by high $^{87}Sr/^{86}Sr$ (>0.710) and $\delta^{18}O$ (+10/+16 ‰) associated with low neodymium (<0.5122) and hafnium (ε_{Hf} < ca.-6) while the presence of interlayered mafic metamorphic rocks (amphibolites) within the source rocks is suggested by the anomalous high contents of CaO, FeO, MgO and TiO_2 “not consistent with experimental partial melts of metasedimentary protoliths” (DINI, FARINA, 2018). Several data lead the researchers to hypothesize the formation of mid-crustal (15-10 km depth) large reservoirs (several hundred km^3) feeding smaller plutons (tens to hundred km^3) above 8-6 km depth (DINI *et al.*,2018). New U-Pb zircon ages in agreement with $^{40}Ar/^{39}Ar$ results indicate that Larderello geothermal field is a multipulse magmatic system embracing five events: 3.8-3.6 Ma; 3.3-3.1 Ma; 2.7-2.5 Ma; 1.9- 1.6 Ma and a present-day event (DINI *et al.*,2018). $^{40}Ar/^{39}Ar$ ages of 1.23 ± 0.13 Ma and 1.27 ± 0.22 Ma were also obtained on muscovites from the monzogranite of sample Carboli C bis 4200 and the syenogranite of sample Carboli C bis 4304 respectively (DINI *et al.*, 2005).

3 PT CONDITIONS OF THE SUPERCRITICAL MAGMATIC SYSTEM

Recently ENEL Green Power public company drilled the well Venelle 2 located in the hottest area of the Larderello geothermal field 1.7 km from San Pompeo 2 well (see Fig.1), the latter characterized by extrapolated well bottom temperatures of 450-460°C and supra-hydrostatic pressures (CAVARRETTA, PUXEDDU, 1990). From Venelle 2 geochemical, isotope and fluid inclusion data reveal that tourmaline-rich veins and breccias crystallized at T = 450-550°C, P = 400-800 bars (40-80 MPa) (DINI *et al.*, 2018). In this well, HJELSTUEN et al. (2018) report a measured temperature of 372.9°C at 2,610m depth and

443.6°C at 2,810m depth with a gradient of 35.35°C/100m. The highest homogenization temperatures observed with the method of synthetic fluid inclusions indicate a present-day well bottom (2,900 m depth) temperature of 510 ± 10°C and pressures of 42 ± 3 MPa (RUGGIERI *et al.*, 2018). The temperature increase of 66.4°C from 443.6°C at 2810m depth up to 510 ± 10°C at 2,900 m depth testifies a sudden doubling of the geothermal gradient in the deepest 90 m up to 73.78°C/100m. Temperature of 394°C and pressure of 212 bars (estimated P ≥ 240 bars at well bottom, 2930 m depth) were measured at 2560m depth in San Pompeo 2 well (BATINI et al.,1983). If the same gradient of 73.78°C/100m observed between 2810 m and 2900 m depth in Venelle 2 well characterize also the deepest 90 m of the San Pompeo 2 well between 2840 m and 2930 m depth, and the same gradient of 35.35°C/100m observed between 2610 m and 2810 m depth in the Venelle 2 well probably occur also between 2560m (measured T of 394°C) and 2840 m depth in the San Pompeo 2 well, the following temperatures can be calculated for San Pompeo 2 well: 411.7°C at 2610m depth, 493°C at 2840m depth and 559.4°C at 2930m depth (well bottom). Cogenetic aqueous-carbonic and multiphase hypersaline fluid inclusions in San Pompeo 2-2270 sample yielded past T =495-510°C, P = 70-82 MPa as indicated by the intersection of the isochores (RUGGIERI, 2018). The application of the empirical biotite-tourmaline geothermometer (COLOPIETRO, FRIBERG, 1987) on 27 pair of the two minerals from the well bottom sample San Pompeo 2-2930 yielded 21 temperature values in the range 540-585°C, 4 values in the range 518-540°C, and two values of 618°C and 622°C (unpublished data CAVARRETTA, PUXEDDU, 1990). The last values are consistent with the nearby occurrence of corundum and xenoblastic sanidine generated by the muscovite breakdown that took place at T = 610-620°C and P = 1 kb (100 MPa) (DEL MORO *et al.*, 1982). All data collected in well San Pompeo 2 suggest that tourmaline and associated dumortierite in Rad 29-4548 were deposited during a previous thermal event (~ 1.3-1.2 Ma in Carboli C bis?) at PT conditions estimated to be 518-618°C (see above the temperatures of the geothermometer biotite-tourmaline), 100MPa (1kb CAVARRETTA, PUXEDDU 1990) very similar to present day temperatures of 510-559°C and only slightly lower pressures of 42 ± 3 MPa instead of 70-82 MPa of fluid inclusions in San Pompeo 2-2270 (see above RUGGIERI 2018) or 100 MPa estimated owing to the appearance of corundum (1kb CAVARRETTA, PUXEDDU 1990).

4 TECTONIC SETTING IN THE LIGHT OF SEISMIC SURVEYS

The Larderello granites crossed by several deep drillings (Radicondoli and Carboli C bis) produced magmatic supercritical fluids with temperatures slightly lower than granite solidus in hydrothermal environment characterized by lithostatic pressures and separated from the shallower meteoric system of the exploited reservoir by an impermeable barrier (CAVARRETTA, PUXEDDU, 1990). The impermeable barrier was discovered by BATINI et al. (1983) during drilling of San Pompeo 2 well. The

authors stated: “No fractured zones were discovered between 2,300 m and about 2,930 m, at which depth the well encountered a permeable horizon containing fluids of extremely high pressure and temperature” and “No pressure and temperature measurements were possible as each time this horizon was reached the well blew out causing the formation to cave-in and fill the borehole with hundreds of metres of debris”. This fractured horizon corresponds to an ubiquitous seismic reflecting horizon of the bright spot type well known in literature as the K horizon. Probably drilling of San Pompeo 2 well for the first time reached this fractured horizon filled with supercritical mostly magmatic fluids at a very shallow depth of 2,930 m. Seismic surveys reveal that the present day exploited reservoir is coincident with a shallower reflecting horizon also known in literature as the H horizon. CASINI and CIUFFI (2018) estimated depths of 2,750-2,800 m and of 3,150-3,200 m for the H and K horizons respectively in Venelle 2 well. The last value indicates a deepening of the K horizon from the 2,930 m depth of San Pompeo 2 well down to the 3,150-3,200 m depth of Venelle 2 well. The coexistence of two hydrothermal systems, a shallower one containing meteoric fluids with hydrostatic pressures and a deeper one magmatic with lithostatic pressures was proposed by TAYLOR (1974) for porphyry copper deposits. The remarkable analogy between geothermal fields and porphyry copper deposits due to the presence at depth of an intrusive body or magma chamber as the heat and fluid source is of great economic interest and can give useful indications for the research of both present-day systems (geothermal fields) and fossil systems (porphyry copper deposits).

5 EVOLUTION OF THE SUPERCRITICAL MAGMATIC SYSTEM

The Larderello granites are syenogranites to monzogranites with 73.8 to 78.7 wt % SiO_2, 11.9 to 13.9 wt % Al_2O_3, 4.65 to 5.38 wt % K_2O, 2.50 to 3.65 wt % Na_2O (DINI *et al.*, 2005). These granitic melts, at the end of crystallization generated supercritical fluids strongly enriched in B, Li, F. Li in supercritical fluids is revealed by extremely low eutectic temperatures ranging from – 78 to – 65°C typical of the $LiCl{\cdot}5H_2O$ system, while ice melting temperatures of – 25°C indicates a mean salinity of ~ 30 wt % LiCl equivalent (CATHELINEAU *et al.*, 1994). High Li contents are also revealed by tourmaline crystal cores in the leucogranitic centimetre-thick dyke of sample VC 11 -2946 (Fig. 3) whose compositions show a trend towards tourmalines from Li-rich granitoid pegmatites and aplites (CAVARRETTA, PUXEDDU, 1990). A confirmation of the high F contents of the Larderello granites is given by the occurrence of abundant grains of fluorite and fluorapatite and by the unusual very high average F content of dumortierite (0.15 wt %) generally lower than 0.05 wt %. Extremely high F contents were found in muscovites from the Larderello granites particularly in the last silicic differentiates, such as syenogranite Carboli C bis 4304 in which several muscovites exceed the world record of 2.13 wt % F found in a muscovite from the Macusani ignimbrite (PICHAVANT *et al.*, 1988, Table 5 sample MH 7

analysis n.16), attaining a maximum value of 2.93 wt % (DINI *et al.*,2005). B does not show high contents in the Larderello granites probably because its concentration, with progressing crystallization, was generally enriched only in the last residual fluids that gave origin to dumortierite along the grain boundaries and tourmaline in breccias and miarolitic cavities (Fig. 3). The abundance of boron in the Larderello granites and in the whole Tuscan Magmatic Province is explained by the metasedimentary nature of the source rocks located in the fertile lower crust. Moreover, the Larderello granites are also remarkably enriched in Li and F. In these cases (see Fig 4) the granite solidus (DINI *et al.*, 2005) is more and more leftwards shifted even for some hundreds T°C as testified by the experimental granite solidus for the Macusani glass (MAC), Harding pegmatite (HAR), Beauvoir granite (BV) and for the synthetic granitic melts with 1 wt % B_2O_3, 2 wt % F (PICHAVANT *et al.*, 1988, p.319, Fig.17*)*,lowering the crystallization for muscovite-bearing granites to the temperature range ~ 550-630°C for pressures just slightly above and below 100 MPa (elliptical field). The contemporaneous rightwards shifting of the pure muscovite-out reaction (Ms Ab As Kfs vapor solid line) towards that of two Macusani muscovites with 0.68 and 2.13 wt % F (PICHAVANT *et al.*, 1988, Fig. 17, Table 5: sample MH8 analysis n. 14, sample MH 7 analysis n.16 respectively) lowers the intersection with the solidus of B-, F-, Li-rich granites towards lower and lower pressures comparable with those of the present-day supercritical magmatic fluids with only a concomitant slight temperature increase of the muscovite-out reaction. All the currently available data from geochemistry and petrology, included the most recent ones, confirm the hypothetical position of the LAR granite solidus in the PT range depicted with the shaded area between the dashed lines of Fig 4. It must be emphasized that estimated present day temperatures of 510-559°C are slightly lower and almost coincident with the hypothetic solidus temperatures of the underlying Larderello granite (elliptical field in Fig. 4) whose top must be only some tens to hundreds metres below 2.9 km depth.

6 FIGURE CAPTIONS

Fig. 1: Thermal structure of the Larderello-Travale geothermal field from Fig 2 in Dini et al. (2005) updated with inclusion of San Pompeo 2 and Venelle 2 wells.

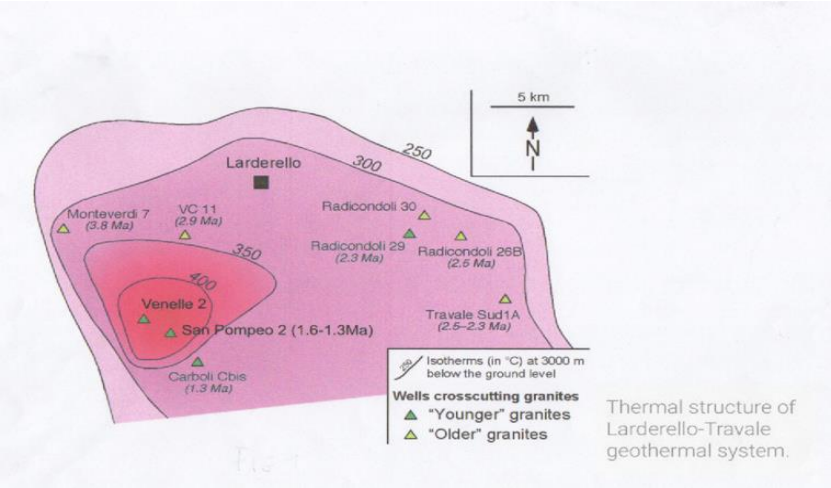


Fig. 2: photomicrographs od dumortierite crystals: a) reddish brown squat prism and small grains of dumortierite; b) greenish blue fibrous dumortierite. Parallel polars.

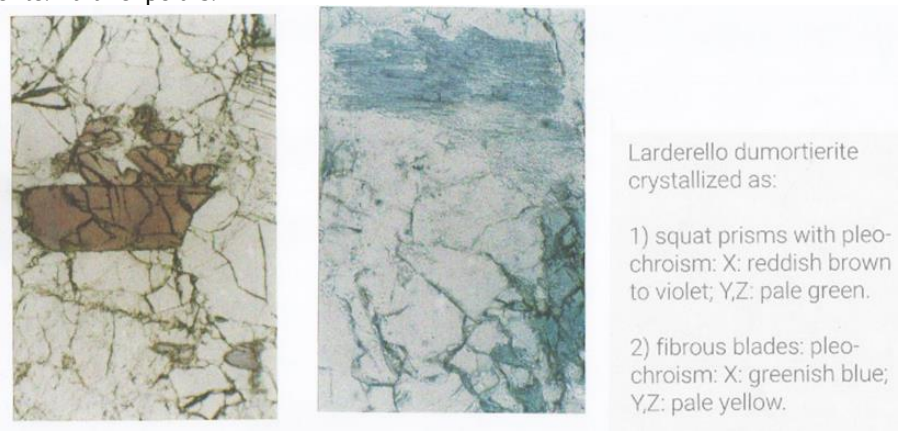


Fig. 3: whitish aplitic cm-sized dyke crossing a fine-grained dark brownish gneiss, from bottom of well VC 11, 2946m depth. Scattered black spots are miarolitic cavities filled with tourmaline.

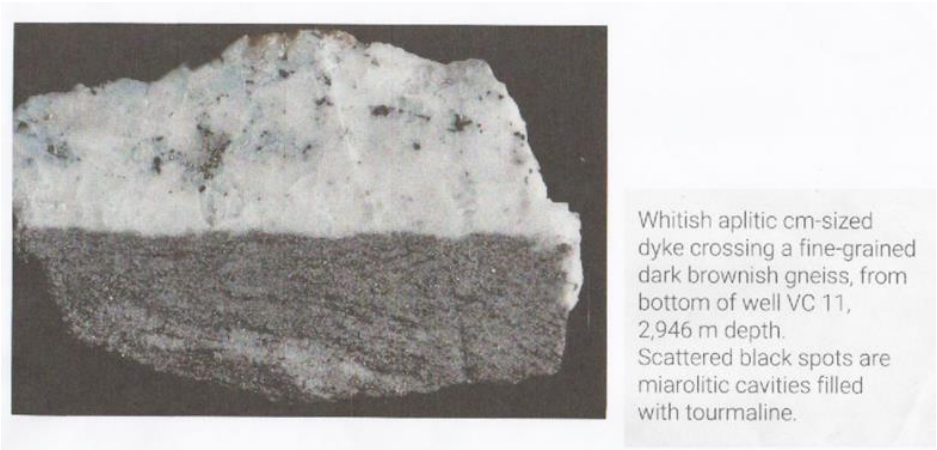
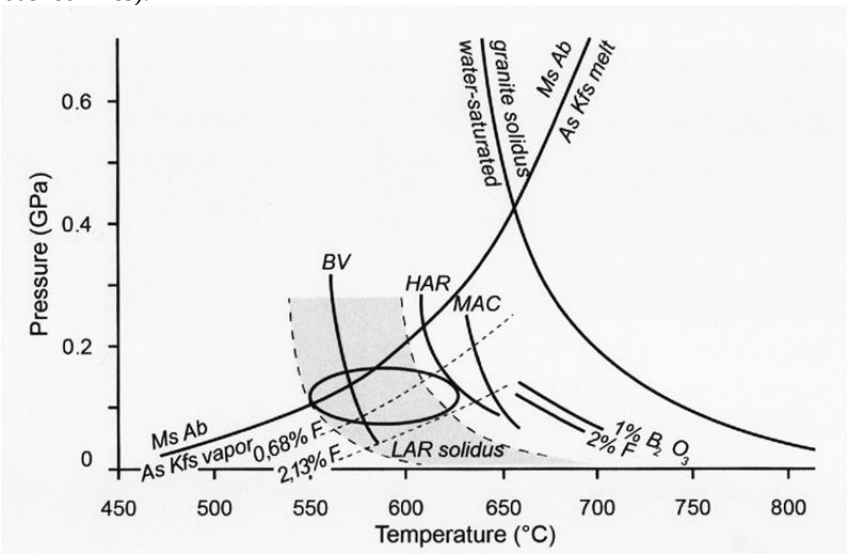


Fig. 4: Evolution of the Larderello granitic system of melts from the water saturated granite solidus towards the solidus of melts more and more enriched in B, Li, F. Muscovite-out reaction (Ms Ab vs AS Kfs vapor) for pure end member (solid line) and with 0.68 and 2.13 wt % F (dotted lines): experimental granite solidus (thick lines) for Macusani glass (MAC), Harding pegmatite (HAR), Beauvoir granite (BV) and for synthetic granites with addition of 1 wt % B_2O_3 and 2 wt % F (PICHAVANT *et al.*, 1988); crystallization field of muscovite granite (open elliptical field), hypothetical position of the LAR granite solidus (grey field bounded by dashed lines).



REFERENCES

BATINI F., BERTINI G., BOTTAI A., BURGASSI P.D., CAPPETTI G., GIANELLI G., PUXEDDU M. (1983) - San Pompeo 2 deep well: a high temperature and high pressure geothermal system. Proc.3rd Intern. Seminar Results EC Res. and Demonstration. Projects in the field of. geothermal energy EUR8853EN, Munich, W. Germany, 29 November - 1 December 1983, 341 - 353.

CASINI M., CIUFFI S. VSP and drilling target definition. . **Drilling in dEep, Super-CRitical AMBient of continentaL Europe** (DESCRAMBLE) Final Conference, Pisa, 28 March 2018- Proceedings, p.5**,** 2018.

CAVARRETTA G., PUXEDDU M. Schorl-dravite-ferridravite tourmalines deposited by hydrothermal magmatic fluids during early evolution of the Larderello geothermal field (Italy). **Econ. Geol.,** 85, p. 1236-1251, 1990.

CATHELINEAU M., MARIGNAC C., BOIRON M.C., GIANELLI G., PUXEDDU M. Evidence for Li-rich brines and early magmatic fluid-rock interaction in the Larderello geothermal system. **Geochim. Cosmochim. Acta,** 58, p.1083-1099, 1994.

COLOPIETRO M.R., FRIBERG L. M. Tourmaline-biotite as a potential geothermometer for metapelites. Black Hills, South Dakota. **Geol. Soc. Amer. Abstr. Progr.** 140176, 1987.

DEL MORO A., PUXEDDU M., RADICATI DI BROZOLO F., VILLA I.M. Rb-Sr and K-Ar ages on minerals at temperatures of 300°-400°C from deep wells in the Larderello geothermal field (Italy). **Contrib. Mineral. Petrol.** 81, p. 340 – 349, 1982.

DINI A., BOSCHI C., FARINA F., LAURENZI M., PERUZZO L., RUGGIERI G., SHALTEGGER U. Pre-drilling resource assessment: insights from granite, hydrothermal vein and metamorphic basement petrology. **Drilling in dEep, Super-CRitical AMBient of continentaL Europe** (DESCRAMBLE) Final Conference, Pisa, 28 March 2018- Proceedings, p. 10-11**,** 2018.

DINI A., FARINA F. Isotopic constraints on crustal partial melting in the roots of Larderello geothermal field. **Drilling in dEep, Super-CRitical AMBient of continentaL Europe** (DESCRAMBLE) Final Conference, Pisa, 28 March 2018- Proceedings, p. 39**,** 2018.

DINI A., GIANELLI G., PUXEDDU M., RUGGIERI G. Origin and evolution of Pliocene-Pleistocene granites from the Larderello geothermal field (Tuscan Magmatic Province, Italy). **Lithos** 81, p. 1-31**,** 2005.

HJELSTUEN M., VEDUM J., RØED M. H., STAMNES Ø. N., LIVERUD A., KOLBERG S., DALGARD S., KNUDSEN S., NORDHAGEN H.O., HALLADAY N. A novel high temperature wireline logging tool for measuring temperature and pressure in supercritical geothermal wells. **Drilling in dEep, Super-CRitical AMBient of continentaL Europe** (DESCRAMBLE) Final Conference, Pisa, 28 March 2018- Proceedings, p. 15-17**,** 2018.

MONGELLI F., PALUMBO F., PUXEDDU M., VILLA I.M., ZITO G. Interpretation of the geothermal anomaly of Larderello, Italy. **Mem. Soc. Geol. Ital.** 52, p. 305-318, 1998.

PICHAVANT M., KONTAK D.J., HERRERA J. V., CLARK A. H. The Miocene-Pliocene Macusani Volcanics, I. Mineralogy and magmatic evolution of a two-mica aluminosilicate-bearing ignimbrite suite. **Contrib Mineral Petrol** 100, p. 300-324, 1988.

RUGGIERI G. Predictive characterization of pressure-temperature condition of the K-horizon from fluid inclusion studies on quartz-tourmaline veins from the Larderello geothermal ystem. **Drilling in dEep,**

Super-CRitical AMBient of continetaL Europe (DESCRAMBLE) Final Conference, Pisa, 28 March 2018- Proceedings, p.70-71**,** 2018.

RUGGIERI G., DINI A., ORLANDO A., PERUZZO L.Post-drilling characterization of pressure-temperature conditions in the Venelle 2 well from petrographic studies and synthetic fluid inclusion analyses. **Drilling in dEep, Super-CRitical AMBient of continetaL Europe** (DESCRAMBLE) Final Conference, Pisa, 28 March 2018- Proceedings, p. 29-30**,** 2018.

TAYLOR H.P. Jr. The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. **Econ. Geol.** 69, p. 843-883, 1974.