Geochemistry of geothermal waters in the La Selva, NE Spain – modeling -

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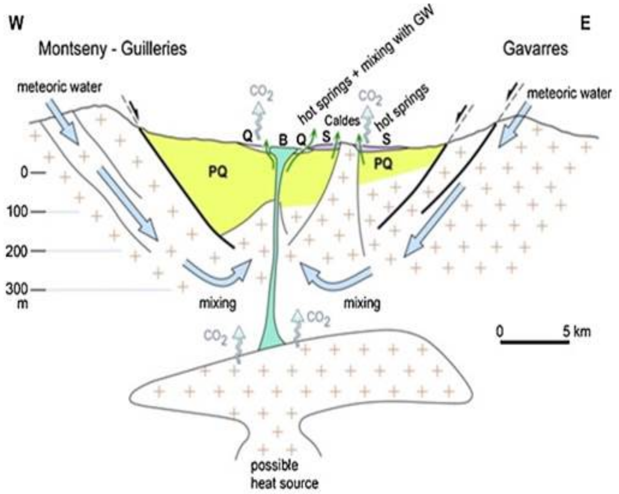
Study area

Map of Study Area (Navarro,2011)

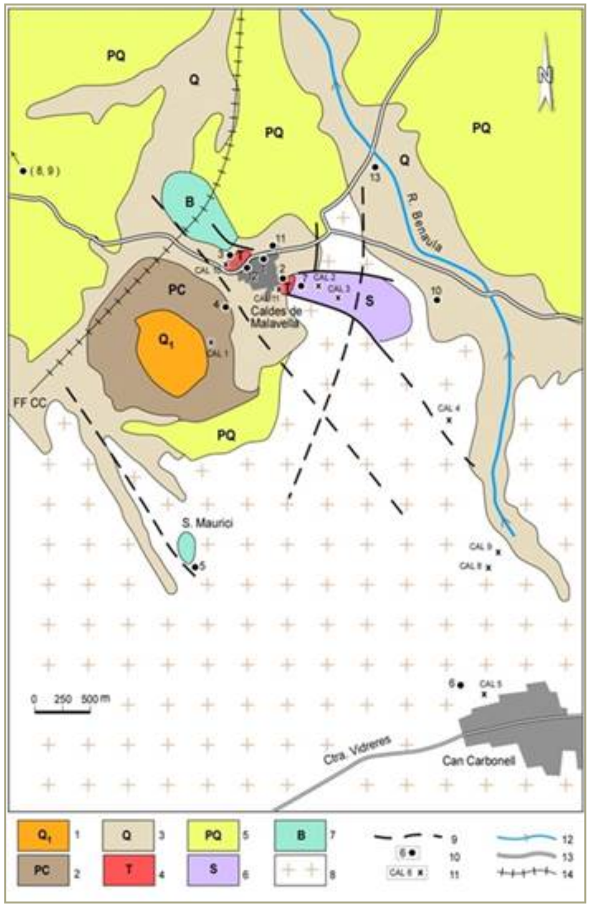


Geological cross-section showing the groundwater flow in the geothermal system. Depth scale in m under the sea level (Navarro,2011)

- The La Selva geothermal system, located 20km south of Girona and 200m above sea level (Fig.1), is a complex unit that includes a granitic and metamorphic besament, Pliocene arkoses sediments, including silicified deposits and travertine, and Quaternary alluvial sediments in the upper part, with a thickness of 12-300m, depending of the area.

- The system works by refilling meteoric waters that penetrate the earth in high areas, move underground and reach an unknown thermal hot spot, where they heat up and acquire CO2, and probably metals as well. Afterwards the water leaches out (dissolve) the host rocks and flows out from the upwelling. In this process waters naturally pick up pollutants.

Sampling



Detailed geological map and soil and grondwater location samples; (1) Lacustrine sediments on the Malavella volcanic crater; (2)Pyroclastic and braccia deposits of the Malavella volcanic crater; (3) Quaternary alluvial deposits; (4) Present deposits (Navaro,2011)

Groundwater samples were collected from hot springs(1-7 and12), water supply and agricultural wells (samples 10,11, and13) and nerby low thermal discharges (samples 8 and 9), the depth of which ranged from 0-35m from a saturated zone of variable thickness.

In this presentation samples from site 1 (hot spring) and 4 (cold groundwater) are used.

Previous Data

	T	pH	Eh(mV)	HCO3	SO4	Cl	NO3	F	Br	
1.Saint Narcis	54	6.9	68	1740	46.5	632	0.2	7.88	2.9	
2.Font Vaca	12.3	7.62	72	360	111	114	69.09	0.31	0.38	
	Na	**K**	**Ca**	**Mg**	**Si**	**Li**	**Ag**	**Ba**	**As**	**Cd**
1.Saint Narcis	1138	53	56	9.4	42000	1660	<2	525	58.3	0.3
2.Font Vaca	76	2.3	150	35	26900	41	<0.02	320	2.25	<0.01
	Fe	**Ni**	**Cu**	**Pb**	**Sb**	**Zn**	**Se**	**Rb**	**Mn**	**Cr**
1.Saint Narcis	<100	5	16	0.3	0.1	9	37	266	22	<5
2.Font Vaca	<10	0.3	3.4	8.02	0.01	3.1	4.3	10.3	0.2	1.4

In the table are shown concentration of anion and cations used for modeling. Main cations and trace elements in groundwater are shown in µm/L, except Na, K, Ca and Mg, they are shown in mg/L and anions are shown in the same unit (mg/L).

. Piper Diagram

Piper diagram used to classify water on the basis of its chemical composition, Faure,Pg.374

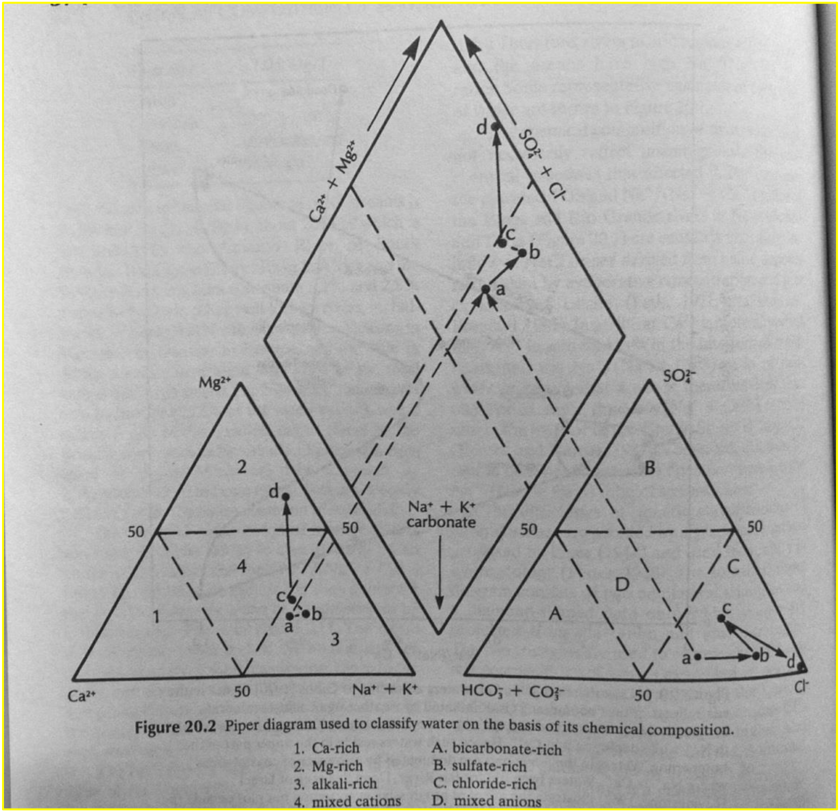
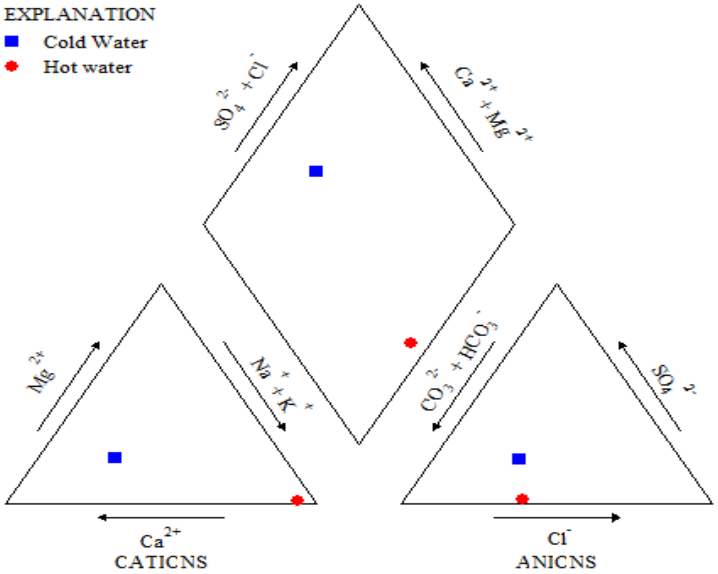


Figure 20.2 Piper diagram used to classify water on the basis of its chemical composition.

1. Ca-rich
2. Mg-rich
3. alkali-rich
4. mixed cations

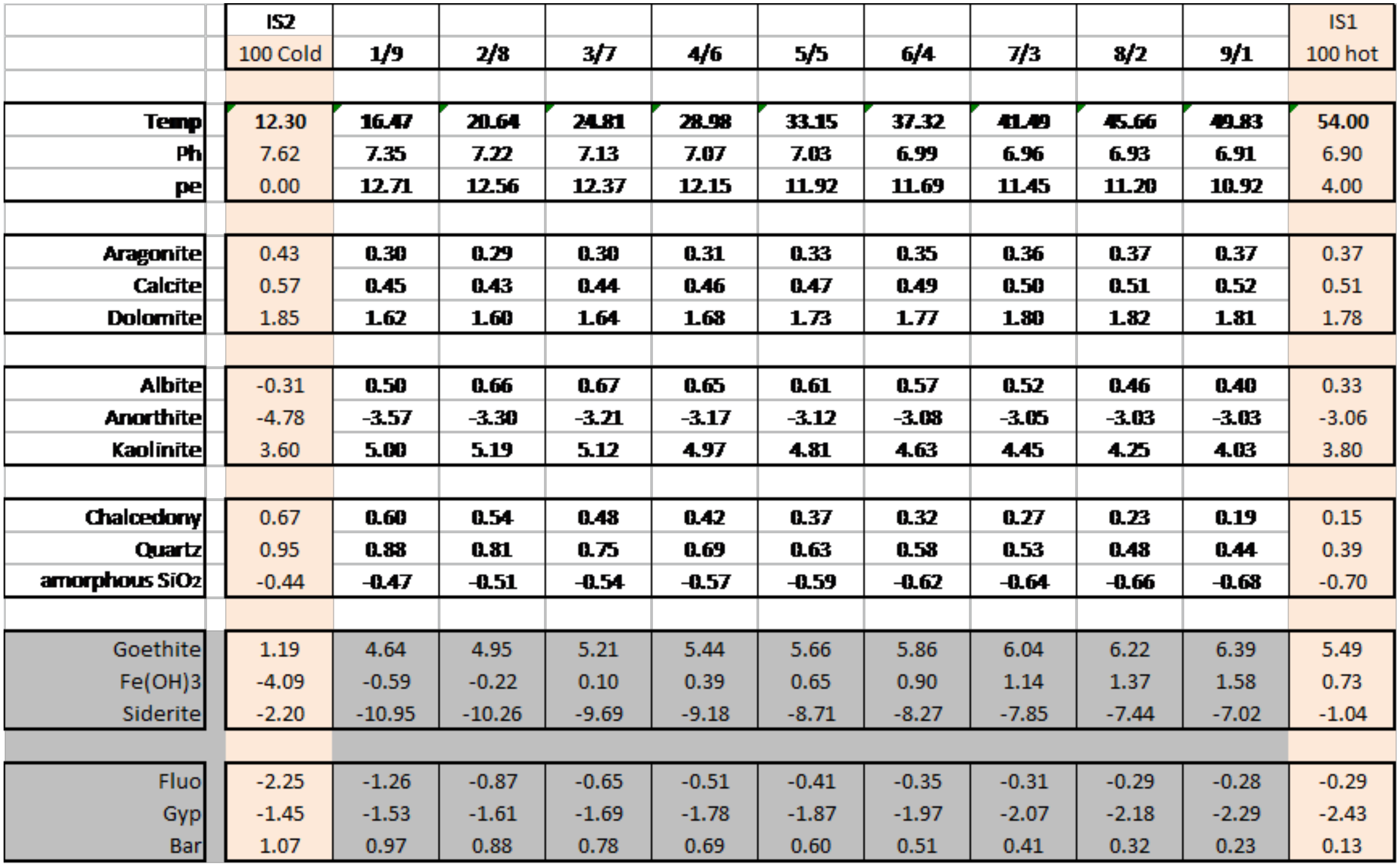
A. bicarbonate-rich
B. sulfate-rich
C. chloride-rich
D. mixed anions



Distribution of water samples on a Piper diagram

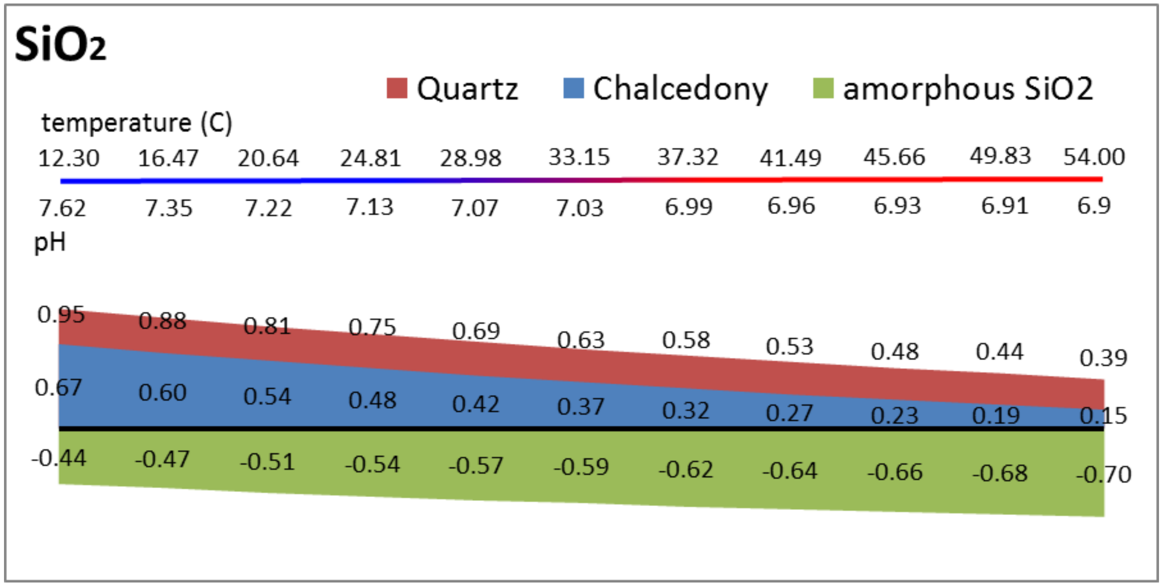
Modeling

Hot spring (Saint Narcis) and cold groundwater (Font Vaca) mix



	IS2										IS1
	100 Cold	**1/9**	**2/8**	**3/7**	**4/6**	**5/5**	**6/4**	**7/3**	**8/2**	**9/1**	100 hot
Temp	12.30	**16.47**	**20.64**	**24.81**	**28.98**	**33.15**	**37.32**	**41.49**	**45.66**	**49.83**	54.00
Ph	7.62	**7.35**	**7.22**	**7.13**	**7.07**	**7.03**	**6.99**	**6.96**	**6.93**	**6.91**	6.90
pe	0.00	**12.71**	**12.56**	**12.37**	**12.15**	**11.92**	**11.69**	**11.45**	**11.20**	**10.92**	4.00
Aragonite	0.43	**0.30**	**0.29**	**0.30**	**0.31**	**0.33**	**0.35**	**0.36**	**0.37**	**0.37**	0.37
Calcite	0.57	**0.45**	**0.43**	**0.44**	**0.46**	**0.47**	**0.49**	**0.50**	**0.51**	**0.52**	0.51
Dolomite	1.85	**1.62**	**1.60**	**1.64**	**1.68**	**1.73**	**1.77**	**1.80**	**1.82**	**1.81**	1.78
Albite	-0.31	**0.50**	**0.66**	**0.67**	**0.65**	**0.61**	**0.57**	**0.52**	**0.46**	**0.40**	0.33
Anorthite	-4.78	**-3.57**	**-3.30**	**-3.21**	**-3.17**	**-3.12**	**-3.08**	**-3.05**	**-3.03**	**-3.03**	-3.06
Kaolinite	3.60	**5.00**	**5.19**	**5.12**	**4.97**	**4.81**	**4.63**	**4.45**	**4.25**	**4.03**	3.80
Chalcedony	0.67	**0.60**	**0.54**	**0.48**	**0.42**	**0.37**	**0.32**	**0.27**	**0.23**	**0.19**	0.15
Quartz	0.95	**0.88**	**0.81**	**0.75**	**0.69**	**0.63**	**0.58**	**0.53**	**0.48**	**0.44**	0.39
amorphous SiO_2	-0.44	**-0.47**	**-0.51**	**-0.54**	**-0.57**	**-0.59**	**-0.62**	**-0.64**	**-0.66**	**-0.68**	-0.70
Goethite	1.19	4.64	4.95	5.21	5.44	5.66	5.86	6.04	6.22	6.39	5.49
$Fe(OH)_3$	-4.09	-0.59	-0.22	0.10	0.39	0.65	0.90	1.14	1.37	1.58	0.73
Siderite	-2.20	-10.95	-10.26	-9.69	-9.18	-8.71	-8.27	-7.85	-7.44	-7.02	-1.04
Fluo	-2.25	-1.26	-0.87	-0.65	-0.51	-0.41	-0.35	-0.31	-0.29	-0.28	-0.29
Gyp	-1.45	-1.53	-1.61	-1.69	-1.78	-1.87	-1.97	-2.07	-2.18	-2.29	-2.43
Bar	1.07	0.97	0.88	0.78	0.69	0.60	0.51	0.41	0.32	0.23	0.13

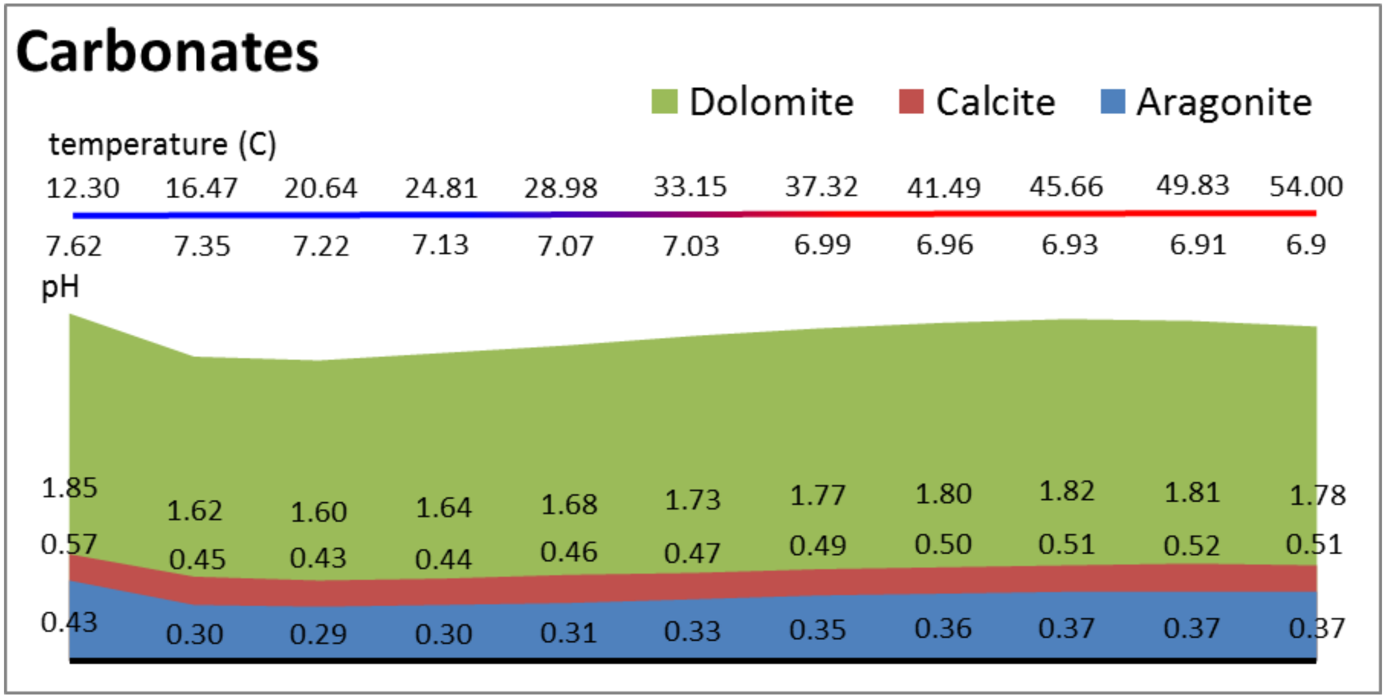
Saturation Index of groundwater for the chief minerals (carbonates, silica and aluminosilicates)



SI(quartz)>SI(chalcedony)>SI(amorphous)

(crystalline>cryptocrystalline>amorphous)

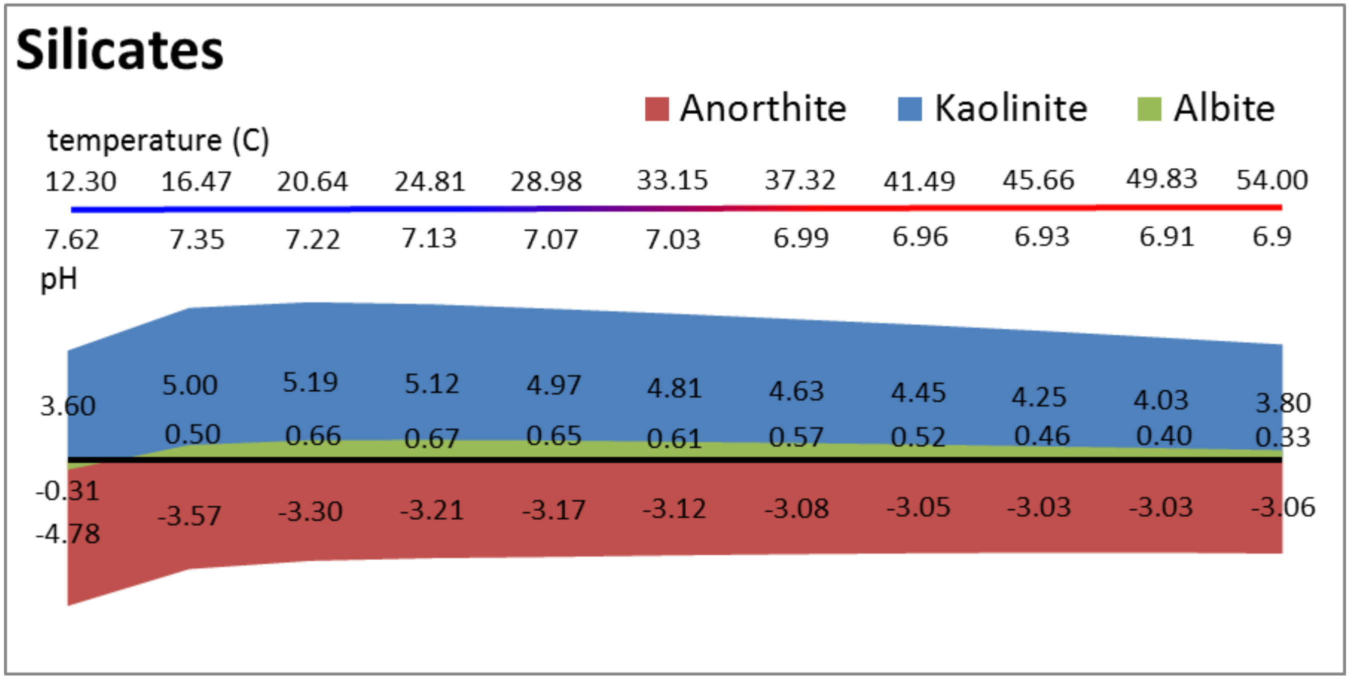
Carbonates



Both samples are oversaturated with respect to calcite, dolomite, and aragonite. Aragonite and calcite are very close to reach equilibrium, explaining precipitates of the geothermal system.

SI (Dolomite)>SI (Calcite)>SI (Aragonite)

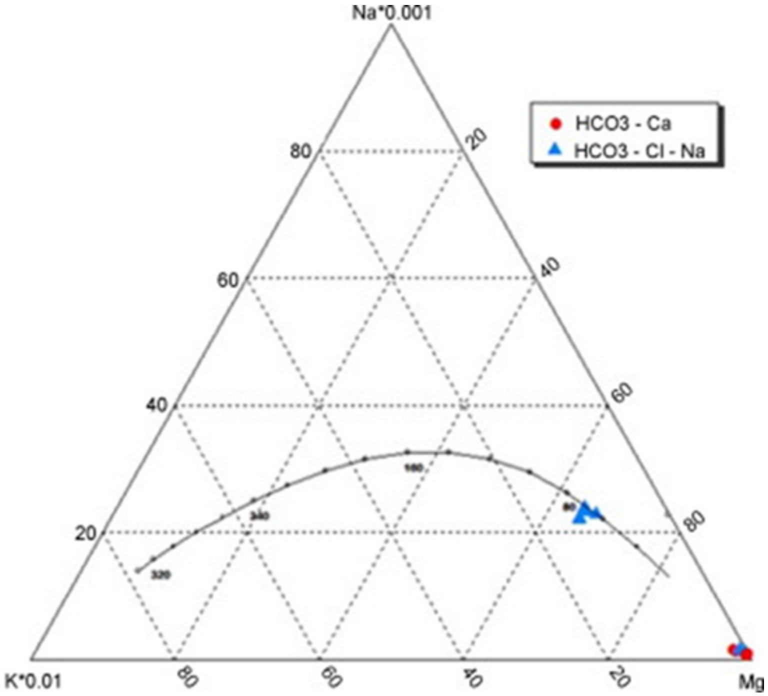
Aluminosilicates



SI (Kaolinite0>SI(Albite)>SI(Anorthite)

Gigginbach geothermometers (Giggenbach,1988)

- Where fluids reach the surface by way of hot springs, fumaroles or wells, their chemical composition may often be used to deduce sub-surface temperatures.
  - Concentrations of the constituents that relate to deep temperatures are called chemical geothermometers and are very useful as a prospecting tool especially in the exploration and development stages



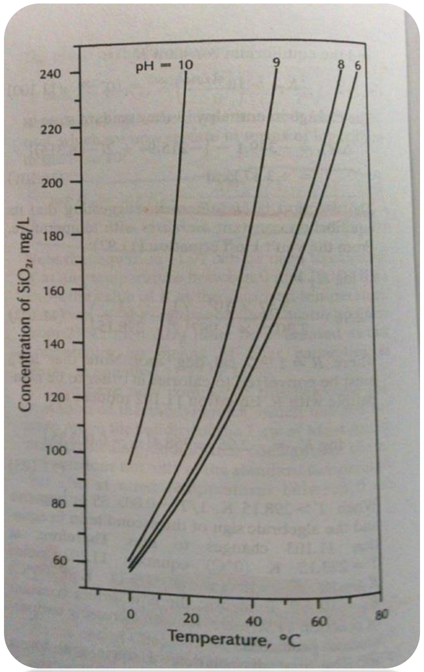
Geothermometers have been classified into two groups:

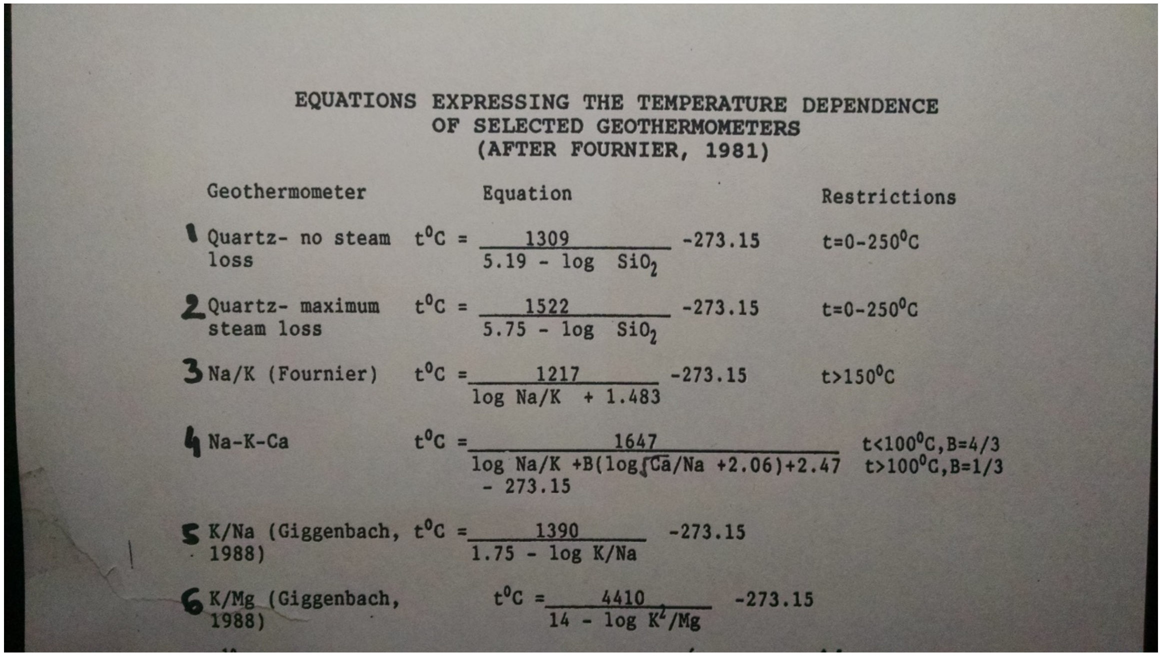
1. Chemical geothermometars
    - Solute and
    - Gas geothermometers

2. Isotope geothermometers

Silica geothermometars

Solubility of silica varies with pH and T, and can be used as a geothermomether, to estimate temperatures. The resulting curves indicate that the concentration of SiO2 in milligrams per liter in saturated solutions of amorphous silica in water increases both with increasing temperature and pH. (Faure,1991).





EQUATIONS EXPRESSING THE TEMPERATURE DEPENDENCE
OF SELECTED GEOTHERMOMETERS
(AFTER FOURNIER, 1981)

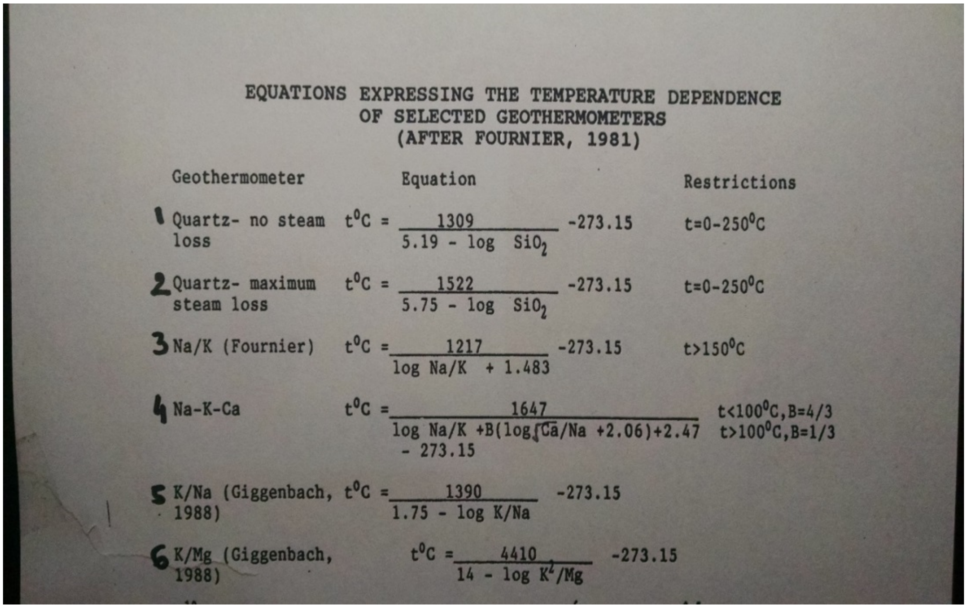
	Geothermometer	Equation	Restrictions
1	Quartz- no steam loss	$t^{0}C = \frac{1309}{5.19 - \log SiO_2} - 273.15$	$t=0-250^{0}C$
2	Quartz- maximum steam loss	$t^{0}C = \frac{1522}{5.75 - \log SiO_2} - 273.15$	$t=0-250^{0}C$
3	Na/K (Fournier)	$t^{0}C = \frac{1217}{\log Na/K + 1.483} - 273.15$	$t>150^{0}C$
4	Na-K-Ca	$t^{0}C = \frac{1647}{\log Na/K + B(\log \sqrt{Ca}/Na + 2.06) + 2.47} - 273.15$	$t<100^{0}C, B=4/3$ $t>100^{0}C, B=1/3$
5	K/Na (Giggenbach, 1988)	$t^{0}C = \frac{1390}{1.75 - \log K/Na} - 273.15$	
6	K/Mg (Giggenbach, 1988)	$t^{0}C = \frac{4410}{14 - \log K^2/Mg} - 273.15$	

Na/K geothermometars

The main advantage of this geothermometer is that

- it is less affected by dilution and steam separation than other geothermometers
- the flow rate of a spring may be less than that required for the application of the quartz geothermometer

. Na-K geothermometer, (>180°C), Fournier 1981, it is used in all phases and applied on spring and deep well samples, (Formula3). Na-K geothermometer, Giggenbach 1988, (t>180°C), it is used in the exploration and development phases, applied on spring and deep well samples, (Formula5).



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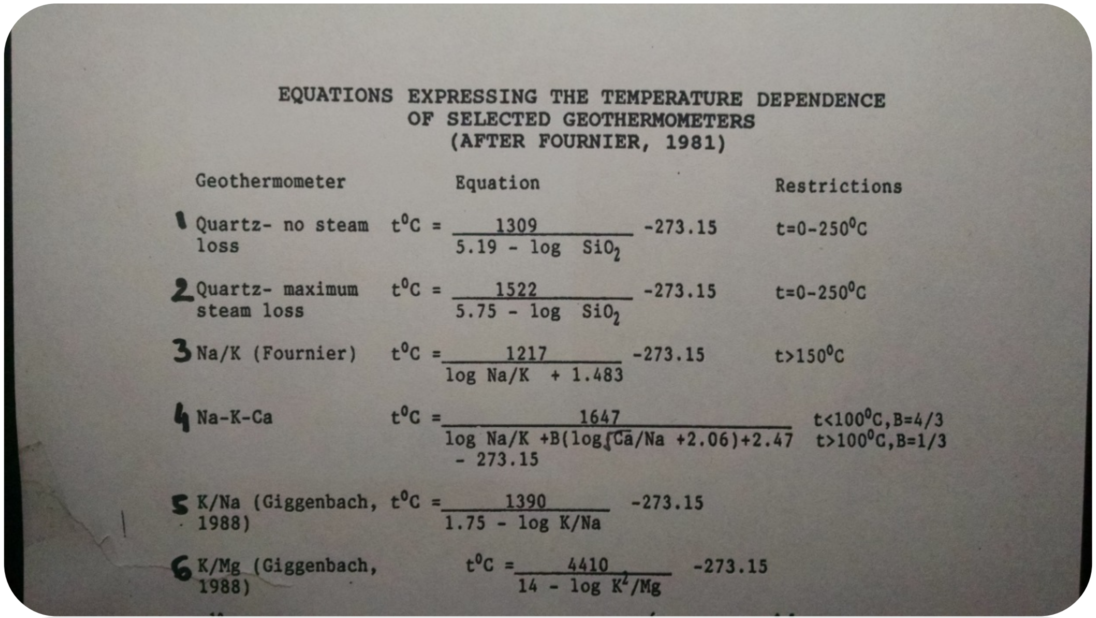
K-Mg geothermometers

Giggenbach 1988, is used in all phases and applied in spring and deep well samples. The K and Mg concentration are expressed in mg/kg (ppm), (Formula6).



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Na-K-Ca Geothermometer

This geothermometer is affected by boiling and dilution.The main consequence of boiling is calcite (CaCO3) precipitation which reduces the dissolved calcium concentration. A correction for fluids containing high concentrations of magnesium exists (Fournier and Potter, 1979; Giggenbach,1988). (Formula 4)

Conclusion

The PHREEQC is used for modeling and for a calculation saturation index of the effluents.

- SI of mixed shows the amorphous SiO2 form is always under-saturated, while Chalcedony is near saturation and quartz is oversaturated .The SI of the silica minerals is in following order:
  SI(quartz)>SI(chalcedony)>SI(amorp)
- All samples are oversaturated with respect to calcite, dolomite, and aragonite. Aragonite and calcite are very close to reach equilibrium, explaining precipitates of the geothermal system.
  SI (Dolomite)>SI (Calcite)>SI (Aragonite)
- **SI (Kaolinite0>SI(Albite)>SI(Anorthite)**
- Water is saturated with the respect to barite and fluorite
- Similarities between the geochemical characteristic could indicate a single origin for the metals present in those deposits and fluids

Thank You !

Questions???