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## Water Rock Interaction [WRI 14]

# Origin of salinity in a coastal karst system: La Clape massif, SE France

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### Abstract

Recent increases in groundwater salinity, exceeding the guidelines for irrigation, prompted this investigation on the origin of mineralisation in the La Clape karst aquifer (SE France). The La Clape massif (Aude) is a typical Jurassic and Cretaceous carbonate aquifer that was deeply karstified during the Messinian crisis. The massif is affected by the vicinity of the Cevennes lithospheric fault, and numerous normal faults related to the Oligocene distension event. Potential sources of salinity are seawater intrusion, upward migration of deep saline waters, as well as dissolution of Triassic evaporites. A contribution from halite can be ruled out on the basis of the measured Br/Cl ratios that are similar to that of seawater and deep saline waters. Sr concentrations suggest mixing with an end member slightly more enriched in Sr than current seawater. Ranging from 0.707852 to 0.708875, <sup>87</sup>Sr/<sup>86</sup>Sr ratios of groundwaters are lower than that of modern Mediterranean seawater (0.709163), and higher than that of the carbonate matrix, ranging from 0.707276 to 0.707477. Those ratios tend towards that of deep saline groundwaters observed at the nearby site of Balaruc. <sup>36</sup>Cl/Cl ratios measured on a few samples agree with a mixing hypothesis of superficial karst waters with deep saline water at secular equilibrium with the carbonate matrix. Including dissolution of carbonate and mixing with a saline end member, PHREEQ C modelling confirms that Balaruc-type waters are a likely end member. Calculated parts of mixing range from 0 to 16% of deep saline water. This suggests that seawater intrusion in the karst system is prevented by thick off-shore sedimentary deposits. The deeply faulted and karstified La Clape system is likely to favor the upward movement of deep saline waters. At the regional scale, saline groundwaters of three coastal karst aquifers located along the Gulf of Lion show <sup>87</sup>Sr/<sup>86</sup>Sr ratios tending towards a Sr isotopic ratio of 0.70847. This may suggest a similar origin for the observed salinities in these coastal karst systems, by upward movement of deep saline waters.

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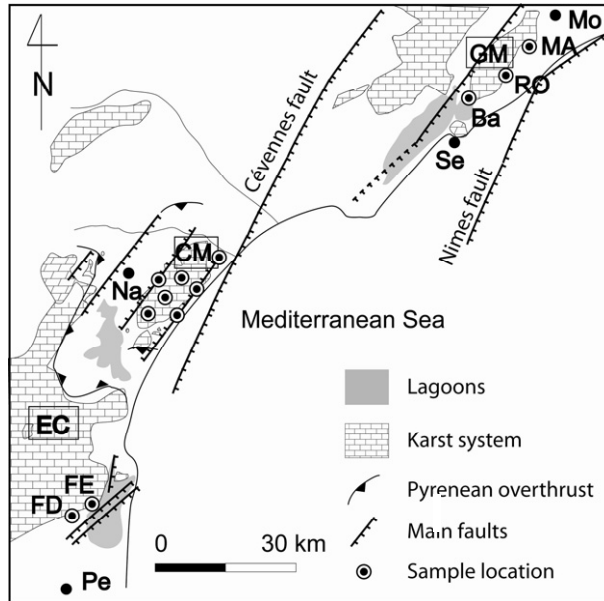
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## 1. Introduction

Increasing water usage from karst aquifers in carbonated formations outcropping along the Mediterranean coast increases the threat of water salinization. Along the Gulf of Lion sea shore, outcrop 3 carbonate massifs of Lower Cretaceous and Upper Jurassic age (Fig.1).



**Fig. 1.** Location, along the Mediterranean coast, of 3 highly karstified massifs (GM, La Gardiole; CM, La Clape; ECM, Eastern Corbières) constituted of limestones and dolomitic limestones of Lower Cretaceous and Upper Jurassic age. Mo, Montpellier; Na, Narbonne; Pe, Perpignan; Se, Sète; Ba, Balaruc. Saline springs: FE, Font Estramar; FD, Font Dame; RO, La Roubine; MA, La Madeleine.

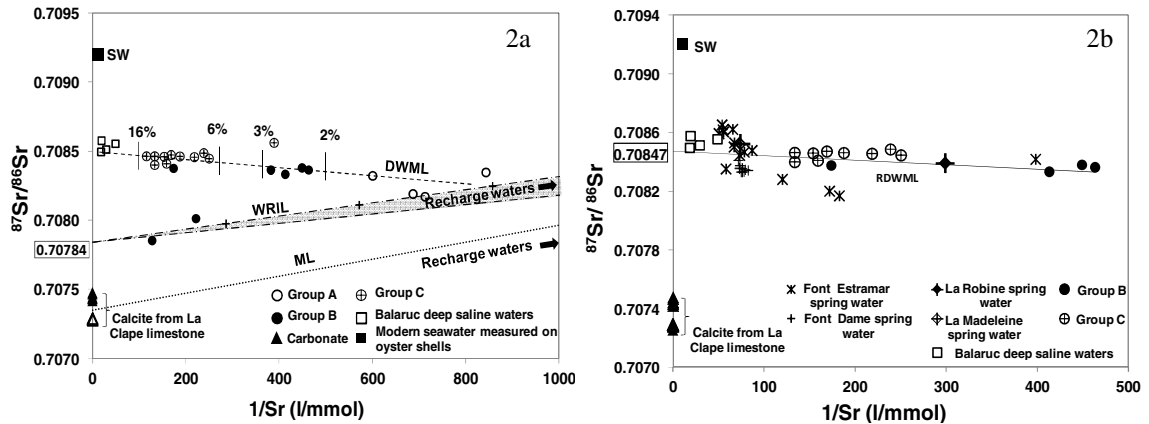
In the studied area, after the Variscan structuration of the basement, the main geodynamic evolution occurred during the Tertiary, with the Eocene compressive Pyrenean phase at the origin of the eastern Corbières overthrust, followed by the Oligocene extensional phase (horsts, grabens, opening of the Gulf of Lion). Coastal carbonate massifs were deeply karstified during the Upper Cretaceous and the Messinian event.

## 2. Results

Groundwaters from La Clape massif range from fresh to brackish waters (400-1800 mg/l). Three groups of waters are identified, spring waters of group A ( $0.7 < \text{Cl} < 1.2$  mmol/l), weakly salted groundwaters of group B ( $0.8 < \text{Cl} < 1.9$  mmol/l) and mostly brackish groundwaters of group C ( $4.5 < \text{Cl} < 20.5$  mmol/l). Groundwaters show Br/Cl ratio ranging from 1.3 to  $2.2 \times 10^{-3}$  similar to that of seawater, this exclude the influence of Triassic halite ( $\text{Br}/\text{Cl}_{\text{molar}} = 0.11 \times 10^{-3}$ ).

On a Sr mixing diagram (Fig. 2a), dots of La Clape groundwaters define a mixing line DWML, with superficial spring waters (Group A) and Balaruc deep saline waters [1] as end members. In contrast, there is no trend towards the Sr isotopic composition of modern seawater. Considering Balaruc-type waters as the saline end-member, mixing parts are calculated with several tracers (Cl and Sr contents, Sr mixing diagram) for La Clape groundwaters (Fig. 2a). Mixing parts obtained with the different tracers are coherent, showing that Cl and Sr isotopic data are in agreement with the hypothesis of mixing with deep

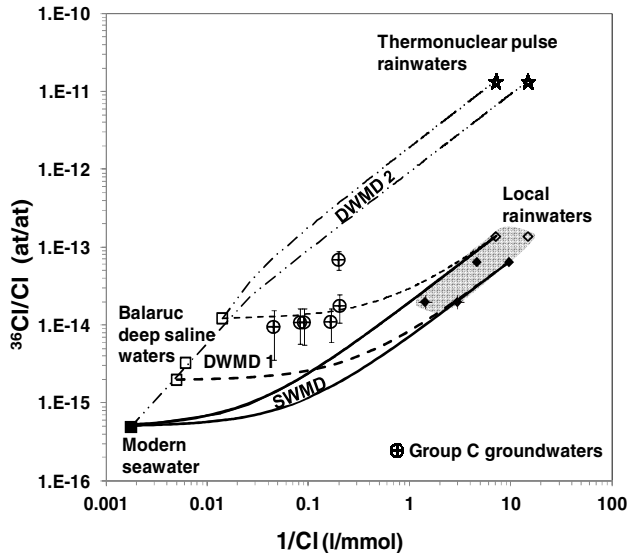
saline waters. The mixing parts range between 0 and 3% of deep saline waters for group B waters and 3 to 16% for group C waters respectively. On the same diagram (Fig. 2a) another mixing line is defined (WRIL) between local meteoric waters and Sr isotopic composition of calcite from limestones as end-members. Superficial karst groundwaters with rapid recharge (springs of Group A and karst conduit connected with a sinkhole) fall on the WRIL mixing line and do not show influence of deep saline waters. Furthermore, considering the Ca activity,  $P_{CO_2}$  and T°C for studied groundwaters, PHREEQ C modeling shows that waters from group C can be modeled by mixing with deep saline groundwater similar to that of Balaruc. The hypothesis of mixing with current seawater does not fit with the observed data.



**Fig. 2** a and b. (2a) Plot of La Clape groundwaters on an  $^{87}\text{Sr}/^{86}\text{Sr}$  vs  $1/\text{Sr}$  diagram define 2 mixing lines DWML and WRIL (see text); (2b) on a  $^{87}\text{Sr}/^{86}\text{Sr}$  vs  $1/\text{Sr}$  diagram, groundwaters of 3 coastal highly karstified massifs outcropping along the Gulf of Lion define a mixing line RDWML in agreement with the rises of similar deep saline waters in the considered karst aquifers.

To further constrain the nature of the saline end member  $^{36}\text{Cl}/\text{Cl}$  ratios were measured on a selection of groundwater samples from group C. On a  $(^{36}\text{Cl}/\text{Cl})-(1/\text{Cl})$  diagram (Fig. 3) are shown the possible mixing end members: evaporated meteoric waters, modern seawater [2] and Balaruc type deep saline waters [1].

**Fig. 3.** On a  $^{36}\text{Cl}/\text{Cl}$  vs  $1/\text{Cl}$  diagram, dots of La Clape groundwaters fall mostly on the domain DWMD1, defined by mixing lines, between Balaruc deep saline waters [1] and local modern meteoric waters. Contribution of precipitation contaminated by the thermonuclear pulse is possible for one of the observed data (DWMD2 domain). Mixing lines between modern seawater and local modern meteoric waters define a 3rd mixing domain (SWMD), shown for comparison.



The  $^{36}\text{Cl}$  fallout of  $31\text{at/m/s}$  is calculated based on Phillips approach [3]. Cl concentrations in meteoric waters range between  $0.09$  and  $0.31$  mmol/l for coastal and inland local waters respectively [4]. Hence the  $^{36}\text{Cl}/\text{Cl}$  ratio ranges between  $9 \times 10^{-15}$  and  $65 \times 10^{-15}$  at/at, in agreement with  $^{36}\text{Cl}/\text{Cl}$  ratio measured in Perpignan [5]. Following the nuclear bomb test pulse,  $^{36}\text{Cl}$  fallout and  $^{36}\text{Cl}/\text{Cl}$  ratio is 10 to 1000 times higher than natural fallout [3]. Ranging between  $9.5 \pm 1.4$  and  $17.7 \pm 1.8 \times 10^{-15}$ , most  $^{36}\text{Cl}/\text{Cl}$  ratios from selected group C waters, fall in a mixing domain DWMD 1, defined by mixing lines between local meteoric waters and Balaruc deep saline waters [1]. One outlier dot shows higher  $^{36}\text{Cl}$  content, which is likely to be due to the influence of the thermonuclear bomb test implying a non negligible component of groundwater recharged during the nuclear bomb peak period.

At a regional scale, the more or less saline groundwaters ([1], [6], [7]) of 3 coastal karstified massifs (La Gardiole, La Clape, eastern Corbières) are plotted on a Sr mixing diagram (Fig. 2b) and define a mixing line (RDWML) which suggests again that the salinity of these coastal aquifers is not related to intrusions of present-day seawater but is rather due to the rises of deep saline waters.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio ( $0.70747$ ) of this end member is comprised between those of recent Mediterranean seawater and of calcite from limestone matrix (Fig 2b). Introduction of ancient seawater during and after Flandrian transgression, followed by water-rock interaction with carbonated rocks of similar ages (Upper Jurassic and Lower Cretaceous) could explain the occurrence of saline waters in coastal karst aquifers outcropping along the Gulf of Lion sea shore.

### 3. Conclusion

Increasing salinity in groundwaters from the La Clape coastal massif is mainly due to mixing with ancient evolved seawater rising from deep parts of the karst aquifer. A combination of Cl, Sr, and  $^{36}\text{Cl}$  data and PHREEQ C modeling allow characterizing the saline end member waters. The absence of current seawater intrusion suggests that thick off shore sediment deposits act as an efficient impermeable screen preventing modern seawater intrusions. Based on Sr isotopic data, similar processes may affect karst saline groundwaters of other coastal karstified massifs outcropping along the Gulf of Lion. The Sr mixing diagram revealed again to be a suitable tracer for the origin of salinity.

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