

## Genesis and rates of fluid flow at the Mercator mud volcano, Gulf of Cadiz

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Mud volcanism is a widespread phenomenon in the Gulf of Cadiz (GoC) and provides a window into deep structural and diagenetic processes [1]. Sediment pore fluids from the Mercator mud volcano (MMV), located in the El Arraiche mud volcano field offshore Morocco, are extremely enriched in chloride reaching up to 5.3 M (thus, exceeding normal seawater values by a factor of 9). Na/Cl ratios are close to 1 suggesting halite dissolution by the ascending fluid. This is corroborated by 3D seismic data that shows an active anticline below the eastern flank of the MMV, which can only be explained by a rising salt diapir. Additionally, the fluids are highly enriched in Li and B indicating a deep fluid source from mineral dewatering reactions at elevated temperatures (>100 °C). A deep fluid source is also supported by a radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr porewater signal of 0.7106 as well as the morphology of quartz and gypsum crystals transported within the ascending mud matrix. These crystals are probably of Triassic origin. Hence, the geochemical and the 3D seismic data suggest that the Triassic salt province 500 km further south on the Moroccan Margin might extend further north than previously known and that halokinesis has to be considered as a driving force for mud volcanism in the GoC.

Finally, a 1-D transport-reaction model has been applied to constrain the fluid advection rates. The numerical simulations of conservative porewater compounds Cl, Li, and B reveal upward fluid flow rates of ~6 cm/a at the top of the MMV, gradually decreasing to 0.3 cm/a towards the rim. In addition, a CTD mounted onto a video sled system provided bottom water salinity and temperature information (about 2 m above the seafloor) from tracks crossing the MMV. In combination with the numerical porewater analysis, this unique spatial data set allows to constrain the overall budgets for the release of water, methane, and other porewater constituents as well as the heat flow of the MMV.

### References

- [1] Hensen C., Nuzzo M., Hornibrook E., Pinheiro L.M., Bock B., Magalhaes V.H. and Brückmann W., (2007), *Geochim. Cosmochim. Acta* **71**, 1232-1248.

## Arsenic mineralogy in high-As wastes at historic gold mine sites, New Zealand

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The studied mine processing sites are part of the Phoenix Mine and the Blackwater Mine, which are historic gold mines hosted within the Otago schist and Greenland Group schist, respectively. The processing of arsenopyrite ore produced very arsenic rich residues (up to 40 wt% As) and no rehabilitation was undertaken after mine closure at either mine. Thus, the studied sites possess suitable conditions for the study of the physical and chemical characteristics of secondary arsenic minerals, especially with respect to time. At the Blackwater Mines all arsenic was originally present as arsenolite (arsenic trioxide polymorph, As<sup>III</sup>), which is a by-product of arsenopyrite roasting. At the Phoenix Battery, where roasting did not take place, arsenopyrite was the original arsenic phase. High dissolved arsenic concentrations derived from the processing residues are temporarily immobilized by the formation of hydrated iron arsenates in the downstream environment. At the Blackwater Mine the hydrated iron arsenate is in the form of scorodite (FeAsO<sub>4</sub>·2H<sub>2</sub>O), whereas at the Phoenix Battery it is in the form of kankite (FeAsO<sub>4</sub>·3.5 H<sub>2</sub>O). In the past the precipitation of hydrated iron arsenates, especially scorodite, has been mainly associated with acidic environments. The studied mine sites are, however, excellent examples for iron arsenate precipitation in a geological setting with high neutralizing capacity and predominant circum-neutral pH. The stability of the hydrated arsenates depends on dissolved arsenic concentrations and is, therefore, controlled by the solubility and availability of the original As phase. In addition, the stability of As is further enhanced by the inherent morphology of the hydrated iron arsenates which precipitates as an interstitial cement, thereby creating an impermeable surface crust and preventing further dissolution of underlying arsenic minerals.