

F-bearing sediments and rocks in the East African Rift: characterization and evaluation of F release capacity

Olaya Cossío (1*), Dídac Navarro-Ciurana (1), Cristina Domènech (1), Àngels Canals (1), Manuela Barbieri (1), Daniele Pittalis (1), Albert Soler (1), Giorgio Ghiglieri (2)

(1) Grup MAiMA, SGR Mineralogia Aplicada, Geoquímica i Geomicrobiologia, Departament de Mineralogia, Petrologia i Geologia Aplicada, SIMGEO UB-CSIC, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), 08028, Barcelona (Spain)

(2) Dipartimento di Scienze Chimiche e Geologiche, Università di Cagliari, 09127, Cagliari (Italy).

* corresponding author: olayacossio@gmail.com

Palabras Clave: Flúor, EARS, rocas volcánicas, lixiviación. | **Key Words:** Fluoride, EARS, volcanic rocks, leaching

INTRODUCTION

Fluoride represents one of the most severe natural contaminant that affects groundwater as well as rivers and soils. More than 200 million people worldwide consume water with fluoride concentration exceeding the WHO guideline of 1.5 mg L⁻¹ (WHO, 2008). Besides dental fluorosis, an excess of fluoride may cause skeletal fluorosis, a bone disease of severe pain. In the East African Rift Valley System (EARS) about 90% of the population exhibit varying degrees of fluorosis symptoms (Yoder et al. 1998) corresponding to over 80 million people (Smedley et al. 2002). FLOWERED (de-FLuoridation technologies for imprOving quality of WatEr and agRo-animal products along the East African Rift Valley in the context of aDaptation to climate change, <http://www.floweredproject.org>) is an H2020 European project whose overall objective is to contribute to the development of a sustainable water management system. The study focus on areas affected by fluoride contamination in water, soils and food in Ethiopia, Kenya and Tanzania, with the aim of improving the living standards for local population. Here we present the study of representative rocks and soils samples with the aim to identify what minerals bear F and what is their alterability and capacity in releasing it to the water.

GEOLOGICAL SETTING

The East branch of the EARS extends from northern Ethiopia to northern Tanzania and corresponds to an active continental rift developed above a mantle plume. The northward drift of Africa explains the existence of flood basalt volcanism in Ethiopia due to the incipient continental break-up, the mature rifting stage results in the magmatism of the Kenya Rift section, and the initial stage of the Rift in the Tanzanian section (Ring, 2014). The intra-continental magmatism of the EARS results in

alkaline igneous rocks that vary slightly according to whether the area is on a continent or not and may present F contents up to 1.2 wt.% (Wang, 2014).

SAMPLING AND METHODOLOGY

Major, minor and trace element (including F) concentrations of 27 fresh rock and weathered samples (12 from Ethiopia, 10 from Kenya, 5 from Tanzania) were determined by XRF and ICP-MS at the Actlabs Laboratories (Canada). Polished thin sections were studied by optical microscopy. XRD measurements were performed at the Centres Científics i Tecnològics of the UB. For leaching experiments, a <2 mm mass of each sample was left in contact with a volume of distilled water for a given time, at 25 °C. pH, conductivity and F aqueous concentration were periodically measured with selective electrodes. Two sets of experiments were done: a) Short experiment with mass: water volume: time: 5g: 50ml: 24 hours; and b) Long experiment: 100g: 400ml: 15 days.

SAMPLES CHARACTERIZATION

Whole rock chemistry

Most samples are volcanic rocks or are derived from them. Ethiopian samples show heterogeneous chemical composition, from basaltic to rhyolitic, while Kenyan samples are mostly rhyolitic to trachi-dacitic and Tanzanian samples mostly trachi-basaltic (Fig.1A). Fluor content in solid samples ranges from 0.02 to 0.30 wt.%. Richest F-bearing samples are those corresponding to obsidian rich rhyolitic samples in Kenya and Ethiopia. Samples show differences of one order of magnitude in total REE concentrations and two normalized patterns (Fig. 1B): samples with lower REE concentrations are richer in LREE and do not present an Eu anomaly (no differences within the three countries) while samples

with higher REE concentrations present an Eu negative anomaly (this pattern is not observed in Tanzania samples).

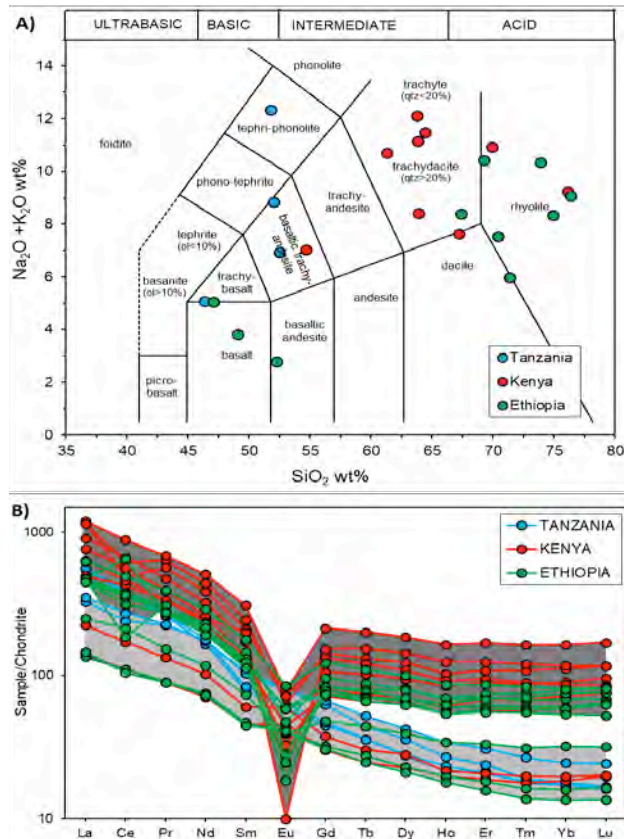


Fig. 1. A) Total alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) vs SiO_2 (TAS; LeBas et al., 1986) diagram for studied samples. **B)** Chondrite-normalized rare earth element (REE) diagram for studied samples. Primitive mantle and chondrite values from Sun and McDonough (1989).

Mineralogy and petrology

Fresh volcanic rocks show a typical porphyry texture with well-defined phenocrysts of K, Na feldspars (mostly sanidine), pyroxene, quartz and/or forsterite in a cryptocrystalline matrix mainly composed of the same minerals. Sometimes F-bearing amphiboles are identified. In weathered samples, crystals are altered to iron oxihydroxides and/or sericite, and textures are more granular and amorphous, depending on the alteration degree. Zeolites and carbonates appear as secondary minerals in some samples.

FLUORIDE LEACHING EXPERIMENTS

Solution pH after short experiments ranges from 6 to 10 (Fig. 2). F concentration in solution is below 2 mg/L in 90% of samples. The highest F concentrations correspond to leaches of dacitic and rhyolitic samples from Kenya and basalt from Tanzania (Fig. 2). The bulk F content of these three samples does not exceed 0.14 wt.% and a F-bearing amphibole has been identified only in one of them. They show, in addition, a high degree of alteration that might be related to the leaching capacity of the fluoride. Preliminary results of long experiments

confirm the range of pH observed in the short experiments.

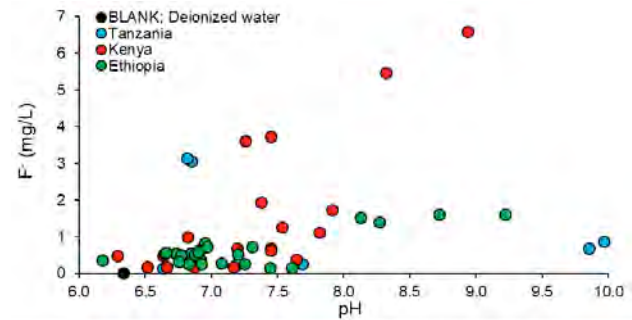


Fig. 2. pH and F concentration obtained in short experiments.

In order to ascertain the role of the rock alteration degree in the F leaching capacity of rocks, the amorphous and cryptocrystalline oxyhydroxide phases need to be further studied in detail.

ACKNOWLEDGEMENTS

This research was financially supported by FLOWERED project (Coordinator G. Ghiglieri), a Horizon 2020 European funded project (Grant Agreement - N. 690378) (www.floweredproject.org).

REFERENCES

- LeBas, M., LeMaitre, R., Streckeisen, A., Zanettin, B. (1986): A chemical classification of volcanic rocks based on the total alkali-silica diagram. *J. Petrol.* **27**, 745–750.
- Ring, U. (2014). The East African Rift System. *Austrian J. Earth Sci.* **107**, 132–145.
- Smedley, P.L., Nkotagu, H., Pelig-Ba, K., MacDonald, A.M., Tyler-Whittle, R., Whitehead, E.J., Kinniburgh, D.G. (2002): Fluoride in groundwater from high-fluoride areas of Ghana and Tanzania. British Geological Survey, Nottingham.
- Sun, S., McDonough, W. (1989): Chemical and isotopic systematics of oceanic basalts: implications for mantle compositions and processes. *Geological Society Special Publications* **42**, 313–345.
- Wang, L. (2014). Halogen (F, Cl and Br) systematics in alkaline to peralkaline magmatic rocks and their constituting minerals. PhD Tübingen University, 125pp.
- WHO (2008) WHO guidelines for drinking-water quality [electronic source]: incorporating 1st and 2nd addenda, 3rd edn. World Health Organization, Geneva.
- Yoder, K., Mabelya, L., Robison, V., Stookey, G., Brizendine, E., Dunipace, E. (1998): Severe dental fluorosis in a population consuming water with negligible fluoride concentration. *Commun. Dent. Oral. Epidemiol.*, **26**, 382–393.