Mars-type mineral assemblages in terrestrial volcanic lake settings

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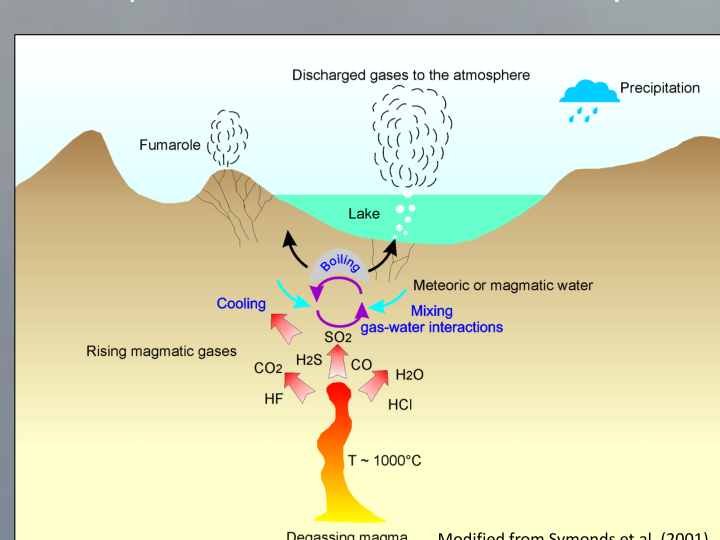
1. INTRODUCTION

Orbital and landed missions have provided evidence for the widespread occurrence of sulfate-rich mineral associations across the Martian landscape (e.g. Swayse *et al.*, 2008; Ehlmann *et al.*, 2011). They must have formed under acidic and oxidizing conditions in the presence of water (Xu *et al.*, 2010). We present evidence that active volcanoes hosting SO_4^- and Cl^- dominated hyperacid crater lakes are promising terrestrial analogues were the formation of Mars-type mineral assemblages can be studied *in situ*. Combined findings at Poás volcano (Costa Rica) and Copahue volcano (Argentina), which include the detection of critical mineral assemblages and results from geochemical modeling, serve as a guide for testing this hypothesis .

Location maps and views of Poás and Copahue volcanos



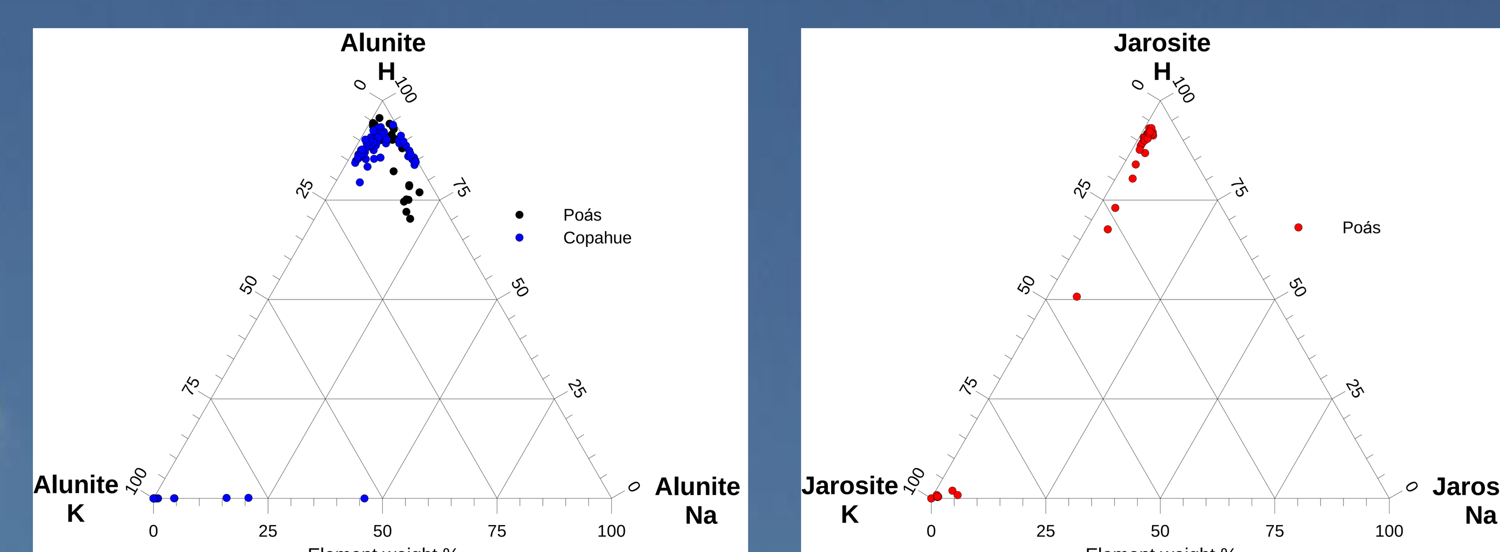
Conceptual model of a volcanic lake

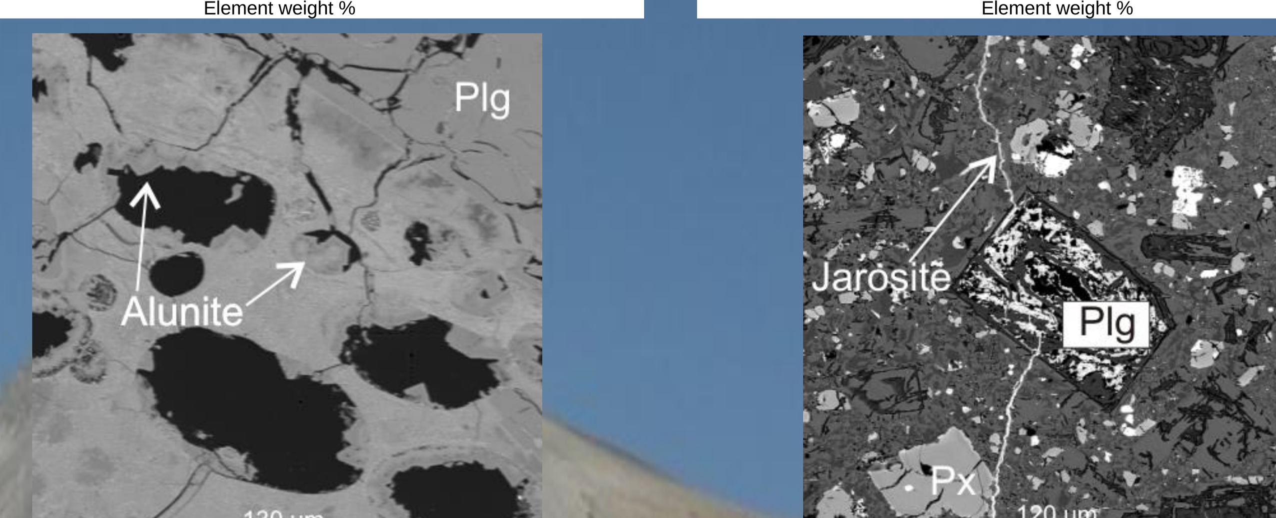
2. SECONDARY MINERALOGY

Amorphous silica, anhydrite and gypsum are conspicuous minerals. Nevertheless, sulfides (pyrite, barite), alunite, jarosite, and other iron and magnesium sulfates are present.

Mineral	Poás	Copahue	Mars	Mineral	Poás	Copahue	Mars
Anhydrite $CaSO_4$	✔		✔	Ferricopiapite $Fe^{3+}_{0.66}Fe^{3+}_4(SO_4)_6(OH)_2{\cdot}20(H_2O)$		✔	possible
Gypsum $CaSO_4{\cdot}2H_2O$	✔	✔	✔	Magnesiocopiapite $MgFe^{3+}_4(SO_4)_6(OH)_2{\cdot}20(H_2O)$	✔	✔	
Jarosite $(K,Na,H)Fe_3(SO_4)_2(OH)_6$	✔	✔	✔	Hexahydrite $MgSO_4{\cdot}6(H_2O)$		✔	✔
Alunite $(K,Na,H)Al_3(SO_4)_2(OH)_6$	✔	✔	✔	Epsomite $MgSO_4{\cdot}7(H_2O)$	✔	✔	✔
Huangite $Ca_{0.5}Al_3(SO_4)_2(OH)_6$	✔			Voltaite $K_2Fe^{2+}_5Fe^{3+}_3Al(SO_4)_{12}{\cdot}18(H_2O)$		✔	
Minamiite $(Na,Ca,K)Al_3(SO_4)_2(OH)_6$	✔			Pertlikite $K_2(Fe^{2+},Mg)_2(Mg,Fe^{3+})_4Fe^{3+}_2Al(SO_4)_{12}{\cdot}18H_2O$		✔	
Rostite $AlSO_4(OH,F){\cdot}5(H_2O)$	✔			Römerite $Fe^{2+}_{0.97}Fe^{3+}_{2.02}(SO_4)_{3.98}{\cdot}13.81(H_2O)$		✔	possible
Halotrichite $FeAl_2(SO_4)_4{\cdot}22H_2O$	✔			Melanterite $FeSO_4{\cdot}7(H_2O)$		✔	✔
Apjohnite $MnAl_2(SO_4)_4{\cdot}22(H_2O)$		✔		Rhomboclase $(H_5O_2)Fe(SO_4)_2{\cdot}2H_2O$	✔		possible
Pickeringite $MgAl_2(SO_4)_4{\cdot}22(H_2O)$		✔		Bilinite $Fe^{2+}Fe^{3+}_2(SO_4)_2{\cdot}22H_2O$	✔		possible
Alunogen $Al_2(SO_4)_3{\cdot}17H_2O$	✔			$Fe_2(SO_4)_3$		✔	✔
Copiapite $Fe^{2+}Fe^{3+}_4(SO_4)_6(OH)_2{\cdot}20(H_2O)$	✔		possible	Khademite $Al(SO_4)F{\cdot}7(H_2O)$			

Sulfates identified by powder XRD at Poás and Copahue, and comparisons with Mars

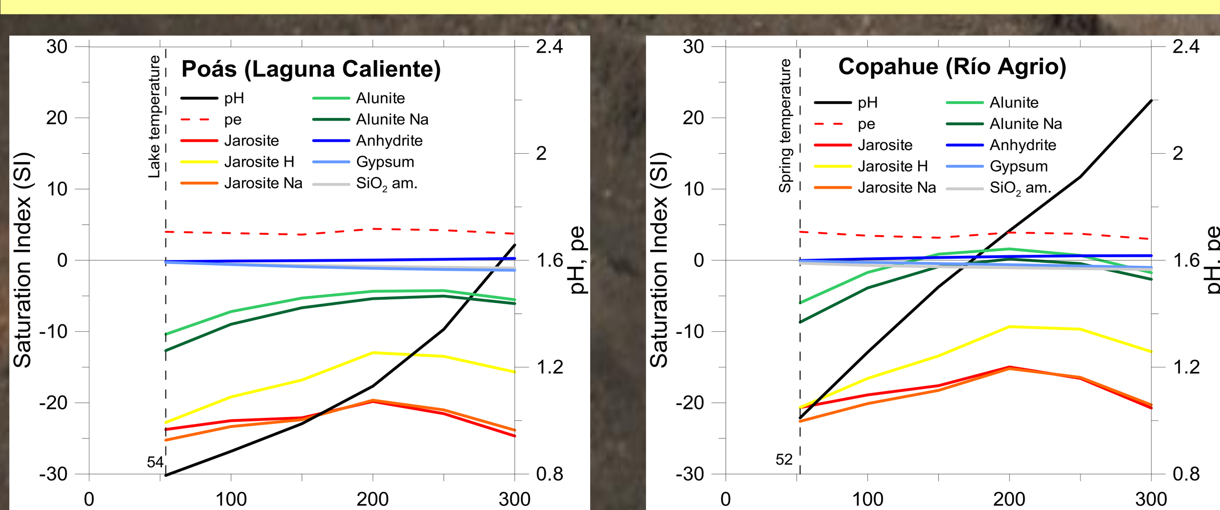




EMPA and EMP images of alunite (Copahue) and jarosite (Poás)

3. SATURATION INDICES

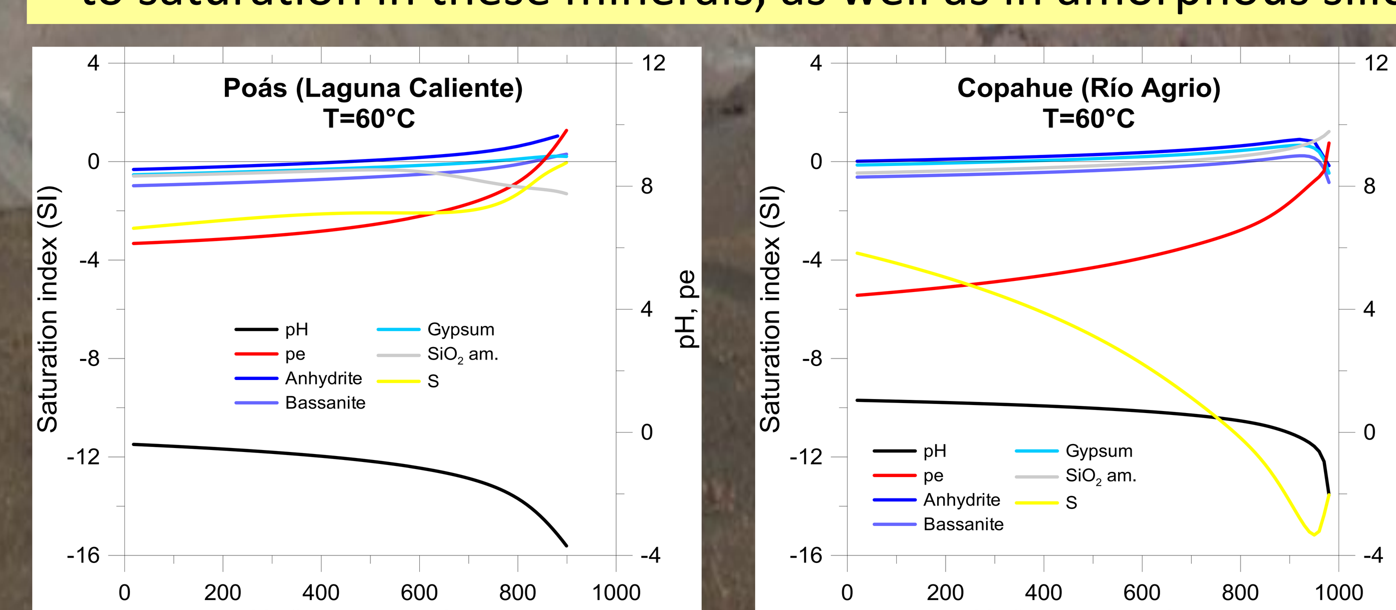
Speciation calculations carried out with PHREEQC (Parkhurst and Appelo, 1999) show that Poás lake (Laguna Caliente) and Copahue spring discharge (Río Agrio) waters are in equilibrium with amorphous silica, anhydrite, cristobalite, sulfur and pyrite; and undersaturated in alunite, jarosite, fluorite and other magnesium and iron sulfates. Increasing temperatures will lead to alunite supersaturation at Río Agrio spring (Copahue).



Mineral saturation states of Poás lake (Laguna Caliente, 30/11/2005) and Copahue (Río Agrio spring, 19/03/2013)

4. REACTION PATH MODELING 1: EVAPORATION

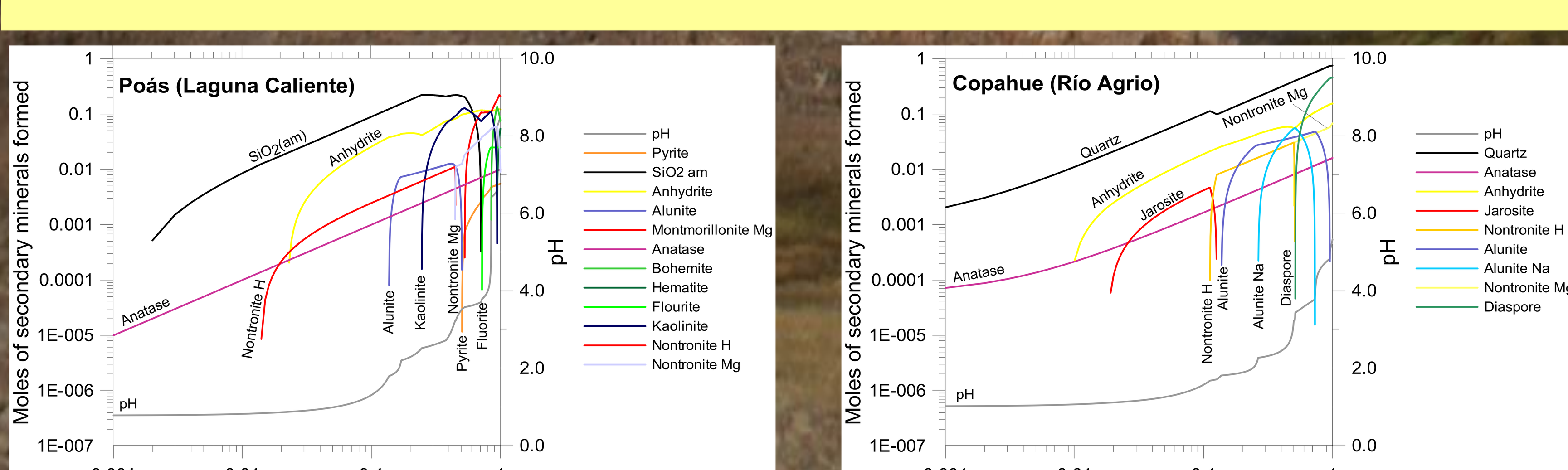
Evaporation at 60°C was modelled with PHREEQC (Parkhurst and Appelo, 1999). Poás waters become oversaturated in anhydrite and eventually in bassanite ($CaSO4{\cdot}0.5H_2O$) and gypsum. Copahue waters are always close to saturation in these minerals, as well as in amorphous silica.



Evaporation models for Poás lake (Laguna Caliente, 27/05/2011) and Copahue (Río Agrio spring, 19/03/2013)

5. REACTION PATH MODELING 2: WATER-ROCK INTERACTION

Reaction between waters and rocks of andesitic composition (Cigolini et al., 1991; Camfield, 2013, pers. com.) were also modeled in PHREEQC (Parkhurst and Appelo, 1999). Anatase, amorphous silica, quartz and anhydrite form at low reaction progress whereas jarosite, alunite, and eventually kaolinite and diaspore with increased rock dissolution.



Water-rock interaction models for Poás lake (Laguna Caliente, 30/11/2005) and Copahue (Río Agrio sring, 19/03/2013)

6. PRELIMINARY CONCLUSIONS

The type of fluids that created the secondary mineral associations at Poás and Copahue are probably chemically similar to the ones that originated some of the sulfate-rich terrains on Mars. In these volcanoes, temperature, redox conditions and extend of reaction (water/rock ratio) play an important role on the type of paragenesis observed.

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