

Mars-type mineral assemblages in terrestrial volcanic lake settings

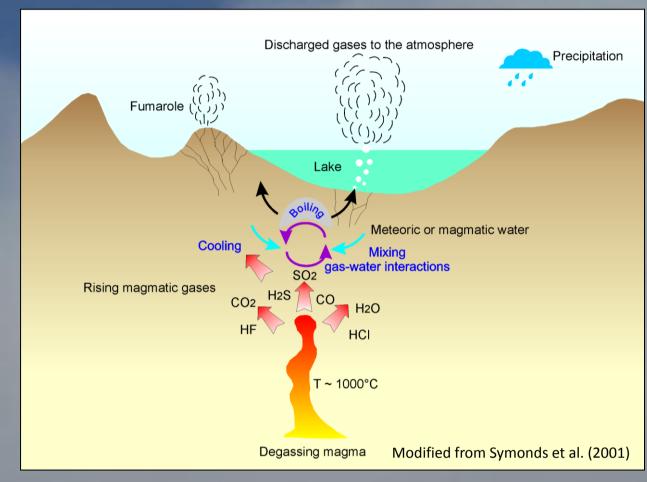
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1. INTRODUCTION

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 SO₄⁻ and Cl⁻ dominated hyperacid crater lakes are promising terrestrial analogues were the formation of Mars-type mineral assemblages can be studied *in situ* (Fig. 1). 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 (Fig. 2).



T ~ 1000°C

Degassing magma Modified from Symonds et al. (2001)

Figure 1. Conceptual model of a volcanic lake

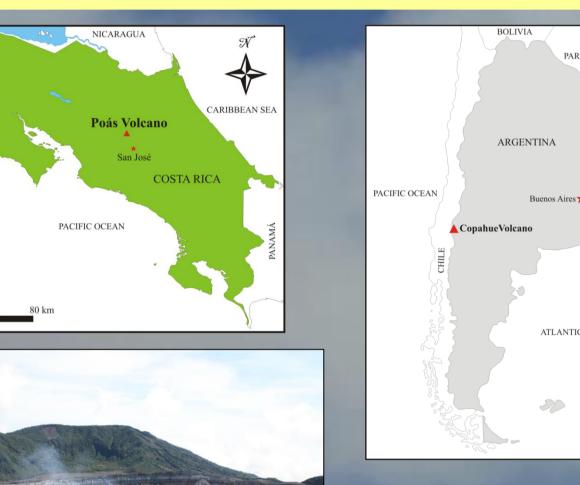
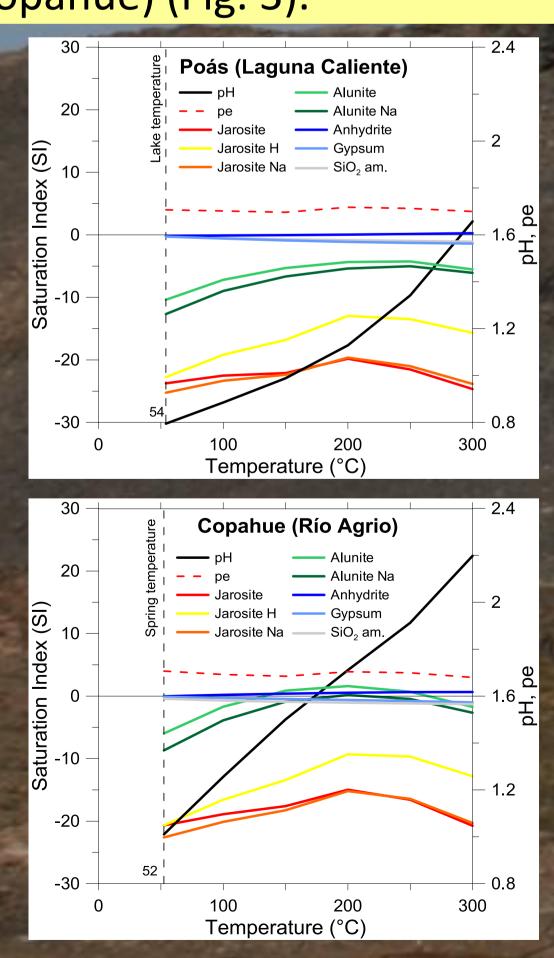


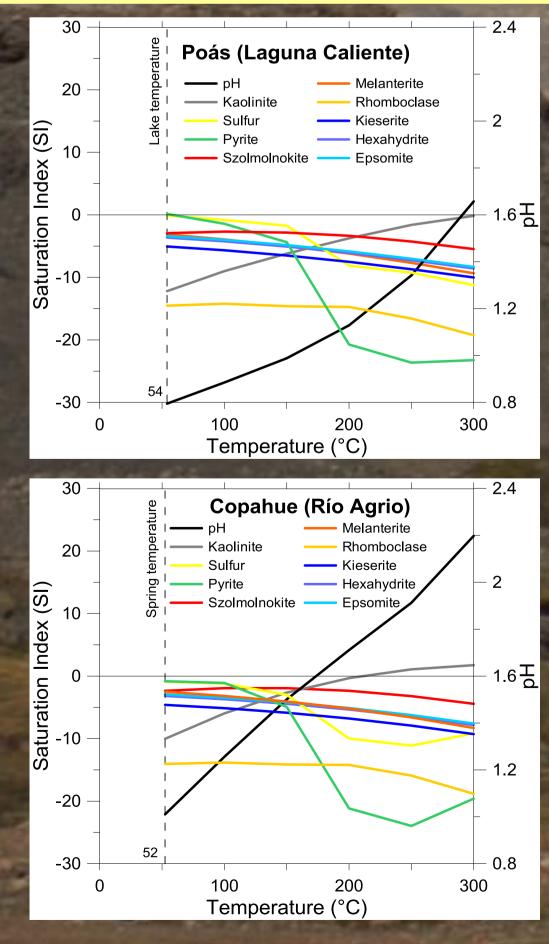


Figure 2. Location maps and views of Poás and Copahue volcanoes

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 would lead to kaolinite, anhydrite and eventually alunite supersaturation in waters with the composition of Río Agrio (Copahue) (Fig. 3).





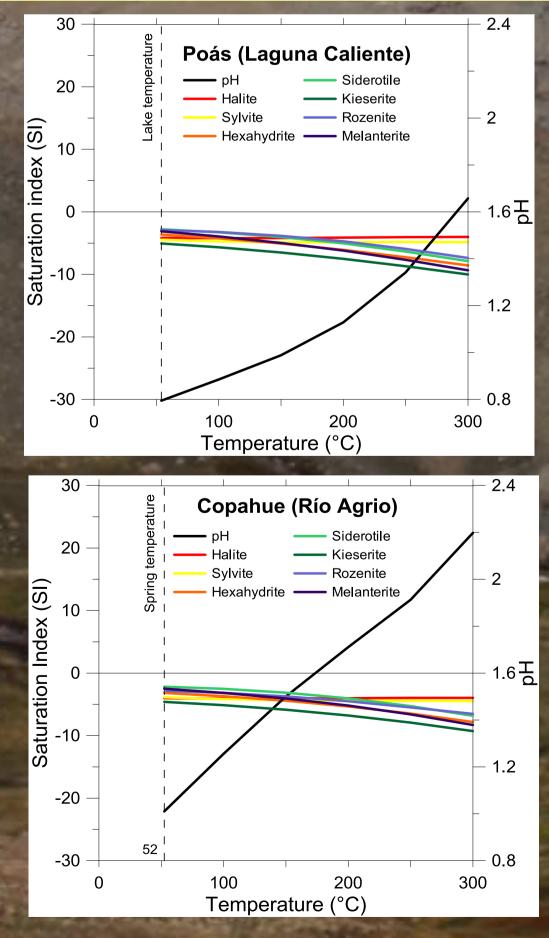


Figure 3. Mineral saturation states of Poás lake (Laguna Caliente, 30/11/2005) and Copahue spring discharge (Río Agrio, 19/03/2013)

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Symonds, R.B., Gerlach, T.M. and Reed, M.H., 2001. Magmatic gas scrubbing: implications for volcano monitoring. Journal of Volcanology and Geothermal Research, 108: 303-341.

Xu, W., Parise, J.B. and Hanson, J., 2010. (H3O)Fe(SO4)2 formed by dehydrating rhomboclase and its potential existence on Mars. American Mineralogist, 95(10): 1408-1412.

2. SECONDARY MINERALOGY

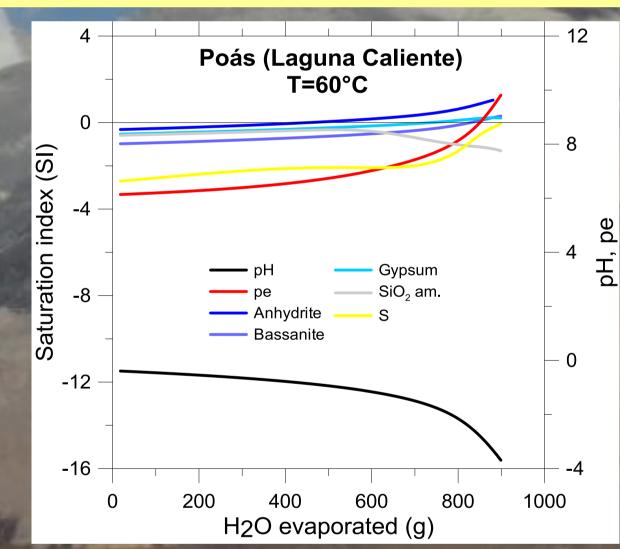
Many sulfate minerals identified at Poás and Copahue have also been recognized on Mars (Table 1).

Table 1. Sulfate minerals identified by SEM, EMPA and XRD at Poás and by XRD at Copahue

Mineral	Poás	Copahue	Mars	Mineral	Poás	Copahue	Mars
Anhydrite CaSO ₄	~		>	Ferricopiapite $Fe^{3+}_{0.66}Fe^{3+}_{4}(SO_{4})_{6}(OH)_{2}\cdot 20(H_{2}O)$		~	possible
Gypsum CaSO ₄ ·2H ₂ O	~	~	~	Magnesiocopiapite MgFe ³⁺ ₄ (SO ₄) ₆ (OH) ₂ ·20(H ₂ O)	✓	>	
Jarosite (K,Na,H)Fe ₃ (SO ₄) ₂ (OH) ₆	✓	>	>	Hexahydrite MgSO ₄ ·6(H ₂ O)		>	✓
Alunite (K,Na,H)Al ₃ (SO ₄) ₂ (OH) ₆	✓	*	>	Epsomite MgSO ₄ ·7(H ₂ O)	✓	>	✓
Huangite Ca _{0.5} Al ₃ (SO ₄) ₂ (OH) ₆	✓			Voltaite K ₂ Fe ²⁺ ₅ Fe ³⁺ ₃ Al(SO ₄) ₁₂ ·18(H ₂ O)		>	
Minamiite (Na,Ca,K)Al ₃ (SO ₄) ₂ (OH) ₆	✓			Pertlikite K ₂ (Fe ²⁺ ,Mg) ₂ (Mg,Fe ³⁺) ₄ Fe ³⁺ ₂ Al(SO ₄) ₁₂ ·18H ₂ O		~	
Rostite AlSO ₄ (OH,F)·5(H ₂ O)	✓			Römerite Fe ²⁺ _{0.97} Fe ³⁺ _{2.02} (SO ₄) _{3.98} ·13.81(H ₂ O)		>	possible
Halotrichite FeAl ₂ (SO ₄) ₄ ·22H ₂ O	✓			Melanterite FeSO ₄ ·7(H ₂ O)		\	~
Apjohnite MnAl ₂ (SO ₄) ₄ ·22(H ₂ O)		~		Rhomboclase (H ₅ O ₂)Fe(SO ₄) ₂ ·2H ₂ O	✓		possible
Pickeringite MgAl ₂ (SO ₄) ₄ ·22(H ₂ O)		~		Bilinite Fe ²⁺ Fe ³⁺ ₂ (SO ₄) ₂ ·22H ₂ O	✓		possible
Alunogen Al ₂ (SO ₄) ₃ ·17H ₂ O	~			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·7(H ₂ O)			

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 (CaSO4-0.5H₂O) and gypsum. Copahue waters are always close to saturation in these minerals, as well as in amorphous silica (Fig. 4).



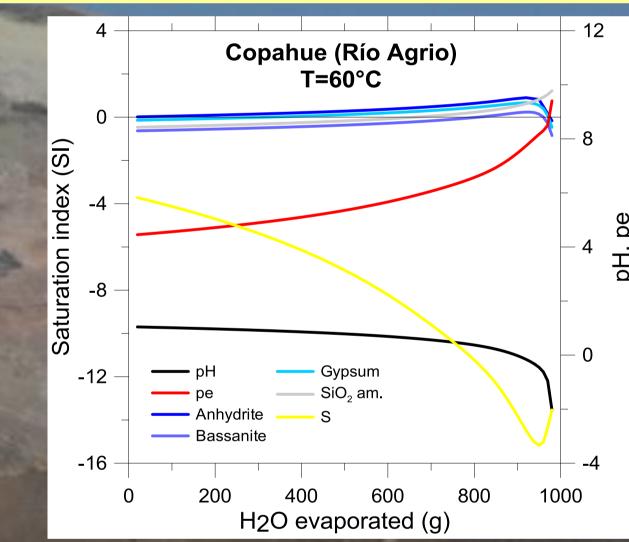
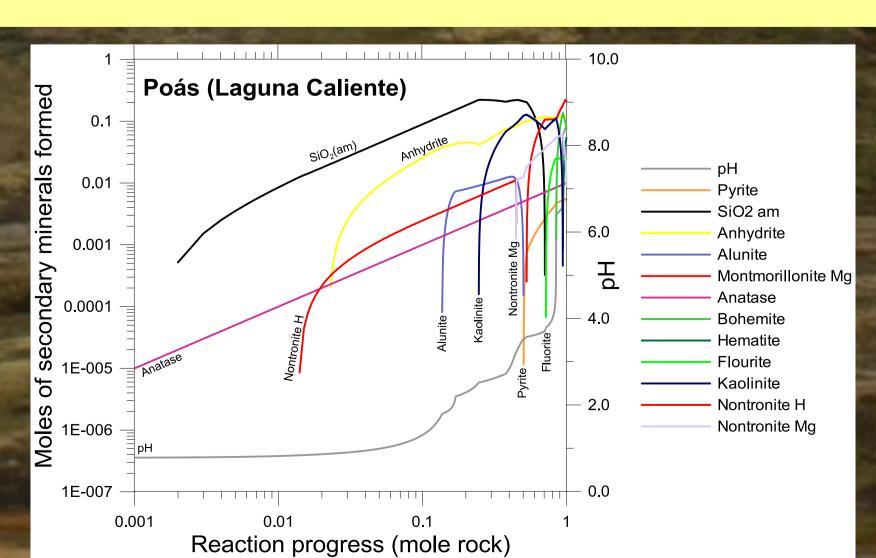


Figure 4. Evaporation models for Poás lake (Laguna Caliente, 27/05/2011) and Copahue spring discharge (Río Agrio, 19/03/2013)

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 and anhydrite form at low reaction progress whereas alunite, kaolinite, and eventually pyrite and fluorite appear with increased rock dissolution (Fig. 5).



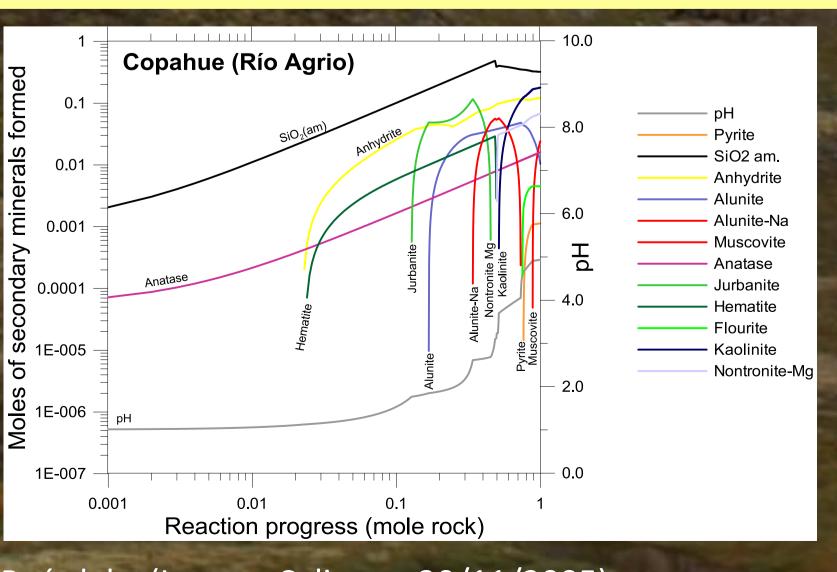


Figure 5. Water-rock interaction models for Poás lake (Laguna Caliente, 30/11/2005) and Copahue spring discharge (Río Agrio, 19/03/2013)