

Natural fluctuation of sulfur species (SO₂, H₂S and S₈⁰) in volcanic fumaroles

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This study describes how the presence of a *dissipative structure*, caused by non-equilibrium conditions in volcanic ducts, is able to reveal relationships affecting the variation in time of concentration of sulfur species SO₂, S₈⁰ and H₂S observed in fumaroles. Based on the general theory of non-equilibrium (Prigogine, 1969) a three components thermodynamic-statistical model is proposed to explain short-time (hours) variations of relative concentrations of sulfur species, while a volcanic fluid rises to the surface. The comparison between theoretically elapsed, and measured concentrations of SO₂, S₈⁰ and H₂S in fluid discharges from different volcanoes (from Italy, Costarica and Mexico) suggests that, in analogy with studies conducted by Prigogine on energy transfer and fluid motion in biological systems, the formation of non-equilibrium *dissipative structures* is able to explain the observed variations in composition in the fumarolic discharges. The most important theoretical result is the identification of relations existing among: *i*) periodicity (hours) of oscillations, *ii*) amplitude of oscillations and *iii*) entropy excess of the *dissipative structure*.

Another important result is that, under the theory of compositional (constrained) data analysis, the sulfur species data-set can be investigated as an independent sub-system, drawn from the whole composition. Consequently, sulfur species are governed by similar laws, when different volcanic systems are considered, and this makes ideal conditions to investigate the role of the *dissipative structures* formed in different fumaroles and different volcanoes.

From a practical point of view an important consequence of our study for the community involved in the geochemical monitoring of volcanic activity is that, the proposed sampling method able to reveal the presence of the *dissipative structure* should (must) be extended to any active volcanic system in the World having SO₂ in the fumarolic gas. In fact, unless an entire period of the natural oscillation covering the dynamic equilibrium caused by the presence of the *dissipative structure* is reached in the relative specific fumarolic field, no reliable data on sulfur species can be gathered.

References

[1] Prigogine, I., 1969. Structure, dissipation and life. In: "Theoretical Physics and Biology", M. Mariolis (ed.), North Holland Publish., Amsterdam, The Nederland, 212 pp