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Jean-Christophe Sabroux, Pierre Briole, Michele Cara

► **To cite this version:**

Jean-Christophe Sabroux, Pierre Briole, Michele Cara. Monitoring hydrogen in soil gases of Mount Etna by means of a new chemical transducer. Meeting on the 1983 Etna eruption, May 1984, Catane (Italie), Italy. hal-04298823

**HAL Id: hal-04298823**

**<https://hal.science/hal-04298823v1>**

Submitted on 21 Nov 2023

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MONITORING HYDROGEN IN SOIL GASES OF MOUNT ETNA BY MEANS  
OF A NEW CHEMICAL TRANSDUCER

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J.C. SABROUX      *Centre des Faibles Radioactivites, C.N.R.S.-C.E.A.,*  
P. BRIOLE        *Avenue de la Terrasse, 91190 Gif sur Yvette, France*  
M. CARA           *Istituto Internazionale di Vulcanologia, C.N.R.,*  
                      *95125 Catania, Italia*

ABSTRACT

A chemical transducer including a marketed solid state sensor, the electrical conductivity of which increases in presence of combustible gases, had been used for monitoring the hydrogen content of soil gas at Mount Etna during the last two months of its 1983 eruption. A significant (almost twofold) decrease of hydrogen concentration was correlated with the end of the eruption. The transducer, due to its high sensitivity, reproducibility, long life expectancy and low cost, proved feasible for long term monitoring of soil gas in volcanic areas.

## INTRODUCTION

The post-May 1980 eruptions of Mount St. Helens clearly demonstrated that accurate monitoring of volcanic activity implies periodic field measurements near the vents together with continuous records provided by telemetered systems (SWANSON *et al.*, 1983). As far as geophysical methods are concerned, such a procedure (e.g. repetition of a geodetic or gravity network in the context of continuous seismic recording) gave rise to some successful predictions. Nevertheless, geochemical surveillance still does not benefit from a transducer — a device converting a chemical potential into an electrical parameter liable to be telemeasured — offering the reliability and versatility of a seismometer. Moreover, volcanic activity often precludes, even on a discontinuous basis, accurate field measurements within the active areas. Up to now, only two gas sensors have been subjected to full scale experiments in the field. The first monitoring station designed for recording the "reducing capacity" (mainly  $H_2$  concentration) of soil gases by means of a small  $H_2/O_2$  fuel cell was established in 1973 in a fumarole in the summit crater of Kilauea, Hawaii, and since then duplicated with significant improvements on several active volcanoes and Californian seismogenic faults. In 1984, most of these monitoring stations are linked with the USGS in Reston, Virginia, via a geostationary satellite (SATO *et al.*, 1983). The feasibility of the second sensor, an oxygen fuel cell using stabilized zirconia as the solid electrolyte, was first demonstrated by SATO and WRIGHT (1966)

in holes drilled into the crust of the Makaopuhi lava lake, Hawaii. A nearly similar sensor design has worked out in a hot (*ca.* 700°C) fumarole of Momotombo volcano, Nicaragua (SABROUX *et al.*, 1983). The results are encouraging, but such experiments, carried out on a small scale, still did not meet with general acceptance.

In order to extend the applicability of geochemical methods to volcanic surveillance, more R & D efforts for designing new chemical transducers are clearly needed. Such transducers should operate reliably in volcanic fluids, *i.e.* in fumarolic, atmospheric or soil gases, thermal springs, crater lakes, etc..., which may carry a chemical information from the depth.

#### HYDROGEN IN VOLCANIC FLUIDS

The chemical transformations undergone by fluids circulating in an active volcano are dominated by the dramatic contrast in redox conditions between the surface ( $P_{O_2} = 0.21$  atm) and the depth (e.g.  $P_{O_2} = 10^{-38}$  atm in a hydrothermal reservoir at 200°C), where reduced gases ( $H_2$ , CO and  $CH_4$ ) are produced at the expense of water and carbon dioxide. These gases are transported towards the surface by diffusion or convection. Changes in permeability and in heat flow, both relevant to volcanic activity, or ascend of magma towards the surface would produce significant changes in the emission rates of these gases and consequently in their concentration in the soil atmosphere. As hydrogen

is more mobile, less soluble and more readily amenable to detection by means of solid state sensors, it is the best candidate for geochemical prediction of volcanic activity. Its modes of occurrence in natural systems are summed up by SATO *et al.* (1983). They will briefly be summarized here with some additional references :

(1) Degassing of a magma body freshly intruded in the upper crust : numerous petrological and field studies showed that they oxidize slowly by means of preferential diffusion of hydrogen towards the surface (SATO, 1978). The depth of crystallization of such a magmatic body seems to control sharply the rate of H<sub>2</sub> loss ( SATO and VALENZA, 1980).

(2) Water-rock or -magma interaction : as reveals the high hydrogen content ( $P_{H_2}/P_{H_2O}=10^{-3}$ ) of most geothermal fluids, ferrous oxides making up minerals reduce liquid water and steam through the mechanism :



Reaction (I) holds even at hydrothermal temperatures (*ca.* 200°C).

Industrial hydrogen production by means of water-magma reaction was theoretically investigated by NORTHROP *et al.*, 1978.

Hydrogen occurrence was also reported from a variety of deep crustal and mantle rocks such as ophiolites at still lower temperatures, in this later case associated with highly alkaline waters (NEAL and STANGER, 1983), high pH and low Eh in this particular environment being close to the water stability lower limit.

(3) Chemisorption of water (even at low temperature) on the surface of freshly crushed silicates : it produces hydrogen through the following mechanism :



SUGISAKI *et al.* conclude that  $\text{H}_2$  concentration could provide clues for relative dating of Quaternary active faults. Continuous monitoring already proved feasible as a means for earthquake prediction (WAKIKA *et al.*, 1980).

Hydrogen is also produced from organic substances during anaerobic decay but simultaneously consumed by other microorganisms in the same habitat (SCHLEGEL, 1974), otherwise, besides  $\text{CO}_2$ , it would be the most important atmos trace gas of organic origin. Due to the low biomass per unit area of volcanic soils in active zones biogenic hydrogen should not interfere with hydrogen of magmatic or hydrothermal origin. Moreover due to its low background concentration (0.5 ppm) atmospheric contamination of hydrogen in soil is not significant.

#### A NEW CHEMICAL TRANSDUCER

Most gas sensors postulated for volcano surveillance (GANTES *et al.*, 1983) are of the electrochemical cell design, which directly converts a difference in chemical activity across an electrolytical membrane into an electric potential. Such cells can operate only when a refe-

rence atmosphere is provided on one side of the membrane. If an internal reference is used, a high impedance voltmeter is to be implemented for measuring the cell's potential in order to lengthen the life expectancy of the reference. Yet since the change in conductance  $G$  accompanying the reversible chemisorption of gases at the surface of certain materials (metals, oxides or chalcogenides) has been discovered (BRATTAIN and BARDEEN, 1953), numerous gas sensors of the non-electrolytical type were experimented. Nevertheless, among the various metal-oxide semiconductor benefiting from the appropriate characteristic,  $\text{SnO}_2$ ,  $\text{ZnO}$  and  $\gamma\text{-Fe}_2\text{O}_3$  are the only ones to have reached a commercial use.

A sintered n-type semiconductor device mainly composed of tin dioxide has been marketed since 1968 by Figaro Engineering Inc. : the TGS (Taguchi Gas Sensor) model 812 is depicted in Fig.1a. The semiconductor material is mounted on a ceramic tube on which platinum electrodes are printed. A heater coil (650 mW) rising the temperature up to a level where reversible chemisorption takes place (*ca.* 200°C) is inserted into the tube. In the presence of combustible gas (hydrogen, carbon monoxide, hydrogen sulfide, hydrocarbons and organic solvent vapours), the conductance of the sensor increases. For example, when exposed to 500 ppm of hydrogen, the increase conductance of the TGS is 45 times its conductance in air at 20°C and 65% relative humidity ( $G_0=70 \text{ k}\Omega$ ). Such a change of conductance in the  $10^{-4} - 10^{-5} \Omega^{-1}$  range does not require a sophisticated circuit to transmit the signal. In the laboratory and in the field we used the basis measuring circuit depicted in Fig.2. The output voltage  $V_m$  is directly proportional to the conductance  $G=1/R$  of the sensor as long as  $R \ll R_s$ .

## GAS DETECTING MACHANISM

A microscopic operating model valid for a thin-film  $\text{SnO}_x$  sensor was developed by WINDISCHMANN and MARK (1979). It can be generalized for a bulk device such as TGS. It assumes that negative ions of oxygen ( $\text{O}^-$  or  $\text{O}_2^-$ ) are chemisorbed on the surface of the semiconductor. From the catalytic oxidation of a combustible gas on the sensor surface by chemisorbed oxygen, it ensues the emission of an electron into the conduction band of the semiconductor, which subsequently lowers its resistance. If  $G_0$  is the conductance of the sensor in air free of combustible gases, its conductance  $G$  in an air mixture with the concentration  $C$  of combustible gas is

$$G = K G_0 C^\alpha \quad (1)$$

with the sensitivity  $\alpha \approx 1/2$ , in the range of concentrations where hold the fundamental assumptions of the model. For example, the combustible gases must remain trace constituents in order not to lower significantly the oxygen partial pressure of the background atmosphere.

## THE TRANSDUCER DESIGN

Despite its ease of handling, long life expectancy, reliability and low cost, all advantages which make it suitable for making up a chemical transducer, the TGS cannot be used directly to monitor the hydrogen (or combustible gas) content of the soil gases in a volcanic area. In order to protect it against groundwater and corrosive gases, it was set

into a Teflon cylinder and allowed to communicate with the outer atmosphere through a Teflon membrane (Fig.1b). The inner volume of the cylinder was filled by silica-gel which buffers the water at a very low value and absorbs slightly polar molecules such as  $\text{SO}_2$  and  $\text{H}_2\text{S}$ .

With regards to the TGS in rough, this design provides a lot of advantages :

- (1) The sensitivity and detectivity are increased more than twofold and a tenfold respectively (Fig:3) when  $P_{\text{H}_2\text{O}} = \text{cte}$ , without altering the repeatability.
- (2) The temperature dependance is lowered (Fig.4) and the sensor is thermally insulated.
- (3) Owing to the permeability characteristics of the membrane, the selectivity of the sensor to hydrogen is enhanced (Fig.5). The relationship (1) becomes linear ( $\alpha=1$ ) in a wide range of low concentrations (say from 1 to 500 ppm),

$$G = K G_0 C \quad (2) \quad (\text{see Fig.6})$$

#### FIRST EXPERIMENTS ON MOUNT ETNA

This transducer was first experimented in the field on Momotombo volcano, Nicaragua (J.C. SABROUX, unpublished results).

The transducer was driven into a 50cm deep hole dug in the soil of Mount Etna at 1736m a.s.l., close by the Geophysical Observatory of Serra la Nave-Pineta where the mains were available for energizing the sensor and the strip chart recorder used for data acquisition (Fig.7). This spot is near by the continuation of the N.S. active fissure which opened on March 28 and delivered the destructive 1983 lava flow (ca.  $10^8 \text{ m}^3$ ). The horizontal distance from the active vents, 700m

higher, is 3.5 km (Fig.8). Figure 9 is a transcription (one point per day) of the records obtained between June 19 and September 2, 1983. Changes in conductance of the sensor during this period reveals variations in hydrogen concentration between 20 and 50 ppm. This figures are within the range of  $H_2$  concentrations found by SUGISAKI *et al.* (1983) in several seismogenic faults of Japan and by SATO and McGEE (1981) in the soil of Mount St. Helens (monitoring site 1.2 km from the nearest fumaroles) although in this later case, most measurements yielded "negative" concentrations relative to ambient air used as reference, and often richer in  $H_2$  than soil gas<sup>(1)</sup>. This certainly occurs on Mount Etna, where strong  $CO_2$  anomalies above the normal atmospheric background had been detected (CARBONNELLE *et al.*, 1982), but does not jeopardizes the relevance of our measurements since our transducer dispense with a reference.

Although the results shows a conspicuous decrease in  $H_2$  concentration accompanying the end of the eruption (6 August 1983), this feature is difficult to interpret in the absence of any other correlative observations (e.g. seismicity, tiltmetry or gravimetry). A withdrawal of the magma from the dike feeding the lava flow is the most straightforward explanation of the hydrogen concentration decrease in the soil atmosphere. On the other hand, the regular increase of concentration between June 19 and July 29, not amenable to the "transitional period" of the sensor

(1) This drawback has been avoided since by feeding the sensor by bottled oxygen (SATO *et al.*, 1984).

(a few days in this case), has not yet received a satisfactory explanation and ought to be examined in the light of existing geophysical observations. An instrumental shift can be ruled out as  $G_0$  of the transducer in hydrogen-free air as well as its sensitivity did not vary between the beginning and the end of the experiment. Obviously the duration of this test, satisfactory for technological evaluation, was too short for deriving sound volcanological interpretation of the data and more experience is to be gained in other volcanic areas.

## CONCLUSION

In designing a sensor for monitoring a chemical parameter in volcanic fluids, one has to keep in mind that repeatability and detectivity of the sensor are more needed than its accuracy and selectivity. Based on a marketed sensor detecting combustible gases, the chemical transducer we designed and tested in our laboratory and in the field displays the whole set of features — including low cost — required for such an equipment. Its relatively high steady electrical consumption (650mW) is certainly a drawback for autonomous monitoring stations including a teletransmitting system, but is below the performances of currently available solar-panels. On the other hand, such a transducer does not need a reference to operate and seems to be recalibration-free for long periods (say, several months). The preliminary data obtained with this transducer on Mount Etna during the last two months of the 1983 eruption are encouraging as they revealed significant variations of hydrogen content in the soil, well within the range of concentration attainable by the transducer. For the one who agrees with the statement of SATO *et al.*, (1983), "that monitoring

hydrogen in volcanic areas would give the earliest indication of the intrusion of a fresh, unoxidized magma into the upper crust", a longer test on a smaller volcano, already continuously monitored by means of a dense geophysical network, cannot seem nothing but worthwhile.

#### ACKNOWLEDGEMENTS

We thank Prof. BLANCO, Director and the staff of the Geophysical Observatory of Serra la Nave-Pineta who provided field facilities for implementing our gas monitoring station on Mount Etna. This research was granted by the PIRPSEV of the French C.N.R.S.

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## CAPTIONS OF FIGURES

Figure 1a. Photographie of the TGS, Figaro Engineering Inc., Tokyo

Figure 1b. Cross section of the sensor. The choice of inner volume and membrane thickness is a matter of compromise between life expectancy of silica-gel and response time of the transducer, the later being of minor importance as long as slow variations are concerned. For the Etna experiment we chose a  $50\mu$  thick Teflon membrane.

Figure 2. Diagram of the hydrogen monitoring circuit. The choice of  $R \ll R_s$  allows tension  $v_m$  to be proportionnal to the TGS conductance in a wide range of concentrations.

Figure 3. Response curve of the transducer obtained by successive injections of hydrogen in the experimental circuit. Each level corresponds to an increase of 5ppm.

Figure 4. Relationship between conductance and temperature for several hydrogen concentrations.

Figure 5. Response curves against several combustible gases at the same concentration (50ppm). Furthermore the shape of the curves allows one to appreciate the response time of the transducer provided with a  $50\mu$  thick membrane.

Figure 6. Relationship between conductance and hydrogen concentration (deduced from Fig.3). The relation is linear except at very low hydrogen concentrations.

Figure 7. Observatory of Serra la Nave-Pineta into which data acquisition systems were established during the eruption of Mount Etna, 1983.

Figure 8. Sketch map of the lava flow close by the monitoring station.

Figure 9. Relative variations of conductance of the sensor set in the soil of Mount Etna (increase of conductance is approximately propor-

tionnal to hydrogen concentration). The vertical arrow indicates the end of effusive activity (morning of August 6).  $G/G_0 = 12$  corresponds approximately to 25ppm of hydrogen ( $G_0 \approx 400k\Omega$ ).