

**MARS OXIDANT: PROOF OF CONCEPT AND QUANTITATIVE ANALYSIS.** Friedemann Freund<sup>1</sup>, Aaron Staple<sup>2</sup>, Paul Gosling<sup>3</sup>, and Warren Belisle<sup>4</sup>; <sup>1</sup>NASA Ames Research Center, Moffett Field, CA 94035 (ffreund@mail.arc.nasa.gov); <sup>2</sup>Stanford University, <sup>3</sup>San Jose State University, <sup>4</sup>Lockheed-Martin Engineering.

**Introduction:** Textbooks make us believe that in every silicate mineral, on Earth, Mars and elsewhere, the oxygen anions exist in just one oxidation state, namely 2- as in  $O^{2-}$ . Yet, a surprisingly large fraction of the oxygen anions in rock-forming minerals may exist in a more oxidized form, namely the 1- state, as  $O^-$  in peroxy. This has far-reaching consequences for understanding the Mars soil oxidant and its biocompatibility.

The change from the 2- oxidation state to the 1- states starts with hydroxyls  $O_3Si-OH$  that become incorporated into nominally anhydrous minerals whenever such minerals crystallize in an  $H_2O$ -laden magma [1]. Magmatic systems on Mars are surely  $H_2O$ -laden. During cooling, probably between 400-600°C, as the structures of the minerals are already frozen with respect to major diffusional rearrangements,  $O_3Si-OH$  pairs reshuffle their electrons in such a way as to turn into peroxy links,



This reaction is a classical redox reaction. What is quite unusual about it is (1) it takes place in the mineral structure, (2) oxygen acts as the electron donor, reducing hydroxyl protons to  $H_2$ , while oxidizing oxygen from  $O^{2-}$  to  $O^{1-}$ , and (3)  $H_2$  molecules may diffuse out over geological time, leaving the rock (system) with excess oxygen in form of peroxy.

Because this redox reaction takes place when the minerals are no longer in equilibrium, it is thermodynamically allowed. Thus, even minerals that are considered reduced and that do contain reduced transition metal cations can acquire peroxy during their cooling from magmatic temperatures. If  $H_2$  molecules diffuse out, the peroxy left behind represent a true oxygen excess.

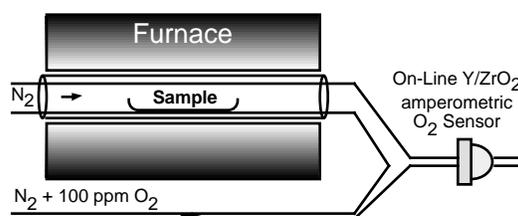
For some time we thought that the concentration of peroxy in common rock-

forming minerals would be relatively small, maybe in the tens ppm range. Using a new analytical technique we are now finding unexpectedly high peroxy concentrations. For instance in  $MgO$  crystals, grown from a highly reduced melt, the peroxy concentration exceeds 10,000 ppm per  $10^6 O^{2-}$ . In a granite from Barre, VT, we find an average peroxy content around 3,000 ppm. In andesite, a volcanic rock believed to be present on Mars, we find a lower but still significant peroxy concentration of about 300 ppm.

Our analytical technique is simple. We take advantage of the fact that peroxy becomes thermally unstable upon heating above 400-600°C, disproportionating [2]:

$$O_3Si^{OO}/SiO_3 \rightarrow O_3Si^{O}/SiO_3 + 1/2 O_2 \quad (2)$$

For analysis we crush minerals or rocks to a fine powder and heat them (9°C/min) in a stream of  $N_2$  (40 ml/min containing 50 vol.-ppm  $O_2$ ), measuring the  $O_2$  evolution by means of an amperometric Y/Zr  $O_2$  oxygen sensor developed for Mars [3].



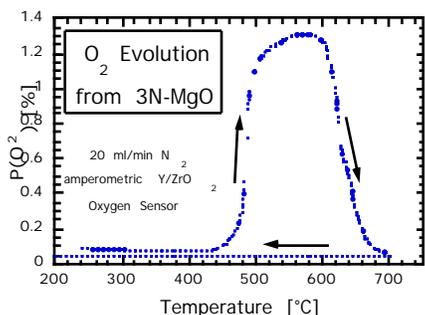
**Figure 1:**  $O_2$  evolution experiment using an amperometric Y/ZrO<sub>2</sub> oxygen sensor.

**Figure 1** shows the set-up for the  $O_2$  evolution measurements. The two gas streams, 20 ml/min each, one of pure  $N_2$  and the other of  $N_2 + 100 \text{ ppm } O_2$ , are combined after the furnace, because the operation of the Y/Zr  $O_2$  oxygen sensor requires a small  $O_2$  partial pressure.

**Figure 2** shows the  $O_2$  evolution from a crushed high purity (99.9%)  $MgO$  single crystal, measured with the Y/Zr  $O_2$  oxygen sensor and verified by GC

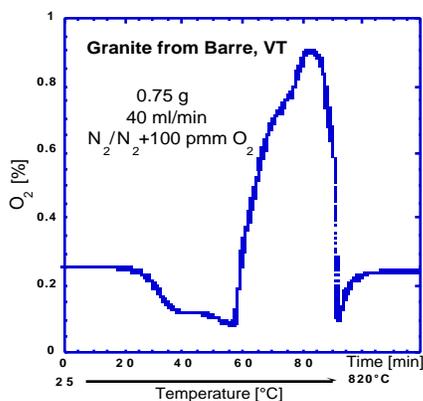
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analysis. The  $O_2$  evolution begins around  $500^\circ\text{C}$  and continues up to  $600^\circ\text{C}$ .



**Figure 2:**  $O_2$  evolution from a crushed melt-grown  $MgO$  crystal.

The total amount of  $O_2$  released indicates that more than 1% of all  $O^{2-}$  anions in the  $MgO$  structure had converted to peroxy,  $O_2^{2-}$ . At the same time, as predicted by eq. (1), this  $MgO$  crystal contains  $H_2$  molecules which give rise to a distinct IR band of H-H stretching combining with a lattice phonon at  $4150\text{ cm}^{-1}$ . Given the fact that the  $MgO$  crystal had been grown the under extremely reducing conditions of a carbon arc furnace, the occurrence of peroxy is a confirmation of the type of redox conversion postulated by eq. (1).



**Figure 3:**  $O_2$  evolution from granite from Barre, Vermont.

**Figure 3** shows the  $O_2$  evolution from a crushed sample of a granite from Barre, VT, measured in the same manner.

The amount of  $O_2$  released corresponds to about 3,000 ppm peroxy oxygen. At the time of writing of this abstract we do not yet know which minerals in granite are the peroxy-bearing and how much peroxy they contain.

**Figure 3** also shows that, during heating, some  $O_2$  in the carrier gas is consumed by side reactions either due to the combustion of reduced gases that evolve (CO or organics) or due to the oxidation of  $Fe^{2+}$  and other transition metal cations.

Mars is believed to have once been replete with water. Therefore, martian magmatic systems most surely were and may still be  $H_2O$ -laden. The minerals in martian igneous rocks that make up the surface regolith are likely to contain the same peroxy links as terrestrial rocks from similar environments.

**Conclusion:** (1) The amperometric Y/Zr  $O_2$  oxygen sensor [3] could be used to assess the amount of reduced gases and of molecular oxygen evolving from the Mars soil on heating. (2) Understanding the role the peroxy may play in igneous rocks on the surface of Mars may be crucial to understand the nature of the Mars oxidant. (3) This is crucial to understanding the properties of Mars soil and its biocompatibility.

### References:

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3. Sridhar, K. R., and Blanchard, J. A., Electronic conduction in low oxygen partial pressure measurements using an amperometric zirconia oxygen sensor, *Sensors and Actuators B* 59.1 (1999): 60-67.