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Ozone generation by rock fracture: Earthquake early warning?

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We report the production of up to 10 ppm ozone during crushing and grinding of typical terrestrial crust rocks in air, O_2 and CO_2 at atmospheric pressure, but not in helium or nitrogen. Ozone is formed by exoelectrons emitted by high electric fields, resulting from charge separation during fracture. The results suggest that ground level ozone produced by rock fracture, besides its potential health hazard, can be used for early warning in earthquakes and other catastrophes, such as landslides or land shifts in excavation tunnels and underground mines. © *2011 American Institute of Physics*. [doi:10.1063/1.3660763]

Earthquakes can inflict enormous costs in lost lives and property damage. Although they are unpredictable due to their chaotic nature, earthquakes may be detected early through multiple phenomena that precede them by up to several days. Researchers have been actively seeking reliable identification of seismic precursors with the goal of using them to enable early warnings to help minimize tragedy. So far, phenomena associated with rock deformation or fracture, including the emission of electromagnetic (EM) waves, atmospheric ions, and radon,[1] have been unsuccessful as early warnings to minimize tragedy.[2] On the other hand, there is ample (mostly anecdotal) evidence that animals can anticipate earthquakes,[3–5] but the cause of this sensitivity is elusive, with no conclusive correlations with physical precursors that could be used for earthquake early warning.

Could the link between pre-seismic animal behavior and electrical phenomena be ozone? This gas, easily detectable at ~7 ppb by humans,[6] is a by-product of electrical discharges in air, which could accompany rock fracture. In fact, ozone has been reported to appear months prior to an earthquake in the vicinity of the epicenter.[3]

Here, we present evidence for ozone generation during rock fracture in air, advance a model that accounts for its production, and propose that rock fracture may be a frequent source of ground ozone pollution in different environments.

We fractured single igneous and metamorphic rocks in air at atmospheric pressure within a small (~5 L) acrylic chamber with a 0.2 cm^2 vent. Chamber gases were pumped at 1 L/m into a dual-beam photoelectric ozone monitor (2B Technologies 205) before, during, and after fracture. The detector has an accuracy of 2% or 1 ppb, and a sensitivity of 0.1 ppb; it is crosschecked with an ozone calibrator (Eco Sensors OG-3). The time constant for ozone decay is ~300 s, determined by the chamber volume, pumping speed and adsorption, desorption and reactions from walls, and the sample and rock fragments. Background ozone is measured to fluctuate around 1.5 ppb.

Initial experiments were done by compression in a vice until fracture, and recording the ozone emission in real time. Fig. 1 shows results for a piece of granite, ~30 mm × 30 mm × 15 mm in size. We found a strong variability in ozone production (a factor of 4) likely due to uneven contact of the rough rocks with the vice, in addition to the inconstant amount of pre-existing cracks in the samples. Therefore, we devised a more controlled method of fracture, systematic grinding, a method known to result in the emission of EM waves.[7]

Fracturing was done with a 7.1 mm silicon carbide grinding stone attached to a vertical high-speed (30 k rpm) Dremel. Similar results were obtained with an alumina bit. The rocks, fixed in a polytetrafluoroethylene jig, were abraded for 260 s, after which the chamber atmosphere was pumped into the ozone detector through a 5-6 μm PTFE particle filter. Figure 2 shows the results of the grinding experiments on rocks of differing petrology. Initially, the ozone signal increases due to the transit time of the gas to the detector, then peaks and decays as gas is pumped from the chamber. The strongest measured signal after 260 s grinding was 10 600 ppb, from rhyolite (for context, an extended exposure to 100 ppb ozone is considered unhealthy for most humans[8] and lowers the yield of agricultural crops[9]). The total amount of ozone produced in the 260 s grinding can be estimated from the integral of the peaks and the pumping speed and are (in micro moles): 0.12 (basalt), 0.1 (gneiss), 0.4 (granite), 0.7 (rhyolite), and 0.3 (schist).

The fact that similar levels of ozone were produced both in compression fracture with the vice and, by grinding with two different bit materials, show that fracture, and not bit-rock rubbing, is the cause of ozone production. It also rules out heating during grinding as a significant factor in ozone production, besides the fact that heating is not a plausible mechanism of ozone production from rocks.

To determine if the production of ozone is dependent primarily on atmospheric oxygen, silicate material, or gas released during rock fracture, we measured the effects of varying the gas environment. Gasses with and without oxygen were chosen for the study. For these experiments, we ground rhyolite for 260 s at 1 atm, detecting ozone during rock fracture only in air and in oxygen, and to a lesser extent, in carbon dioxide atmospheres. No ozone was detected when grinding in nitrogen or helium, as shown in Fig. 3. This implies that oxygen in the environment of the fracture region is necessary for the production of ozone.

We propose the mechanism for ozone generation is fractoemission of electrons, a processes initiated by large electric fields induced by charge separation due to fracture, which

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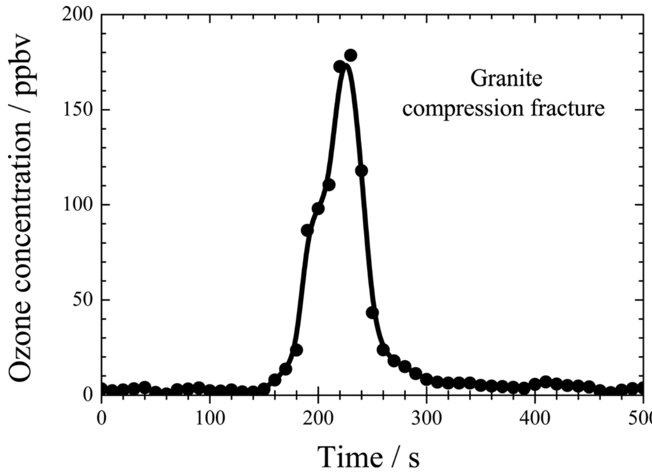

FIG. 1. Ozone emission during compression fracture of granite. The onset of ozone production coincides with fracture.

can also result in luminescence and EM waves.[10] Charge separation occurs in patches,[11] by a statistical imbalance of ions at the new surfaces, either intrinsic to the mineral lattice or charged impurities. Microscopically, an imbalanced surface charge density σ produces an electric field,

$$E = \sigma/\varepsilon_0 = 1.8 \times 10^{-6}\sigma \mathrm{V/cm},$$

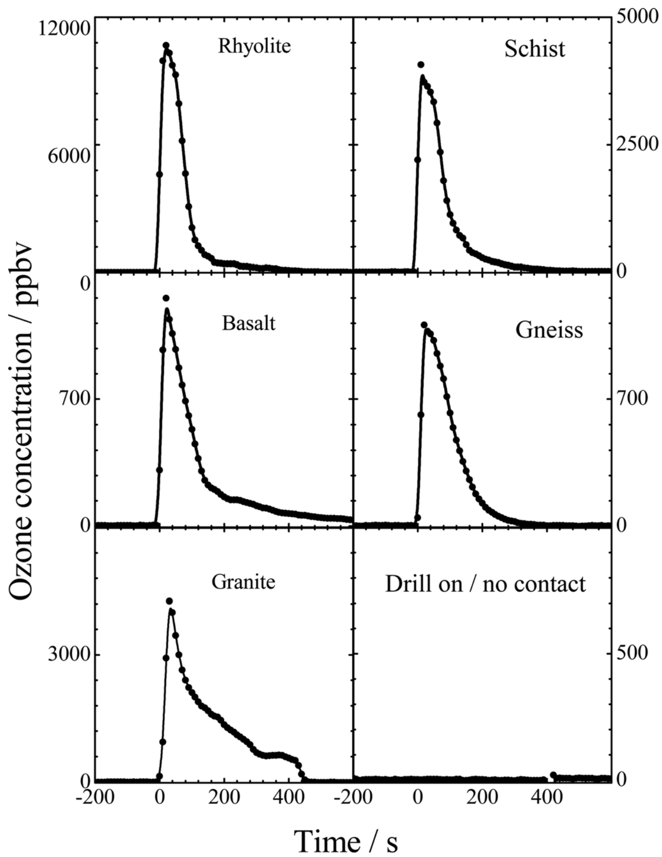

FIG. 2. Ozone production after grinding for 260 s. During grinding, the chamber is isolated from the detector. Immediately after finishing grindings, time zero, a valve is open to allow the detector to begin pumping chamber gases. The decay of the signal with time is due to pumping at 1 L/m with possible contribution from surface reactions. A dry run with no sample shows no ozone produced above background.

where ε_0 is the permittivity of vacuum and σ is in units of the elementary charge, which lead to an increasing voltage V as the fracture walls separate. Typically, electric breakdown of air requires $E = 30$ kV/cm, which can result from charge separation of $\sigma = 1.7 \times 10^{10}/\mathrm{cm}^2$, a very small number compared with the density of ions or atoms at the fracture wall ($\sim 10^{15}/\mathrm{cm}^2$). At these values of E, electrons can be ejected from surface traps by field emission. These values of charge density are consistent with those reported in experiments of fracture of granite and quartz by Molchanov and Hayakawa,[12] and Takeuchi and Nagahama.[13,14]

We distinguish three possible energy ranges relevant for producing ozone. Even electrons in the eV range can break down oxygen molecules by dissociative electron attachment,

$$e^- + O_2 \rightarrow O + O^-,$$

$$e^- + CO_2 \rightarrow CO + O^-.$$

The resulting oxygen atom may then undergo further reaction with an oxygen molecule to form ozone,

$$O + O_2 + M \rightarrow O_3 + M,$$

where M is a third body (another molecule) that ensures momentum conservation.

The O-atom precursors to ozone formation can also be formed by high-energy electrons. The electric field due to unbalanced charge causes a corresponding voltage that increases with gap separation until an electrical discharge can produce electrons that neutralize the surface charge. Excitation of gas during rock fracture at atmospheric pressure has been demonstrated by Brady and Rowell.[15] Energetic electrons can also produce ions, which have been previously observed in rock fracture.[16,17]

The third alternative for ozone formation is an electrical discharge characterized by Townsend multiplication, of the type observed during fracture of granite, diorite, and basalts.[18] For a discharge to strike, the voltage across the gap between fracture walls must reach a minimum, $\sim$330 V (Paschen's law for air) when the gap $\times$ pressure $\sim$ 7.5 μm-atm. However, when the gap opens up at the beginning of fracture, a much smaller voltage is required due to enhanced field emission by ions on the crack walls.[19] The significance of the existence of electrical discharges is that that they increase the ionic concentration in air and generate radio waves, which have also been postulated as useful pre-seismic signals,[20,21] but different from that of ozone production proposed here.

Finally, another possible mechanism is field ionization, with the field produced by the accumulation of holes generated by stress-induced peroxide defects in the rock.[20] Even though the precise mechanism of exoemission has not been elucidated after decades (different processes may operate in different cases), the variety of effects observed, including the emission of ozone reported here, all point to a root cause in charge separation.

Implications of these results are manifold. The production of ozone (and possibly other gases, such as NO_x) should arise in a wide variety of scenarios, some with possible

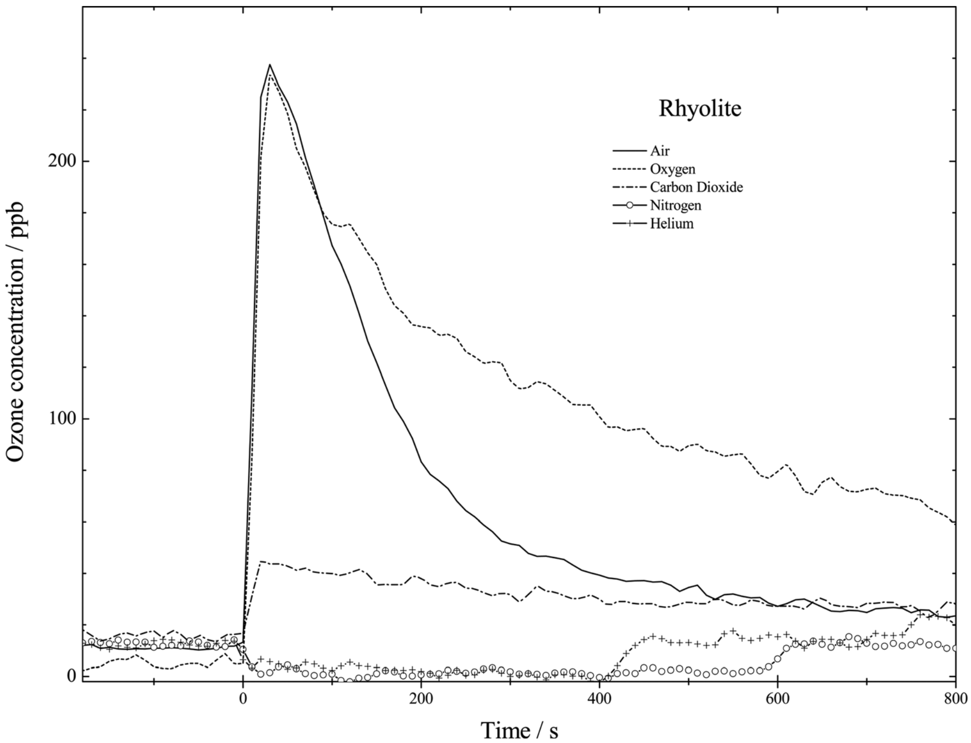

FIG. 3. Same as Figure 2 but for rhyolite in different gaseous environments (1 atm). Ozone is produced in oxygen, carbon dioxide, and air.

health consequences: mines, quarries, industrial drilling, as well as natural occurrences such as earthquakes, volcanoes, and dust storms. The increase in ozone from rock fracture in the troposphere is not connected with a decrease in mesospheric ozone observed above earthquake epicenters.[22]

If future field research shows a positive correlation between ground-level ozone near geological faults and earthquakes, an array of interconnected ozone detectors could monitor anomalous patterns when rock fracture induces the release of ozone from underground and surface cracks. Such an array, located away from areas with high levels of ground ozone, could be useful for identification of locations of seismic risks and give early pre-seismic warning. Detection of an increase of ground ozone might also be used to anticipate disasters in tunnel excavation, landslides, and underground mines.

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