

MDAG.com Internet Case Study 66

Pondering the Role of Quartz in Rock Reactivity, ML-ARD, and Minesite-Drainage Chemistry

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It is worthwhile to repeat two important quotations from MDAG Case Studies 63 and 64 (Morin, 2020a and 2020b):

It has been known for over two centuries that the solid and liquid Earth and its atmosphere are almost permanently electrified. (National Research Council, 1986)

EMFs (electrical and magnetic fields) are all around us, occurring naturally in every atom of matter. The surface of the Earth is covered with a natural electric field, created by electrical charges in the upper atmosphere. Similarly, a powerful electric field is required to keep the cells of living organisms alive. (Hydro Québec, 2011)

Abstract

Quartz is a common crystalline form of SiO₂ in many rocks and at many minesites around the world. From a geochemical perspective, quartz has relatively low solubility. From an electrochemical and electrical perspective, it has relatively low electrical conductivity and is thus often considered like an electrical resistor. As a result, quartz is often considered relatively passive or unimportant in rock reactivity, metal leaching (ML), acid rock drainage (ARD), and minesite-drainage chemistry.

However, quartz and many other minerals have another property that could indirectly, but potentially significantly, affect rock reactivity, ML-ARD, and drainage chemistry, namely *piezoelectricity*. For these minerals and their surfaces, piezoelectricity includes (1) the development of electrical charges during the application or withdrawal of pressure or mechanical stress and (2) the reversed effect of physical deformation during the application or withdrawal of an electrical field.

The microphotograph in this MDAG case study leads to the question: why did a pyrite cube deeply embedded in quartz “fall out”? This presumably eventually led to all six surfaces of the cube oxidizing and generating acidity, rather than just the exposed surface, which in turn can increase the severity of ARD. Based on piezoelectrical values for quartz, some plausible explanations (among many) include the following.

- 1) The oxidation of the pyrite cube created secondary minerals such as gypsum and ferric oxyhydroxides, which have much larger volumes per mole of sulphur and iron as they take O and H from air and water. This “swelling” upon oxidation caused the cube to “pop out”.
- 2) The periodic piezoelectric distortion of the surrounding quartz by variable large-scale earth currents eventually loosened the cube and it fell out.
- 3) The initial intense pressure caused by blasting during mining, followed by the release of compressive strength during excavation, followed by ongoing burial and increasing weight on the rock prior to collection caused the quartz and other piezoelectrical minerals to create electrical potentials that could accelerate the oxidation of the pyrite cube. This is basically the acceleration of the first explanation above.
- 4) There may have been some synergistic combination of the previous three.
- 5) Like a loose tooth, the pyrite cube just fell out.

Because the answer is not clear, it remains possible that piezoelectricity played some role in the ejection of the pyrite cube from the rock, which could have later increased the severity of acidity generation. Nobody knows because apparently no one has checked for significant piezoelectricity in minesite components.

Therefore, we are left to ponder whether the piezoelectricities of quartz and other minerals have any significant effects on rock reactivity, ML-ARD, and drainage chemistry at minesites. If so, these effects are not included in current evaluations and predictions.

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1. Introduction

Quartz is a common crystalline form of SiO_2 in many rocks and at many minesites around the world. Except for some impurities, it is mostly SiO_2 with a solubility around 6 mg/L.

Other crystalline, cryptocrystalline, and amorphous forms of SiO_2 exist. This MDAG case study can be extended to some of them, but the focus remains primarily on quartz.

From a geochemical perspective, quartz has relatively low solubility. From an electrochemical and electrical perspective, it has relatively low electrical conductivity and is thus often considered like an electrical resistor. As a result, quartz is often considered relatively passive or unimportant in rock reactivity, metal leaching (ML), acid rock drainage (ARD), and minesite-drainage chemistry.

However, quartz has another property that could indirectly but potentially significantly affect rock reactivity, ML-ARD, and drainage chemistry, namely *piezoelectricity*.

2. Piezoelectricity of Quartz

2.1 Definition of Piezoelectricity

Wikipedia (2021) succinctly explains:

“Piezoelectricity is the electric charge that accumulates in certain solid materials (such as crystals . . . in response to applied mechanical stress. The word piezoelectricity means electricity resulting from pressure and latent heat. . . . The piezoelectric effect is a reversible process: materials exhibiting the piezoelectric effect (the internal generation of electrical charge resulting from an applied mechanical force) also exhibit the reverse piezoelectric effect, the internal generation of a mechanical strain resulting from an applied electrical field.”

2.2 Implications of Piezoelectricity for Quartz and Other Minerals

One of the best known and most common examples of piezoelectricity is our “relatively passive” quartz crystals. This is why quartz is used as a timing crystal in watches and other electronic devices. Also, quartz crystals are used in gas stoves and cigarette lighters, where a small “hammer blow” on the quartz creates a piezoelectric-generated spark that ignites the gas.

In addition to quartz, dozens of other minerals including tourmaline generate piezoelectricity (e.g., Encyclopædia Britannica, 2021; Parkhomenko, 1967 and 1971; Jose, 1979; Saigusa, 2017). In fact, 20 of the 32 crystal classes produce piezoelectricity (Wikipedia, 2021). Thus, piezoelectrical behaviour could be considered normal and common for many minerals and rock. Beyond that, other compounds known to be piezoelectric include table sugar, some polymers, DNA, and viral proteins.

As explained above, piezoelectricity includes (1) the development of electrical charges during the application or withdrawal of pressure or mechanical stress and (2) the reversed effect of physical deformation during the application or withdrawal of an electrical field.

In the first case, imagine a piece of quartz-bearing rock being blasted during mining, followed by the release of confining pressure from surrounding rock, and then being progressively buried, day after day, year after year, by more rock or tailings. Alternatively, a crushed-rock sample with quartz might initially be heavily compressed for testing in a laboratory, with the compressive force then released. This will result in electrical potentials arising in the quartz and the other piezoelectric minerals.

In the second, reversed case, imagine a quartz mineral physically “vibrating” in a cyclical electro(chemical) field. In fact, there are cyclical electrical fields in and around minesite components at many wavelengths all the time (e.g., Morin, 2016, 2018, 2019, 2020a, and 2020b; see also the quotations at the beginning of this case study). This can cause complex physical vibrations of quartz and other piezoelectric minerals.

2.3 Magnitude of Piezoelectrical Effects

One author (Repas, 2008) reported that 1 cm³ of quartz could produce a voltage of 12,500 V when struck in a certain way with 2000 N (~500 pounds). No supporting evidence was given for this, plus I note that such a small quartz crystal would be smashed to pieces under that weight. Anyway, it is a starting point for characterizing the potential magnitude of piezoelectrical effects in quartz-bearing rock.

The piezoelectric coefficient (“d”) represents the proportion between physical and electrical effects. It can be complex as a three-dimensional tensor with at least two subscripts for various polymorphs of quartz (Parkhomenko, 1971; Wikipedia, 2021). This is because crystal orientation relative to the direction of pressure application determines the exact piezoelectrical response.

With the hope of avoiding oversimplification here, the piezoelectrical coefficient (d) for quartz is often reported around 2×10^{-12} Coulombs/Newton (e.g., Encyclopædia Britannica, 2021), which is dimensionally equivalent to 2×10^{-12} m/V. This is also roughly equivalent to 2×10^{-8} Coulombs/tonne of overlying rock or tailings and 2×10^{-13} moles e⁻/tonne of overlying rock or tailings. The piezoelectrical potential of quartz has been observed to decay with time, so the generated voltage does not persist indefinitely.

The objective here is to roughly estimate whether the piezoelectricity of quartz can be significant. Thus, $d = 2 \times 10^{-12}$ m/V simplistically means that, for each volt applied to quartz, its surface will flex and distort 2×10^{-12} m. Because it is reversible, for each 2×10^{-12} m that a quartz surface is distorted, 1 Volt would be generated.

The diameters of atoms are roughly 1×10^{-10} m and larger to a factor of about 5. Therefore, for a quartz surface to flex the width of one atom, roughly 100 V has to be applied. In turn, if a quartz surface is distorted by pressure or physical stress to the width of one atom, then the generated piezoelectrical potential would be roughly 100 V. This is likely the basis for the unsubstantiated example given at the beginning of this subsection.

Interestingly, local small-scale electrical potentials due to factors like self potential, electrochemical reactions, and cathode-anode reactions of sulphide minerals are typically tens to thousands of mV, or ~0.01-10 V (Morin 2020a). Based on the calculations above, this voltage might make quartz and other piezoelectrical minerals flex only on a sub-atomic scale, but can have major effects on aqueous concentrations (Morin, 2020a). Thus, local potentials likely make little contribution to, and receive little effects from, piezoelectricity.

On the other hand, atmospheric electricity and polarity reversals during storms can reach hundreds to thousands of volts (Morin, 2020a). Therefore, the larger-scale electrical potentials and their variations can cause quartz and other piezoelectric minerals to flex and distort distances equivalent to the diameter of one to many atoms. As a result, larger-scale potentials can significantly contribute to, or be affected by, piezoelectricity. After years of such periodic flexing and distortion, significant effects can be envisioned for adjacent and nearby minerals, like pyrite.

Finally, the initial intense pressure caused by blasting during mining, followed by the release of compressive strength during excavation, followed by ongoing burial and increasing weight in a rock pile or tailings impoundment on quartz would lead to large variations in piezoelectrical potential, which could affect the reaction rates of some minerals like pyrite.

2.4 A Piezoelectrical Point to Ponder

In Microphotograph 2-1 below, there is a cube-shaped “pit” about 10 um across, apparently surrounded by mostly quartz with some ferric-iron staining. Based on the mineralogy of this net-acid-generating waste rock, the missing cube was likely pyrite.

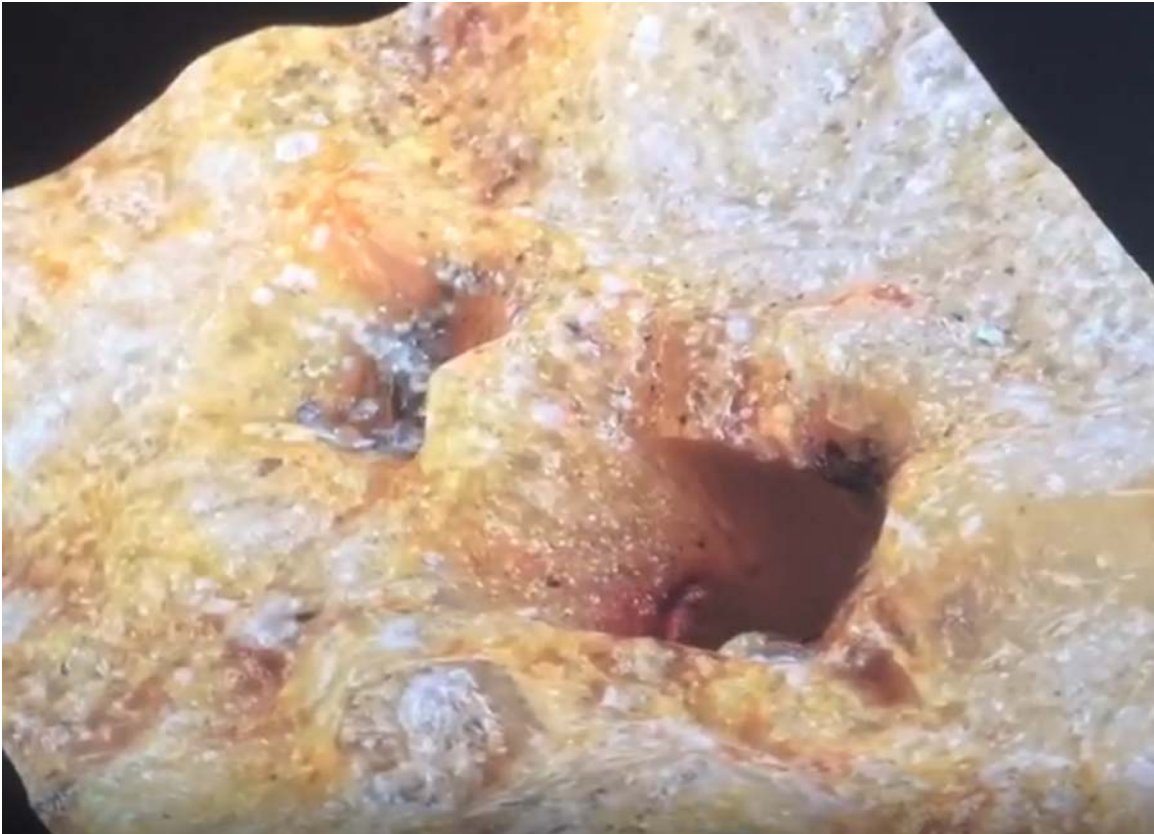
When embedded in the rock, only one surface of the cube and some edges were likely exposed to air and thus generated acidity. Now outside the pit, all six sides could be exposed, potentially leading to greater per-unit-time oxidation and acidity.

What caused this pyrite cube to “fall out” of its pit (Dr. W.A. Price, personal communication, 2021)? Here are some (among many) plausible explanations.

- 1) The oxidation of the pyrite cube created secondary minerals such as gypsum and ferric oxyhydroxides, which have much larger volumes than pyrite per mole of sulphur and iron as they remove O and H from air and water. This “swelling” upon oxidation caused the cube to “pop out”.
- 2) The periodic piezoelectric distortion of the surrounding quartz by variable large-scale earth currents eventually loosened the cube and it fell out.
- 3) The initial intense pressure caused by blasting during mining, followed by the release of compressive strength during excavation, followed by ongoing burial and increasing weight on the rock prior to collection caused the quartz and other piezoelectrical minerals to create electrical potentials that could accelerate the oxidation of the pyrite cube. This is basically the acceleration of the first explanation above.
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Microphotograph 1. A microphotograph of a pit approximately 10 μm across in quartz-bearing rock from which a cube of pyrite is apparently missing (photo courtesy of the National Research Council Canada).

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