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# Explanations for Poregas $CO_2$ Variability Relative to $O_2$ in the Equity Silver Waste-Rock Pile

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**Acknowledgments**
Many thanks to my colleagues and co-authors at the National Research Council Canada for re-directing my attention back to this previously unresolved issue.

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# Abstract

For the Equity Silver waste-rock pile, roughly 17 years of poregas monitoring for $O_2$ and $CO_2$ have produced more than 4000 values for each gas, distributed laterally and vertically through the pile. Earlier work identified a generally linear, inverse correlation between the two gases. Simple oxygen consumption during pyrite oxidation to produce acidity, followed by neutralization with carbonate minerals, could not reliably explain the inverse correlation or the variability of $CO_2$ at a particular level of $O_2$. In fact, the Equity Silver waste-rock pile mostly releases strong ARD and relatively little pH-neutral water, suggesting greater complexity.

The re-evaluation here of the poregas monitoring data has shown that the observed inverse correlation can be explained by carbonate neutralization of acidity, but only when various degrees of neutralization are considered. Most poregas values indicate at least one-half of the acidity was neutralized (0.5:1 partial neutralization), although a few datapoints showed virtually no neutralization. Many values indicate pH was initially neutralized to above pH ~ 6.4, followed by re-acidification along downgradient flowpaths.

This re-evaluation also found these neutralization processes likely create a partial vacuum within the waste rock. The assumption that this partial vacuum is filled by ambient air comes close to explaining the average trend between $O_2$ and $CO_2$.

For no readily apparent reason, the variability of $CO_2$ within a particular range of $O_2$ displays a generally normal statistical distribution. The means and standard deviations generally increase as $O_2$ decreases.

The National Research Council of Canada (NRC) is conducting detailed evaluations and modelling of this waste-rock pile, with seasonal mechanisms already explained. This case study provides geochemical support for the current NRC findings.

# 1. Introduction

Based on 23 years of accumulated monitoring, Morin et al. (2010 and 2012) and Morin (2016) described and interpreted thousands of water analyses, flows, internal temperatures, and poregas levels of carbon dioxide ($CO_2$) and oxygen ($O_2$) within the Equity Silver waste-rock pile. One observation was that a general inverse correlation was seen between $O_2$ and $CO_2$, but an explanation for the variability of $CO_2$ relative to $O_2$ was not apparent. Liu et al. (accepted) carried this further, by finding abundant inverse correlations of $O_2$ and $CO_2$, laterally and with depth at the individual "P" poregas monitoring ports, within a correlation matrix of $O_2$ and $CO_2$.

Depicted originally on a logarithmic scale, the inverse correlation between $O_2$ and $CO_2$ was generally linear (Figure 1-1), with a best-fit equation of:

$$\%CO_2 = -0.27586 * \%O_2 + 5.5317 \quad \text{(correlation coefficient = 0.73)} \qquad \text{(Eq. 1-1)}$$

Nevertheless, variability of $CO_2$ at a particular level of $O_2$ was often a factor-of-two above and below the best-fit equation.

The atmospheric oxygen level of approximately 21%$O_2$ was asymptotically approached, but not exceeded in Figure 1-1, as $CO_2$ levels decreased. Also, most $CO_2$ levels were substantially above atmospheric levels of ~0.04%$CO_2$, and often clustered around 2-10%$CO_2$ where oxygen was below one-half atmospheric (<10%$O_2$). This was generally consistent with some neutralization, by carbonate minerals, of the strong ARD that flows through and drains from the waste-rock pile.

However, the correlation between $O_2$ and $CO_2$ was not 1:1 and thus not balanced. Carbon dioxide did not increase by the same amount as oxygen decreased. Therefore, although some type of inverse correlation was geochemically plausible, this non-proportional correlation suggested significant complexity. For example, the non-proportionality meant a partial vacuum developed as $O_2$ decreased, meaning air and/or poregas were drawn from elsewhere into these locations. Also, the significant variability of $CO_2$ suggested sources of $CO_2$ other than carbonate neutralization.

This MDAG.com Case Study 50 re-examines the relationship of $O_2$ to $CO_2$ in the Equity Silver waste-rock pile to explain the observed trend and variability.

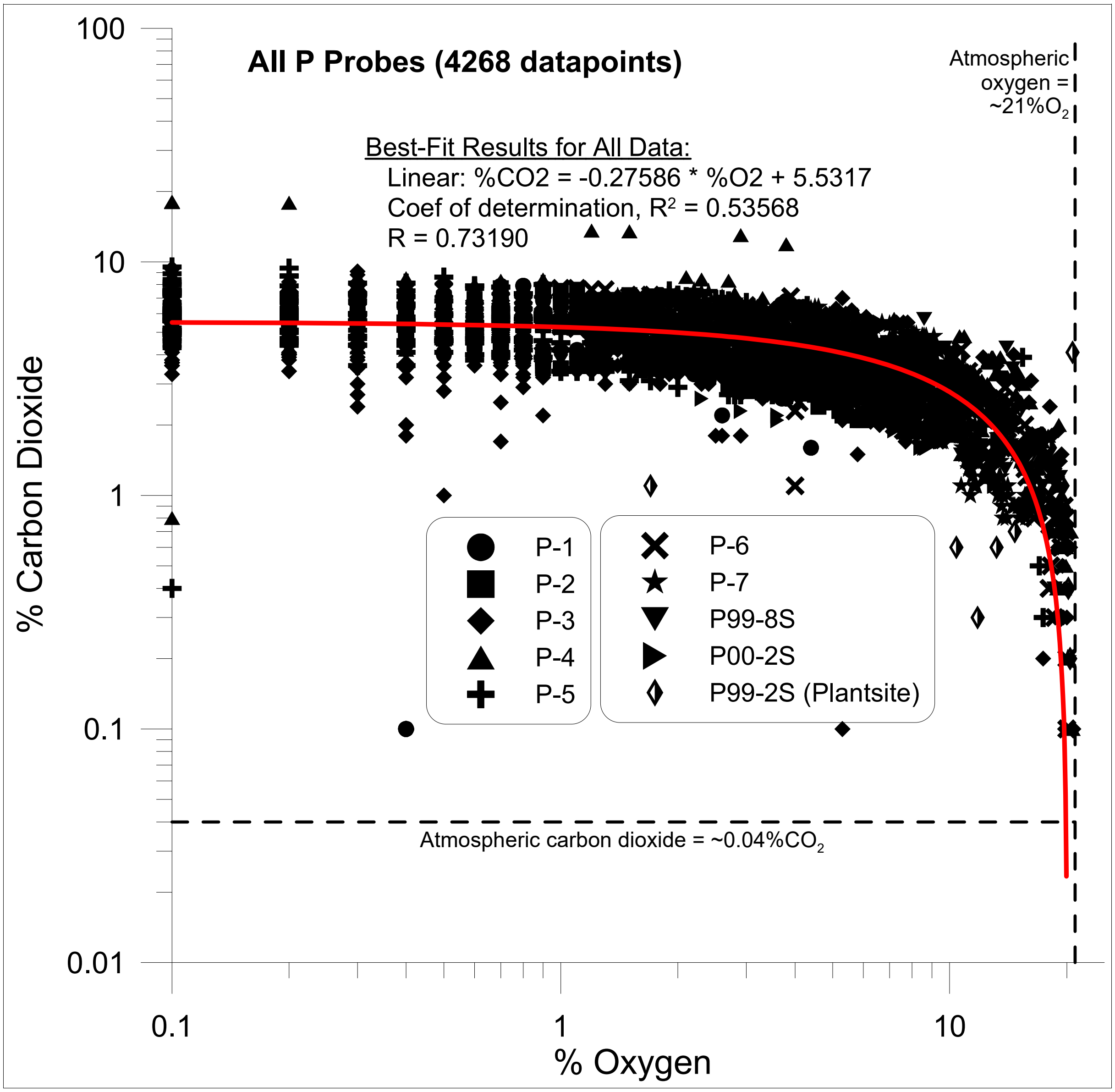


**Figure 1-1. Pore-gas carbon dioxide vs. oxygen at all P locations and depths in the Equity Silver waste-rock pile, with the best-fit equation for the overall linear trend (from Morin et al., 2010 and 2012).**

## 2. Description of "P" Poregas Monitoring at Equity Silver

The Equity Silver waste-rock pile contains more than 50 depth-specific ports for collecting poregas $O_2$ and $CO_2$ within the waste rock. These depth-specific ports are at specific spatial locations identified with a "P" prefix for poregas probes (Figures 2-1 and 2-2).

In general, P-5, P-3, P-6, P-1, P-7 (with the hottest internal temperatures), and P-2 extend from east to west through the pile, generally parallel to the lateral portion of westward ARD drainage. P-3 and P-5 are within the Southern Tail Pit backfilled with waste rock. P-4 is also located within the backfilled Southern Tail Pit, near the south end of the waste rock. P99-8 (shallow and deep) and P00-02 are located on the north end of the waste rock. P99-2S is found farther north near the former plantsite.

## 3. Detailed Description of Poregas Monitoring Results and Partial Vacuums

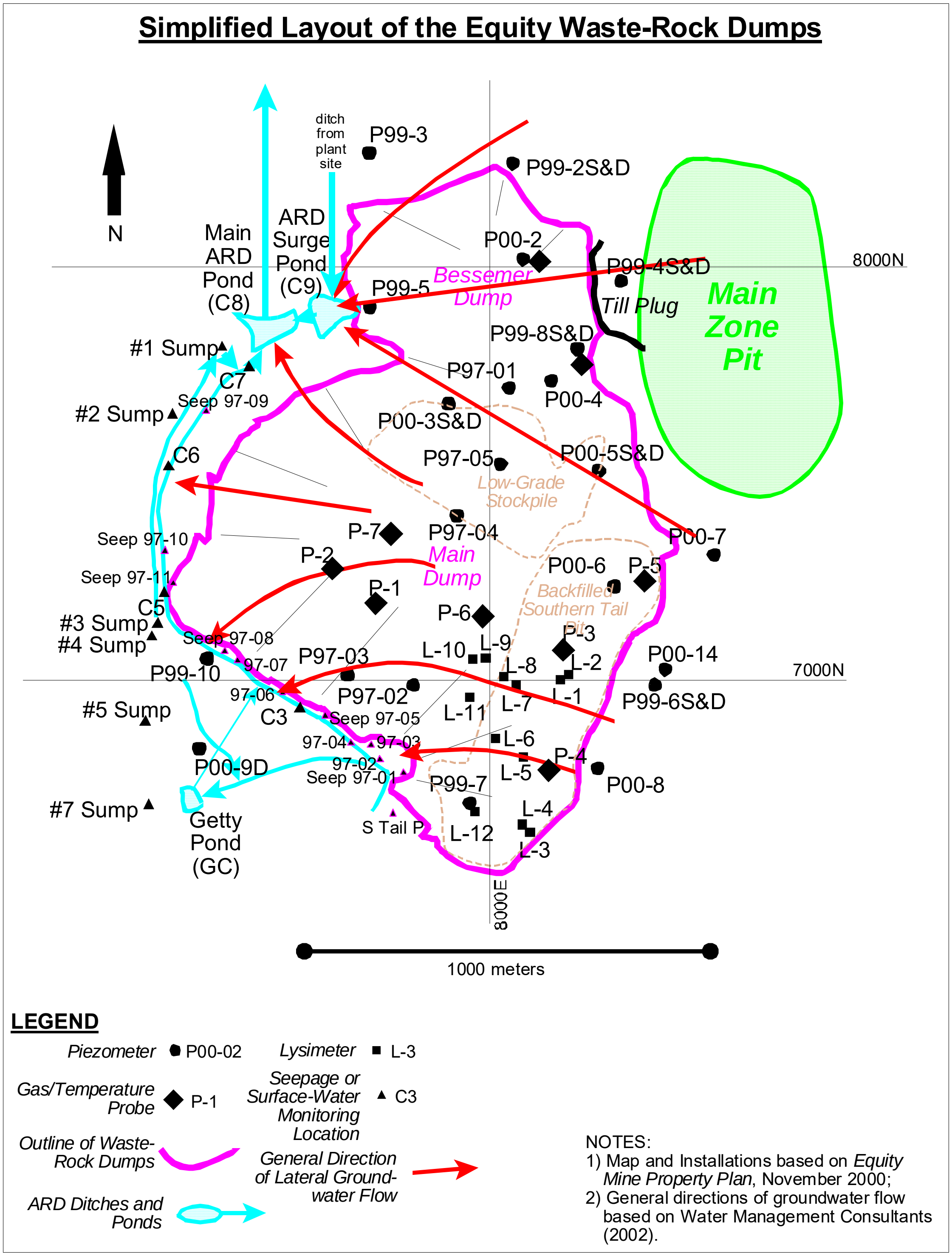
Figure 1-1 depicts nearly 4300 data pairs of $O_2$ and $CO_2$ from the "P" ports, spanning roughly 17 years. The conversion of that original depiction, from logarithmic axes to arithmetic axes (Figure 3-1), adds a few more datapoints that have zero values, and slightly changes the linear best-fit equation (the red line in Figure 3-1) to:

$$\%CO_2 = -0.29335*\%O_2 + 5.6951 \quad \text{(correlation coefficient = 0.74)} \qquad \text{(Eq. 2-1)}$$

The variability of $CO_2$ at a particular $O_2$ level (any vertical slice in Figure 3-1) increases as $CO_2$ decreases. However, the point remains that there is no 1:1 inverse correlation: $O_2$ is consumed in a proportionally greater amount than $CO_2$ replaces it. This makes sense, as explained below with equations, because a significant amount of $O_2$ is removed from the gas phase and incorporated into solid-phase minerals like oxyhydroxides (e.g., $Fe(OH)_3$) and sulphates (e.g., $CaSO_4{\bullet}2H_2O$).

This excess loss of poregas $O_2$ also means a partial vacuum develops (Figure 3-2). As a result, air and/or poregas is drawn from elsewhere, leading to convection within the waste rock. This convection in waste-rock piles, also driven by thermal and barometric gradients, has been known for decades (e.g., Morin et al., 1991). Perhaps the partial vacuum and its subsequent filling can account for the variability of $CO_2$ relative to $O_2$, but there is also another, more successful explanation.

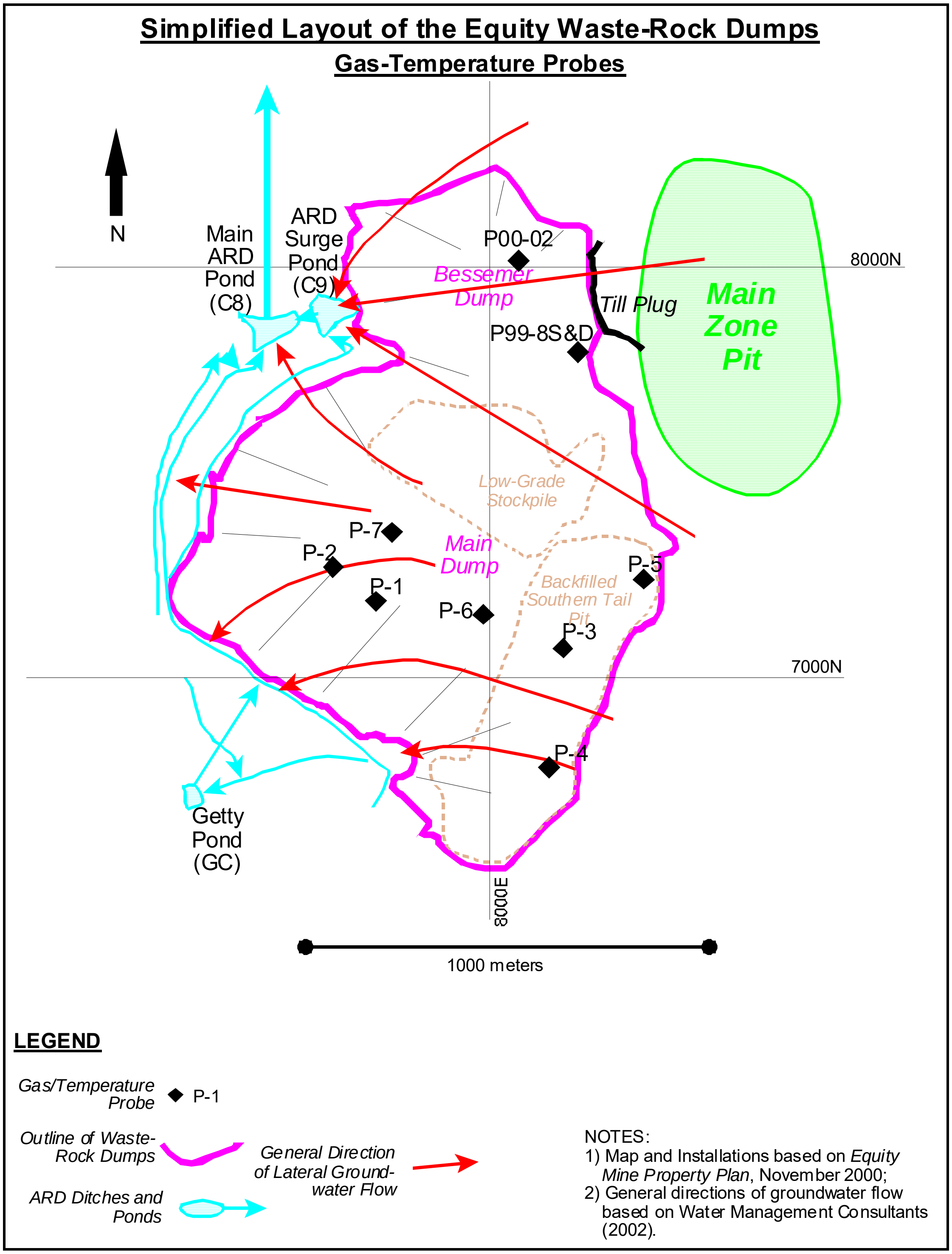
Statistical distributions do not provide helpful explanations. Oxygen is generally lognormally distributed (Figure 3-3), showing oxygen is typically depleted substantially from atmospheric levels within the waste rock. In contrast, carbon dioxide is generally normally distributed (Figure 3-4), and highly enriched above atmospheric levels. The difference in the two distributions suggests a minor relationship, but there is more to this story.



Simplified Layout of the Equity Waste-Rock Dumps

NOTES:
1) Map and Installations based on *Equity Mine Property Plan*, November 2000;
2) General directions of groundwater flow based on Water Management Consultants (2002).

Figure 2-1. Locations of the "P" poregas probes within the Equity Silver waste-rock pile, consisting of two merged waste-rock dumps, a low-grade ore stockpile, and the backfilled and buried Southern Tail Pit.



NOTES:
1) Map and Installations based on *Equity Mine Property Plan*, November 2000;
2) General directions of groundwater flow based on Water Management Consultants (2002).

**FIGURE 2-2. A simplified version of Figure 2-1, showing only the "P" poregas probes in the Equity Silver waste-rock pile, with each probe containing two to eight depth-specific monitoring ports.**

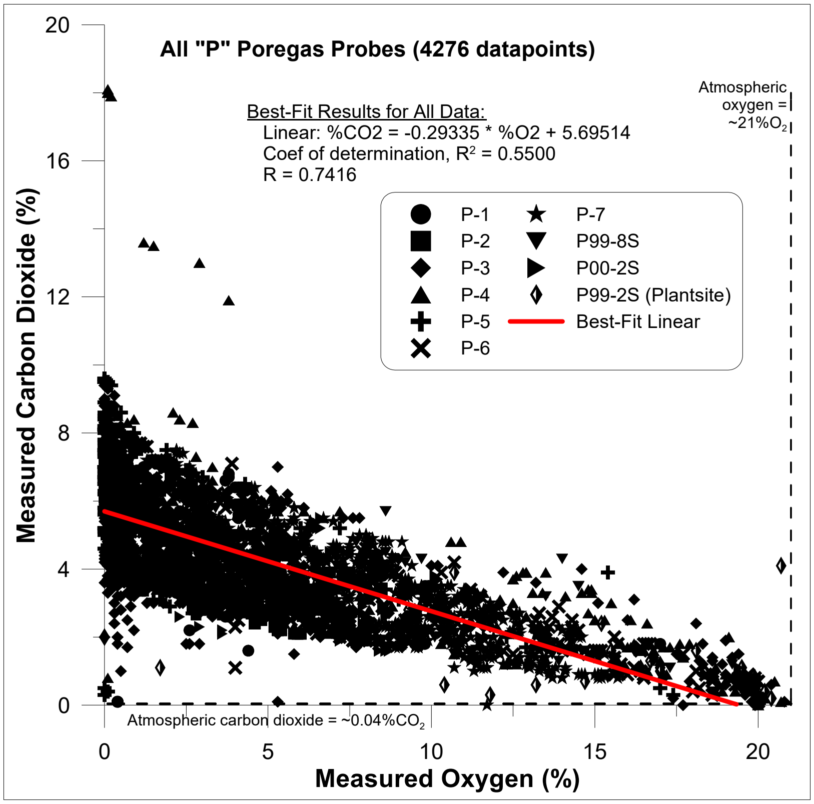


Figure 3-1. Scatterplot of measured oxygen and measured carbon dioxide, with the best-fit linear line shown in red.

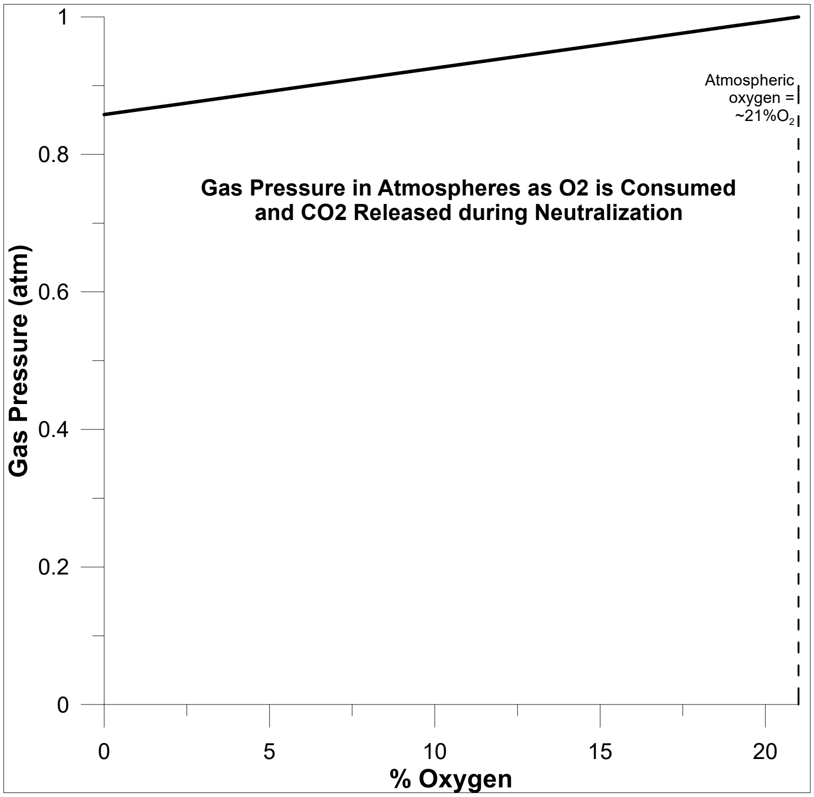


Figure 3-2. Trend of increasing partial vacuum as oxygen decreases, due to the lack of 1:1 replacement by carbon dioxide.

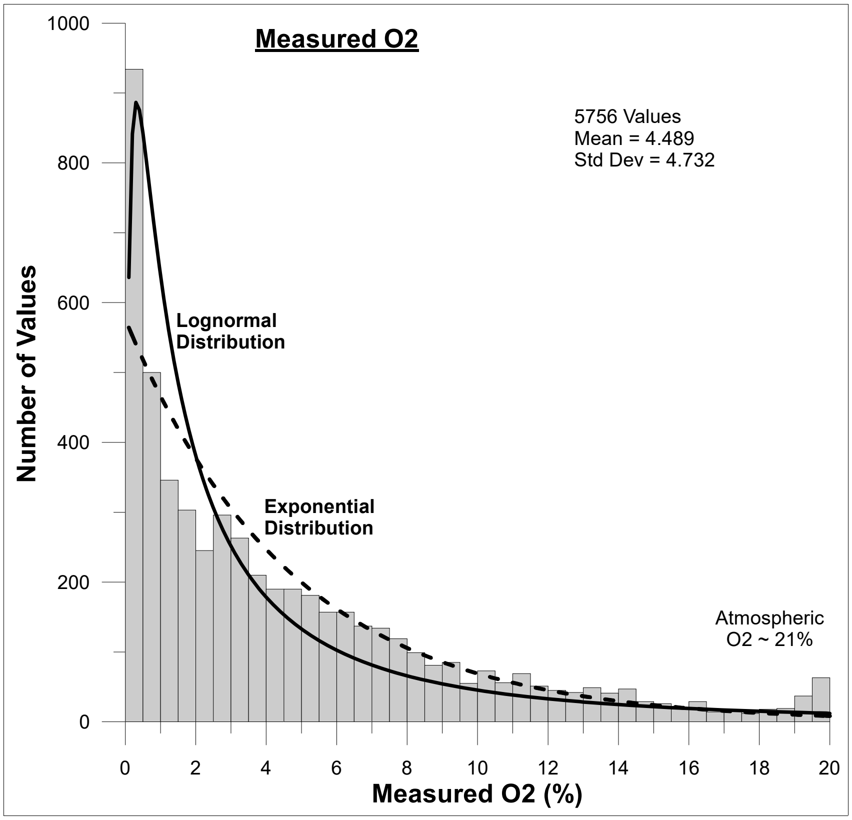


Figure 3-3. Statistical histogram of poregas oxygen levels.

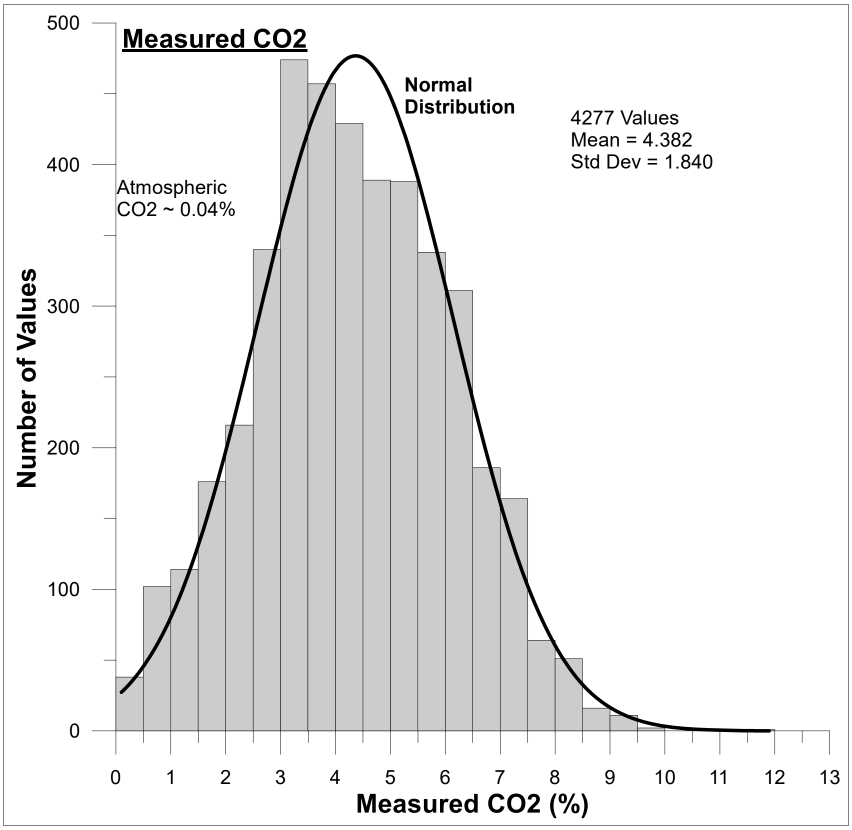


Figure 3-4. Statistical histogram of poregas carbon dioxide levels.

## 4. The Geochemical Explanation for the Inverse Correlation of Oxygen and Carbon Dioxide, and for the Significant Variability of Carbon Dioxide

The most successful explanation for the inverse correlation of $O_2$ and $CO_2$, and the significant variability of $CO_2$, lies in aqueous geochemistry. Here is the first important equation.

$$H_2O + CO_{2(gas)} \rightleftarrows H_2CO_3^0 \rightleftarrows H^+ + HCO_3^- \qquad \text{(Eq. 4-1)}$$

Equation 4-1 is a basic equation of the aqueous carbonate system, which appears simple but is very complex due to reversible and acid-base buffering reactions. At pH < ~6.4, the left side dominates, with most carbon occurring as $CO_2$ gas and aqueous $H_2CO_3^0$. At pH > ~6.4, the right side dominates, with little $CO_2$ and $H_2CO_3^0$ occurring. Here are the relevant neutralization equations.

If neutralization pH remains less than ~6.4,

$$FeS_2 + 15/4O_2 + 3/2H_2O + 2CaCO_{3(solid)} \rightarrow Fe(OH)_{3(solid)} + 2Ca^{2+} + 2SO_4^{2-} + 2CO_{2(gas)} \qquad \text{(Eq. 4-2a)}$$

$$FeS_2 + 15/4O_2 + 7/2H_2O + 2CaCO_{3(solid)} \rightarrow Fe(OH)_{3(solid)} + 2Ca^{2+} + 2SO_4^{2-} + 2H_2CO_3^0 \qquad \text{(Eq. 4-2b)}$$

*If all reacted carbon occurred as $CO_2$ gas (Equation 4-2a, which is unlikely), the molar ratio of $O_2$ to produce $CO_2$ would be 2 mole $CO_2$ produced for every 15/4 moles$O_2$ consumed, or -0.53. The corresponding volume/mass ratio would be 88 g $CO_2$ to 120 g $O_2$ consumed, or -0.73. This is labelled here "ideal 2:1 neutralization". Because not all carbon becomes $CO_2$ gas, the molar and weight ratios would realistically be less negative. Also, if there is insufficient $CaCO_3$ for neutralization of all acidity by Equation 4-2, then the weight-based ratio would again be less negative than -0.73 and perhaps close to zero. Thus, a less negative value than 2:1 neutralization is expected, such as "1:1 neutralization" with about one-half the negative slope around -0.3. Note the linear correlation slopes in Figures 1-1 and 2-3 are ~-0.29.*

If pH increases above ~6.4 to a maximum around 9 in a closed system so that all $CO_2$ remained in the water (Equation 4-2b),

$$FeS_2 + 15/4O_2 + 7/2H_2O + 4CaCO_{3(solid)} \rightarrow Fe(OH)_{3(solid)} + 4Ca^{2+} + 2SO_4^{2-} + 4HCO_3^- \qquad \text{(Eq. 4-3)}$$

*If this neutralized water with pH above 6.4 subsequently becomes acidic again along flowpaths, the reversal of Equation 4-1 would ideally produce 4 moles of $CO_2$, . However, re-acidification would require additional $O_2$ to be consumed to generate the additional acidity. Also, not all $CO_2$ remains in the water of an open system (Equation 4-2a) like a relatively coarse waste-rock pile, which means Equation 4-3 would overestimate $CO_2$ production upon re-acidification. This can become complicated and convoluted, so it is easier to use the net effect, which is Equation 4-2.*

With atmospheric conditions representing a starting point (21% $O_2$ and 0.04% $CO_2$), the linear correlation equations for neutralization to pH <~6.4 (Equation 4-2a) allowing for about 10% of carbon to remain in water as $H_2CO_3^0$ and dissolved $CO_2$ are:

1:1 neutralization: CO2(%) = -0.323*O2(%) + 6.823 (Eq. 4-4)
0.5:1 neutralization: CO2(%) = -0.162*O2(%) + 3.442 (Eq. 4-5)
1.5:1 neutralization: CO2(%) = -0.485*O2(%) + 10.225 (Eq. 4-6)
2:1 neutralization: CO2(%) = -0.647*O2(%) + 13.627 (Eq. 4-7)
These are shown in Figure 4-1.

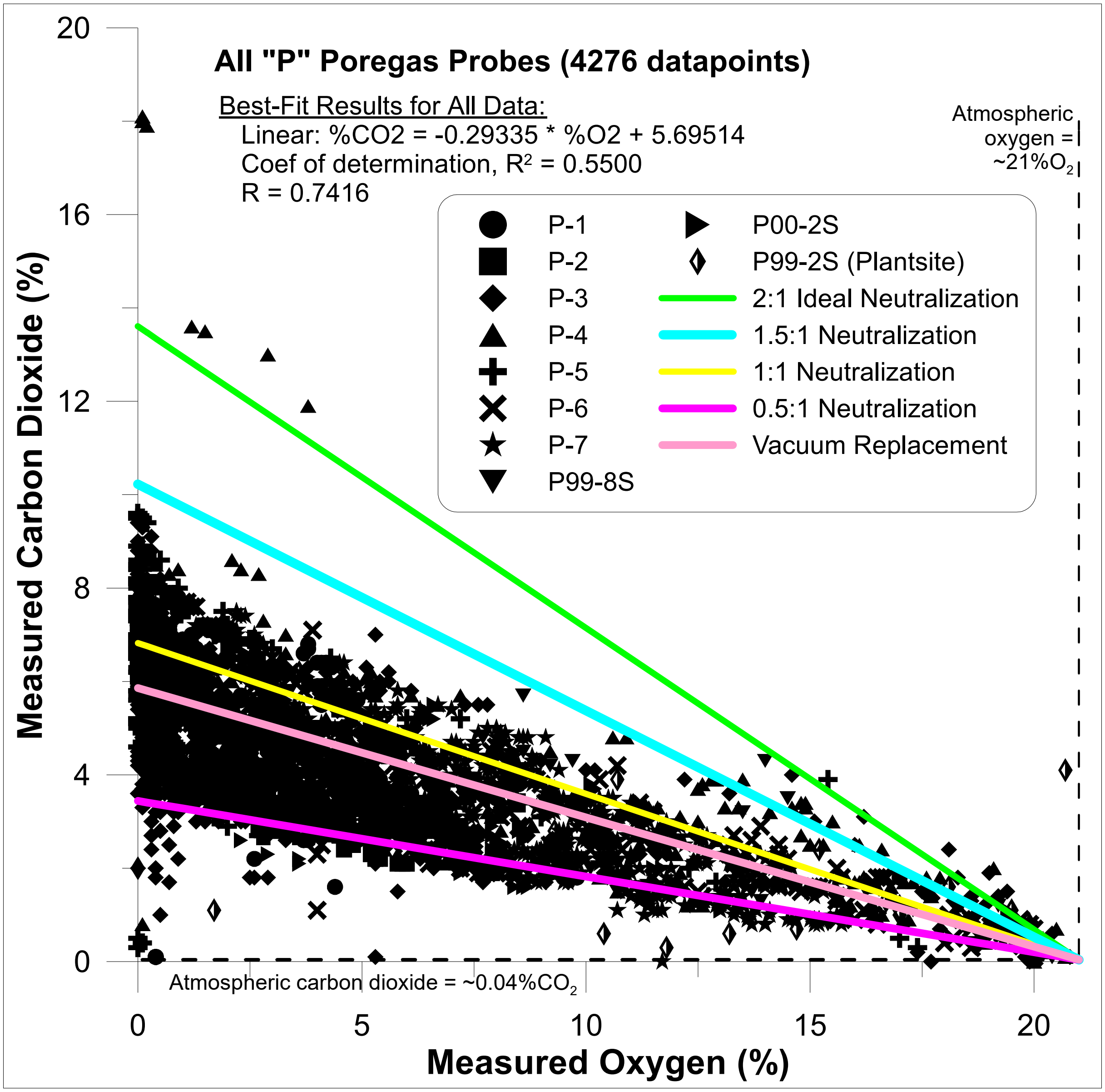


**Figure 4-1. Scatterplot of measured oxygen and measured carbon dioxide, with straight lines representing various degrees of neutralization and with "vacuum replacement" representing carbon dioxide after the partial vacuum is filled with air.**

Figure 4-1 leads to several observations.

- The ideal 2:1 neutralization generally represents the upper bound for the rare high values of $CO_2$ associated with significant $O_2$ in the Equity Silver waste-rock pile.

- 1.5:1 neutralization generally overestimates $CO_2$ levels, except at higher levels of $O_2$.

- 1:1 neutralization is within the typical variability of $CO_2$, but somewhat on the high side.

- "Vacuum replacement" where ambient air (0.04% $CO_2$) is drawn in to fill the partial vacuum after 1:1 neutralization is more centrally located within the $CO_2$ variability.

- 0.5:1 neutralization is the general lower bound of measured $CO_2$, indicating ARD from the Equity Silver waste-rock pile is typically at least 50% internally neutralized.

By "P" location, measurements from P-1 and P-2 in the western portion showed their poregas was typically low in $O_2$ and reflected predominantly partially neutralized (less than 1:1 neutralization) conditions (Figure 4-2). P-7 with the highest temperatures and P-6 showed large ranges of $O_2$ and neutralization (Figure 4-3).

P-3 and P-5 in the backfilled Southern Tail Pit tended to have very low values of $O_2$ with a relatively large range of neutralization at those low $O_2$ levels (Figure 4-4). P-4 also in the backfilled Southern Tail Pit had a more even distribution of $O_2$ levels than P-3 and P-5, with a few datapoints near and above the ideal 2:1 neutralization suggesting some closed-system neutralization nearby (Figure 4-5).

P99-8S on the north side of the waste-rock pile produced a nearly full range of $O_2$ values (Figure 4-6), with $CO_2$ mostly reflecting less than 100% neutralization. Most datapoints for P00-2S also on the north side of the waste-rock pile indicated $O_2$ was typically 3-10% and typically partially neutralized somewhat above 50% (Figure 4-6).

P99-2S near the former plantsite generally produced $O_2$ less than 5% with some partially neutralized $CO_2$ levels approaching zero neutralization (Figure 4-7).

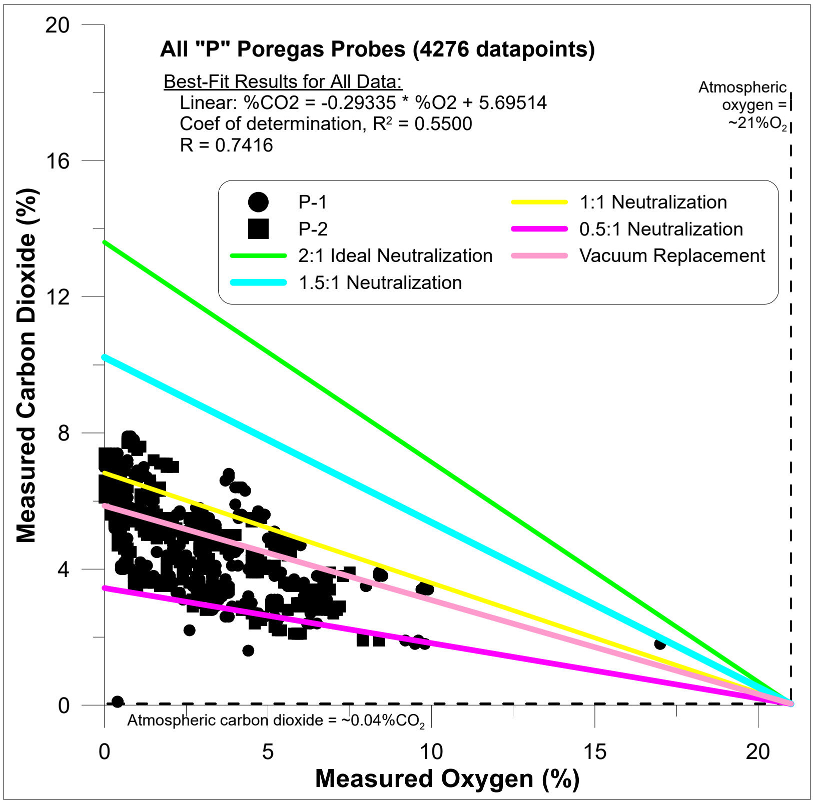


Figure 4-2. Scatterplot of measured oxygen and measured carbon dioxide for P-1 and P-2.

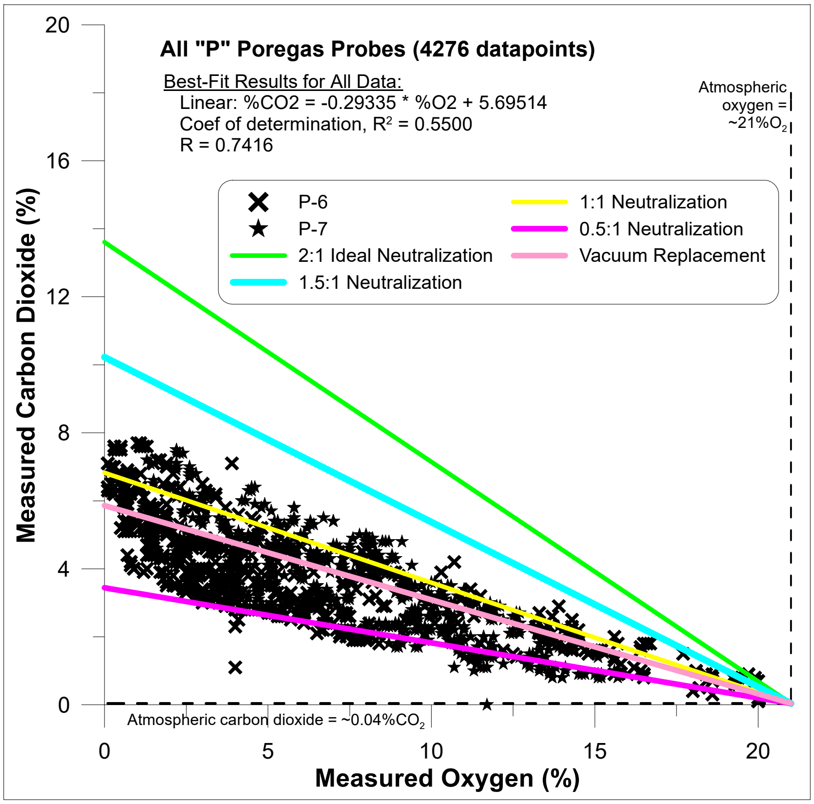


Figure 4-3. Scatterplot of measured oxygen and measured carbon dioxide for P-6 and P-7.

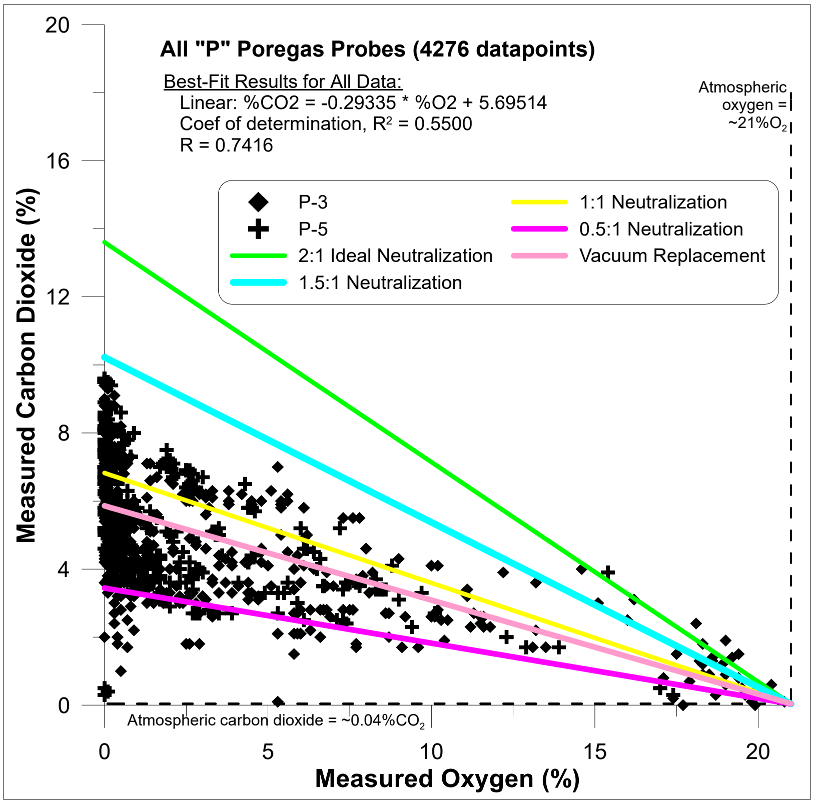


**Figure 4-4. Scatterplot of measured oxygen and measured carbon dioxide for P-3 and P-5.**

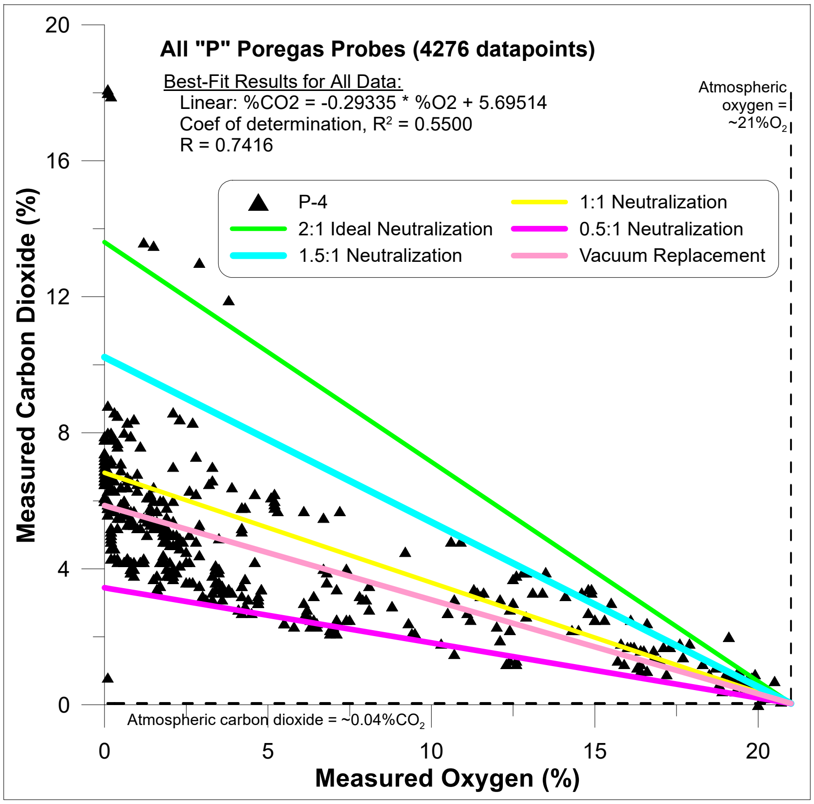


**Figure 4-5. Scatterplot of measured oxygen and measured carbon dioxide for P-4.**

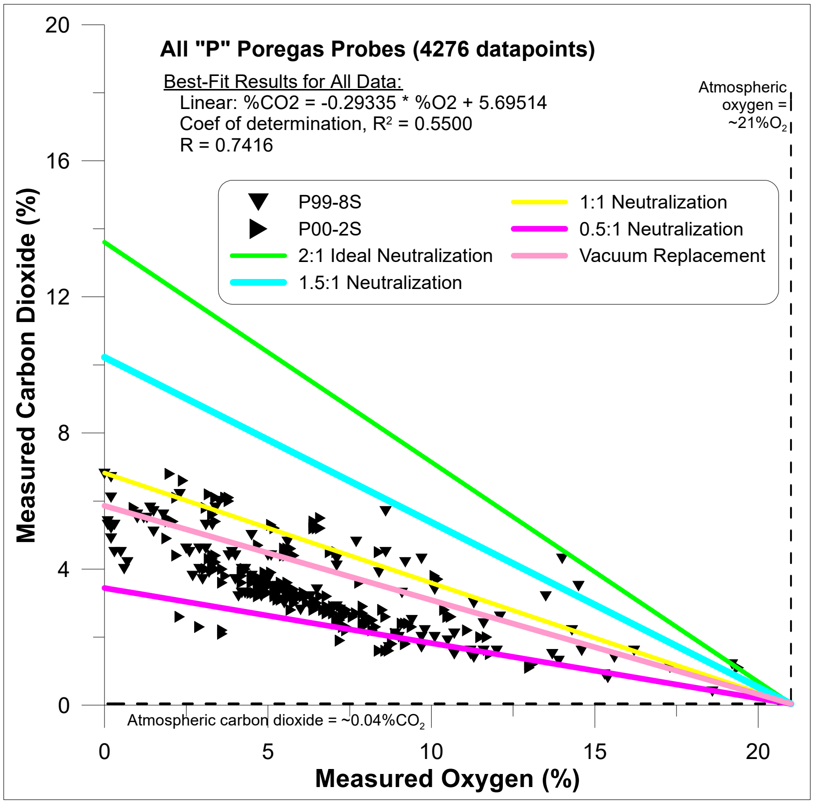


**Figure 4-6. Scatterplot of measured oxygen and measured carbon dioxide for P99-8S and P00-2S.**

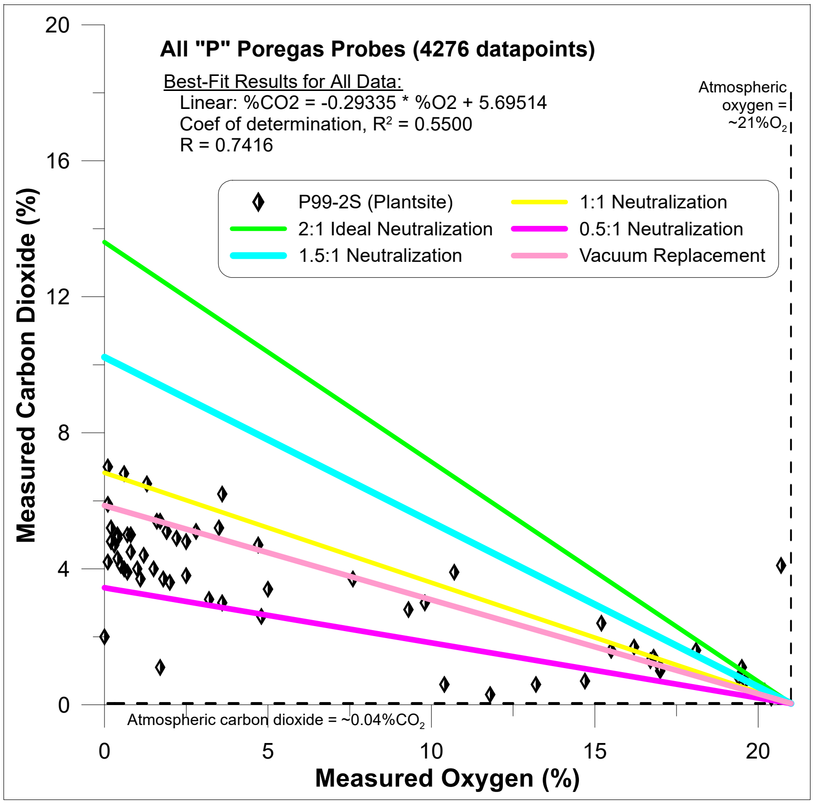


**Figure 4-7. Scatterplot of measured oxygen and measured carbon dioxide for P99-2S (Plantsite).**

## 5. Statistical Central Tendencies within the Geochemical Explanation for the Significant Variability of Carbon Dioxide

As explained in Section 4, various degrees of acidity neutralization by carbonate minerals within the Equity Silver waste-rock pile can explain the observed inverse correlation between $O_2$ and $CO_2$. The various degrees can also explain the observed variability of $CO_2$ levels at a specific $O_2$ level. This section looks more closely at the statistics.

To start, it is important to note that there is no obvious reason to expect $CO_2$ to vary in a regular statistical manner within a particular range of $O_2$. However, it does so in the Equity Silver waste-rock pile.

Based on 1:1 neutralization (Equation 4-4) providing the "predicted" $CO_2$ at a particular $O_2$ level, the statistical distribution of (measured $CO_2$ minus predicted $CO_2$) resembles a normal distribution (Figure 5-1). The mean is nearly -1% $CO_2$ and thus 1:1 neutralization does not represent the exact mean or average neutralization in this waste-rock pile. In other words, more measurements indicate partial neutralization of acidity at Equity Silver.

When the partial vacuum (Figure 3-2) is assumed to be replaced by ambient air (0.04% $CO_2$) after 1:1 neutralization (Figure 5-2), the mean is closer to zero (-0.237% $CO_2$). However, both Figures 5-1 and 5-2 are not good statistical indicators, because they combine the low degree of variability at high $O_2$ with the high degree at low $O_2$ (e.g., Figure 4-1). In other words, lumping tightly gathered datapoints at higher $O_2$ with more scattered datapoints at lower $O_2$ can be misleading.

To resolve this, the statistical distributions of $CO_2$ within $O_2$ ranges of zero to 4.9% (Figures 5-3 and 5-4), 5 to 9.9% (Figures 5-5 and 5-6), and 10 to 21% (Figures 5-7 and 5-8) were checked. The results show that, as $O_2$ decreases, the means and standard deviations generally increase, but all still resemble normal distributions.

The reason is not obvious for these generally regular statistical distributions and trends of poregases within the Equity Silver waste-rock pile. The reason may become apparent as the National Research Council of Canada continues its evaluations of this site, with seasonal mechanisms already explained by Liu et al. (accepted).

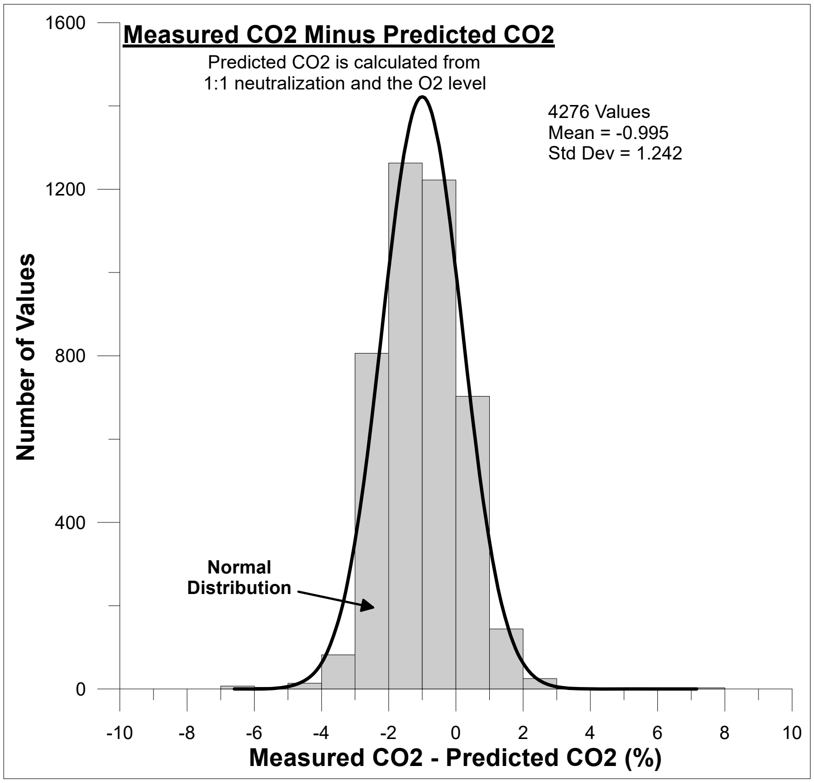


**Figure 5-1. Histogram of measured $CO_2$ minus predicted $CO_2$ from $O_2$, based on 1:1 neutralization.**

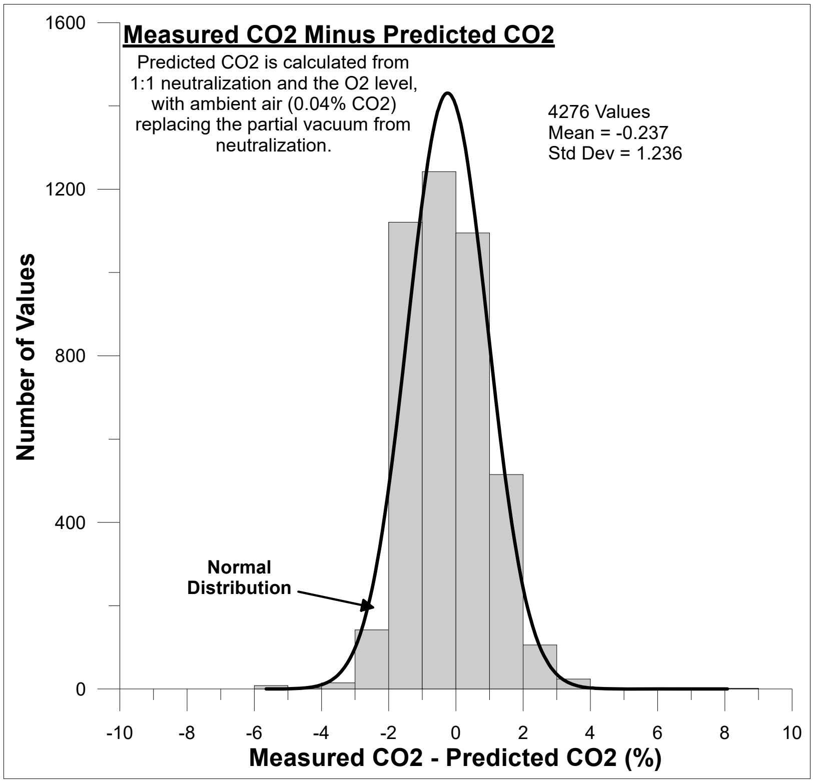


**Figure 5-2. Histogram of measured $CO_2$ minus predicted $CO_2$ from $O_2$, based on the replacement of partial vacuum during 1:1 neutralization by ambient air (0.04% $CO_2$).**

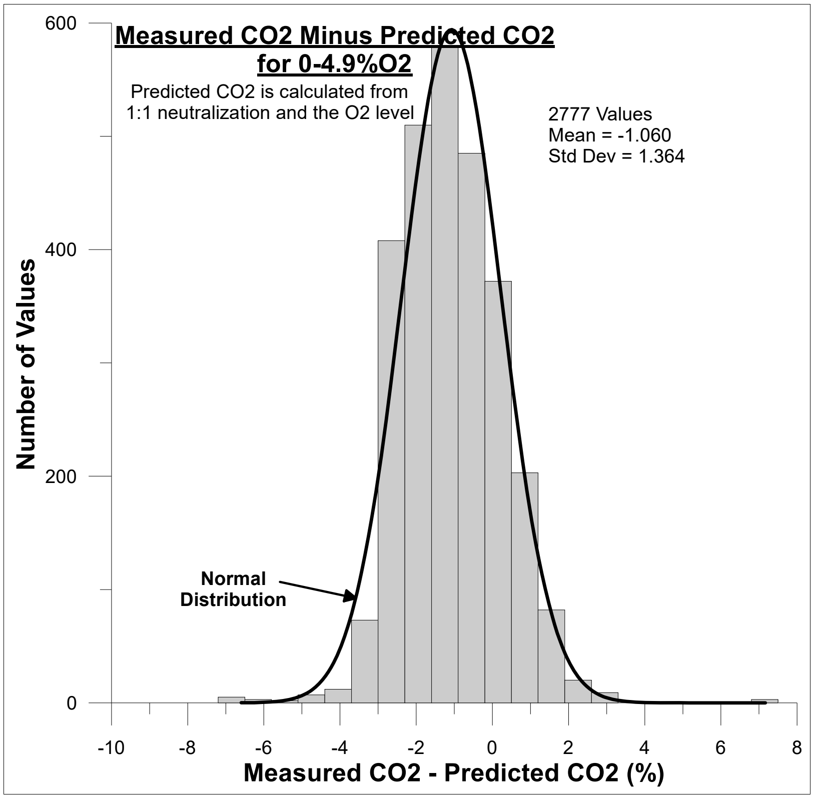


**Figure 5-3. Histogram of measured $CO_2$ minus predicted $CO_2$ from 0-4.9% O2, based on 1:1 neutralization.**

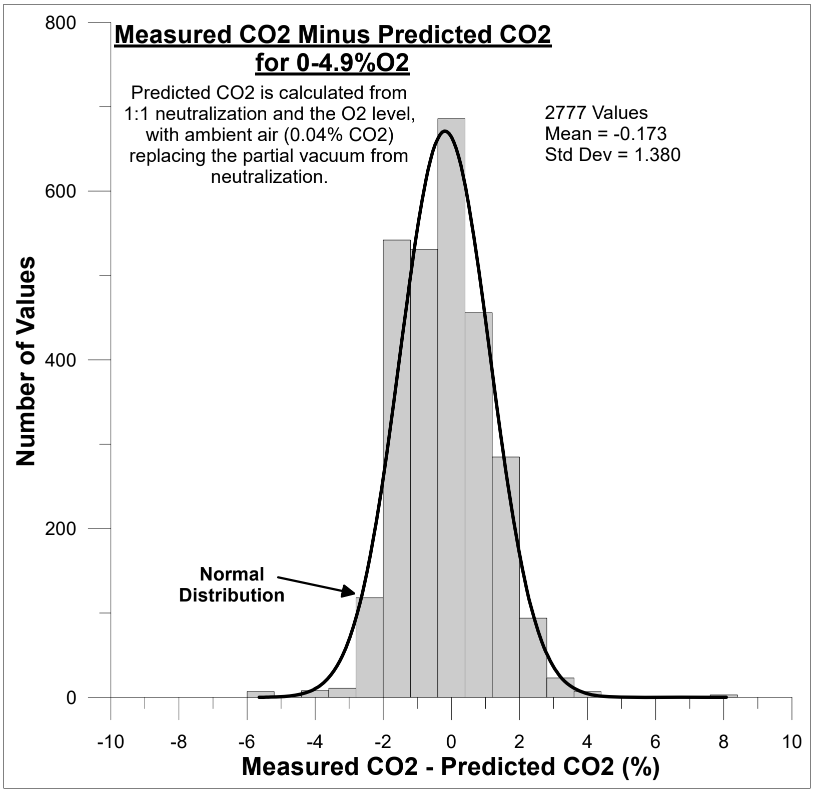


**Figure 5-4. Histogram of measured $CO_2$ minus predicted $CO_2$ from 0-4.9% $O_2$, based on the replacement of partial vacuum during 1:1 neutralization by ambient air (0.04% CO2).**

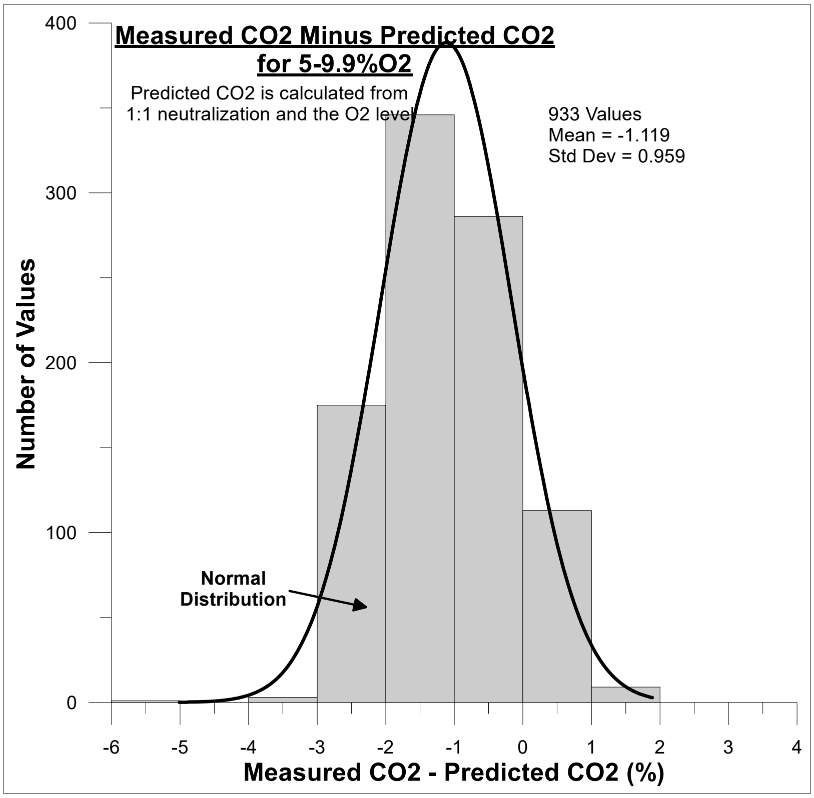


Figure 5-5. Histogram of measured $CO_2$ minus predicted $CO_2$ from 5-9.9% $O_2$, based on 1:1 neutralization.

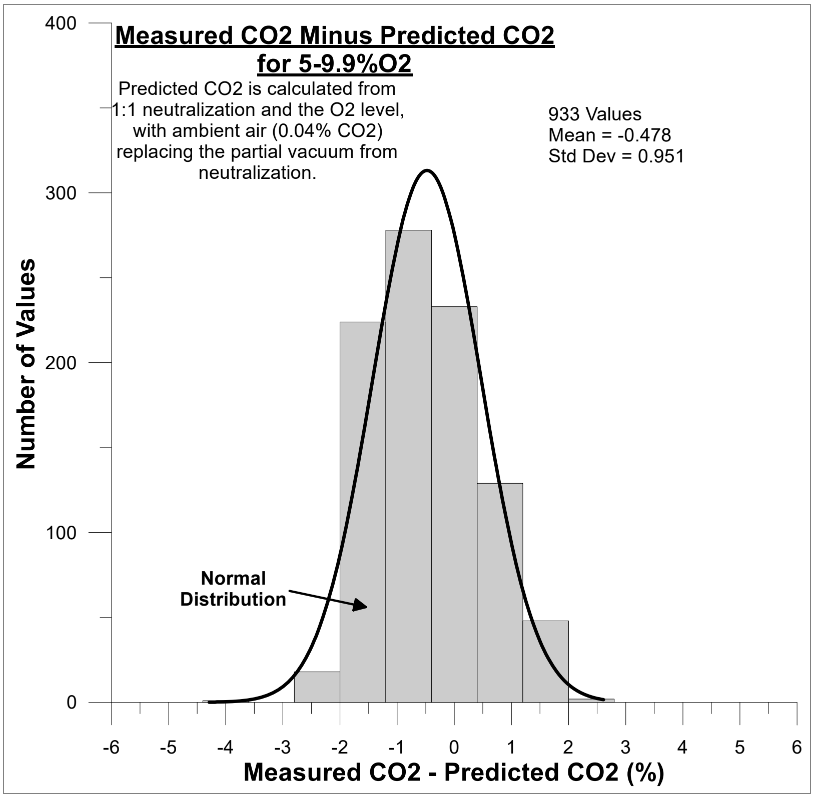


Figure 5-6. Histogram of measured $CO_2$ minus predicted $CO_2$ from 5-9.9% $O_2$, based on the replacement of partial vacuum during 1:1 neutralization by ambient air (0.04% $CO_2$).

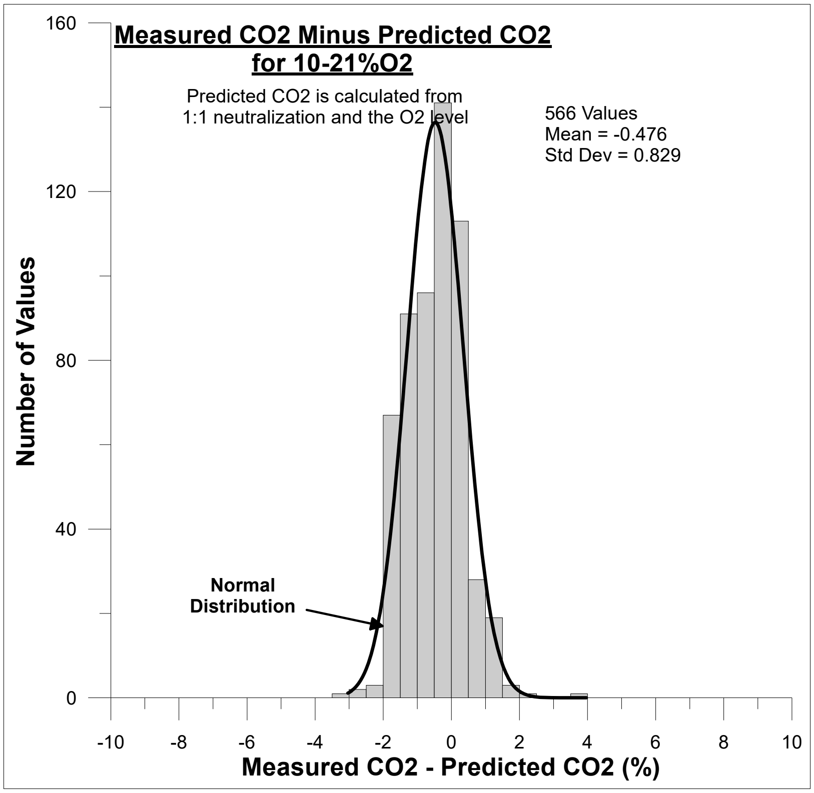


**Figure 5-7. Histogram of measured $CO_2$ minus predicted $CO_2$ from 10-21% $O_2$, based on 1:1 neutralization.**

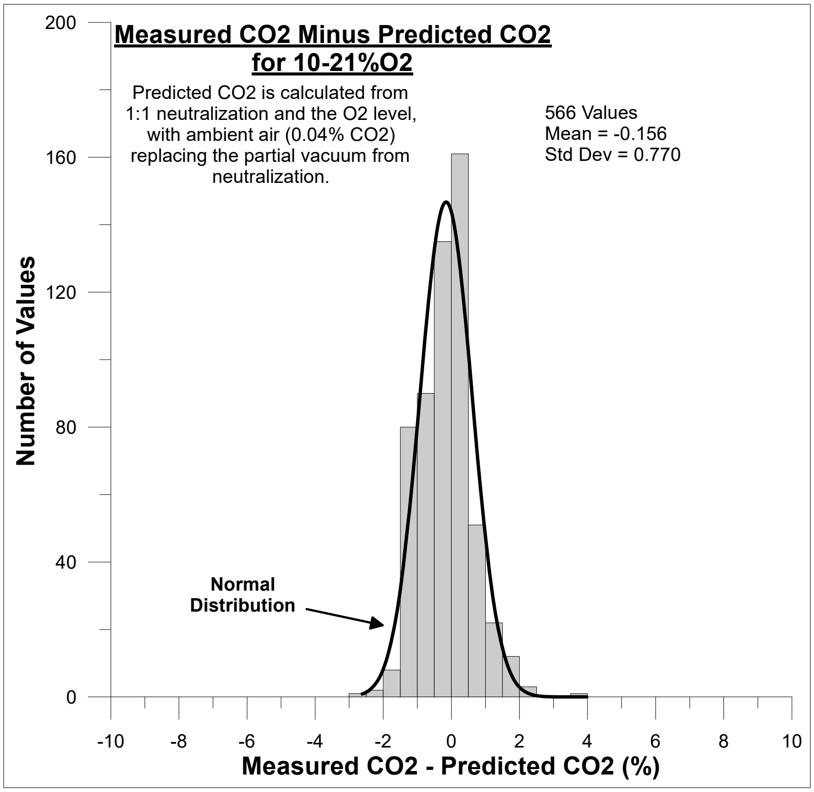


**Figure 5-8. Histogram of measured $CO_2$ minus predicted $CO_2$ from 10-21% $O_2$, based on the replacement of partial vacuum during 1:1 neutralization by ambient air (0.04% $CO_2$).**

# 6. Conclusion

Poregas monitoring data from the Equity Silver waste-rock pile have been re-evaluated here to explain observed trends in $O_2$ and $CO_2$. The observed inverse correlation of these two gases can be explained by carbonate neutralization of acidity, but only when various degrees of neutralization are considered. Most poregas values indicate at least one-half of the acidity is neutralized (0.5:1 partial neutralization), although a few datapoints indicate virtually no neutralization. Many values indicate pH was initially neutralized to above pH ~ 6.4, followed by re-acidification along downgradient flowpaths.

This re-evaluation also showed that these neutralization processes likely create a partial vacuum within the waste rock. The assumption that this partial vacuum is filled by ambient air comes close to explaining the average trend between $O_2$ and $CO_2$.

Although there is no readily apparent reason, the variability of $CO_2$ within a particular range of $O_2$ displays a generally normal statistical distribution. The means and standard deviations generally increase as $O_2$ decreases.

The National Research Council of Canada (NRC) is conducting detailed evaluations and modelling of this waste-rock pile, with seasonal mechanisms already explained. This case study provides geochemical support for the current NRC findings.

# 7. References

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