

MDAG.com Internet Case Study 50

Explanations for Poregas CO₂ Variability Relative to O₂ in the Equity Silver Waste-Rock Pile

by K.A. Morin

© 2017 Kevin A. Morin

www.mdag.com/case_studies/cs50.html

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.

TABLE OF CONTENTS

Abstract	2
1. Introduction	3
2. Description of “P” Poregas Monitoring at Equity Silver	5
3. Detailed Description of Poregas Monitoring Results and Partial Vacuums	5
4. The Geochemical Explanation for the Inverse Correlation of Oxygen and Carbon Dioxide, and for the Significant Variability of Carbon Dioxide	10
5. Statistical Central Tendencies within the Geochemical Explanation for the Significant Variability of Carbon Dioxide	16
6. Conclusion	21
7. References	22

Abstract

For the Equity Silver waste-rock pile, roughly 17 years of poregas monitoring for O₂ and CO₂ 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 CO₂ at a particular level of O₂. 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 O₂ and CO₂.

For no readily apparent reason, the variability of CO₂ within a particular range of O₂ displays a generally normal statistical distribution. The means and standard deviations generally increase as O₂ 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 2013) and Morin (2016) described and interpreted thousands of water analyses, flows, internal temperatures, and poregas levels of carbon dioxide (CO₂) and oxygen (O₂) within the Equity Silver waste-rock pile. One observation was that a general inverse correlation was seen between O₂ and CO₂, but an explanation for the variability of CO₂ relative to O₂ was not apparent. Liu et al. (accepted) carried this further, by finding abundant inverse correlations of O₂ and CO₂, laterally and with depth at the individual “P” poregas monitoring ports, within a correlation matrix of O₂ and CO₂.

Depicted originally on a logarithmic scale, the inverse correlation between O₂ and CO₂ was generally linear (Figure 1-1), with a best-fit equation of:

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

Nevertheless, variability of CO₂ at a particular level of O₂ was often a factor-of-two above and below the best-fit equation.

The atmospheric oxygen level of approximately 21%O₂ was asymptotically approached, but not exceeded in Figure 1-1, as CO₂ levels decreased. Also, most CO₂ levels were substantially above atmospheric levels of ~0.04%CO₂, and often clustered around 2-10%CO₂ where oxygen was below one-half atmospheric (<10%O₂). 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 O₂ and CO₂ 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 O₂ decreased, meaning air and/or poregas were drawn from elsewhere into these locations. Also, the significant variability of CO₂ suggested sources of CO₂ other than carbonate neutralization.

This MDAG.com Case Study 50 re-examines the relationship of O₂ to CO₂ in the Equity Silver waste-rock pile to explain the observed trend and variability.

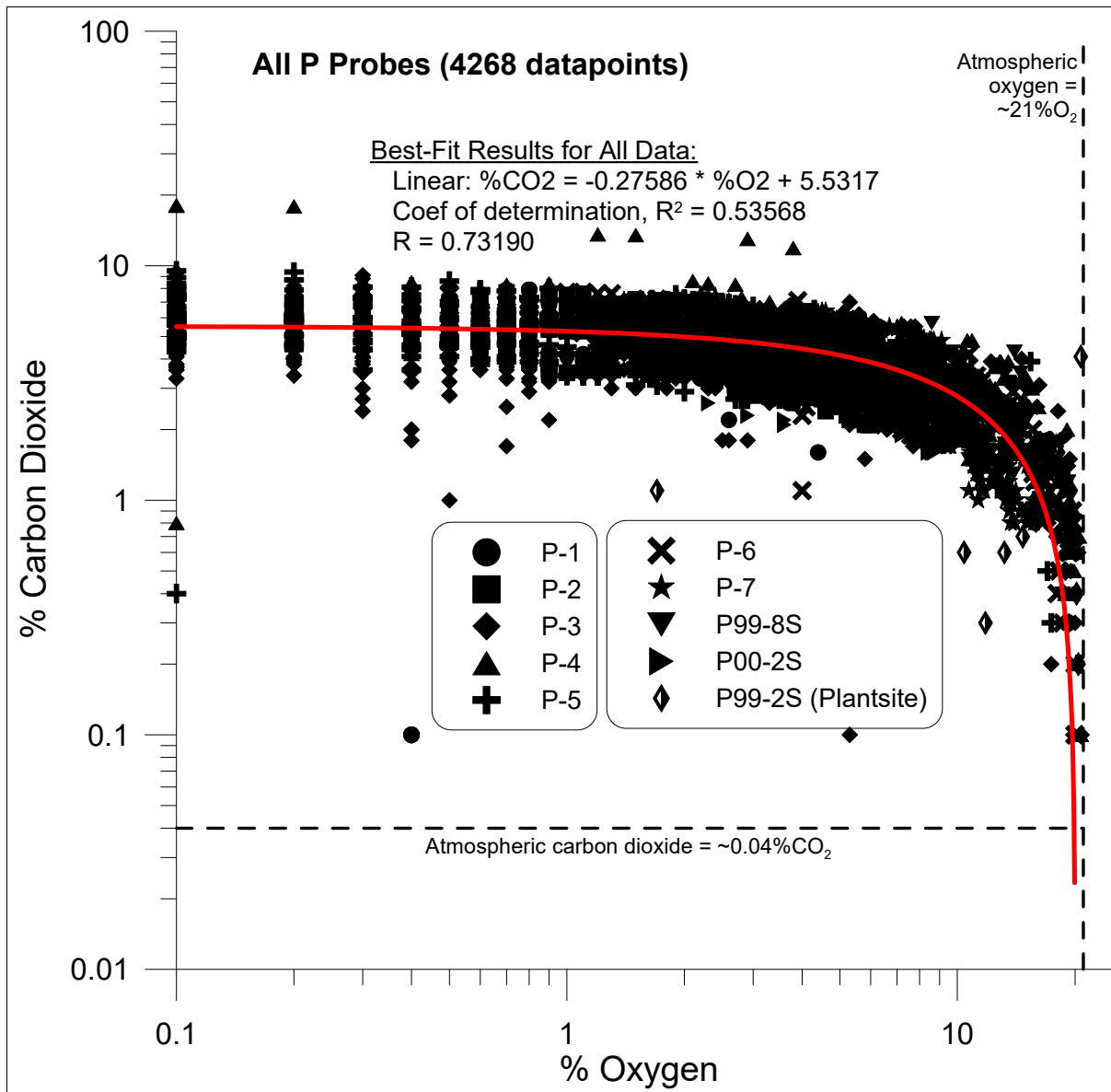


Figure 1-1. Pore-gas carbon dioxide vs. oxygen at all P locations and depths in the Equity Silver waste-rock pile, with the best-fit equation for the overall linear trend (from Morin et al., 2010 and 2012).

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 O₂ and CO₂ 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 O₂ and CO₂ 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:

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

The variability of CO₂ at a particular O₂ level (any vertical slice in Figure 3-1) increases as CO₂ decreases. However, the point remains that there is no 1:1 inverse correlation: O₂ is consumed in a proportionally greater amount than CO₂ replaces it. This makes sense, as explained below with equations, because a significant amount of O₂ is removed from the gas phase and incorporated into solid-phase minerals like oxyhydroxides (e.g., Fe(OH)₃) and sulphates (e.g., CaSO₄•2H₂O).

This excess loss of poregas O₂ 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 CO₂ relative to O₂, 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.

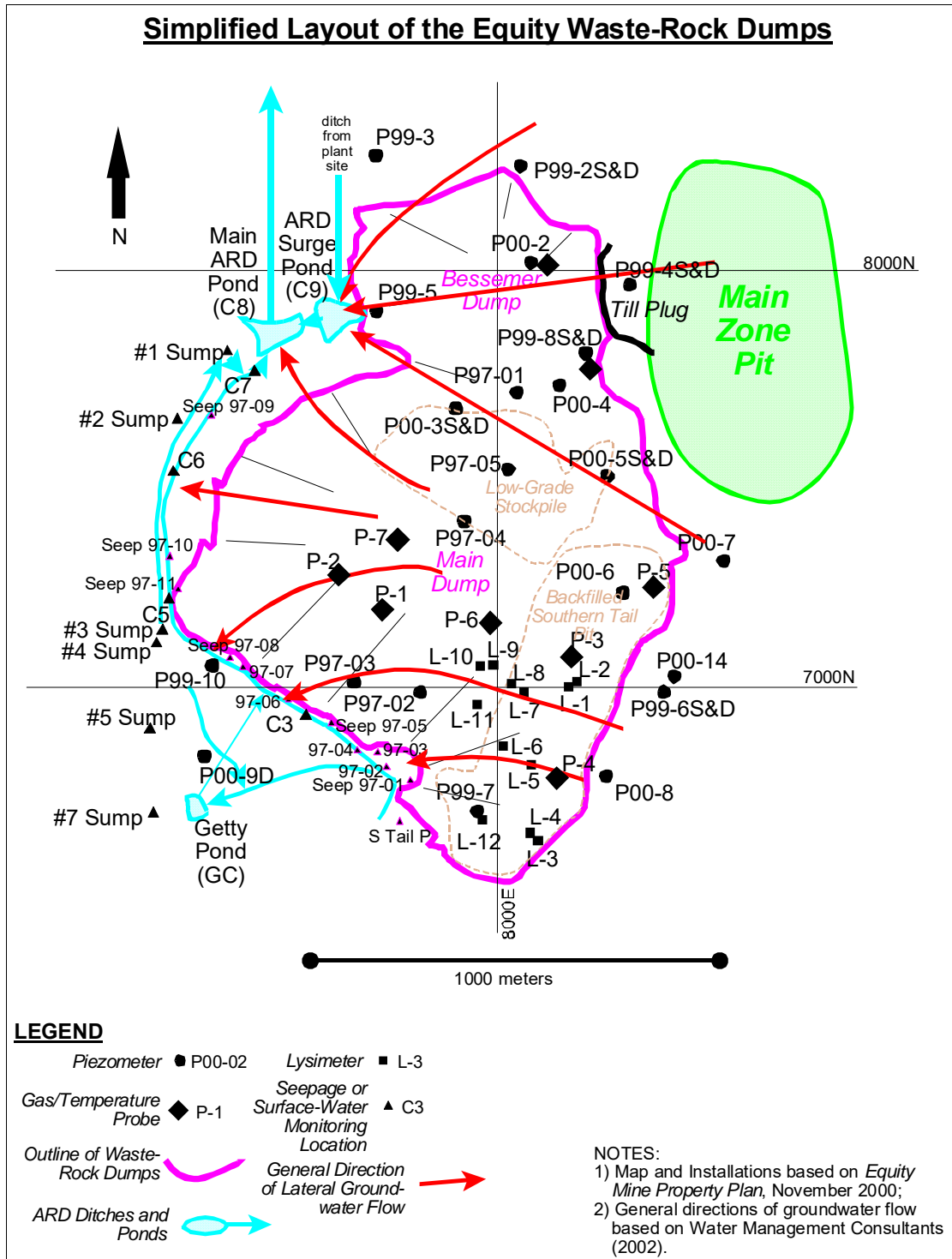


Figure 2-1. Locations of the “P” poregas probes within the Equity Silver waste-rock pile, consisting of two merged waste-rock dumps, a low-grade ore stockpile, and the backfilled and buried Southern Tail Pit.

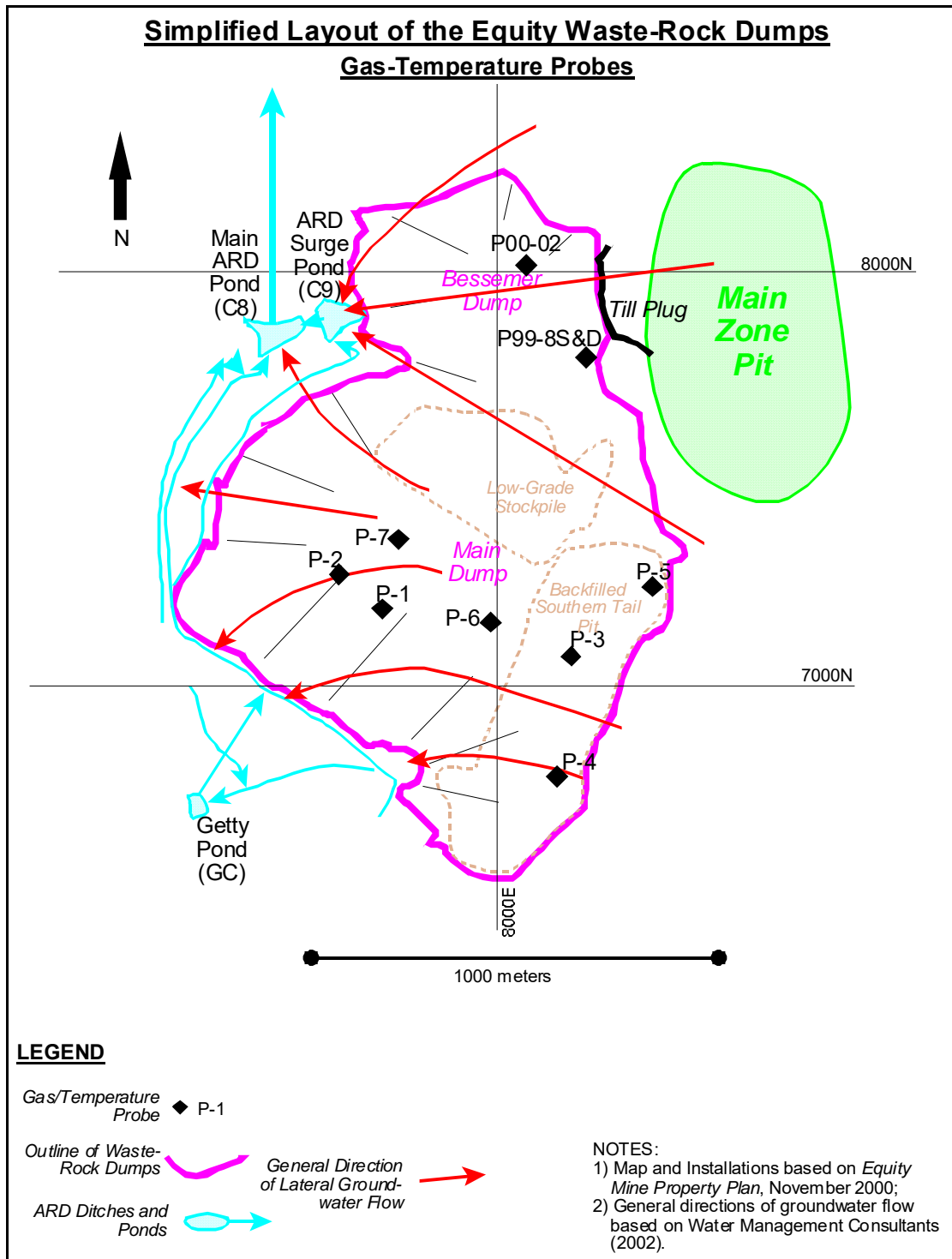


FIGURE 2-2. A simplified version of Figure 2-1, showing only the “P” poregas probes in the Equity Silver waste-rock pile, with each probe containing two to eight depth-specific monitoring ports.

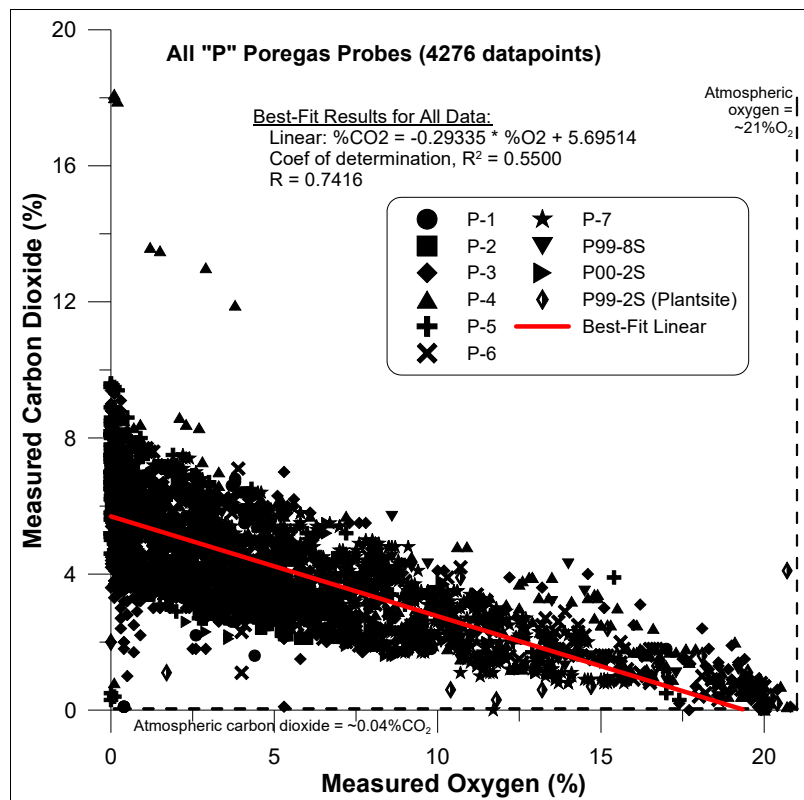


Figure 3-1. Scatterplot of measured oxygen and measured carbon dioxide, with the best-fit linear line shown in red.

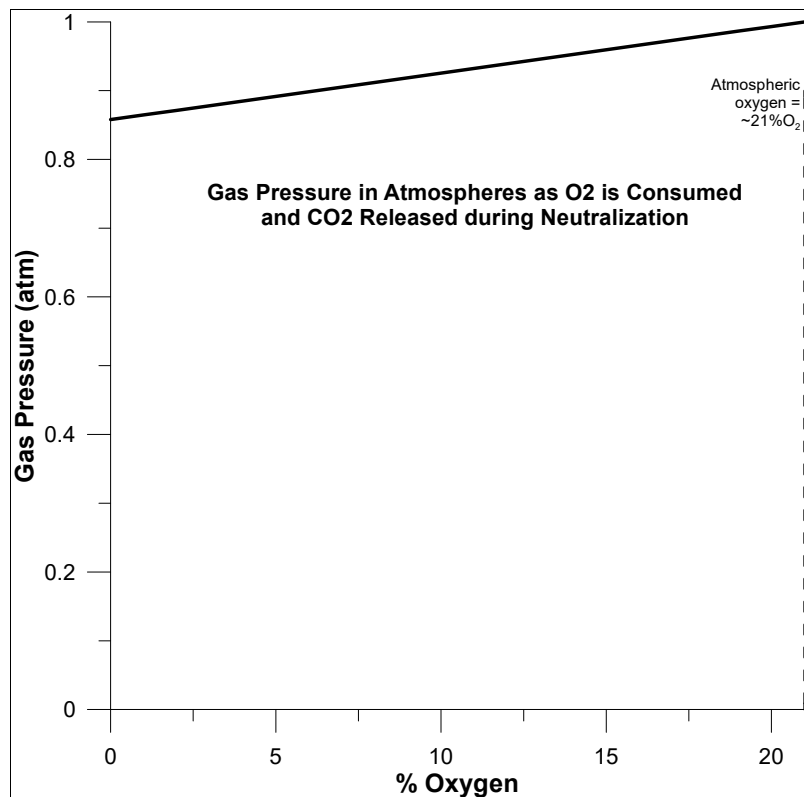


Figure 3-2. Trend of increasing partial vacuum as oxygen decreases, due to the lack of 1:1 replacement by carbon dioxide.

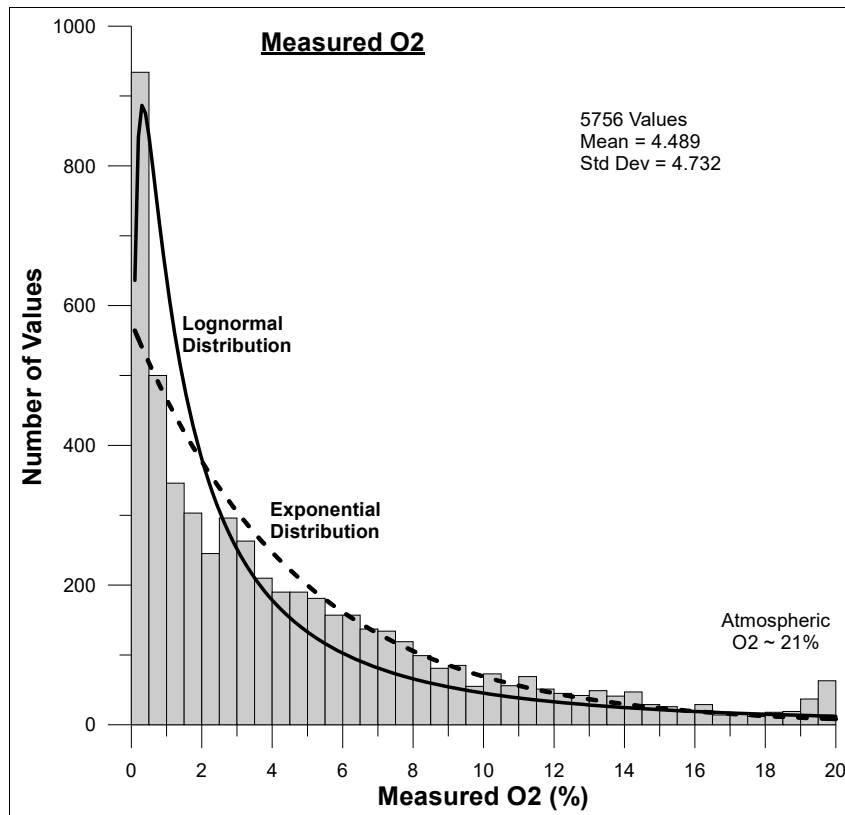


Figure 3-3. Statistical histogram of poregas oxygen levels.

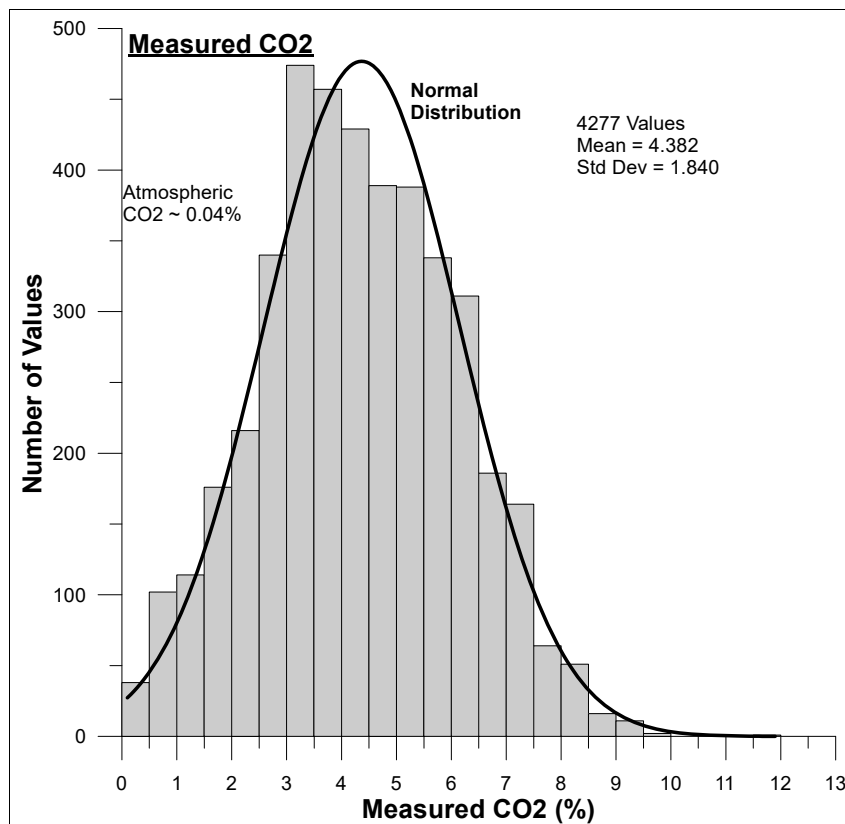


Figure 3-4. Statistical histogram of poregas carbon dioxide levels.

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

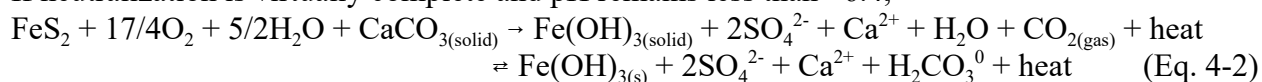
The most successful explanation for the inverse correlation of O₂ and CO₂, and the significant variability of CO₂, lies in aqueous geochemistry. Here is the first important equation.



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 CO₂ gas and a lesser amount as aqueous H₂CO₃⁰. At pH > ~6.4, the right side dominates, with little CO₂ and H₂CO₃⁰ occurring. The important point is to know aqueous pH in advance so that the relevant forms of carbonate can be considered.

When the ARD contacts some carbonate minerals, neutralization occurs. However, neutralization may or may not raise pH above 6.4. Here are two relevant neutralization equations.

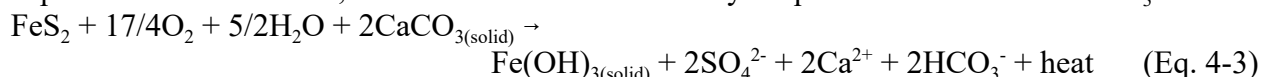
If neutralization is virtually complete and pH remains less than ~6.4,



With most of the CO₂ occurring as gas, the molar consumption ratio of O₂ to produce CO₂ would be 1 mole CO₂ produced for every 17/4 moles O₂ consumed, or -0.235. The volume/mass ratio would be 44 g CO₂ to 136 g O₂ consumed, or -0.323. Note the linear correlation coefficients in Figures 1-1 and 2-1 are ~-0.28.

If there is insufficient CaCO₃ for Equation 4-2, then the consumption ratio would be closer to zero and less negative than -0.323. For example, half neutralization would produce a ratio of -0.162.

If pH increases above 6.4, then this neutralization ideally¹ requires twice as much CaCO₃,



If this water with pH above 6.4 subsequently becomes acidic along flowpaths, the reversal of Equation 4-1 would ideally produce twice the CO₂, representing a volume/mass consumption ratio of 88g CO₂ to 136 g O₂ consumed, or ideally -0.646. This would only happen when the neutralized water is later re-acidified along flowpaths; otherwise, the consumption ratio would be close to zero because little CO₂ would be released to the poregas above pH 6.4. The Equity Silver waste-rock pile releases little near-neutral drainage and most drainage is strongly acidic, so re-acidification along flowpaths is possible. Again, rarely is the ideal ratio of -0.646 achieved¹, so a realistic ratio would be between -0.646 and -0.323, such as halfway at -0.485.

With atmospheric conditions representing a starting point (21% O₂ and 0.04% CO₂), the correlation equations for full neutralization to pH <~6.4 (“1:1 neutralization”), one-half neutralization (“0.5:1 neutralization”), and non-ideal neutralization to pH >~6.4 with subsequent re-acidification (“1.5:1 neutralization”) are:

$$1:1 \text{ neutralization: } \text{CO}_2(\%) = -0.323 * \text{O}_2(\%) + 6.823 \quad (\text{Eq. 4-4})$$

$$0.5:1 \text{ neutralization: } \text{CO}_2(\%) = -0.162 * \text{O}_2(\%) + 3.442 \quad (\text{Eq. 4-5})$$

$$1.5:1 \text{ neutralization: } \text{CO}_2(\%) = -0.485 * \text{O}_2(\%) + 10.225 \quad (\text{Eq. 4-6})$$

These are shown in Figure 4-1.

¹ “Ideally” is a long and complicated explanation. Suffice to it to say “ideally” is rarely achieved, particularly in open systems like waste-rock piles, and some amount less than twice is more often consumed.

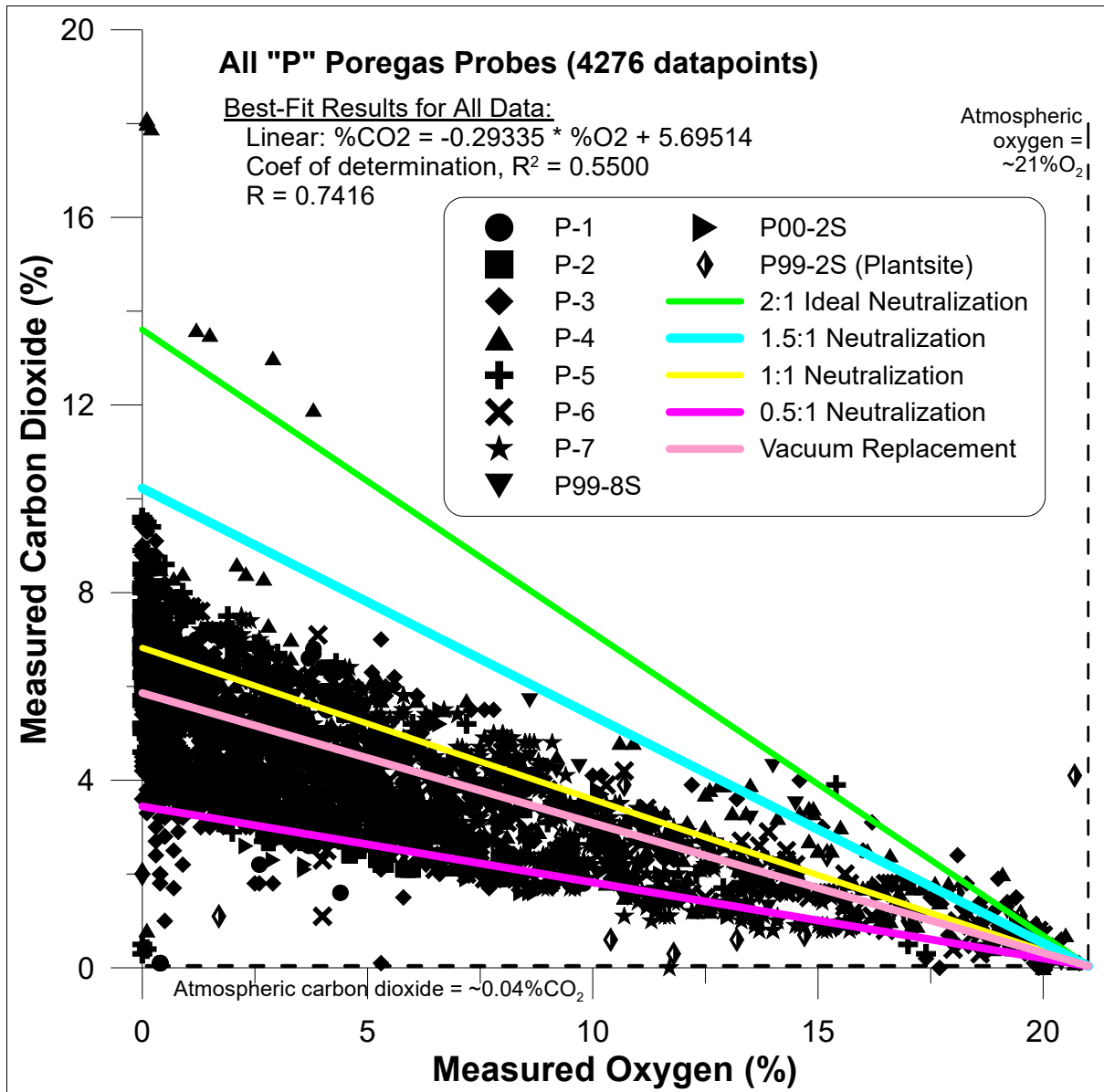


Figure 4-1. Scatterplot of measured oxygen and measured carbon dioxide, with straight lines representing various degrees of neutralization and with “vacuum replacement” representing carbon dioxide after the partial vacuum is filled with air.

Figure 4-1 leads to several observations.

- The ideal 2:1 neutralization generally represents the upper bound for the rare high values of CO₂ associated with significant O₂ in the Equity Silver waste-rock pile.
- 1.5:1 neutralization generally overestimates CO₂ levels, except at higher levels of O₂.
- 1:1 neutralization is within the typical variability of CO₂, but somewhat on the high side.
- “Vacuum replacement” where ambient air (0.04% CO₂) is drawn in to fill the partial vacuum after 1:1 neutralization is more centrally located within the CO₂ variability.
- 0.5:1 neutralization is the general lower bound of measured CO₂, 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 O₂ 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 O₂ and neutralization (Figure 4-3).

P-3 and P-5 in the backfilled Southern Tail Pit tended to have very low values of O₂ with a relatively large range of neutralization at those low O₂ levels (Figure 4-4). P-4 also in the backfilled Southern Tail Pit had a more even distribution of O₂ 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 O₂ values (Figure 4-6), with CO₂ mostly reflecting less than 100% neutralization. Most datapoints for P00-2S also on the north side of the waste-rock pile indicated O₂ was typically 3-10% and typically partially neutralized somewhat above 50% (Figure 4-6).

P99-2S near the former plantsite generally produced O₂ less than 5% with some partially neutralized CO₂ levels approaching zero neutralization (Figure 4-7).

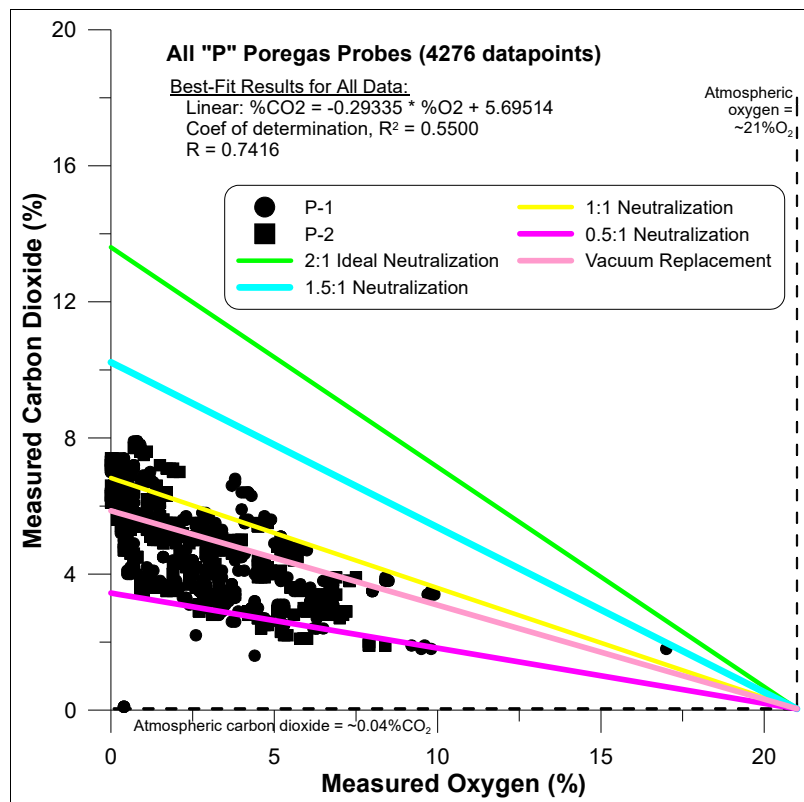


Figure 4-2. Scatterplot of measured oxygen and measured carbon dioxide for P-1 and P-2.

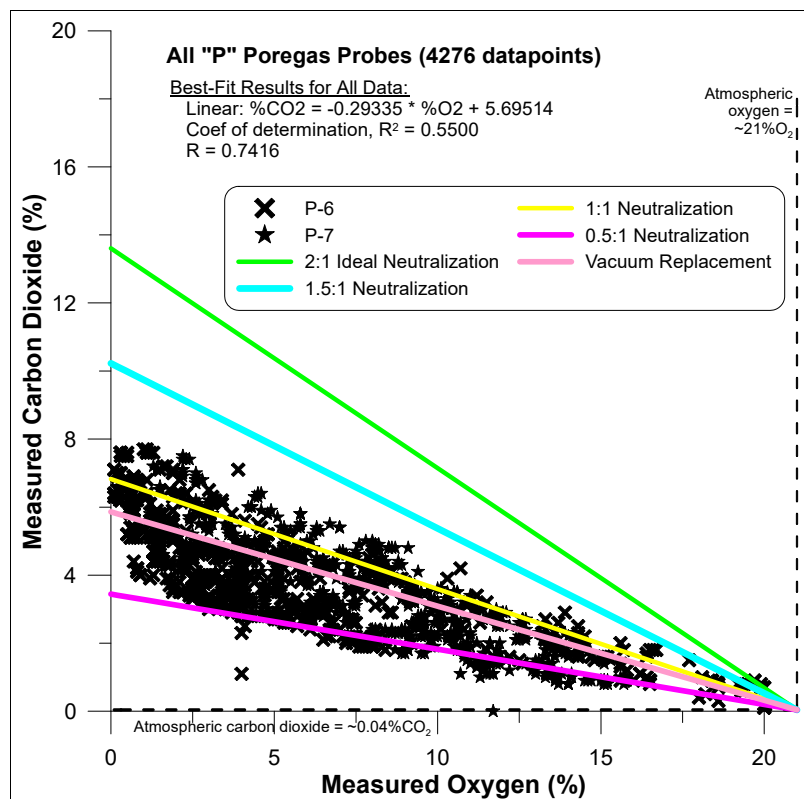


Figure 4-3. Scatterplot of measured oxygen and measured carbon dioxide for P-6 and P-7.

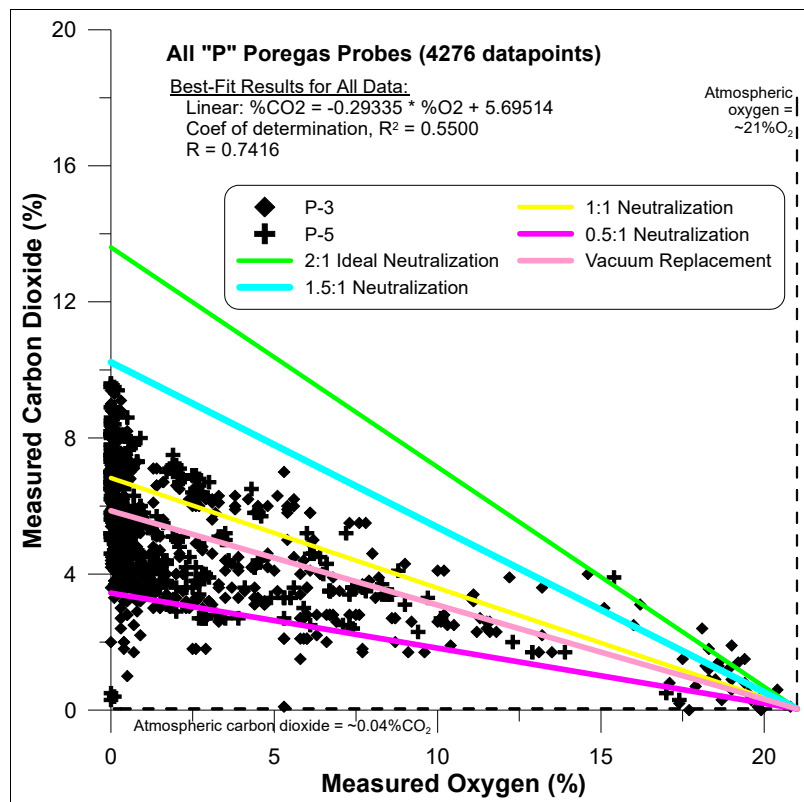


Figure 4-4. Scatterplot of measured oxygen and measured carbon dioxide for P-3 and P-5.

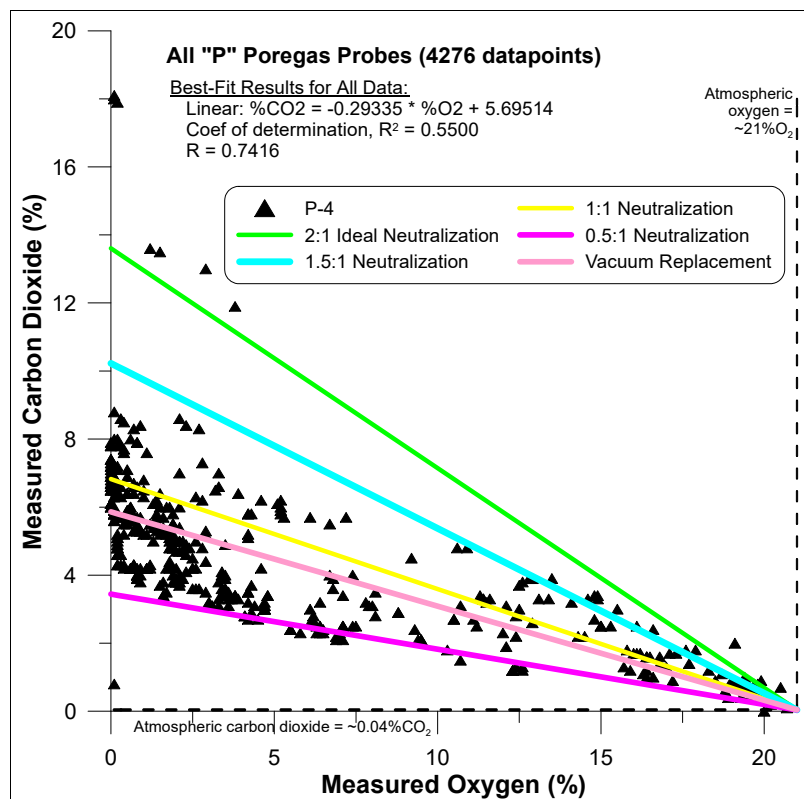


Figure 4-5. Scatterplot of measured oxygen and measured carbon dioxide for P-4.

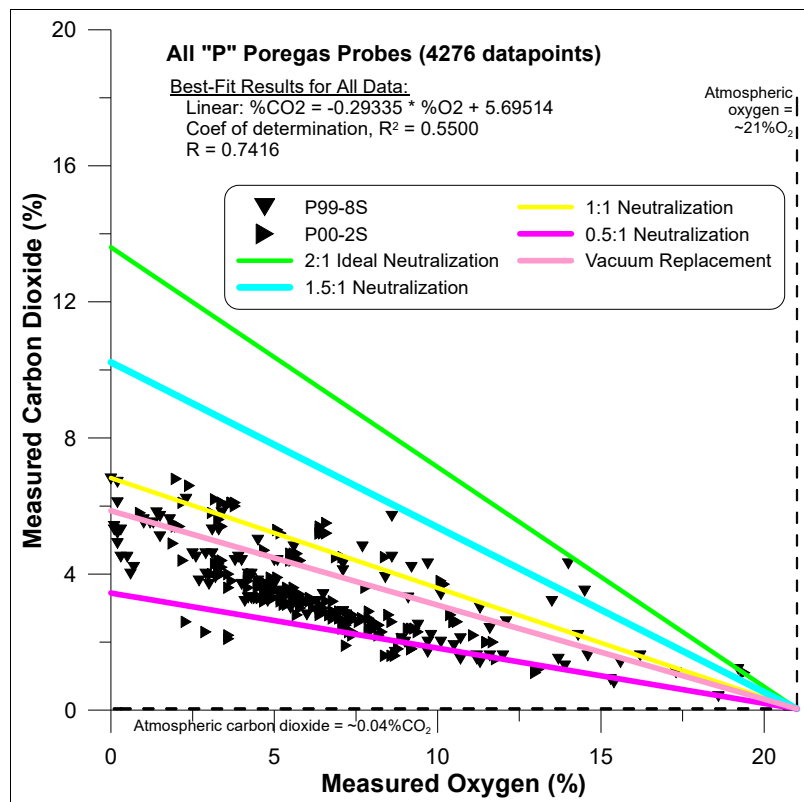


Figure 4-6. Scatterplot of measured oxygen and measured carbon dioxide for P99-8S and P00-2S.

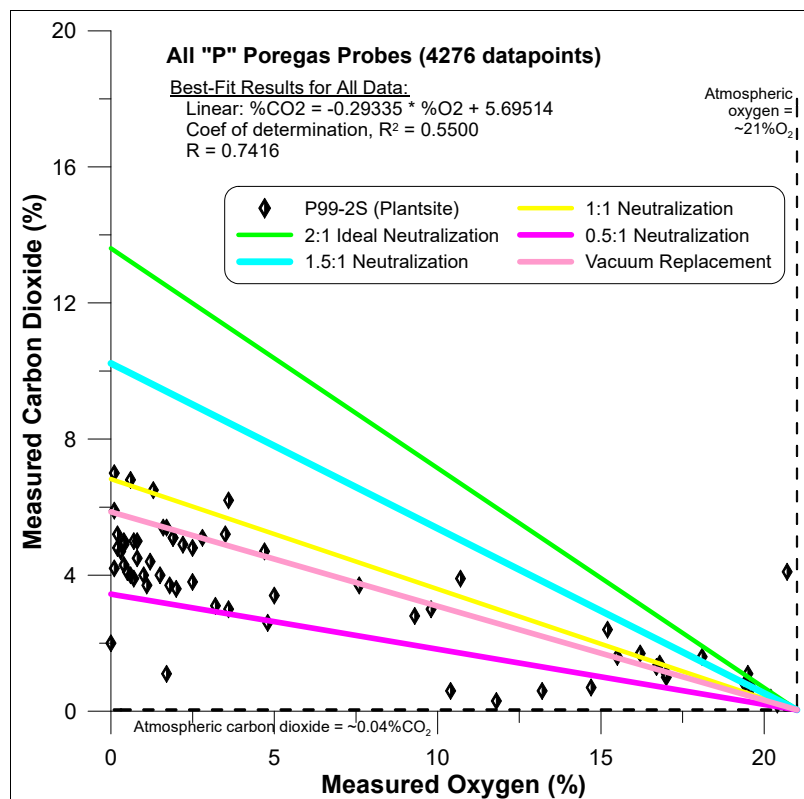


Figure 4-7. Scatterplot of measured oxygen and measured carbon dioxide for P99-2S (Plantsite).

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 O₂ and CO₂. The various degrees can also explain the observed variability of CO₂ levels at a specific O₂ level. This section looks more closely at the statistics.

To start, it is important to note that there is no obvious reason to expect CO₂ to vary in a regular statistical manner within a particular range of O₂. However, it does so in the Equity Silver waste-rock pile.

Based on 1:1 neutralization (Equation 4-4) providing the “predicted” CO₂ at a particular O₂ level, the statistical distribution of (measured CO₂ minus predicted CO₂) resembles a normal distribution (Figure 5-1). The mean is nearly -1% CO₂ 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% CO₂) after 1:1 neutralization (Figure 5-2), the mean is closer to zero (-0.237% CO₂). However, both Figures 5-1 and 5-2 are not good statistical indicators, because they combine the low degree of variability at high O₂ with the high degree at low O₂ (e.g., Figure 4-1). In other words, lumping tightly gathered datapoints at higher O₂ with more scattered datapoints at lower O₂ can be misleading.

To resolve this, the statistical distributions of CO₂ within O₂ 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 O₂ 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).

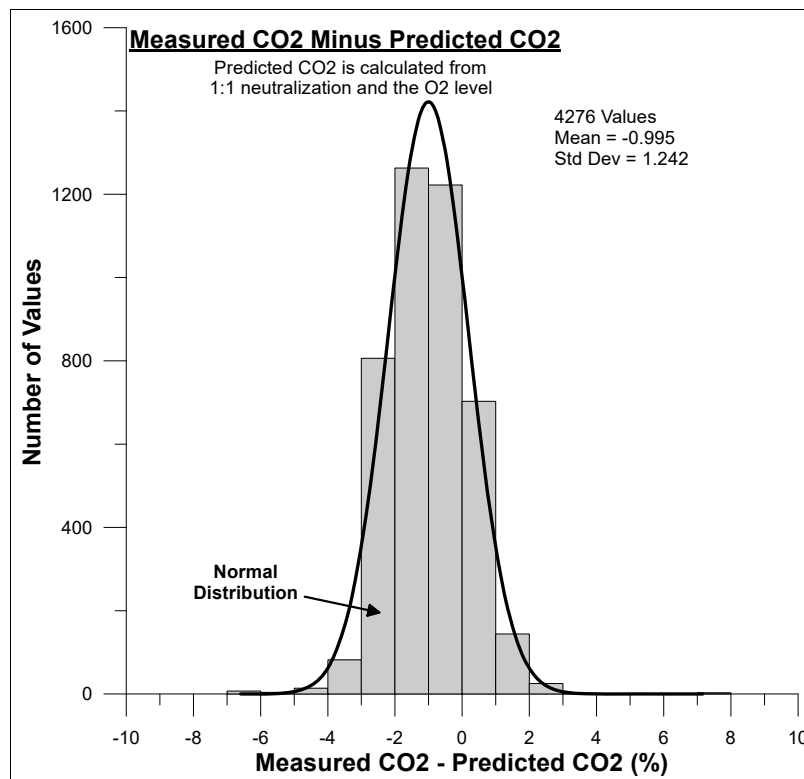


Figure 5-1. Histogram of measured CO₂ minus predicted CO₂ from O₂, based on 1:1 neutralization.

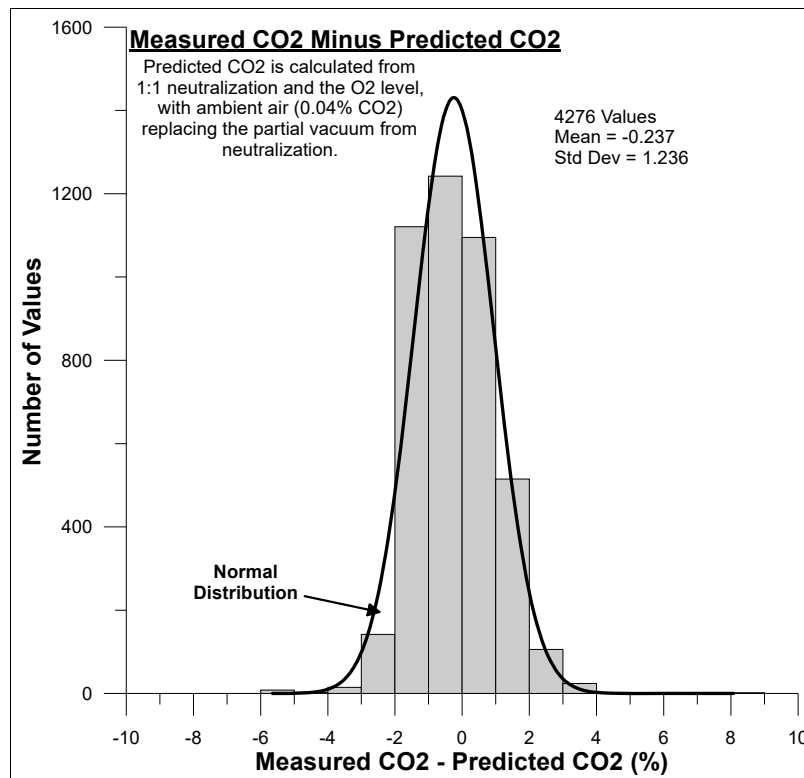


Figure 5-2. Histogram of measured CO₂ minus predicted CO₂ from O₂, based on the replacement of partial vacuum during 1:1 neutralization by ambient air (0.04% CO₂).

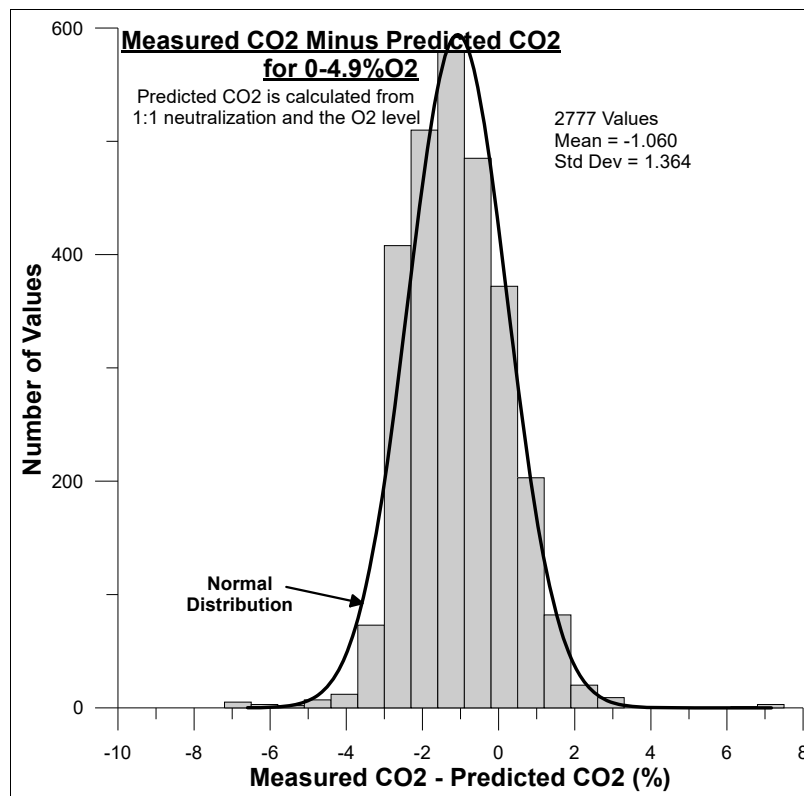


Figure 5-3. Histogram of measured CO₂ minus predicted CO₂ from 0-4.9% O₂, based on 1:1 neutralization.

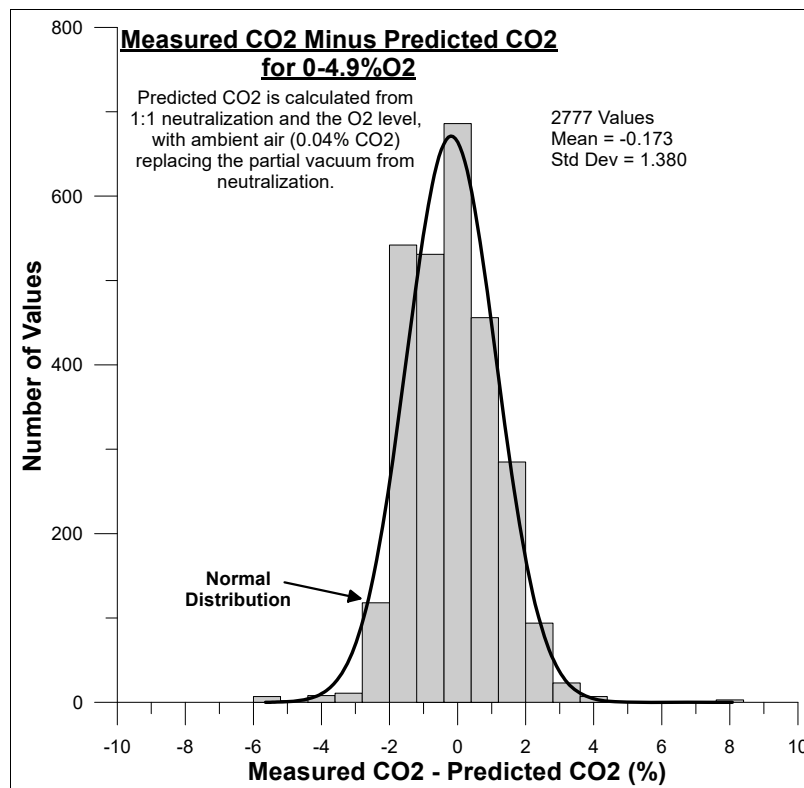


Figure 5-4. Histogram of measured CO₂ minus predicted CO₂ from 0-4.9% O₂, based on the replacement of partial vacuum during 1:1 neutralization by ambient air (0.04% CO₂).

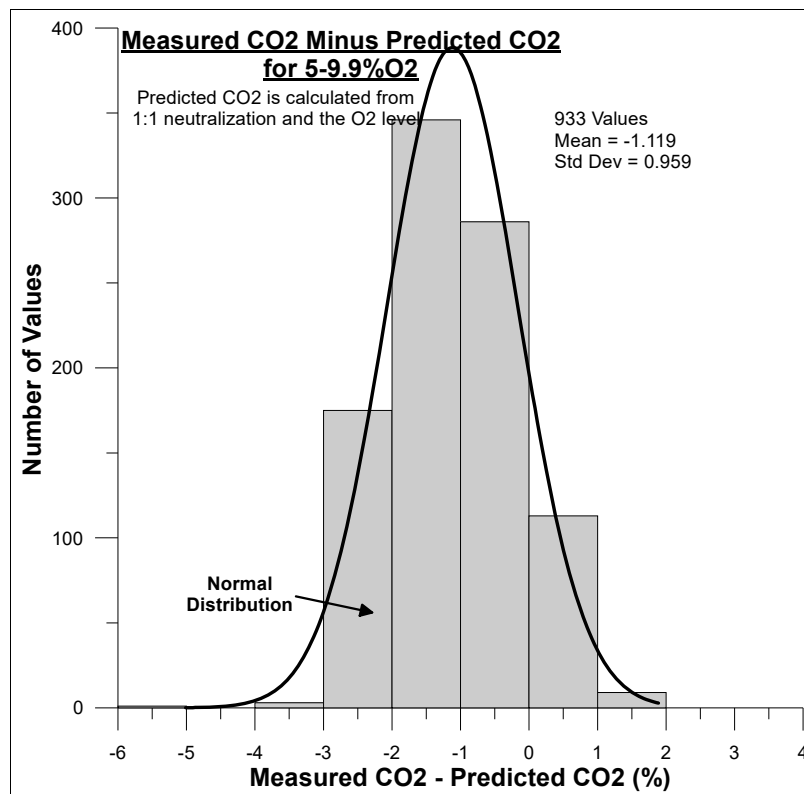


Figure 5-5. Histogram of measured CO₂ minus predicted CO₂ from 5-9.9% O₂, based on 1:1 neutralization.

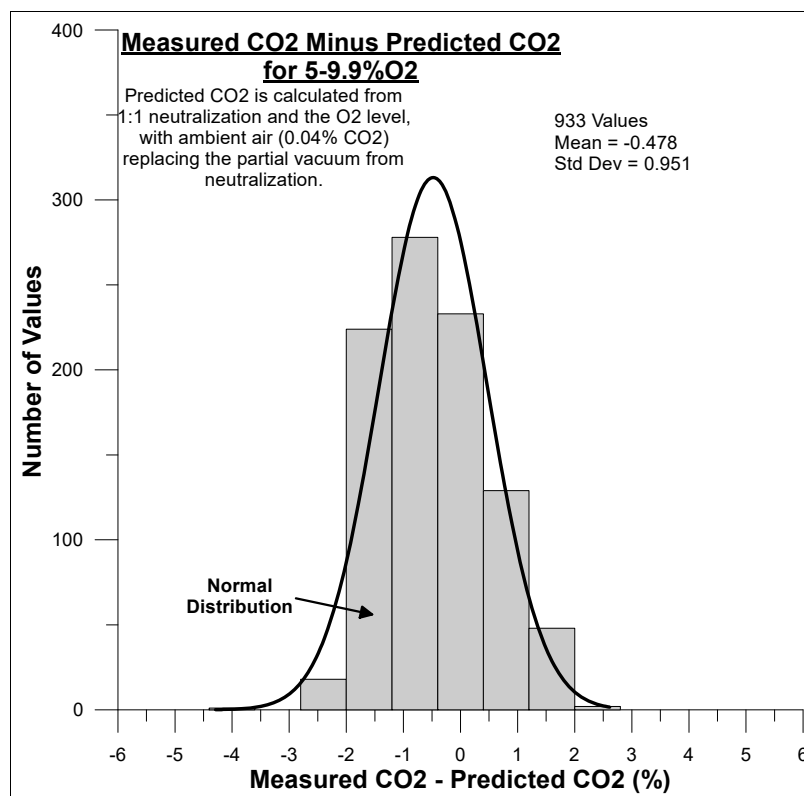


Figure 5-6. Histogram of measured CO₂ minus predicted CO₂ from 5-9.9% O₂, based on the replacement of partial vacuum during 1:1 neutralization by ambient air (0.04% CO₂).

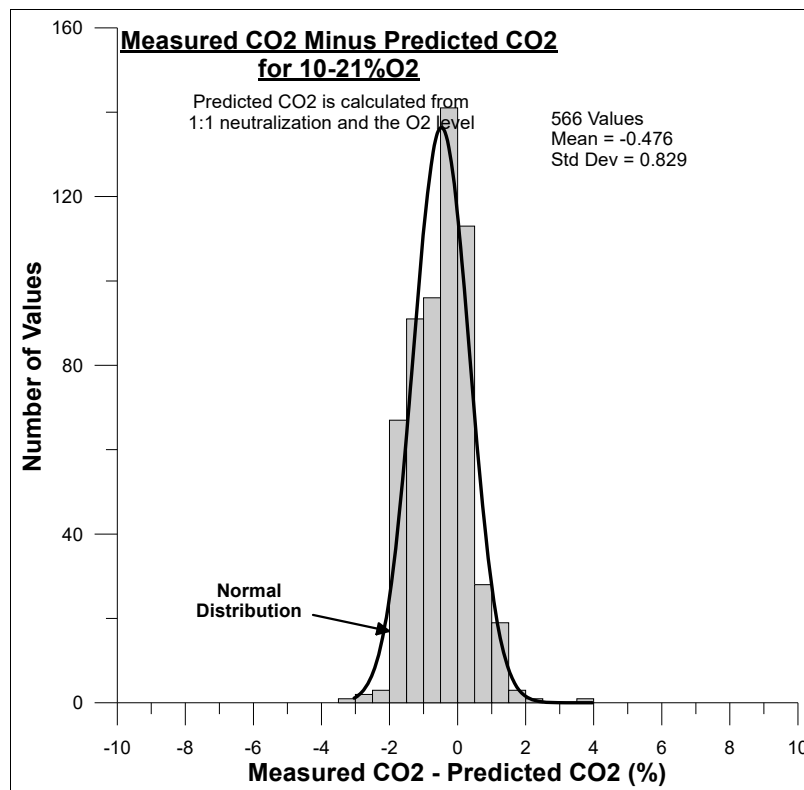


Figure 5-7. Histogram of measured CO₂ minus predicted CO₂ from 10-21% O₂, based on 1:1 neutralization.

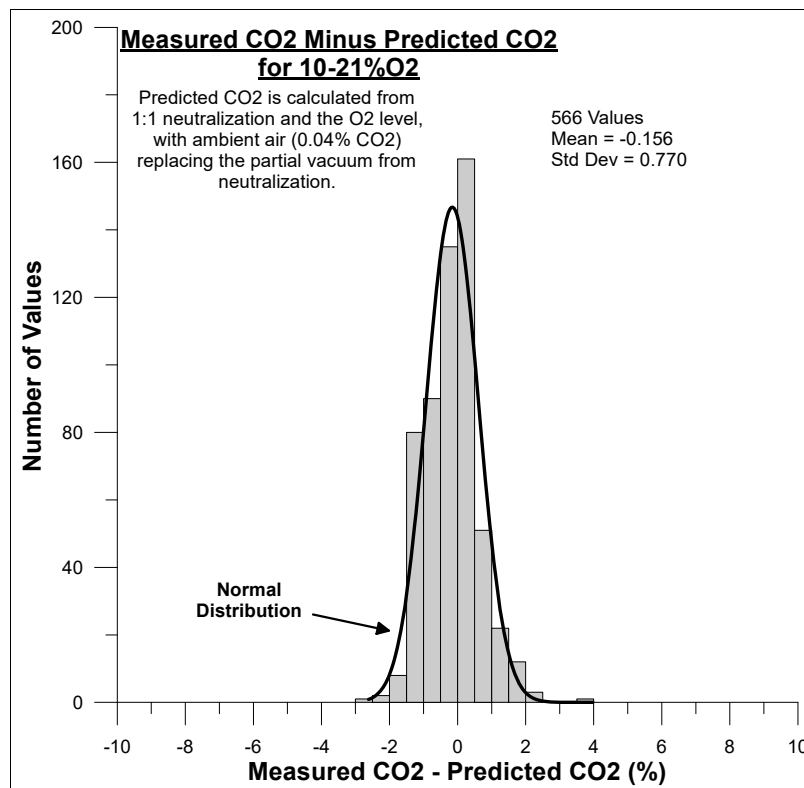


Figure 5-8. Histogram of measured CO₂ minus predicted CO₂ from 10-21% O₂, based on the replacement of partial vacuum during 1:1 neutralization by ambient air (0.04% CO₂).

6. Conclusion

Poregas monitoring data from the Equity Silver waste-rock pile have been re-evaluated here to explain observed trends in O₂ and CO₂. 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 O₂ and CO₂.

Although there is no readily apparent reason, the variability of CO₂ within a particular range of O₂ displays a generally normal statistical distribution. The means and standard deviations generally increase as O₂ 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

- Liu, Z-S, C. Huang, L. Ma, and K.A. Morin. Accepted. Observations and explanations from the monitoring data of Equity Silver Mine, Canada. IN: 9th Australian Workshop on Acid and Metalliferous Drainage, 20-23 November 2017, Burnie, Tasmania.
- Morin, K.A. 2016. Spectral Analysis of Drainage from Highly Reactive Geologic Materials. Morwijk-MDAG Publishing, Surrey, Canada. ISBN 978-0-9952149-1-0. www.MDAG.com/spectral-book.html
- Morin, K.A., N.M. Hutt, and M. Aziz. 2012. Case studies of thousands of water analyses through decades of monitoring: selected observations from three minesites in British Columbia, Canada. IN: Proceedings of the 2012 International Conference on Acid Rock Drainage, Ottawa, Canada, May 22-24.
- Morin, K.A., N.M. Hutt, and M.L. Aziz. 2010. Twenty-Three Years of Monitoring Minesite-Drainage Chemistry, During Operation and After Closure: The Equity Silver Minesite, British Columbia, Canada. MDAG Internet Case Study #35, www.mdag.com/case_studies/cs35.html
- Morin, K.A., E. Gerencher, C.E. Jones, and D.E. Konasewich. 1991. Critical Literature Review of Acid Drainage from Waste Rock. MEND Report 1.11.1.