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**Accounting for cyanide and its degradation products at three Nevada gold mines:
Constraints from stable C- and N-isotopes**

by

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Accounting for cyanide and its degradation products at three Nevada gold mines: Constraints from stable C- and N-isotopes*

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ABSTRACT

An understanding of the fate of cyanide (CN⁻) in mine process waters is important for addressing environmental concerns and for taking steps to minimize reagent costs. The utility of stable isotope methods in identifying cyanide loss pathways has been investigated in case studies at three Nevada gold mines.

Freshly prepared barren solutions at the mines have cyanide $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values averaging -4 ‰ and -36 ‰, respectively, reflecting the nitrogen and carbon sources used by commercial manufacturers, air and natural gas methane. Pregnant solutions returning from ore heaps display small isotopic shifts to lower $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values. The shifts are similar to those observed in laboratory experiments where cyanide was progressively precipitated as a cyanometallic compound, and are opposite in sign and much smaller in magnitude than the shifts observed in experiments where HCN was offgassed. Offgassing is inferred to be a minor cyanide loss mechanism in the heap leach operations at the three mines, and precipitation as cyanometallic compounds, and possibly coprecipitation with ferric oxides, is inferred to be an important loss mechanism.

Isotopic analysis of dissolved inorganic carbon (DIC) shows that uptake of high $\delta^{13}\text{C}$ air CO₂ has been important in many barren and pregnant solutions. However, DIC in reclaim pond waters at all three mines has low $\delta^{13}\text{C}$ values of -28 to -34 ‰ indicating cyanide breakdown either by hydrolysis or by other chemical pathways that break the C-N bond. Isotope mass balance calculations indicate that about 40 % of the DIC load in the ponds, at a minimum, was derived from cyanide breakdown. This level of cyanide hydrolysis accounts for 14-100 % of the dissolved inorganic nitrogen species present in the ponds. Overall, isotope data provide quantitative evidence that only minor amounts of cyanide are lost via offgassing and that significant amounts are destroyed via hydrolysis and related pathways. The data also highlight the possibility that significant cyanide may be either retained in the ore heaps or destroyed via other chemical pathways.

INTRODUCTION

Dilute solutions of cyanide (CN⁻) are used at a large number of mines to leach gold from ores. The basic process is well known, having been used on a commercial scale for more than a century (von Michaelis, 1985).

It is important to understand the fate of cyanide in process waters because of its toxicity and because of increasing environmental concerns. Cyanide levels are regulated in mine discharge (Smith and Struhsacker, 1988), and cyanide use at U.S. mines will soon be subject to Toxic Chemical Release Inventory (TRI) reporting as a consequence of the extension to metal mining facilities of Section 313 of the Emergency Planning and Community Right-to-Know Act and Section 6607 of the Pollution Prevention Act. Mines will need to give an annual accounting for the

* This report contains the text of a talk that was delivered at the Geological Society of America annual meeting in Toronto, Ontario on October 26, 1998. An abstract of the talk was published previously (Johnson et al., 1998).

cyanide imported on-site including quantities treated for destruction, quantities accumulated, and quantities released to the environment. A second reason to understand the fate of cyanide in process waters is that this will identify steps to conserve it and minimize mining costs (Botz and others, 1995).

Cyanide chemistry is complex, and there are several pathways by which it can be lost or degraded in process waters (Smith and Mudder, 1991). The operative loss pathways can be difficult to identify, however, so accurate TRI reporting is going to be a formidable task at many mines. We have been investigating the utility of stable isotope methods for identifying specific loss pathways and for quantifying the amounts of cyanide lost. The purpose of this report is to provide an overview of case studies that were carried out at active cyanidation operations at the Lone Tree, Pinson, and Getchell mines in north-central Nevada. We are grateful to Newmont Gold Company, Pinson Mining Company, and the Getchell Gold Corporation for access and assistance in carrying out the work.

DESCRIPTIONS OF THE HEAP LEACH CIRCUITS, SAMPLES TAKEN, AND PROBABLE CYANIDE LOSS MECHANISMS

At the three mines, barren cyanide solutions with pH about 10.5 are sprayed onto the ore heaps. The solutions percolate through the crushed ores and dissolve gold as the cyanide complex, $\text{Au}(\text{CN})_2^-$. They then hit an impermeable pad beneath the heaps, and are channelled outward and through a series of tanks containing activated carbon. The carbon adsorbs the gold, and the barren solutions then flow out to a holding pond where they are amended with fresh cyanide and base for another pass through the heaps. The activated carbon is removed from the tanks periodically for gold stripping.

At each mine, water samples were taken at several different points in the heap leach circuit over a time period of an hour or two, so the samples represent snapshots of the circuits. The heap leach operations were the primary focus of the study, but for comparison purposes mill reclaim pond waters were also sampled at each of the mines as were mill process waters at Pinson.

Smith and Mudder (1991) have reviewed a large number of laboratory and case studies that were carried out to determine the chemical pathways by which cyanide can be lost in heap leach circuits. The results of these studies indicate that the loss pathways likely to be important at Lone Tree, Pinson, and Getchell are:

- 1) offgassing as HCN,
- 2) hydrolysis, which is a term that we will use in this report for a family of oxidative pathways, some mediated by bacteria, that break the C-N bond to form dissolved inorganic carbon and nitrogen species,
- 3) sulfidation to thiocyanate (SCN^-),
- 4) precipitation of insoluble cyanometallic compounds, and
- 5) adsorption or coprecipitation on solid phases.

ISOTOPIC ANALYSES OF CYANIDE AND IMPLICATIONS FOR CYANIDE LOSS PATHWAYS

Figure 1 shows carbon and nitrogen isotopic analyses of dissolved cyanide from the three mines. Cyanide was separated from the samples by reflux distillation to an alkaline trap following standard techniques (USEPA, 1986). The cyanide in the trap was then precipitated and analyzed isotopically by a method described by Johnson (1996). The analyses are of total cyanide which includes the CN^- anion and aqueous HCN (the relative proportion of which changes with pH) and cyanide complexed with metals.

The isotopic compositions are expressed in δ -notation relative to internationally recognized standards where δ (in ‰) = $(R_{\text{SA}}/R_{\text{ST}} - 1) \times 1000$. For nitrogen, R_{SA} and R_{ST} refer to the ratio $^{15}\text{N}/^{14}\text{N}$ in the sample and air N_2 , respectively; for carbon, R_{SA} and R_{ST} refer to the ratio $^{13}\text{C}/^{12}\text{C}$ in

the sample and Vienna Pee Dee Belemnite (VPDB), respectively. The reproducibility of the measurements is typically within ± 0.5 ‰.

Barren solutions and fresh cyanide as delivered to the mines define a triangular field with average values of -4 ‰ for nitrogen and -36 ‰ for carbon. Overall, these compositions reflect the sources used in the common manufacturing processes, air for nitrogen and natural gas methane for carbon (Kroschwitz, 1993). The small shift downward from the 0 ‰ air $\delta^{15}\text{N}$ value indicates that the manufacturing process fractionates the isotopes of nitrogen slightly. Also shown in Figure 1 are analyses of cyanide from the mill operation at Pinson and the mill reclaim pond. The $\delta^{13}\text{C}$ values for these samples are -49 to -53 ‰, much lower than in the heap leach operations. This discrepancy illustrates the fact that the natural gas methane used to manufacture cyanide can span a very broad $\delta^{13}\text{C}$ range, from -20 to -65 ‰, depending on its point of origin (Schoell, 1988). The Nevada mines periodically change cyanide suppliers and the low $\delta^{13}\text{C}$ values in the pond likely reflect the $\delta^{13}\text{C}$ of an earlier batch of cyanide from a different supplier.

The pregnant solutions returning from the heaps show wider isotopic ranges than the barren solutions. For some samples, the isotopic compositions are indistinguishable from the starting barren solutions, but for others there was a shift to lower $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values along a slope of about unity. This shift is a fingerprint of the cyanide loss pathways in the ore heaps.

Figure 2 shows the variation in cyanide $\delta^{15}\text{N}$ values with the fraction of cyanide remaining (relative to the barren solution concentrations at a given mine). The curve is a least squares fit to the Lone Tree mine data using a Rayleigh distillation model. At the time of our sampling, cyanide losses were high at all three mines. The losses produced negative (downward) isotopic shifts meaning that the heavier isotope ^{15}N was preferentially lost as the solutions travel through the ore heaps. This is the opposite of chemical reactions that are kinetically controlled. The implications of this behavior will be discussed below.

The cyanide behaved differently depending on whether the solutions encountered oxidized ores or sulfide ores in the heaps. Figure 3 shows a correlation between cyanide concentration, or cyanide $\delta^{15}\text{N}$, and thiocyanate (SCN^-). Thiocyanate forms from intermediate valence sulfur species during the oxidation of sulfide minerals, and its concentration can be taken as an index of the amount of sulfide ore that a solution encounters in the heaps. Where thiocyanate is low (where the solutions encountered predominantly oxidized ores) the cyanide losses were greatest and the $\delta^{15}\text{N}$ values were shifted downward. Where thiocyanate is high (where the solutions encountered sulfide ores) the cyanide losses were less and $\delta^{15}\text{N}$ was unchanged from the original values in the barren solutions. As a point of reference, the highest thiocyanate levels observed in the solutions would account for about 10 % of the cyanide loss in one pass through the ore heaps. Unless thiocyanate has a very fast removal rate, the results suggest that sulfidation is a minor cyanide loss mechanism at these mines.

Where sulfide minerals are present in the heaps, solution pH usually drops and metals are taken into solution. Figure 4 shows the variation in dissolved iron with thiocyanate concentration. There is a large increase moving into the sulfide ores (note that iron is plotted on a log scale). The horizontal line in Figure 4 is the iron concentration sufficient to accommodate all the cyanide in the starting barren solutions as an iron complex. The solutions that encountered sulfide ores clearly have the capacity to complex large amounts of cyanide.

Figure 4 also shows the concentrations of several other metals (Mn, Zn, Ni, Co, Cd, and Ag) that are known to combine with the ferri- or ferrocyanide complexes to form insoluble compounds. These metals also increase as more sulfidic ores are encountered. The data in Figure 4 don't prove that the cyanide in these heap leach operations is precipitating as insoluble cyanometallic compounds, but they are at least permissive evidence that precipitation is an important cyanide loss pathway in portions of the heaps that contain sulfide ores.

Another point to be made with respect to Figure 4 is that the iron concentrations are very low in the solutions that encountered predominantly oxidized ores (the low thiocyanate solutions). The reason for this is that large amounts of ferric oxy/hydroxides are precipitated. Discrete cyanometallic compounds may not have precipitated from these solutions, but coprecipitation of cyanide with ferric oxides, or adsorption onto ferric oxides, may have been important.

To determine whether the isotopic shifts observed at the three mines (Figures 1 and 2) are compatible with the cyanide precipitation or coprecipitation hypothesis, we carried out experiments in the laboratory in which we precipitated copper(II)ferrocyanide from simple solutions and then measured the isotopic shifts in the residual free cyanide. The results are shown in Figure 5, and they match reasonably well the small, non-kinetic isotope fractionations that were observed at the mines. It is important to remember though that the samples with the greatest cyanide losses and the lowest $\delta^{15}\text{N}$ values have encountered mainly oxidized ores and they are low in metals. The fact that these samples follow the same trend on Figure 5 as the samples with higher metal contents (and correspondingly greater cyanide complexing capacity) suggests that coprecipitation of cyanide with ferric oxides may produce similar small, non-kinetic fractionations. This is a question that needs further investigation.

Another cyanide loss pathway favored by lower pH is offgassing of HCN. One of our original hypotheses was that offgassing would be analogous to the evaporation of water which is kinetically controlled and in which the lighter isotopes are preferentially lost (Dansgaard, 1964). We confirmed this by conducting offgassing experiments in the laboratory using simple solutions, and the results are illustrated in Figure 5. Cyanide concentrations declined, and $\delta^{15}\text{N}$ (and $\delta^{13}\text{C}$) values of the residual cyanide progressively increased. Note that the isotopic shifts are quite large.

The absence of similar increases in $\delta^{15}\text{N}$ at the mines indicates that HCN offgassing is not an important mechanism at Lone Tree, Pinson, and Getchell. It is possible that some offgassing did take place, and that the resulting positive $\delta^{15}\text{N}$ shifts were offset by negative shifts caused by precipitation or coprecipitation reactions. Still though, offgassing could only have been a minor pathway because the largest downward $\delta^{15}\text{N}$ shifts that we have observed, some 4 to 6 ‰, would be offset by offgassing of only 10 or 20 % by analogy with our experiments.

Hydrolysis and related pathways may be more important where solutions encounter sulfide than where they encounter oxidized ores. Figure 6 shows the relationship between thiocyanate and ammonium, and there is an increase toward sulfide ores. Ammonium concentrations depend not only on production from cyanide but also on any non-cyanide sources and on ammonium loss pathways. At these mines though we believe that the increase is related to production from cyanide because i) other possible sources, such as explosive residues, would be uniformly distributed in the heaps and while they might contribute ammonium they would not lead to higher concentrations in sulfide ores than in oxidized ores, ii) offgassing of ammonia would likely be uniformly low because the pregnant solutions all have pH well below the ammonia-ammonium pK_a , and iii) oxidation of ammonia would be expected to proceed at a uniform rate independent of the ore types encountered. As a point of reference, the highest ammonium levels observed in pregnant solutions are equivalent to the amount of cyanide lost in one cycle through the heaps.

ISOTOPIC ANALYSES OF DISSOLVED CO_2 AND NITRATE AND IMPLICATIONS FOR CYANIDE LOSS PATHWAYS

Another way to monitor cyanide loss by hydrolysis and related pathways is to measure the isotopic composition of the degradation products. Figure 7 shows the $\delta^{13}\text{C}$ value of dissolved inorganic carbon, or dissolved CO_2 , in barren solutions, pregnant solutions, and reclaim pond waters. Barren solution holding ponds range from -19 to -28 ‰, and the pregnant solutions range from -9 to -27 ‰. Reclaim ponds at all three mines are low in $\delta^{13}\text{C}$. If cyanide was the only source of dissolved CO_2 in these solutions, then one could measure the CO_2 contents and calculate the amount of cyanide degraded. There are other sources though, and their $\delta^{13}\text{C}$ values are given in Figure 7. They are atmospheric CO_2 , carbonaceous compounds which are indigenous to the ores at all three of the mines, carbonate minerals, the activated carbon used for gold adsorption, and cyanide, through several different pathways. Offgassing to the atmosphere and bacterial reduction are sinks.

Looking just at CO_2 production, the full equation for carbon isotope mass balance would involve the five sources shown in Figure 7, their isotopic compositions, and any isotopic fractionations. This is far too many unknowns to determine the contribution from cyanide.

However, cyanide is distinctive its low $\delta^{13}\text{C}$ value (Figure 7), so one can look at a limiting case of binary mixing between cyanide carbon and the next lowest $\delta^{13}\text{C}$ source, either activated carbon or carbonaceous matter depending on the mine. This case will give a minimum amount of CO_2 from cyanide. The calculation isn't useful for many barren or pregnant solutions because the dissolved CO_2 is dominated by air CO_2 , which is high in $\delta^{13}\text{C}$. The spraying procedure used to administer the solutions to the ore heaps undoubtedly enhances air uptake. But the reclaim pond waters have not exchanged as thoroughly with air because they sit static, and a low $\delta^{13}\text{C}$ cyanide component is required to explain their isotopic compositions (Figure 7). The results of the binary mixing calculations (Table 1) indicate that about 40 %, at a minimum, of the dissolved CO_2 in the ponds is cyanide-derived at all three of the mines.

For each carbon atom produced by cyanide breakdown, there must have been a nitrogen atom produced. So one can calculate an equivalent amount of dissolved inorganic nitrogen ($\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$) from the CO_2 data, and the results are shown in Table 1. Cyanide breakdown accounts for all, 20 % and 14 % of the inorganic nitrogen inventory of the ponds. As with the dissolved CO_2 results, these are minimum values.

One can do a parallel isotopic analysis of nitrate, and we have just begun doing that. The few data that we have at this time are shown in Figure 8. It would be premature to give an interpretation of the results, but it is clear that nitrate is important in constraining the cyanide budget because there is enough to account for large quantities of cyanide, some three times the amount that is lost in one pass through the heaps. The critical question is whether it is all cyanide-derived.

CONCLUSIONS

To conclude, where cyanide solutions encounter oxidized ores, the lack of $\delta^{15}\text{N}$ increases indicates that offgassing of HCN is not an important loss pathway. We hypothesize that coprecipitation with ferric oxides is a major loss pathway. Where cyanide solutions encounter sulfide ores, the dissolved metal contents suggest that precipitation of cyanometallic compounds may be important. The $\delta^{15}\text{N}$ values do not show downward shifts though, and although it is possible that negative shifts were offset by positive shifts caused by HCN offgassing, the amount of offgassing could not have been more than 10 or 20 %.

Cyanide hydrolysis and sulfidation are more important loss pathways in sulfide ores than in oxidized ores. Where solutions sit ponded, isotopic analyses of dissolved CO_2 place lower bounds on the amount of hydrolysis occurring, and it is considerable. Isotopic analysis of dissolved nitrate may allow better quantification of hydrolysis and related pathways, and this is an area that we are currently pursuing.

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Isotopic analyses of total cyanide

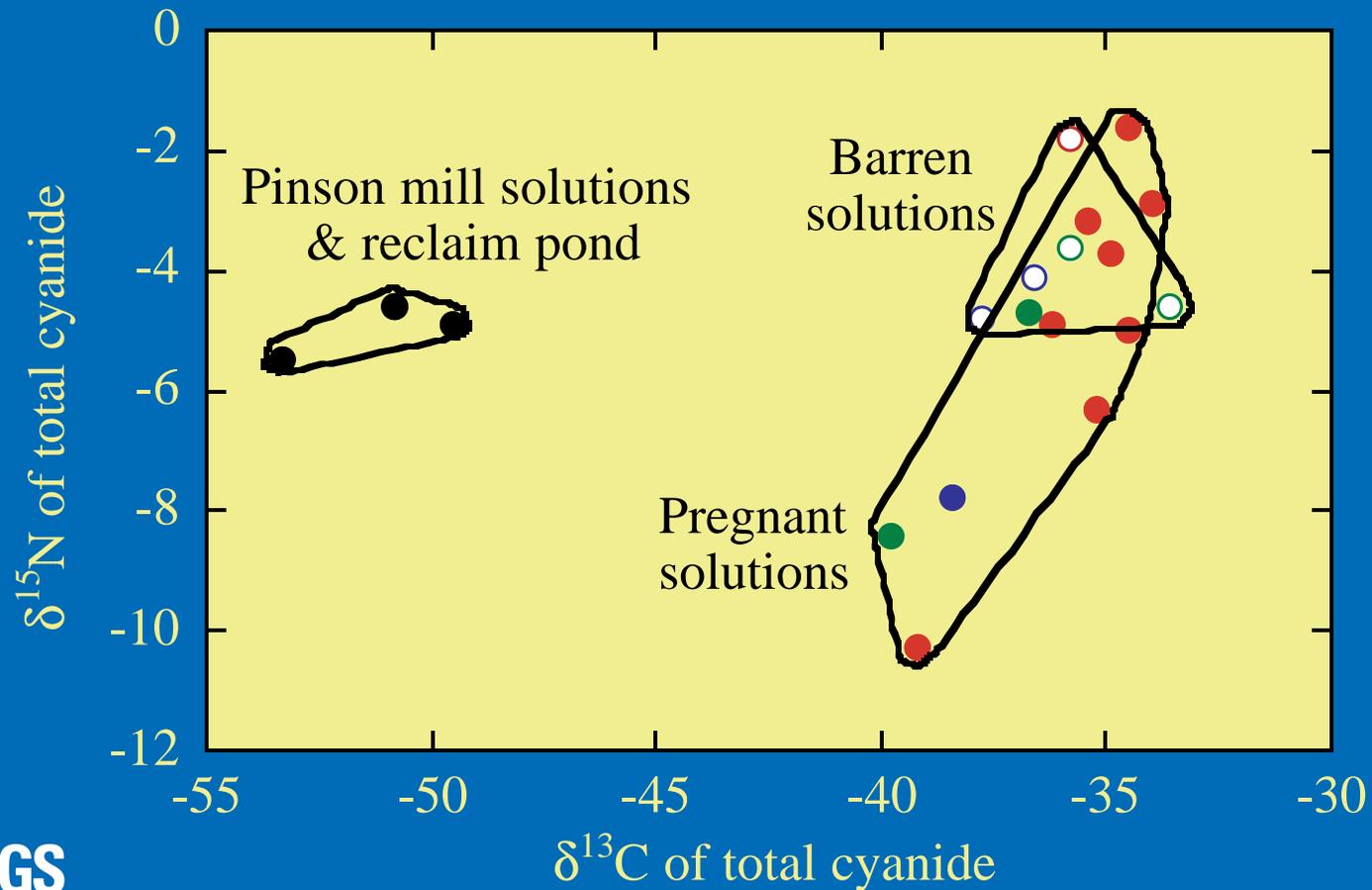


Figure 1. Carbon and nitrogen isotopic analyses of total cyanide in process water samples from the Pinson (blue symbols), Lone Tree (red symbols), and Getchell (green symbols) mines.

Cyanide loss fractionates isotopes

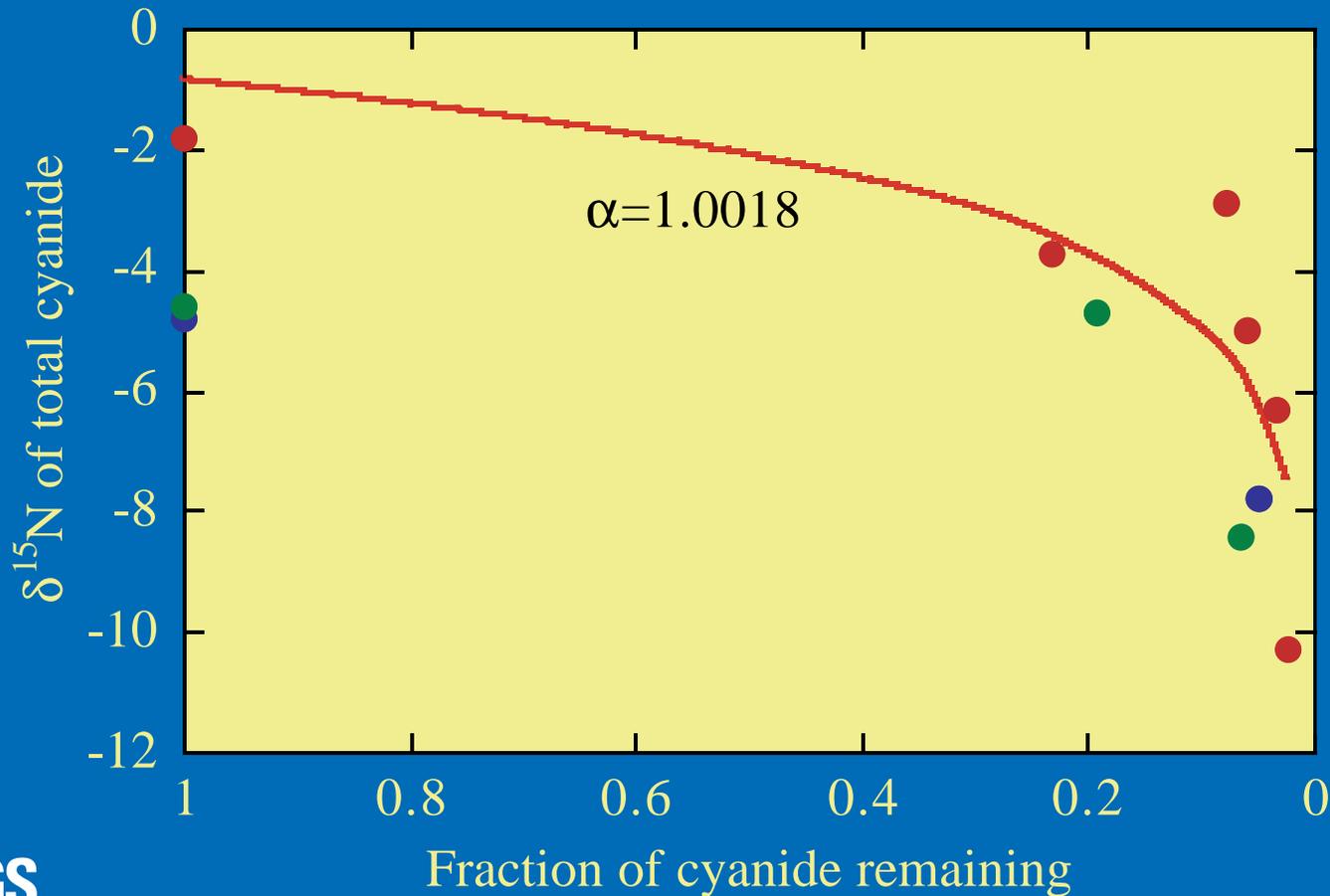


Figure 2. Variation in $\delta^{15}\text{N}$ of total cyanide with the fraction of cyanide remaining. The curve is a least squares fit to the data from the Lone Tree mine using a Rayleigh distillation model. Data from Pinson are shown in blue, Lone Tree in red, and Getchell in green.

Oxidized vs sulfide ores

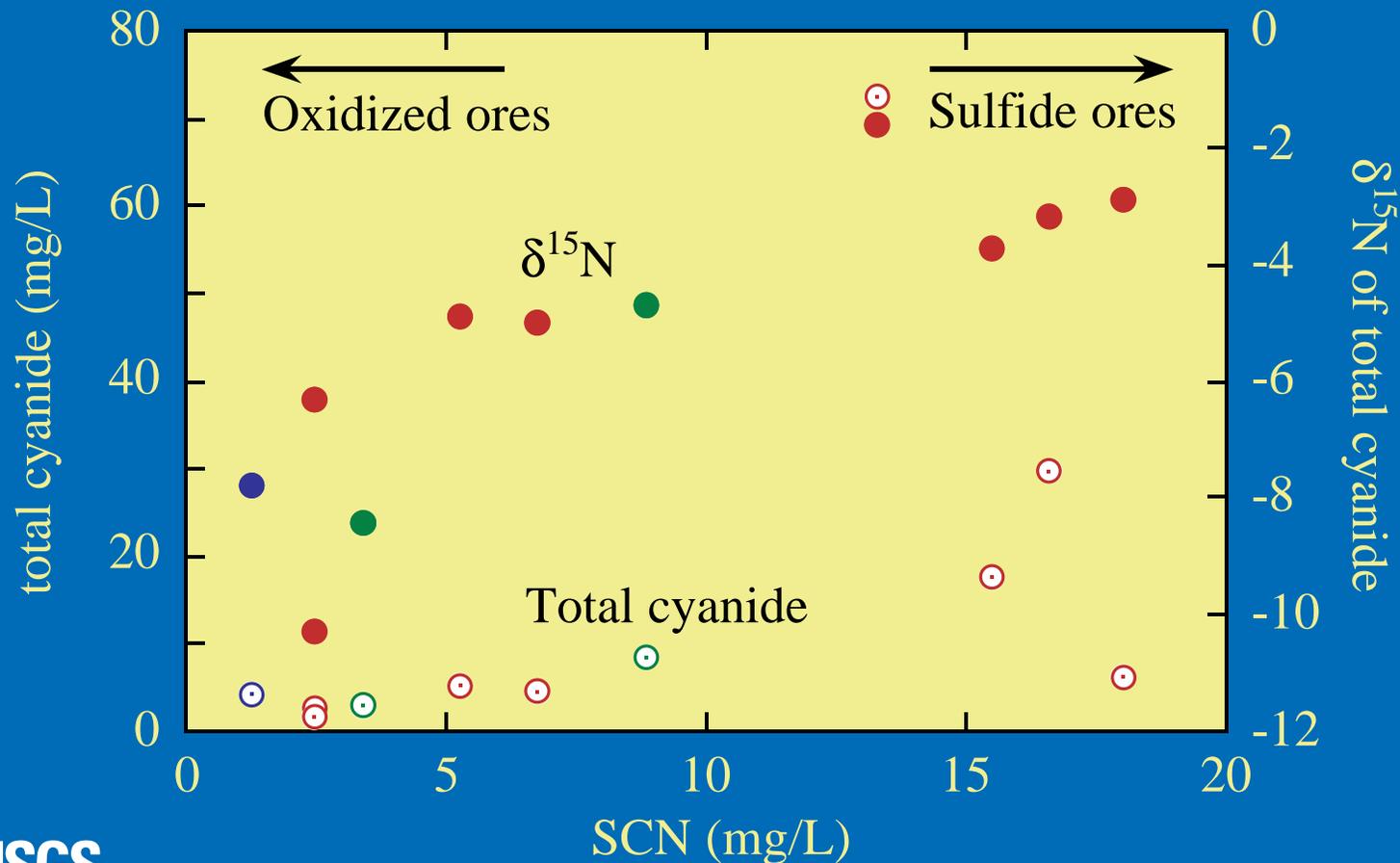


Figure 3. Variation in total cyanide concentrations and $\delta^{15}\text{N}$ values with thiocyanate showing that there is a systematic change in the behavior of cyanide depending on the amount of sulfide ore that a solution encounters in the ore heaps. Data from Pinson are shown in blue, Lone Tree in red, and Getchell in green.

Precipitation & coprecipitation

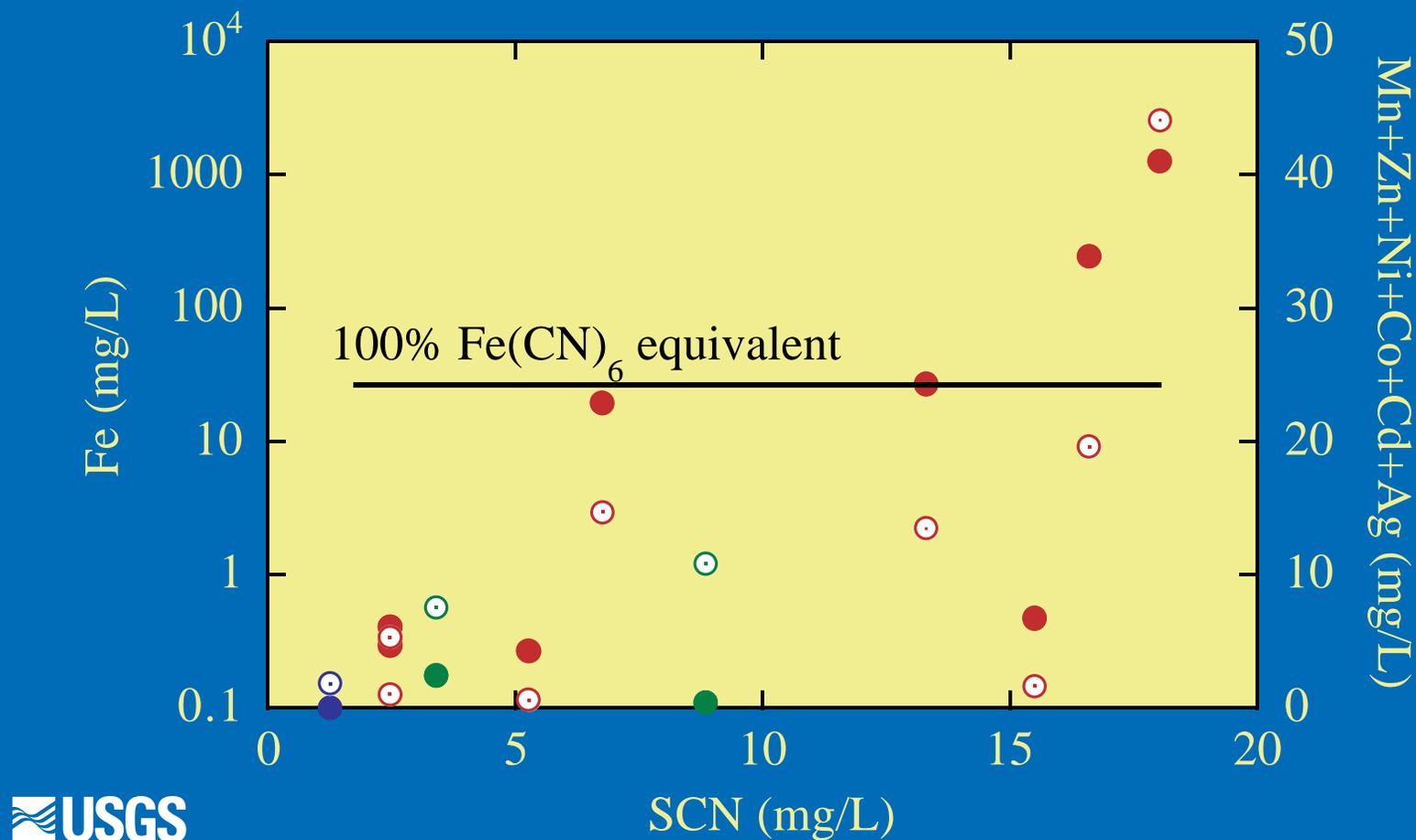


Figure 4. Variation in iron and other metals with thiocyanate. As they encounter increasing amounts of sulfide ores, the solutions show an increasing capacity to carry metals. The horizontal line is the iron concentration sufficient to accommodate all the cyanide in the barren solutions as the ferri- or ferrocyanide complex. Iron concentrations are plotted as filled circles, combined minor metals are plotted as open circles. Data from Pinson are shown in blue, Lone Tree in red, and Getchell in green.

Comparison with lab experiments

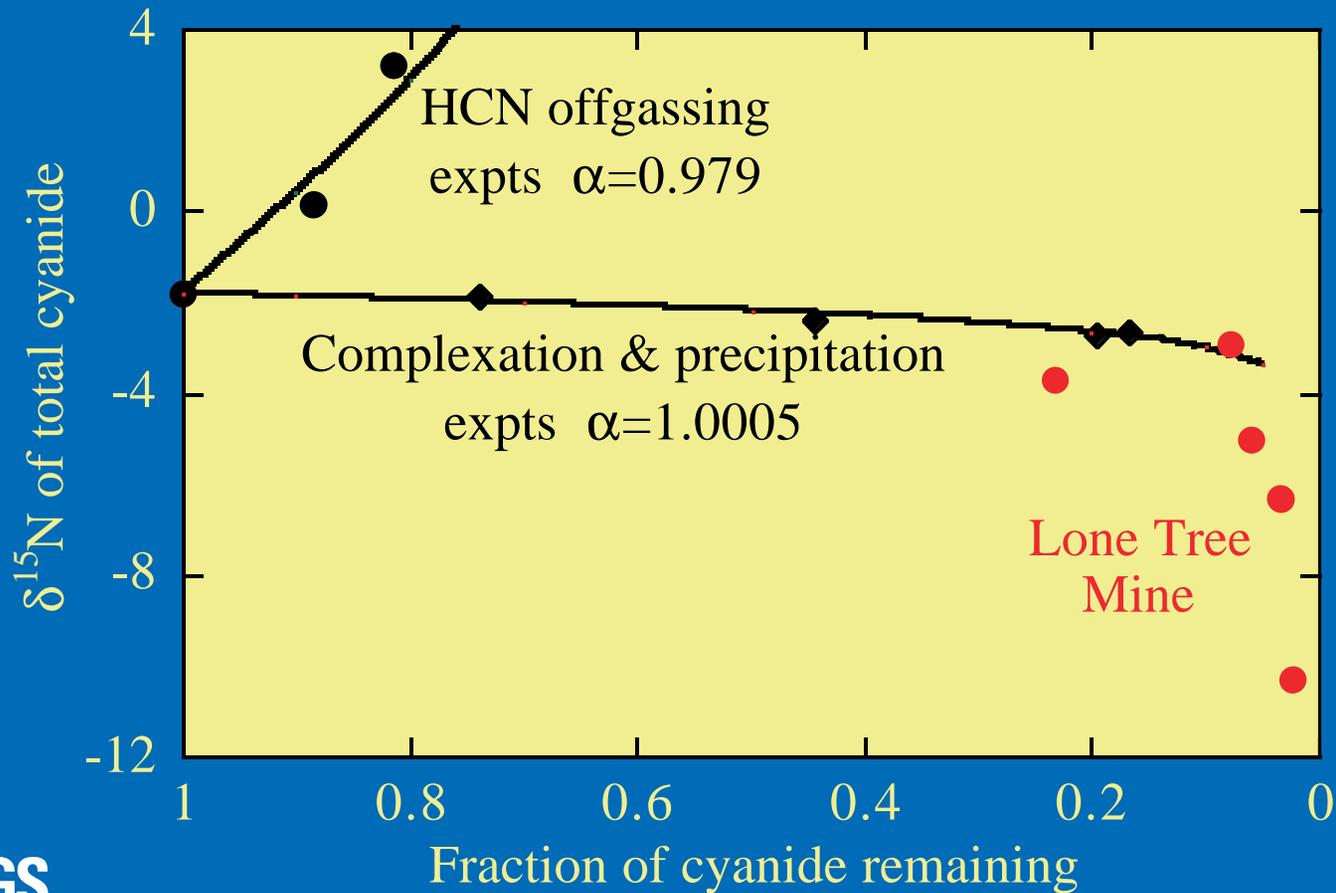


Figure 5. Comparison of the isotopic shifts observed in the Lone Tree mine pregnant solutions with those observed in laboratory experiments where cyanide was offgassed or precipitated as a cyanometallic complex. The Lone Tree data are compatible with cyanide loss by precipitation, but not with cyanide loss by offgassing. Experimental results are plotted in black, data from Lone Tree are plotted in red.

Hydrolysis and related pathways

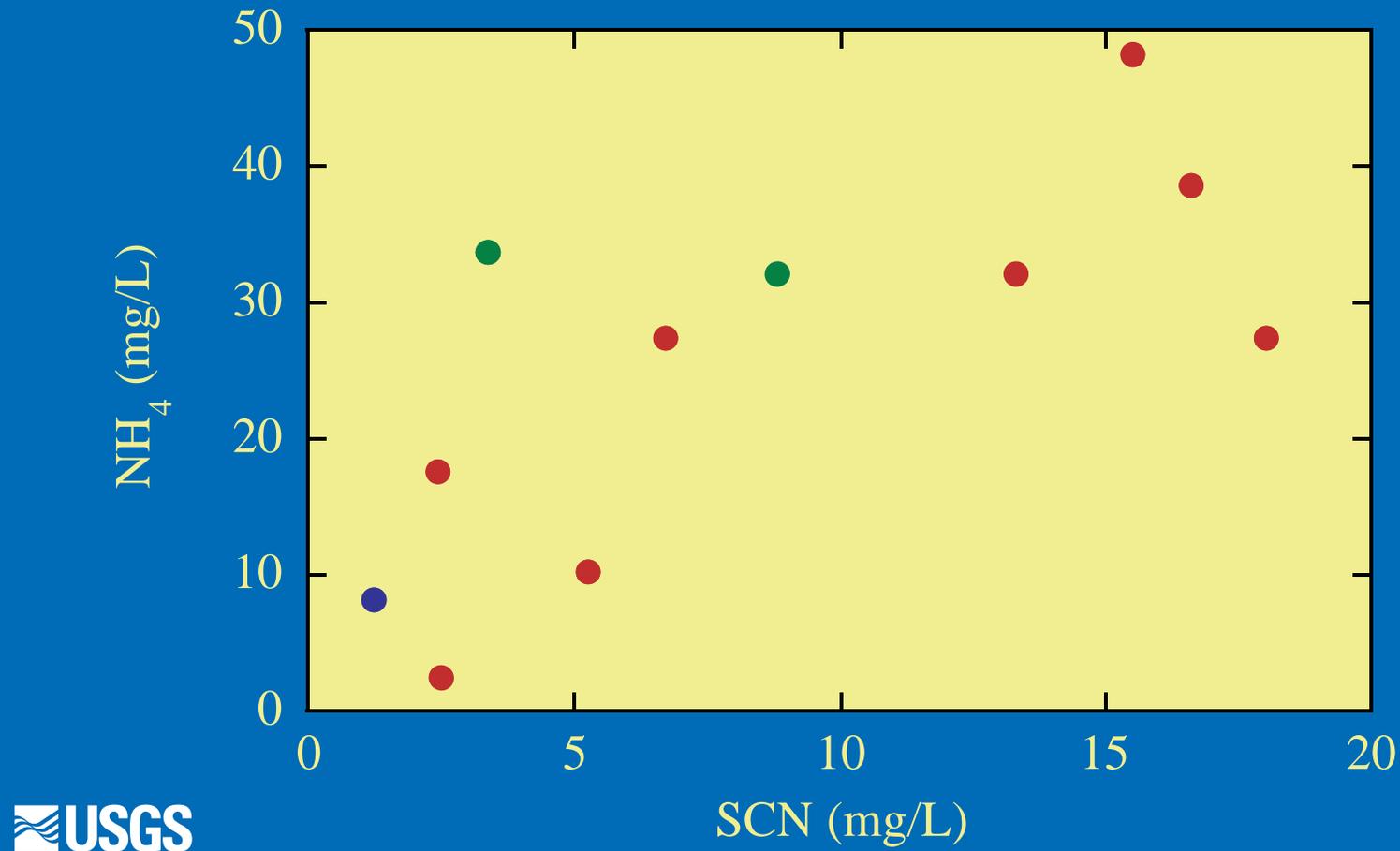


Figure 6. Variation in ammonium with thiocyanate. Hydrolysis and other pathways which break the C-N bond appear to be more important where solutions encounter sulfide ores than where they encounter oxidized ores, but the possibility of non-cyanide sources and a poor understanding of ammonium sinks makes this conclusion tentative. Data from Pinson are shown in blue, Lone Tree in red, and Getchell in green.

Dissolved CO₂

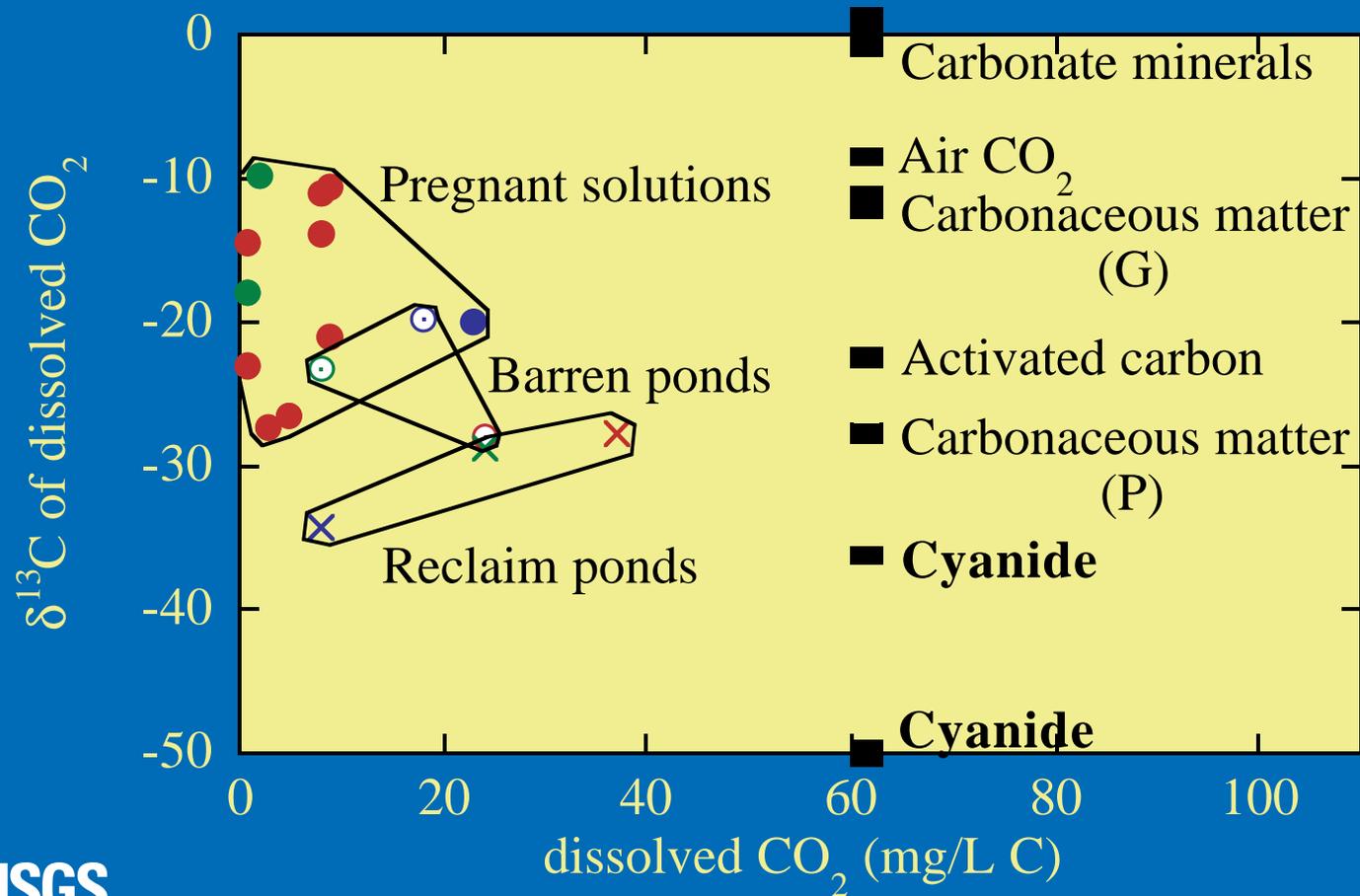


Figure 7. Carbon isotopic compositions of dissolved CO₂ in barren solution holding ponds, pregnant solutions, and reclaim pond waters. The isotopic compositions of the potential CO₂ sources were taken from the literature or from our own unpublished measurements. Reclaim pond waters have low $\delta^{13}\text{C}$ values, which is a fingerprint of cyanide breakdown. Data from Pinson are shown in blue, Lone Tree in red, and Getchell in green.

Nitrate

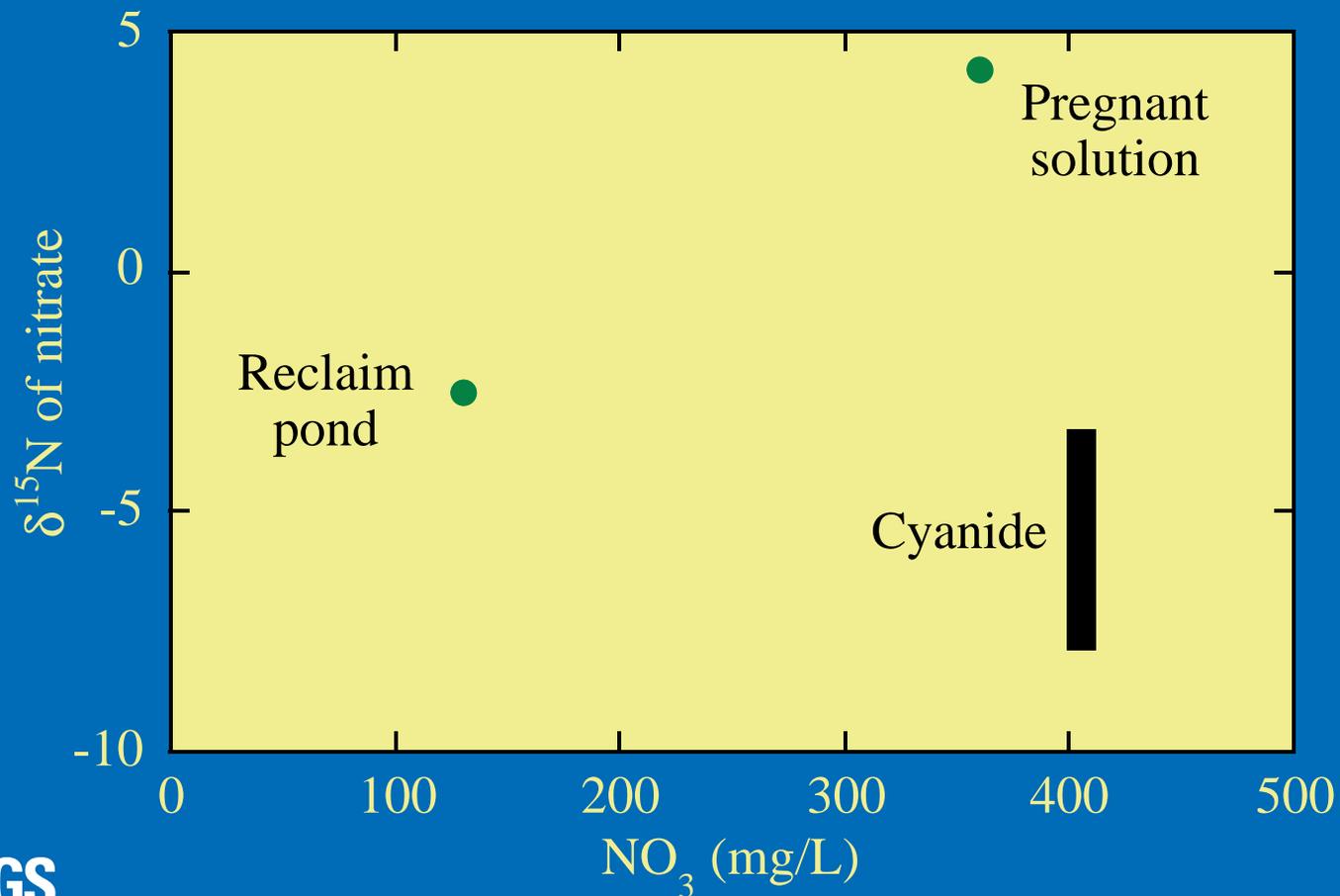


Figure 8. Nitrogen isotopic compositions of nitrate in a pregnant heap leach solution and in reclaim pond water from the Getchell mine. The reclaim pond isotopic composition resembles the composition of the cyanide in use at the Getchell mine, but the pregnant solution has a substantially higher δ -value.

Table 1.-*Minimum percentages of dissolved inorganic carbon ($CO_2+HCO_3^-+H_2CO_3$) and dissolved inorganic nitrogen ($NH_4^++NO_2^-+NO_3^-$) derived from cyanide in reclaim ponds*

Mine	Dissolved inorganic carbon	Dissolved inorganic nitrogen
Pinson	40	100
Lone Tree	43	20
Getchell	38	14