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# THE PRODUCTION OF CONDENSED PHASE CO IN QUIESCENT MOLECULAR CLOUDS

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## ABSTRACT

The high abundance of condensed phase CO in cool quiescent molecular clouds is not reproducible by our standard two-phase and three-phase gas-grain chemical models. We consider changes to the models designed to enhance the predicted abundance of condensed phase CO. We find that the use of the so-called "high-metal" elmental abundances to describe the initial composition of the gas leads to higher condensed phase CO abundances, which are in better agreement with observation, by reducing the surface hydrogenation rate of CO into methanol ($CH_3OH$). We also confirm, however, that high-metal elemental abundances depress the gas phase production of complex organic molecules. This problem can be removed by using initial conditions with metallic elements, especially sulfur, predominantly on grain surfaces rather than in the gas.

*Subject headings:* dust, extinction — ISM: clouds — ISM: molecules — molecular processes

## 1. INTRODUCTION

More than 90 different molecules have been discovered in interstellar and circumstellar clouds (Winnewisser & Herbst 1993). Existing in both the gaseous state and in dust particles, these molecules present clues to the physical and chemical states of the clouds in which they are found. Although much attention has been paid to an understanding of the abundances of gas phase molecules, less attention has been paid to condensed phase molecular species. Observations of molecules in cold, interstellar grain mantles, however, constrain chemical models that include both gas phase and grain surface chemistry. We (Hasegawa, Herbst, & Leung 1992; Hasegawa & Herbst 1993a, b) have previously published two types of gas-grain chemical models for quiescent dense interstellar clouds. In the first type (Hasegawa et al. 1992; Hasegawa & Herbst 1993a), dust particles consist of two phases, labeled the core and the "surface." All condensed phase chemistry takes place on the surface, which can have up to 100 monolayers. In the second type (Hasegawa & Herbst 1993b), dust particles consist of three phases: the core, the mantle, and the surface. The mantle here consists of adsorbed and processed material that lies beneath the outermost layer, labeled the surface. All chemistry occurs in the outermost layer, so that adsorbed material is chemically inert once additional material is adsorbed atop it. Our two-phase and three-phase models utilize two sets of initial conditions depending principally on whether the hydrogen is atomic or molecular. The material is initially either in the gas or contained in the cores of dust particles. As time progresses, both gas phase and condensed phase chemistry occur. The temperature remains constant, typically at 10 K, and the cloud is homogeneous. The gas density $n$, defined by the relation

$$n = 2n(H_2) + n(H) , \tag{1}$$

remains effectively constant at $2 \times 10^4$ cm$^{-3}$. Except in our first publication, cosmic rays induce nonthermal desorption of surface molecules back into the gas (Léger, Jura, & Omont 1985). We utilize the so-called "low-metal" elemental abundances to describe material not in the cores of dust particles and initially present in the gas. Defined originally by Graedel, Langer, & Frerking (1982), this set of elemental abundances contains 100 times reductions of assorted "real" metals (e.g., sodium and iron), as well as sulfur and silicon. We have found that low-metal abundances are necessary to form significant abundances of complex organic molecules in the gas phase (Herbst & Leung 1989).

Although all of our models reproduce the large observed abundances of condensed-phase water at virtually all times, we are less successful at reproducing the large condensed-phase abundances of CO seen in cool regions such as the Taurus dark cloud complex, where the abundance ratio of condensed phase to gaseous CO is approximately $\frac{1}{4}$ (Whittet & Duley 1991) so that the fractional abundance of condensed phase CO with respect to $n/2$ exceeds $10^{-5}$. This large CO condensed phase abundance is important because it signifies that CO desorption from grain particles is not particularly efficient at low temperatures. Our models with atomic hydrogen present initially destroy condensed phase CO so rapidly via surface hydrogenation that little ever exists. Although some past models with $H_2$ present initially do contain large amounts of condensed phase CO, the exclusion of the surface atomic hydrogen scavenger $HN_2$, recently found to be unstable, has led to predictions of very low condensed phase CO abundances. Specifically, our latest three-phase model result (Hasegawa & Herbst 1993b) of a few $\times 10^{-7}$ for the condensed phase fractional abundance of CO at all times past $10^5$ yr lies two orders of magnitude below that observed in Taurus.

In this paper, we consider changes to our model to raise predicted abundances of condensed phase CO while maintaining the high calculated abundances of water and other condensed phase species such as methanol. In particular, we consider the use of "high-metal" elemental abundances in two contexts. First, we simply raise the initial gas phase abundances of the affected metals, sulfur, and silicon. We will refer to such models as high-metal models. The rationale is that since we now include both gas phase and surface chemistry, it may be more appropriate to start with the standard, or high-metal, abundances and allow depletions of metals to occur naturally over the course of time. Second, we use the depleted, or low-metal, abundances as initial conditions in the gas phase but start with material on the surfaces of dust grains made up of the difference for at least one of the elements between high-metal and low-metal abundances, based on the assumption that a selective depletion of heavy elements from the gas phase occurred in some previous low-density, high-temperature epoch. We will refer to these latter models as depleted high-metal models. In all models, we assume that the initial form of hydrogen is $H_2$ and that all other elements are in atomic form. The fixed temperature and density are as assumed in previous papers; viz, $T = 10$ K and $n = 2 \times 10^4$ cm$^{-3}$.

## 2. HIGH-METAL MODELS

Figure 1 shows the calculated surface CO abundance $n_s$(CO) with respect to $n/2$ as a function of time for assorted two-phase models. It can be seen that the surface CO abundance in the high-metal model, labeled HM, exceeds that in the low-metal model, labeled LM, by an order of magnitude or more at most epochs. Specifically, in the important "early-time" interval $10^5$–$10^6$ yr when calculated gas phase abundances of complex molecules are at their peak values (Herbst & Leung 1989), the fractional surface CO abundance in HM, referred to $0.5n$, reaches the enhanced value of $10^{-6}$. This value is still a factor of $\approx 25$–30 below the observed value in Taurus, which, in our view, is uncertain by a factor of $\approx 5$ (see also Whittet & Duley 1991). As always in two-phase models, condensed phase species such as CO which react with atomic hydrogen are eventually hydrogenated. The calculated abundances for surface CO decrease strongly after $10^6$ yr.

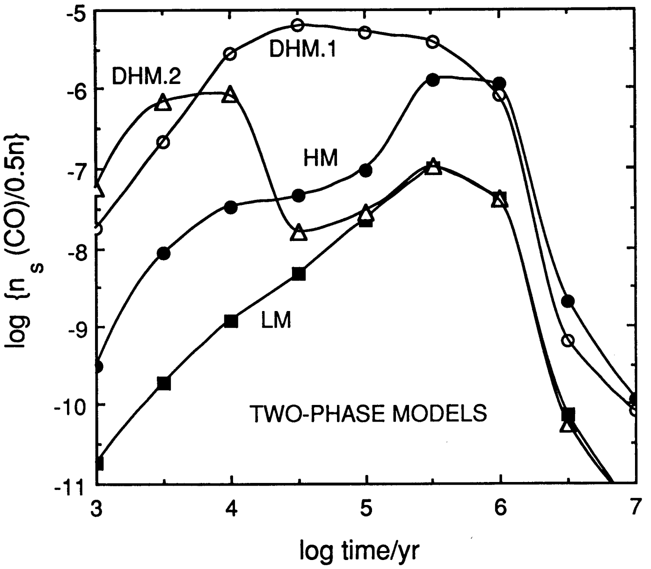

FIG. 1.—The abundance $n_s$(CO) of surface CO with respect to $n/2$ is plotted vs. time for four different two-phase models. Model LM contains low-metal initial abundances in the gas phase, model HM contains high-metal initial abundances in the gas phase, model DHM.1 contains high-metal initial abundances depleted onto the surfaces of dust particles so that only low-metal abundances are left in the gas, and model DHM.2 contains the same initial elemental abundances as does DHM.1 except that the surface sulfur abundance is cut by a factor of 10.

Figure 2 shows analogous results for our three-phase models. Here the condensed phase (surface + mantle) CO fractional abundance in the high-metal case is 1–2 orders of magnitude higher than in the low-metal case, achieving a value of $10^{-6}$ by $10^5$ yr and reaching a plateau at $\approx 5 \times 10^{-6}$ at times past $10^6$ yr, close to the observed value. Because the condensed phase CO is buried in unreactive mantles in the three-phase models, its fractional abundances does not decline due to hydrogenation.

There are two reasons why condensed phase CO is enhanced in both the two-phase and three-phase models when high-metal elemental abundances are used. First, and more importantly, the increasing elemental abundance of sulfur allows more atomic sulfur to adsorb onto grain surfaces, where it catalytically reduces the atomic hydrogen abundance through the series of reactions (Tielens & Hagen 1982):

$$H + S \rightarrow HS , \qquad (2)$$

$$H + HS \rightarrow H_2S , \qquad (3)$$

$$H + H_2S \rightarrow H_2 + HS . \qquad (4)$$

Second, the enhanced abundance of sulfur leads to higher abundances of condensed phase OCS and SO, which are surface precursors to CO. In the low-metal models, virtually all condensed phase CO stems from adsorption after production in the gas.

Although the high-metal abundances elevate the calculated condensed phase abundance of CO, as desired, they hinder the formation of complex molecules via gas phase reactions, as is

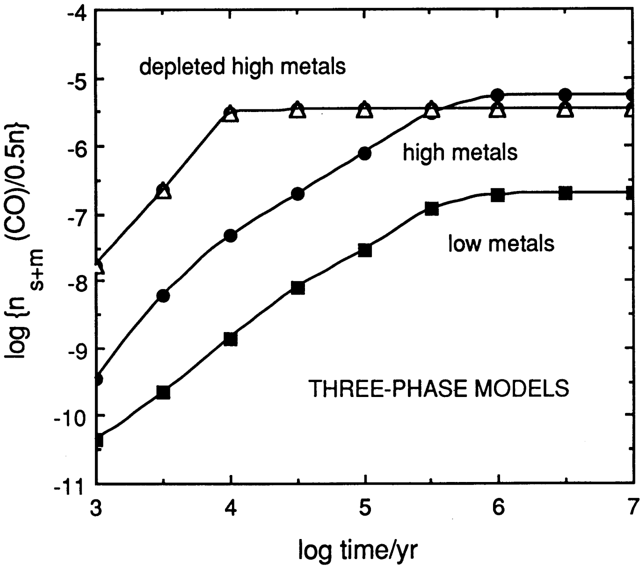

FIG. 2.—The abundance $n_{s+m}$(CO) of condensed phase (surface + mantle) CO with respect to $n/2$ is plotted vs. time for three different three-phase models with, respectively, low-metal initial abundances in the gas phase, high-metal initial abundances in the gas phase, and a high initial sulfur abundance on grain surfaces ("depleted high metals").

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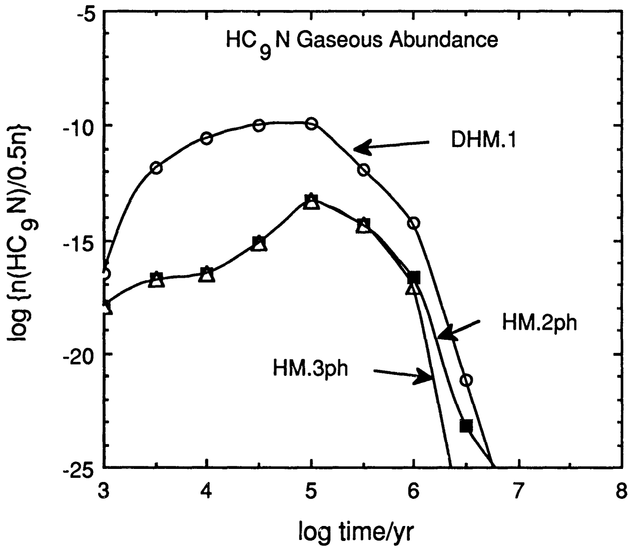

FIG. 3.—The abundance $n(HC_9N)$ of gaseous $HC_9N$ with respect to $n/2$ is plotted vs. time for three different models. The designations HM.2ph and HM.3ph refer to two-phase and three-phase models, respectively, with high-metal initial abundances in the gas phase. The designation DHM.1 refers to a two-phase model with high-metal initial abundances depleted onto the surfaces of dust particles so that only low-metal abundances are left in the gas.

well known (Herbst & Leung 1989; Leung, Herbst, & Huebner 1984). Figure 3 shows gaseous abundances of the complex molecule $HC_9N$ for assorted calculations. The HM.2ph and HM.3ph models, referring to two-phase and three-phase models, respectively, show peak early-time ($10^5$ yr) fractional abundances of only $5 \times 10^{-14}$, approximately four orders of magnitude below the result for low-metal models. The high-metal result, not appropriate for the dark cloud TMC-1, could be more generally appropriate in the Taurus complex since high abundances of the cyanopolyynes are confined to TMC-1, whereas the high abundance of condensed phase CO is widespread (Whittet & Duley 1991). The enhanced production of cyanopolyynes in TMC-1 must then be regarded as not understood. As regards the chemistry of TMC-1, there are other undesirable aspects stemming from the use of high-metal initial abundances (Herbst & Leung 1989). For example, the calculated abundance of the ion $HCO^+$ is much too low.

The use of high-metal abundances does not affect the condensed phase concentrations of abundant molecules significantly, although the concentrations of other species can be affected. Water remains the dominant condensed phase species, and the abundance of methanol, the hydrogenation product of CO, still remains high. Interestingly, the condensed phase abundance of methane ($CH_4$) is surprisingly large in all three-phase model calculations that exclude $HN_2$.

In Table 1 we compare the early-time ($10^5$ yr) gas phase and condensed phase abundances (with respect to $H_2$) of assorted molecules for low-metal (LM) and high-metal (HM) two-phase models. Selected gas phase abundances observed in TMC-1 are also shown.

## 3. DEPLETED HIGH-METAL MODELS

If we use initial conditions in which the gas phase contains low-metal elemental abundances but the surface contains the high-metal abundances with a correction for what is present in the gas, we expect differences from the previous results. Results for condensed phase CO and gaseous $HC_9N$ are shown in Figures 1 and 3, respectively, for a two-phase model labeled DHM.1, the initials of which refer to depleted high-metal abundances. It can be seen that the low-metal abundances used for the gas phase allow the gas phase chemistry to produce complex molecules efficiently; in particular, the $HC_9N$ fractional abundance at early time reaches the $10^{-10}$ value achieved in previous low-metal models (Hasegawa et al. 1992). At the same time, the high abundance of sulfur on grain surfaces lowers the atomic hydrogen concentration and allows that of CO to become high. The fractional abundance of surface CO depicted in Figure 1, peaks at $\approx 6 \times 10^{-6}$ during the early-time period, a value larger than achieved in the simple two-phase high-metal model and close to the observed value. The surface abundances of water and methanol remain high. Model DHM.1 at early time is therefore capable of simultaneously reproducing the gas phase molecular abundances of TMC-1 and the condensed phase abundances of both water and carbon monoxide observed throughout the Taurus region. An additional benefit is that the high abundance of sulfur leads

TABLE 1

SELECTED FRACTIONAL ABUNDANCES WITH RESPECT TO $H_2$ AT EARLY TIME CALCULATED WITH TWO-PHASE MODELS

| CHEMICAL SPECIES | TMC-1[a] Gas | LM Gas | LM Surface | HM Gas | HM Surface | DHM.1 Gas | DHM.1 Surface |
|---|---|---|---|---|---|---|---|
| CS ................ | 1 (−08) | 7.1 (−09) | 1.1 (−12) | 1.5 (−06) | 1.2 (−12) | 9.7 (−09) | 5.3 (−11) |
| SO ................ | 5 (−09) | 1.0 (−09) | 2.6 (−14) | 1.8 (−07) | 5.7 (−13) | 1.5 (−09) | 3.1 (−11) |
| HCN ............ | 2 (−08) | 9.3 (−08) | 2.9 (−07) | 3.4 (−07) | 3.2 (−06) | 8.3 (−08) | 3.3 (−06) |
| HNC ............ | 2 (−08) | 5.1 (−08) | 2.9 (−06) | 1.3 (−07) | 1.7 (−06) | 4.1 (−08) | 1.1 (−08) |
| $NH_3$ ............. | 2 (−08) | 1.6 (−07) | 3.2 (−06) | 1.7 (−08) | 1.2 (−07) | 1.5 (−08) | 4.9 (−09) |
| $C_5H$ ............. | 4 (−10) | 4.3 (−09) | 2.4 (−20) | 6.0 (−11) | 2.3 (−22) | 4.2 (−09) | 2.8 (−20) |
| $CH_3CHO$ ........ | 6 (−10) | 1.4 (−11) | 5.4 (−12) | 1.8 (−13) | 1.5 (−11) | 1.4 (−11) | 5.3 (−10) |
| $C_6H$ ............. | 1 (−09) | 2.1 (−09) | 9.8 (−21) | 9.4 (−12) | 2.7 (−23) | 2.0 (−09) | 1.1 (−20) |
| $HC_5N$ ........... | 3 (−09) | 5.4 (−09) | 6.9 (−12) | 1.9 (−09) | 6.3 (−12) | 5.1 (−09) | 5.9 (−10) |
| $HC_7N$ ........... | 1 (−09) | 1.2 (−09) | 1.3 (−12) | 2.4 (−12) | 7.6 (−15) | 1.1 (−09) | 1.1 (−10) |
| $HC_9N$ ........... | 3 (−10) | 1.4 (−10) | 1.4 (−13) | 5.5 (−14) | 1.7 (−16) | 1.3 (−10) | 1.3 (−11) |
| $HCO^+$ ........... | 8 (−09) | 5.0 (−09) |  | 1.8 (−10) |  | 5.2 (−09) |  |
| $HCS^+$ ........... | 6 (−10) | 1.9 (−11) |  | 3.6 (−10) |  | 2.8 (−11) |  |

NOTE.—$a(-b)$ means $a \times 10^{-b}$.

[a] Irvine, Goldsmith, & Hjalmarson 1987, except for the molecules $C_5H$ and $C_6H$; see Cernicharo et al. 1987.

to a large fractional abundance of surface $H_2S$ at early time in the range $5 \times 10^{-6}$–$8 \times 10^{-6}$, which agrees nicely with the gas phase fractional abundance detected by Minh et al. (1990) in the Orion hot core, assuming that the gas phase $H_2S$ in this source stems from sudden evaporation of mantles due to the onset of the protostellar source IRc2 (Caselli, Hasegawa, & Herbst 1993). Selected gas phase and condensed phase abundances for the two-phase model DHM.1 at early-time are shown in Table 1. The high condensed phase abundances of the cyanopolyynes in this model indicate how strongly the abundance of surface H has been reduced, since these species are depleted primarily by reaction with surface hydrogen.

In model DHM.1, the initial elemental sulfur abundance on grain surfaces corresponds to $6 \times 10^6$ sulfur atoms per dust particle. Since there are typically $10^6$ binding sites per particle, model DHM.1 initially contains six monolayers of sulfur atoms. About $\frac{1}{3}$ of the sulfur is converted into $H_2S$ via hydrogenation; much of the remainder is oxidized into $SO_2$ due to the large initial abundance of oxygen atoms. The amount of surface sulfur is so large, however, that some is available for conversion into $H_2S$ when the surface abundance of atomic hydrogen eventually increases. It is the $H_2S$ which is necessary to reduce the amount of surface hydrogen via reaction (4) since gas phase reactions continue to produce significant abundances of atomic hydrogen for adsorption.

To determine how sensitive the surface concentrations, especially that of CO, are to the high sulfur elemental abundances, we have run several models in which the initial sulfur condensed phase abundance has been reduced. If the initial elemental sulfur on grain surfaces is reduced by a factor of 10, grain surfaces start with roughly a single monolayer of sulfur atoms. More than 90% of this sulfur is conveerted into $SO_2$. Because little $H_2S$ is formed, the surface abundance of H remains high and the surface CO abundance, shown in Figure 1 under the label DHM.2, is significantly lower than in model DHM.1, except at very early times when there is little atomic hydrogen and before the surface sulfur is totally oxidized. If the initial surface abundance of sulfur is decreased by another order of magnitude, so that about 0.1 of a monolayer is present initially, a significant percentage of sulfur once again forms $H_2S$, because the surface atoms of hydrogen are more mobile than those of oxygen and compensate for their lower initial concentration by a greater collision frequency with isolated sulfur atoms. Still, the low absolute surface abundance of $H_2S$ produced is insufficient to reduce atomic hydrogen seriously.

In addition to the two-phase models with depleted high metallic elemental abundances, we have attempted to run analogous three-phase models. Since the results from the two-phase models show that large amounts of sulfur, corresponding to six monolayers, are needed to reduce surface hydrogenation rates significantly, we have modified the equations of our three-phase model (Hasegawa & Herbst 1993b) to allow for reactions to occur on a "surface" of more than one monolayer. The differential equations used in the three-phase model cannot accommodate the modification unless the number of reactive layers diminishes with time. Consequently, although we start with six layers of sulfur atoms, we eventually retain only three reactive monolayers. Calculations show that before the adsorption of several more monolayers, a process taking roughly $10^4$ yr, the large abundance of elemental sulfur is converted with $\approx 50\%$ efficiency into $H_2S$, which is then available for conversion of atomic into molecular hydrogen. However, at subsequent times, the $H_2S$ will be covered by newly accreting material and will become chemically inert. The effect on the surface CO abundance will be then be lessened. Still, as shown in Figure 2, the condensed phase CO fractional abundance for this "depleted metal" model quickly reaches a large asymptotic value of $\approx 4 \times 10^{-6}$ by $10^4$ yr. This value is only slightly smaller than the asymptotic CO abundance of the high-metal three-phase model and the peak CO value of the two-phase depleted metal model DHM.1. In addition, the complex gas phase chemistry is, as expected, as efficient as that of low-metal models.

## 4. SUMMARY

Carbon monoxide is a widely detected condensed phase molecule in cool dark interstellar clouds. To maintain high abundances of CO on grains in our models requires some inefficiency in the hydrogenation of CO into methanol by successive hydrogen atom addition reactions. Since we assume that surface atomic hydrogen migrates rapidly via tunnelling the only way in which we can reduce the hydrogenation efficiency is to lower the abundance of H. Even if we utilize the initial condition that all hydrogen is in its molecular form, we have found in previous models that with the molecule $HN_2$ excluded from the set of reactants, gas phase processes followed by adsorption soon produce enough atomic hydrogen on grain surfaces to hydrogenate CO and other unsaturated molecules efficiently. In these previous models, we have used low-metal elemental abundances to describe the initial state of the gas. We have been forced to exclude the molecule $HN_2$ from our list of species because of its calculated instability.

In this paper, we have reported that the use of high-metal, or normal, elemental abundances can reduce the abundance of surface atomic hydrogen. These normal abundances correspond closely to what is observed in diffuse clouds, where grain mantles are not well developed. It is appropriate to use high-metal abundances in dense clouds because our models contain both gas phase and condensed phase chemistry. The element chiefly responsible for reducing the abundance of surface hydrogen is no real metal at all, but is sulfur, which can catalytically convert surface H into $H_2$ via a reaction sequence involving HS and $H_2S$. The additional abundance of elemental sulfur can be initially placed in the gas phase or on dust particle surfaces.

We have first considered both two-phase (dust surface + gas) and three-phase (dust surface + dust mantle + gas) models with additional metals present initially in the gas. In these models, the surface abundance of CO is enhanced, bringing the model abundance closer in line to what is observed, while not worsening the agreement for other condensed-phase species. The gas phase chemistry is adversely affected; in particular, the production of complex organic molecules is strongly curtailed. If these models actually pertain to quiescent interstellar clouds, then the extraordinary complex molecule development in TMC-1 cannot be explained by standard ion-molecule chemistry. If the additional metals are initially placed on dust particle surfaces, the two-phase "depleted high-metal" model results at early time ($10^5$–$10^6$ yr) show that the surface abundance of CO can be enhanced to within a factor of $\approx 5$ of its observed value while the gas phase chemistry remains almost identical to that of low-metal models. This model is successful in simultaneously explaining the widespread nature of surface CO and water in the Taurus and other regions and, at the same time, explaining how complex molecules can be produced in

TMC-1 (see Table 1). An analogous three-phase model with six monolayers of sulfur atoms present initially on grain "surfaces" is almost as successful, although the asymptotic fractional abundance of condensed phase CO is slightly smaller than the peak fractional abundance of the two-phase model. Since TMC-1 is clearly somewhat unique, its uniqueness may lie partially in the set of physical conditions and changes that allowed high-metal abundances to be present on dust surfaces prior to the era explored in our models. We intend in the future to extend the two-phase "depleted high-metal" model to study other environments.

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