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Metals at the surface of last scatter

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Standard big-bang nucleosynthesis (BBN) predicts only a trace abundance of lithium and no heavier elements, but some alternatives predict a nonzero primordial metallicity. Here we explore whether CMB measurements may set useful constraints to the primordial metallicity and/or whether the standard CMB calculations are robust, within the tolerance of forthcoming CMB maps, to the possibility of primordial metals. Metals would affect the recombination history (and thus CMB power spectra) in three ways: (1) Lyα photons can be removed (and recombination thus accelerated) by photoionizing metals; (2) The Bowen resonance-fluorescence mechanism may degrade Lyβ photons and thus enhance the Lyβ escape probability and speed up recombination; (3) Metals could affect the low-redshift tail of the CMB visibility function by providing additional free electrons. The last two of these provide the strongest CMB signal. However, the effects are detectable in the *Planck* satellite only if the primordial metal abundance is at least a few hundredths of solar for (2) and a few tenths of solar for (3). We thus conclude that *Planck* will not be able to improve upon current constraints to primordial metallicity, at the level of a thousandth of solar, from the Lyman-α forest and ultra-metal-poor halo stars, and that the CMB power-spectrum predictions for *Planck* suffer no uncertainty arising from the possibility that there may be primordial metals.

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I. INTRODUCTION

Big-bang nucleosynthesis (BBN) is one of the pillars of the hot standard cosmological model. Comparison of BBN theoretical predictions to observed abundances of the lightest nuclei (D, ^{3}He, ^{4}He and ^{7}Li) uniquely determines the only free parameter of standard BBN, the baryon-to-photon ratio $\eta = (5.7 \pm 0.3) \times 10^{-10}$, or equivalently, given the cosmic microwave background (CMB) temperature today $T_0 = 2.73$ K, the baryon abundance $\Omega_b h^2 = 0.021 \pm 0.001$ (see, e.g., Ref. [1]). The latest results from CMB anisotropy measurements by the WMAP satellite are in excellent agreement, with $\Omega_b h^2 = 0.02249^{+0.00056}_{-0.00057}$ [2].

In the standard BBN scenario, elements heavier than lithium are only produced with trace abundances [3]. It has been shown, however, that significant amounts of heavy elements may be produced in inhomogeneous BBN (IBBN) models [4–6]. IBBN may take place if some nonstandard mechanism leads to large baryon-abundance inhomogeneities on small scales, which are allowed by current observations. It is possible to adjust the IBBN parameters to reproduce the observed abundances of light elements, while producing heavier elements with abundances as large as those in the Sun [6,7]. More generally, it cannot be excluded that some unknown processes may lead to a significant production of metals heavier than lithium. It may therefore be profitable to inquire what empirical constraints to primordial metals might be possible.

Standard methods to constrain metal abundances at high redshifts rely on line emission or absorption measurements, and therefore require some sources to have already formed (typically, high-redshift quasars). The intergalactic medium is therefore already partially enriched by metals produced in the first stars, and extracting limits on the primordial abundances relies on understanding the complex physics of galactic outflows and gas mixing and correctly modeling the ambient radiation field. It would be of great interest to be able to probe the abundance of metals *before* the formation of Population III stars that enriched the intergalactic medium. A few ideas were put forward to probe the metallicity during the dark ages: Ref. [8] suggested using resonant scattering of CMB photons off neutral lithium atoms (later shown to be unobservable because lithium is kept ionized by redshifted Lyman-α photons emitted during primordial hydrogen recombination [9]); Ref. [10] studied the effect of fine-structure transitions of heavy elements in atomic or ionized states on CMB anisotropies; Ref. [11] considered the spectral signatures of carbon and oxygen. In this paper we assess whether heavy elements present during primordial recombination could be detectable from upcoming CMB experiments.

Primordial recombination has recently been the subject of a renewed interest, due to the impact of uncertainties in the standard theory on the predicted CMB temperature and polarization anisotropy power spectrum. Errors in the free-electron fraction $x_e(z)$ as small as a few tenths of a percent near the peak of the visibility function at redshifts $z \sim 1100$ would induce biases of several standard deviations for cosmological parameters estimated from *Planck* data [12,13]. This accuracy requirement has motivated abundant work on radiative transfer in the Lyman lines, in particular, Lyman-α (see, for example, Refs. [14–17] and references therein). The tails of the visibility function are less important, but an accuracy of about 1 percent is still needed, which required implementing an accurate multilevel–atom formulation of the recombination problem [18–21]. Such a high sensitivity to the recombination history can be turned into an asset and serve to probe unusual physics taking place during the recombination history as, for example, the presence of primordial heavy elements. In this paper, we explore this idea, and quantify the impact of neutral metals on the Lyα and Lyβ net decay rates, and of ionized metals on the low-redshift tail of the visibility function.

Below we consider three effects of metals on the recombination history and thus on the CMB visibility function: (1) The removal of Lyman-α photons (and thus acceleration of recombination) by photoionization of metals (Sec. II); (2) the degradation of Lyman-β photons (and thus acceleration of recombination) by the Bowen resonance-fluorescence mechanism (Sec. III); and (3) the contribution to the free-electron abundance at late times by low-ionization metals (Sec. IV). We find that effects (2) and (3) provide the biggest impact on CMB power spectra. However, the effects are visible in *Planck* only if the primordial metal abundance is at least a few hundredths of solar for (2) and a few tenths of solar for (3). Given that the Lyman-alpha forest [22] and ultra-metal-poor halo stars [23] constrain the primordial metal abundance to be at least a few orders of magnitude smaller than solar, we conclude that *Planck* will be unable to improve upon current constraints to the primordial metal abundance or, alternatively, that the standard CMB predictions for *Planck* are robust to primordial metals at the levels allowed by current empirical constraints.

II. EFFECT OF NEUTRAL METALS ON THE LYMAN-α DECAY RATE

All metals (in the proper chemical sense of the term, i.e. not including noble gases, halogens and other nonmetals) have a first ionization energy below 10.2 eV, which corresponds to the Lyα transition in hydrogen. This means that neutral metals can provide continuum opacity in the vicinity of the Lyα line by absorbing Lyα photons in photoionization events. Since the photoejected electrons rapidly thermalize their energy, this results in a net loss of resonant Lyα photons, which would have otherwise been reabsorbed by ground state hydrogen atoms. The presence of metals can therefore speed up hydrogen recombination by increasing the net rate of Lyman-α decays. A similar process was investigated for primordial helium recombination [24,25]: in that case the presence of neutral hydrogen leads to continuum opacity in the He I $2^1P^o - 1^1S$ line. To estimate the impact of continuum opacity on the Lyman-α line, we use the analytic treatment presented for He I recombination in Ref. [26].

A. Continuum opacity in Lyα due to photoionization of neutral metals

The radiative-transfer equation in the vicinity of Lyα for the photon occupation number f_ν, including only true absorptions and emissions (i.e. neglecting resonant scatterings) and continuum opacity is

$$\frac{1}{H\nu_{\mathrm{Ly}\alpha}}\frac{\partial f_\nu}{\partial t}-\frac{\partial f_\nu}{\partial \nu}=\tau_{\mathrm{abs}}\phi(\nu)\left(\frac{x_{2p}}{3x_{1s}}-f_\nu\right)+\eta_c(\mathrm{e}^{-h\nu/T_m}-f_\nu), \tag{1}$$

where we approximated $\nu \approx \nu_{\mathrm{Ly}\alpha}$ in the prefactor on the left-hand-side, τ_{abs} is the Sobolev optical depth for true absorption in the Lyα line, $\phi(\nu)$ is the line profile, and η_c is the continuum differential optical depth, given by

$$\eta_c \equiv \frac{n_{\mathrm{M}^0} c\sigma_{\mathrm{pi}}(\nu_{\mathrm{Ly}\alpha})}{H\nu_{\mathrm{Ly}\alpha}}, \tag{2}$$

In Eq. (2), n_{M^0} is the abundance of neutral metal M^0, and $\sigma_{\mathrm{pi}}(\nu)$ is the photoionization cross section of M^0 at frequency ν. We have assumed that σ_{pi} varies slowly over the Lyα resonance (specifically, over the region which is optically thick for true absorption, which corresponds to a few tens of Doppler widths [14]), so we can approximate $\sigma_{\mathrm{pi}}(\nu) \approx \sigma_{\mathrm{pi}}(\nu_{\mathrm{Ly}\alpha})$. Note that Eq. (1) assumes that the ionization state of M^0 is given by the Saha equilibrium equation (this translates in a ratio of continuum emission to absorption rates equal to $\mathrm{e}^{-h\nu/T_m}/f_\nu$), even though this is not strictly correct (see Sec. II B).

The net rate of $2p \rightarrow 1s$ decays is then obtained as follows:

$$\dot{x}_{2p\rightarrow 1s} = \frac{8\pi\nu_{\mathrm{Ly}\alpha}^2}{c^3 n_{\mathrm{H}}}\int H\nu\tau_{\mathrm{abs}}\phi(\nu)\left(\frac{x_{2p}}{3x_{1s}}-f_\nu\right)d\nu, \tag{3}$$

where the prefactor converts photon occupation numbers to photons per unit frequency per hydrogen atom, and we have approximated $\nu \approx \nu_{\mathrm{Ly}\alpha}$ in the multiplicative factor. Ref. [26] showed that the net decay rate in Lyman-α can be written in the following form:

$$\dot{x}_{2p\rightarrow 1s} = \mathcal{E} \times \dot{x}_{2p\rightarrow 1s}|_{\mathrm{std}}, \tag{4}$$

where

$$\dot{x}_{2p\rightarrow 1s}|_{\mathrm{std}} = \frac{8\pi H\nu_{\mathrm{Ly}\alpha}^3}{c^3 n_{\mathrm{H}}}\left(\frac{x_{2p}}{3x_{1s}} - \mathrm{e}^{-h\nu_{\mathrm{Ly}\alpha}/T_r}\right) \tag{5}$$

is the standard net decay rate in Lyα, in the Sobolev approximation, for a large optical depth and assuming an incoming blackbody radiation field, and $\mathcal{E}$ is a correction factor accounting for continuum absorption in the line. The correction factor $\mathcal{E}(\tau_c)$ depends on the single parameter

$$\tau_c \equiv \frac{\tau_{\mathrm{abs}}\Gamma_{2p}\eta_c}{4\pi^2}, \tag{6}$$

where Γ_{2p} is the total inverse lifetime of the $2p$ state. The dimensionless parameter τ_c can be interpreted as the continuum optical depth within the part of the Lyα line which is optically thick for true absorption. For $\tau_c \to 0$, $\mathcal{E}(\tau_c) \to 1$, and for $\tau_c > 0$, $\mathcal{E}(\tau_c) > 1$, which is what one would expect as continuum opacity increases the net rate of decays in the line, as explained above. For $\tau_c \ll 1$, we have the following approximate expansion (see Eq. (117) of Ref. [26]):

$$\mathcal{E} \approx 1 + 13\tau_c, \qquad \tau_c \ll 1. \tag{7}$$

In order for primordial metals to change the net decay rate in Lyα by $\sim$1% (which is roughly the level detectable by *Planck*), we therefore need $\tau_c \sim 0.001$ near the peak of the visibility function. Extracting the relevant parameters from the multilevel atom code of Hirata [14], we obtain, for $z = 1100$,

$$\tau_c \approx 0.7 \times 10^{-3} \frac{\sigma_{\rm pi}(\nu_{{\rm Ly}\alpha})}{10^{-17}\ {\rm cm}^2} \frac{x_{{\rm M}^0}}{10^{-9}}, \tag{8}$$

where $x_{{\rm M}^0} = n_{{\rm M}^0}/n_{\rm H}$ is the abundance of neutral metals relative to hydrogen. We see that for a characteristic photoionization cross section $\sigma_{\rm pi} = 10^{-17}$ cm^2, a fractional abundance of neutral metals per hydrogen atom as low as $\sim 10^{-9}$ would be potentially detectable.

B. Ionization state of metals and results

We now turn to the evaluation of the fraction of neutral metals $f_{{\rm M}^0} \equiv n_{{\rm M}^0}/n_{\rm M}$. As a first approximation we use the Saha equilibrium value:

$$\frac{(1 - f_{{\rm M}^0})}{f_{{\rm M}^0}}\bigg|_{\rm Saha} = S_{\rm M} \equiv \frac{g_{{\rm M}^+} g_e}{g_{{\rm M}^0}} \frac{(2\pi m_e T_r)^{3/2}}{n_e h^3} {\rm e}^{-\chi_{\rm M}/T_{\rm r}}, \tag{9}$$

where $\chi_{\rm M}$ is the ionization energy of M^0, n_e is the free electron abundance, and the g's are the degeneracy factors for each species. For a standard recombination history, at $z = 1100$, Eq. (9) gives (taking the ratio of degeneracy factors to be unity) $f_{{\rm M}^0} = 5 \times 10^{-3}$, 10^{-4}, 2×10^{-6} and 5×10^{-8} for $\chi_{\rm M} = 10$, 9, 8 and 7 eV, respectively, and we can anticipate that only metals with $\chi_{\rm M} \gtrsim 8$ eV may have some impact on Lyα.

Saha equilibrium assumes that the ionizing radiation field is thermal. During hydrogen recombination, the radiation field develops large distortions in the vicinity of the Lyα line, due to the slow escape of Lyα photons (in fact, thermalization of these distorsions is so inefficient that they survive until today [27]). These nonthermal photons increase the ionization rate with respect to its thermal value, and the neutral fraction of metals is therefore smaller than predicted by the Saha equation (see, for example, Ref. [9] for the case of lithium). The ionization state of the metal M is therefore rather determined by the balance of recombinations and photoionizations (this assumes the steady-state limit, valid so long as the photoionization rate is much larger than the Hubble expansion rate, which is a very good approximation around the peak of the visibility function)

$$n_{{\rm M}^+} n_e \alpha_{\rm M} = n_{{\rm M}^0} \beta_{\rm M}, \tag{10}$$

where $\alpha_{\rm M}$ is the M$^+ \to$ M^0 recombination coefficient and $\beta_{\rm M}$ is the M$^0 \to$ M$^+$ photoionization rate. From Eq. (10), we obtain the neutral fraction,

$$f_{{\rm M}^0} = \left(1 + \frac{\beta_{\rm M}}{n_e \alpha_{\rm M}}\right)^{-1}. \tag{11}$$

The photoionization rate $\beta_{\rm M} = \beta_{\rm CMB} + \beta_{\rm dist}$ comprises a thermal part, due to photoionizations by CMB photons (from the ground state *and* excited states), which is related to the recombination coefficient through the detailed balance relation

$$\beta_{\rm CMB} = S_{\rm M} n_e \alpha_{\rm M}, \tag{12}$$

and a nonthermal part, due to photoionizations from the ground state by distortion photons,

$$\beta_{\rm dist} = \int_{\nu_{\rm M}}^{\infty} \sigma_{\rm pi}(\nu) \frac{8\pi\nu^2}{c^3} \Delta f_\nu d\nu, \tag{13}$$

where $\nu_{\rm M} \equiv \chi_{\rm M}/h$ and $\Delta f_\nu = f_\nu - f_\nu^{\rm (CMB)}$ is the nonthermal distortion to the photon occupation number. The Lyman-α distortion peaks around $z \sim 1400$. We can therefore expect that distortions may start significantly affecting the ionization state of the metal M around redshift $z \sim 1400\chi_{\rm M}/(10.2\ {\rm eV})$. As a consequence, we expect the Saha equilibrium approximation to be quite accurate around $z \sim 1100$ for metals with ionization threshold lower than $\sim$8 eV. For the more interesting metals with $\chi_{\rm M} \gtrsim 8$ eV, however, spectral distortions will lower the neutral fraction with respect to the Saha value at $z \sim 1100$, making their detection more difficult through the effect considered here (we will consider the effect of additional free electrons due to the presence of ionized metals in Sec. IV).

We have computed the neutral fraction of several metals with atomic number $Z \leq 26$, using the fits of Ref. [28] for the photoionization cross sections, and the CHIANTI database for the recombination coefficients [29,30]. We have extracted the Lyα distortion[1] from the two-photon code of Hirata [14]. We show the ionization state of beryllium ($\chi_{\rm Be} = 9.32$ eV), boron ($\chi_{\rm B} = 8.30$ eV) and silicon ($\chi_{\rm Si} = 8.15$ eV) as a function of redshift, for a standard recombination history, in Fig. 1.

We show in Fig. 2 the minimal abundance of metals detectable through its effect on Lyα (i.e. such that $\tau_c \geq 0.001$ at redshift 1100). We see that the smallest detectable abundance would be $x_{\rm Be} \sim 3 \times 10^{-4}$. Because of lack of data, we have not treated the case of other metals with $\chi_{\rm M} > 9$ eV, such as zinc ($\chi_{\rm Zn} = 9.39$), arsenic ($\chi_{\rm As} = 9.79$) and gold ($\chi_{\rm Au} = 9.23$), but do not expect significantly lower

[1] In principle, to be self-consistent, one should account for the continuum optical depth due to metal photoionization above Lyα and between $\nu_{\rm M}$ and $\nu_{{\rm Ly}\alpha}$. Given that we find that this effect should not be detectable anyway, we have not implemented a more subtle treatment.

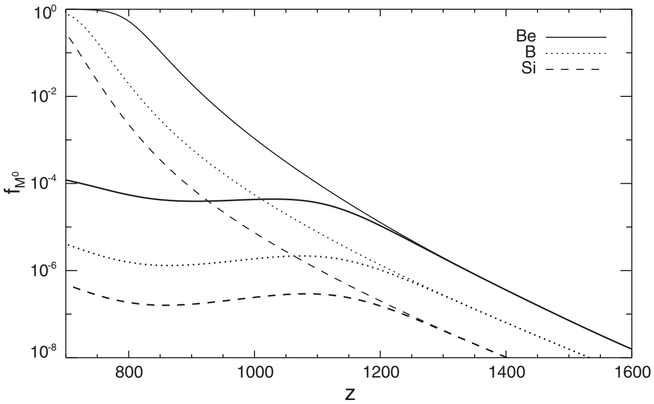

FIG. 1. Neutral fraction of beryllium, boron and silicon as a function of redshift. Thin lines represent the Saha equilibrium value given by Eq. (9). Thick lines represent a more accurate estimate accounting for distortions to the ambient blackbody field near Lyman-α.

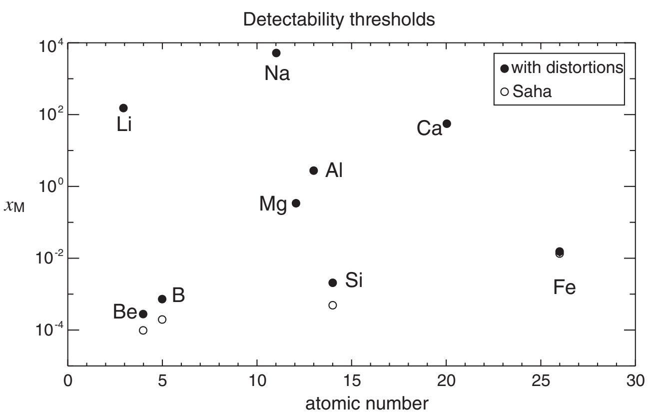

FIG. 2. Minimum abundance of metals relative to hydrogen needed to result in a continuum optical depth in Lyα $\tau_c \geq 0.001$ at $z = 1100$.

detectability thresholds unless they have unusually high photoionization cross sections.

III. THE BOWEN RESONANCE-FLUORESCENCE MECHANISM FOR OXYGEN

There is an accidental coincidence between the hydrogen Lyβ line at 1025.72 Å and the O I $2p^{4\,3}P_2 - 2p^3 3d^3 D_3^o$ line at 1025.76 Å. Lyβ photons may therefore excite neutral oxygen instead of being reabsorbed in the hydrogen line. Neutral oxygen in the $2p^3 3d^3 D_3^o$ state can then either directly decay back to the ground state or first decay to the $2p^3 3p^3 P_2$ state by emitting an infrared photon at 1.13 μm, and subsequently cascade down to the ground state (in principle, atoms in the $2p^3 3d^3 D_3^o$ state can also be excited or photoionized, but there are very few thermal photons energetic enough to do so). The probability of the latter series of events (neglecting stimulated decays) is $p_{1.13\ \mu\mathrm{m}} = A_{1.13\ \mu\mathrm{m}}/(A_{1.13\ \mu\mathrm{m}} + A_{1025.76}) \approx 0.3$. Direct decays of excited oxygen to the ground state do not affect radiative transfer in the Lyβ line, as they do not change the number of Lyβ photons. On the other hand, absorptions in the 1025.76 Å line followed by emission of infrared photons degrade Lyβ photons that would otherwise have been reabsorbed by neutral hydrogen. This effect is similar to the continuum opacity in Lyα discussed in Sec. II, except that this is now a resonant process.

The escape[2] probability in the Lyβ line is enhanced by the probability that a Lyβ photon is absorbed by O I (and then degraded) rather than by H I:

$$\Delta P_{\mathrm{esc}} \approx \frac{\frac{7}{9} n_{\mathrm{OI}} A_{1025.76} p_{1.13\ \mu\mathrm{m}}}{3 n_{\mathrm{HI}} A_{3p,1s}} \approx 0.2 \frac{n_{\mathrm{OI}}}{n_{\mathrm{HI}}}, \qquad (14)$$

where the multiplicative factors are the ratios of the degeneracy factors of the excited levels to those of the ground states. Note that the photon occupation number redward of Lyβ is slightly decreased by this process: $f_- = x_{3p}/(3x_{1s})(1 - \Delta P_{\mathrm{esc}})$. However, as long as $\Delta P_{\mathrm{esc}} \ll 1$, this has no detectable impact on radiative transfer redward of Lyβ.

As oxygen and hydrogen have very similar ionization energies, we can assume that they have the same recombination history. More specifically, the ratio of ionized to neutral oxygen rapidly equilibrates to the corresponding ratio for hydrogen because the continuum above the ionization threshold is optically thick. We therefore have $n_{\mathrm{OI}}/n_{\mathrm{OII}} \approx \frac{9}{8} n_{\mathrm{HI}}/n_{\mathrm{HII}}$ (the 9/8 comes from properly accounting for degeneracy factors, see Eq. (9)) and as a result we obtain $n_{\mathrm{OI}}/n_{\mathrm{HI}} \approx x_{\mathrm{O}}/(1 - x_e/9) \approx x_{\mathrm{O}}$. As long as $x_{\mathrm{OI}} \lesssim 10^{-3}$ the damping wings of the O I 1025.76 Å line are optically thin, and the Bowen mechanism can only affect the net decay rate in the Doppler core of the Lyβ line. The latter is very small anyway, as the radiation field is very close to equilibrium with the 3p-1s ratio over many Doppler widths near line center. We have modified the escape probability from the Doppler core of Lyβ in the recombination code HYREC [26] according to Eq. (14), and found that a minimal abundance of oxygen $x_{\mathrm{O}} \approx 10^{-5}$ is required to affect the recombination history at a potentially detectable level $\Delta x_e/x_e \approx 0.2\%$ at $z \approx 1100$. Note that this would correspond to an enhancement by a factor ~200 from the standard escape probability in the Lyβ Doppler core. This stems from the fact that only a tiny fraction of Lyβ decays occur in the Doppler core of the line, whereas most of them take place in the damping wings. The recombination history is therefore highly insensitive to the exact decay rate in the core.

[2]The term "escape" is somewhat misleading in this situation: photons near the Lyβ frequency do not actually escape more from the resonant region (in fact, their overall escape rate is even lower due to a slightly higher optical depth). They rather only escape reabsorption by neutral hydrogen.

IV. ADDITIONAL FREE ELECTRONS DUE TO IONIZED METALS

If metals remain ionized, they can contribute an additional residual free electron fraction at late times, $\Delta x_e \sim x_{\mathrm{M}^+}$. In fact we have $\Delta x_e = \frac{1}{2} x_{\mathrm{M}^+}$, as we show below. At late times the evolution of the free-electron fraction is given by

$$\dot{x}_e \approx -n_{\mathrm{H}} \alpha_{\mathrm{B}} x_e x_p = -n_{\mathrm{H}} \alpha_{\mathrm{B}} x_e (x_e - x_{\mathrm{M}^+}). \qquad (15)$$

Equation (15) is valid because the free electron fraction is many orders of magnitude above the Saha equilibrium value at late time (for a discussion, see Ref. [26]). If x_e^0 is the unperturbed free electron fraction (i.e. obtained with $x_{\mathrm{M}^+} = 0$) and $x_e = x_e^0 + \Delta x_e$, we obtain

$$\Delta \dot{x}_e = -n_{\mathrm{H}} \alpha_{\mathrm{B}} x_e^0 (2\Delta x_e - x_{\mathrm{M}^+}), \qquad (16)$$

which asymptotes to $\Delta x_e = \frac{1}{2} x_{\mathrm{M}^+}$. The *Planck* satellite will be sensitive to fractional changes $\Delta x_e / x_e \sim 1\%$ at late times. Since $x_e \approx 0.3 - 1 \times 10^{-3}$ for $200 \lesssim z \lesssim 700$, we conclude that a potential detection by *Planck* requires a fractional abundance of metals $x_{\mathrm{M}} \gtrsim 10^{-5}$ (in the case that metals remain fully ionized). Note that for a given Ω_b, the presence of metals also modifies the total abundance of hydrogen, n_{H}, throughout the recombination history. However these modifications are degenerate with a mere change of Ω_b of Y_{He} at the level of a few times 10^{-5} and are therefore undetectable.

V. CONCLUSIONS

We have investigated whether a primordial metal content could sufficiently affect the recombination history to be detectable in upcoming CMB data from *Planck*. We first considered the effect of photoionization of neutral metals by Lyα photons. We showed that although a very small abundance of neutral metals would be enough to significantly affect the net decay rate in Lyα, metals with ionization threshold below Lyα are mostly ionized at $z \sim 1100$, and therefore undetectable. We also considered the Bowen resonance-fluorescence mechanism if primordial oxygen is present. This effect leads to an enhanced escape rate of Lyβ photons and a speedup of recombination. We showed that it could lead to detectable changes for a primordial oxygen abundance of a couple hundredths of solar $x_{\mathrm{O}} \sim 10^{-5}$. Finally, we pointed out that metals that stay ionized until late times provide additional free electrons and therefore change the late-time Thomson scattering optical depth. A fractional abundance $x_{\mathrm{M}} \sim 10^{-5}$ of primordial metals could be detectable through this effect. As a reference, the most abundant metal in the solar photosphere is oxygen ($x_{\mathrm{O}} = 4.9 \times 10^{-4}$), followed by carbon ($x_{\mathrm{C}} = 2.7 \times 10^{-4}$), neon ($x_{\mathrm{Ne}} = 8.5 \times 10^{-5}$), nitrogen ($x_{\mathrm{N}} = 6.8 \times 10^{-5}$), magnesium ($x_{\mathrm{Mg}} = 3.4 \times 10^{-5}$), silicon ($x_{\mathrm{Si}} = 3.2 \times 10^{-5}$), iron ($x_{\mathrm{Fe}} = 3.2 \times 10^{-5}$) and sulfur ($x_{\mathrm{S}} = 1.3 \times 10^{-5}$). Other metals have fractional abundances $x_{\mathrm{M}} < 10^{-5}$ in the Sun [31]. As carbon, nitrogen, oxygen and neon are neutral at late times (due to their high ionization potential), we conclude that *Planck* could potentially detect primordial metals with an abundance at least a few tenths of solar. This is moreover an optimistic estimate, as the effect of metals is likely to be degenerate with the redshift of reionization or other cosmological parameters.

Given that Lyman-alpha-forest measurements and ultra-metal-poor halo stars suggest a primordial metallicity much smaller than 100th solar, we conclude that the CMB can unfortunately not usefully constrain the abundance of primordial metals. At the same time, we also conclude that the CMB predictions for the *Planck* satellite are robust to a primordial metallicity allowed by current empirical constraints.

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