

## Possible in situ tests of the evolution of elemental and isotopic abundances in the solar convection zone

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[1] Helioseismology has shown that the chemical composition of the Sun has changed over its lifetime. The surface abundance of helium and heavy elements is believed to have decreased by up to 10% in relation to their initial values. However, this reduction is too small to be tested by direct observations of the photospheric chemical composition. Here we compare the predicted variations in the solar photospheric composition with precise measurements of abundances in meteorites and the solar wind composition. Although elemental composition ratios can vary by roughly a percent (e.g., for Ca/Mg and Ca/Fe) over the Sun's lifetime, their measurements are rife with uncertainties related to uncertainties in the interpretation of meteoritic measurements, photospheric determinations, and the complex fractionation processes occurring between the upper photosphere and lower chromosphere and the corona. On the other hand, isotopic ratios can be measured much more accurately and are not expected to be affected as much by extrasolar processes, although more work is required to quantify their effect. As the isotopic ratios evolve in the Sun proportionally to the mass ratios of the isotopes, light elements yield the highest variations in isotopic ratios. They are predicted to reach as high as 0.6% for  $^{18}\text{O}/^{16}\text{O}$  and are only slightly lower in the cases of  $^{26}\text{Mg}/^{24}\text{Mg}$  and  $^{30}\text{Si}/^{28}\text{Si}$ . Such a value should be well within the sensitivity of new missions such as

Genesis. *INDEX TERMS:* 7599 Solar Physics, Astrophysics, and Astronomy: General or miscellaneous; 7522 Solar Physics, Astrophysics, and Astronomy: Helioseismology; 7544 Solar Physics, Astrophysics, and Astronomy: Stellar interiors and dynamo theory; *KEYWORDS:* helioseismology, abundances, solar wind, fractionation, isotopic ratios, Sun

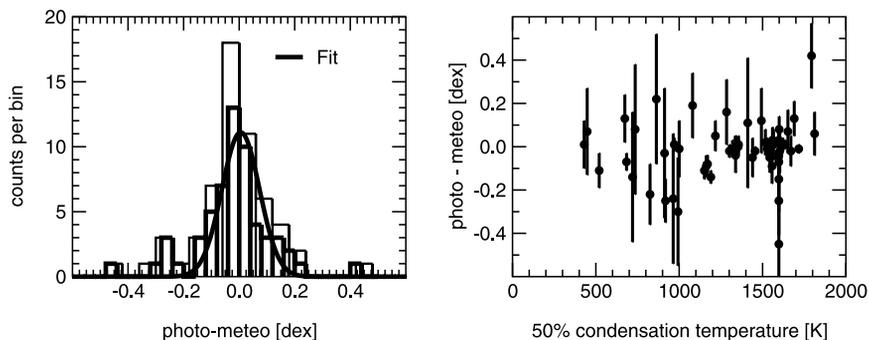
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### 1. Introduction

[2] Modern solar models can be tested to a high degree of accuracy with newly available helioseismic data. Such models infer the speed of sound in the solar interior by comparing measured oscillation modes with model calculations. Because the speed of sound depends on the mean molecular weight of the gas (among other quantities), determining profiles of sound speed yields information about possible compositional inhomogeneities in the interior of the Sun. Indeed, solar models which include effects of elemental segregation succeed much better than those without in reproducing inferred speed profiles [Christensen-Dalsgaard *et al.*, 1996]. In these models, the photospheric abundances of all elements heavier than hydrogen have decreased by up to about 10% over the history of the Sun.

However, this settling of the heavier elements out of the outer convection zone toward the center of the Sun has not been detectable with photospheric abundance measurements. In this work we consider the possibility of directly measuring this effect by measuring the composition of the solar wind.

[3] Lunar soils have preserved an archive of solar wind data dating back to the time of the formation of the lunar regolith. Dust grains that have been exposed to the solar wind retain it with variable fidelity, although the lunar regolith as a whole appears to have preserved the entire solar wind fluence incident on the lunar surface [e.g., Wieler, 1998]. Lunar soils are especially well suited to measure the isotopic and, to a limited extent, the elemental composition of the noble gases and of few other elements, notably nitrogen. Early measurements of the He isotopic composition appeared to show a secular variation of the solar wind  $^3\text{He}/^4\text{He}$  ratio [Geiss, 1973]. This could be interpreted as being due to differences in the solar wind



**Figure 1.** Comparison of CI meteoritic and photospheric abundances normalized to Mg. (right) Plot of the logarithm of the CI meteoritic abundance ratio  $X/Mg$  divided by its corresponding photospheric value plotted versus 50% condensation temperature. (left) Histogram of the abundance values for two different bin sizes and a fit to the histogram. The uncertainties (and hence the width of the histogram) are nearly entirely due to uncertainties in photospheric abundance measurements. For instance, atomic parameters limit measurements to an uncertainty of about 20–30%. Meteoritic uncertainties are smaller, of the order of 3–10% and mainly due to possible sampling biases.

acceleration in the past or due to secular admixture of  $^3\text{He}$  from the  $^3\text{He}$  bulge in the Sun by a slow mixing process beneath the outer convection zone [Bochsler *et al.*, 1990]. The apparent secular change of the isotope ratio  $^3\text{He}/^4\text{He}$  has recently been reinterpreted. Heber [2002] analyzed lunar soil material of various antiquities for their noble gas isotopic composition. Apart from the known changes in He isotope composition, they found a change in the Ne isotope composition which is considerably larger than what could be attributed to the chemical evolution of photospheric composition. According to that work, the apparent secular change is due to slow removal of surface layers of lunar soil grains. The older grains have had more surface material removed, increasing the importance of the deeper-seated and isotopically heavier so-called “SEP” or “HEP” component [Wieler *et al.*, 1986; Wimmer-Schweingruber and Bochsler, 2001a]. Heber [2002] used the measured correlation between Ne and He isotope composition to account for this removal by assuming that the Ne isotope composition did not change over time. Then the apparent secular variation of the He isotopes vanishes and hence the variations of  $^3\text{He}/^4\text{He}$  are not necessarily a test for solar evolution models. Nitrogen is known to have large secular variations in its isotopic composition in lunar soils (see, e.g., Kerridge [1993] for a review). However, recent investigations by Wieler *et al.* [1999] have shown that about 90% of the implanted nitrogen is nonsolar, i.e., due to some other, as yet unidentified, source.

[4] Because there is no unambiguous evidence in lunar soils for secular changes in solar wind composition which could be interpreted as being due to elemental segregation, another approach needs to be chosen. Here we investigate the possibility of comparing the composition of certain, well-determined meteoritic abundance ratios with the same abundance ratios measured in the solar wind. The formation of the solar system about 4.6 billion years ago left compositional signatures in its constituent bodies and in different samples of these bodies. Compositional differences can be used as tracers for formation and alteration processes active mainly in the early solar system but partially continuing to the present day. For example, volatile elements are

extremely depleted in terrestrial samples and in most meteorites. Elements differ in their chemical properties, resulting in variations of elemental abundance ratios in different separates of various solar system samples. Because the Sun contains 99.9% of the mass in the solar system, its composition serves as the reference for solar system composition, and often solar and solar system composition are used synonymously. This information comes from spectroscopic abundance determinations of the solar photosphere or from in situ measurements of the solar wind. However, much of the information available today comes from studies of the composition of meteorites and of meteorite mineral separates or samples from other solar system bodies. On the basis of the comparison of such investigations, the composition of the bulk solar system has become known to a remarkable degree of accuracy. In fact, because of the close match in elemental abundances between solar and CI meteoritic values, CI meteorites are considered the most primitive material in the solar system besides comets or the Sun. Figure 1 illustrates this good agreement by using data from the compilation of Grevesse and Sauval [1998]. The right-hand panel is a plot of the logarithm of the CI meteoritic abundance ratios of element  $X$  with respect to Mg,  $X/Mg$ , divided by its corresponding photospheric value plotted versus 50% condensation temperature [Wasson, 1985]. This quantity is often used to order elemental abundance trends in different classes of meteorites. The comparison of photospheric and CI meteoritic abundance ratios is not reliable for condensation temperatures below about 400 K. For all other elements, with the exception of Li, the agreement between the two different abundance measurements (CI meteoritic and photospheric) is considered remarkably good. This is illustrated in the left-hand panel of Figure 1. It shows a histogram of the abundance ratios,  $(X/Mg)/(X/Mg)_{\text{photo}}$ . The histogram is symmetric around zero, indicating that there is no systematic disagreement between the two sources of solar abundances. The standard deviation of the histogram is 0.084 dex, corresponding to a width of 21.5%. A Gaussian fit with that value for  $\sigma$  is plotted for comparison. The fit is satisfactory, and the result does not change when using a different bin

size for the histogram, e.g., the one shown in thin lines. Assuming the width of the histogram to be representative of the quadratic sum of the uncertainties of CI meteoritic and photospheric, we subtract quadratically the maximum uncertainty of CI meteoritic measurements, 10%, to obtain the expected uncertainty of photospheric abundance determinations,  $\sim 20\%$ . This value is less than that given by *Del Zanna et al.* [2001], 25%–30%, who consider this to be the uncertainties in atomic properties alone. Moreover, uncertainties in the treatment of the thermodynamics of the line-emitting regions in the photosphere and lower chromosphere can be substantial [Holweger, 2001]. Nevertheless, some authors do give smaller uncertainties for certain elements with well-known atomic parameters. Meteoritic uncertainties are generally smaller, of the order of 3%–10% and are mainly due to possible sampling biases and will be considered later. Thus from this discussion, we conclude that abundance ratios of refractory, i.e., nonvolatile, elements offer the best choice of measuring the effect of elemental segregation.

[5] We consider the physics of elemental segregation in section 2 and apply it to solar evolution in section 3, where we also give predictions for the evolution of some elemental and isotopic abundance ratios. We consider possible fractionation processes which would influence measurements in the solar wind and investigate the potential of various solar wind measurements in section 4.

## 2. The Physics of Chemical Evolution in the Sun

[6] The basic structure of the Sun consists of a dynamically stable inner sphere which extends to a little more than 70% of the Sun’s radius and an overlaying convective shell which extends to the photosphere. The turbulent motions in the convection zone are so rapid in comparison with other timescales that one can assume that it is well mixed, leading to a homogeneous composition in its entirety. Compositional changes due to nuclear processing in the convection zone can be excluded because the temperature is too low. Hence changes in the chemical composition have to be generated at the boundaries of the convection zone, either in the dynamically stable region at its base or at the solar surface (through infall of material or mass loss). As any excess or deficit of an element is diluted in the entire convection zone, a variation of, say, 10% in the observed abundance entails that the mass of the element  $i$  in question added or subtracted from the convection zone must be  $M_i = 0.1X_iM_{CZ}$ ,  $X_i$  being the original mass fraction of element  $i$  and  $M_{CZ}$  being the mass of the convection zone (in the current Sun,  $M_{CZ}$  is roughly 2% of the total mass of the Sun [Christensen-Dalsgaard et al., 1996]). For instance, if one terrestrial planet had migrated into the Sun in the early stages of the formation of the solar system, this would have resulted in an increase of solar metallicity by only about 1% using the present-day mass fraction of the convection zone. Note that this process will not alter the relative abundances of refractive elements among themselves. Moreover, in the early Sun, the convection zone was deeper and hence more massive, and a larger flux of matter into it would have been necessary for any observable effect to be expected.

[7] The current mass loss or accretion rates are much too low to have any measurable impact on photospheric abun-

dances. Earlier in the Sun’s life, it is probable that mass loss or accretion rates were higher. Because of the faster rotation of the Sun in the past, dynamo action was enhanced. This made more energy in the form of magnetic fields available to drive the solar wind. Simple calculations show that this could at most have doubled the solar wind fluence over the lifetime of the Moon [Wimmer-Schweingruber and Bochsler, 2001b], commensurate with measurements of solar wind noble gases in lunar soils [Geiss, 1973]. Extrapolating these results to earlier times does not result in a significant increase of mass loss. Moreover, the convection zone was also much more massive in the past. During the Sun’s evolution on the pre–main sequence when mass exchange would be expected to be greatest, the Sun is thought to have been completely convective [Hayashi, 1961]. The hypothesis of large mass loss rates in the young Sun has been examined but is not favored by helioseismology [Morel et al., 1997]. The addition of material that has been processed by nuclear reactions in the dynamically stable core can also be excluded. Again, temperatures are high enough only in its innermost regions, making any exchange at its boundary impossible (with the sole exception of lithium; see section 2.2).

### 2.1. Migration and Separation Processes

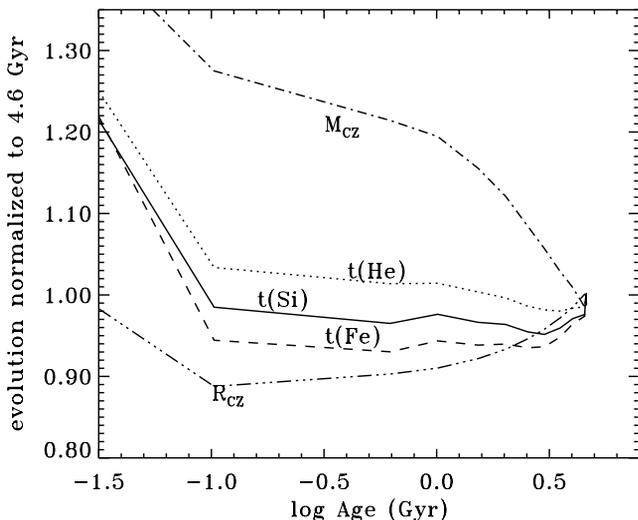
[8] The evolution of abundances in the solar convection zone and in the outer radiative envelope just below it occurs chiefly as a result of the differential effects of gravity on the elements of different mass. In a simple two-component gas, constituted of hydrogen and helium, the inward gravitational pull is 4 times greater on helium than on hydrogen. As a result, helium will gradually settle toward the Sun’s center, and the fractional abundance of hydrogen will rise at the surface. Differential radiation pressure induces a minor correction in the overall chemical evolution in the convection zone, but it plays a dominant role in the evolution of abundance ratios.

[9] The rate at which gravitational settling occurs is determined in a large part by the “friction” within the gas, which is dominated by Coulomb interactions. Because friction increases with the overall ionization state of the plasma, the settling rate generally will decrease as temperature and density rise.

[10] As the evolution of photospheric abundances is governed by the evolution of the abundances at the base of the convection zone, the deeper the convection zone, or the smaller the stable radiative interior, the smaller are the fluxes of elements in and out of the convection zone. This is the combined effect of enhanced interactions between particles leading to smaller diffusion velocities and the geometrical effect of reducing the area of the surface through which particles can flow. Moreover, the dilution of abundance changes in the larger convection zone further increases the timescale for the rate of change of composition. This is important because the depth of convection zone varied strongly as the Sun evolved (as shown in the work of Bahcall et al. [2001]).

[11] The timescale for the evolution of surface abundances can be approximated as [Michaud et al., 1976]

$$\tau = \frac{M_{CZ}}{4\pi(r^2\rho v_{\text{diff}})_{CZ}}, \quad (1)$$



**Figure 2.** Evolution of the timescale for the variation of chemical composition in the convection zone with the age of the Sun; values are normalized to those in the contemporary Sun at  $\log(\text{age}) = 0.66$ . The timescale is element dependent; here helium ( $t(\text{He})$ , normalized to 39 Gyr), silicon ( $t(\text{Si})$ , normalized to 51 Gyr), and iron ( $t(\text{Fe})$ , normalized to 51 Gyr) are shown. Also shown are the evolution of the mass of the convection zone ( $M_{CZ}$ , normalized at the current value of  $0.023M_{\odot}$ ) and the radius of the base of the convection zone ( $R_{CZ}$ , which is currently at  $0.710 R_{\odot}$  in this model).

where  $\rho$  is the density,  $r$  is the radius, and  $v_{\text{diff}}$  is the diffusion velocity all evaluated at the base of the convection zone (CZ). The timescales for helium, silicon, and iron with respect to time shown in Figure 2 illustrate the combined effect of the increases in  $v_{\text{diff}}$  and the radius of the base of the convection zone and the reduction in  $M_{CZ}$ .

[12] The gravitational force exerted on an ion species “ $i$ ” is  $A_i m_H g(r)$ , where  $g(r)$  is the gravitational acceleration at distance  $r$  from the center of the Sun. Radiative pressure is included in the modeling of diffusion by changing the effective gravity felt by different atomic species to  $A_i m_H (g - g_{\text{rad},i})$ , where  $g_{\text{rad},i}$  is the radiative acceleration;  $g_{\text{rad},i}$  is very sensitive to the features of the species spectrum, i.e., to the atomic structure of the ion, on the ionization state of the ion and of other ions competing for the same photons. Completely ionized elements feel practically no radiation acceleration.

[13] The expression for  $g_{\text{rad},i}$  is taken from *Richer et al. [1998]* (please refer to this paper for a detailed discussion) as being

$$g_{\text{rad},i} = \frac{L_r}{4\pi r^2} \frac{\kappa_R}{cX_i} f_{\text{flux}}. \quad (2)$$

In this expression,  $X_i$  is the mass fraction of species  $i$ ,  $f_{\text{flux}}$  is the fraction of the radiative flux which will be transferred to species  $i$  (refer to equation (1) of *Richer et al. [1998]*). The Rosseland mean opacity  $\kappa_R$  is a measure of the opacity of the plasma and determines the total momentum of the radiation field transferred to the absorbing plasma.

[14] The inverse relationship between  $g_{\text{rad},i}$  and the species abundance has an interesting potential consequence for isotopic fractionation. Different isotopes of an element can have large differences in abundance, which would favor the less abundant species. This could potentially create large isotopic anomalies. The condition for such an effect is that the spectral lines of the minor isotope be well separated from the spectral lines of the major isotope and that there would be no coincidence with strong lines from other elements so that  $f_{\text{flux}}$  can become nonnegligible for the minor isotope. This is not the case in the Sun, not even for helium, for which the effect would be the most noticeable. The temperatures below the convection zone where separation by radiative pressure could occur are large enough,  $T > 2 \times 10^6$  K, that the thermal width of the spectral lines is much larger than the line separation for different isotopes of a given element. Therefore  $f_{\text{flux}}$  will be small and will cancel out the effect of the  $1/X_i$  factor.

[15] It follows that in all calculations of the evolution of isotopic ratios in the present paper the  $g_{\text{rad},i}$  will be assumed to be the same for all isotopes of a given element. The radiation pressure will only play a role in the evolution of elemental ratios.

## 2.2. Mixing Below the Solar Convection Zone

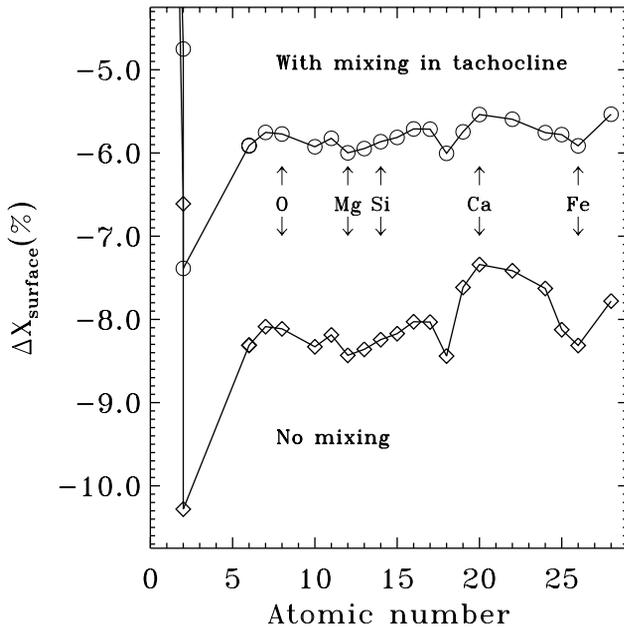
[16] The first evidence for mixing outside of the convection zone came from the strikingly low photospheric lithium abundance. Compared with its meteoritic abundance, it is depleted by a factor of 137 in the photosphere [*Carlsson et al., 1994*]. Solar models without mixing cannot account for this large difference. Modern solar models include various forms of mixing, based on convective overshoot or rotationally driven mechanisms, and can now account for the observed lithium depletion while preserving the observed beryllium abundance and  $^3\text{He}/^4\text{He}$  ratio (see, e.g., *Brun et al. [2000]* and *Richard et al. [1996]*).

[17] Moreover, based on helioseismic results, it appears that diffusion alone is not sufficient to explain the radial profile of the speed of sound in the Sun. There are large discrepancies between older models and measured values, especially around the lower boundary of the convection zone. This can be and has been rectified by including a limited extension of mixing below the convection zone into the stable radiative interior [*Christensen-Dalsgaard et al., 1996*].

[18] Both issues, lithium and sound speed, can be resolved simultaneously by the same mixing mechanism (as in the work of *Brun et al. [2000]*). The mixing occurs in a narrow region at the base of the convection zone in which there is a large gradient in rotational velocity; this region is called the tachocline. Although several mixing processes in that region can match the constraints in the Sun, studies in other solar type stars [*Piau and Turck-Chièze, 2002*] suggest that turbulent mixing caused by the shear due to the rotational velocity gradient [*Spiegel and Zahn, 1992*] is superior to other processes, the most often suggested being convective overshoot [e.g., *Blöcker et al., 1998*].

## 3. Predicted Evolution of the Composition of the Outer Convection Zone

[19] For this work, we have used the models calculated by *Turcotte et al. [1998]* which feature the most detailed



**Figure 3.** Relative change in the surface abundances predicted by the detailed solar models with diffusion, the lower one without mixing and the higher one with an approximate effect of mixing at the base of the convection zone.

treatment of microscopic diffusion in the Sun. The evolution of the abundance of the minor isotopes of elements heavier than carbon have been calculated explicitly. The *Turcotte et al.* [1998] models have also been used by *Bochsler* [2000] to investigate the effect of isotopic fractionation in the Sun on solar wind abundances. He estimated the fractionation based on the basis of isotopic mass differences and the published factors of depletion for the major isotope of each element. In the current paper the full effect of the solar evolution on the net isotopic fraction is taken into account, and an approximate prescription for the effect of mixing beyond the convection zone is also used. The net effect on isotopic ratios is quite similar in the work of *Bochsler* [2000] and here in the absence of mixing. While the *Turcotte et al.* [1998] models do not include the effect of mixing beneath the convection zone, we have approximated how mixing affects the evolution of the photospheric composition by reducing the changes in composition such as to reflect the results of *Brun et al.* [2000], who include mixing in the tachocline in addition to a standard treatment of diffusion.

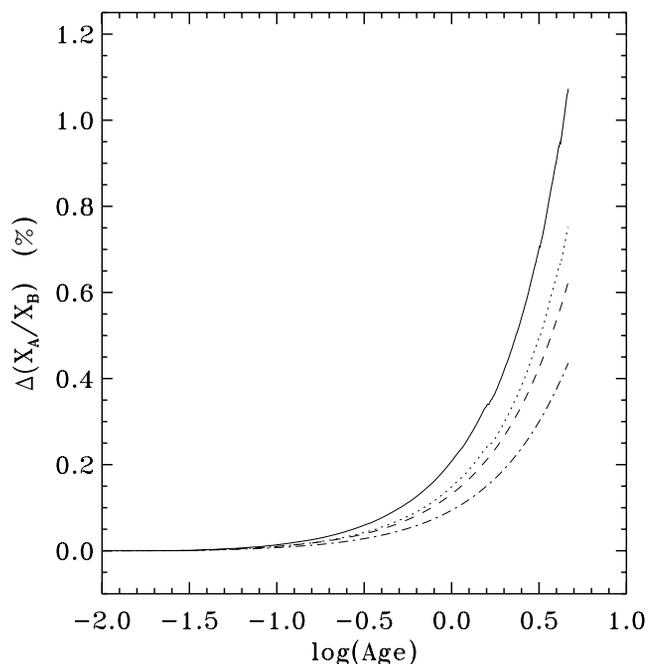
[20] Because of the assumptions on initial composition inherent in the computation of solar models, the absolute values of the abundances predicted by solar evolution models cannot be used, only relative changes are meaningful (with the notable exception of the helioseismic measurements of the helium abundance). Here we assume an initial composition as in the work of *Grevesse and Noels* [1993] calibrated to reproduce a contemporary value of  $Z/X$  of 0.245. This value of  $Z/X$  inferred from the observations is thought to be accurate to 10% at best.

[21] The predicted surface composition at 4.6 Gyr is illustrated in Figure 3, where the difference between the

composition at 4.6 Gyr and the original composition is plotted as a function of the atomic number. The features reflect mostly the effect of the differential radiative forces. These effects are relatively small, however, as the spread in the relative abundance variations spans 8.8% for Ar to 7.6% for Ca. The mean variation in the detailed model is around 8.5%. The model including mixing has a lower relative change, with an adopted value for all estimates done in this work of 71.8% as high as that of the detailed diffusion-only model.

[22] As a consequence of the evolution of the Sun itself, reflected in the decreasing timescales shown in Figure 2, the rate of abundance changes has increased sharply as the Sun has aged. This is illustrated in Figure 4, where the elemental abundance ratio of calcium to iron and the isotopic abundance ratio of  $^{12}\text{C}$  and  $^{13}\text{C}$  are shown to increase exponentially in the near past. One notices that the trends are the same for the elemental and isotopic ratios even though radiative forces are irrelevant in the latter case. One consequence of this rapid recent evolution is that fossil records of the solar wind at different epochs (lunar soils, for example) may possibly contain evidence of the variations of some abundance ratios.

[23] The predicted evolution of isotopic ratios for He, C, N, O, Ne, Mg, Si, and Ar is presented in Table 1. Recalling the discussion on diffusion processes (section 3), one can infer that the only difference of note for isotopes in the context of diffusion is their mass. It is assumed here that all characteristics (i.e., ionization state, radiative forces) for the major isotope were shared by the minor isotopes with the exception of mass.



**Figure 4.** Evolution of the calcium over iron and  $^{12}\text{C}/^{13}\text{C}$  abundance ratios in the solar convection zone over its lifetime. The solid and dotted lines show Ca/Fe with and without mixing, respectively, below the convection zone. The dashed and dot-dashed lines show  $^{12}\text{C}/^{13}\text{C}$  with and without mixing.

**Table 1.** Values of the Relative Variation in Isotopic Abundance Ratios Over the Sun's Life ( $\Delta(A/B)/(A/B)_0$ ) in Percent

A/B	No Mixing, %	With Mixing, %
<sup>3</sup> He/ <sup>4</sup> He	4.10	2.85
<sup>13</sup> C/ <sup>12</sup> C	0.61	0.43
<sup>15</sup> N/ <sup>14</sup> N	0.44	0.31
<sup>17</sup> O/ <sup>16</sup> O	0.37	0.26
<sup>18</sup> O/ <sup>16</sup> O	0.91	0.64
<sup>21</sup> Ne/ <sup>20</sup> Ne	0.26	0.19
<sup>22</sup> Ne/ <sup>20</sup> Ne	0.71	0.50
<sup>25</sup> Mg/ <sup>24</sup> Mg	0.19	0.13
<sup>26</sup> Mg/ <sup>24</sup> Mg	0.57	0.40
<sup>29</sup> Si/ <sup>28</sup> Si	0.13	0.09
<sup>30</sup> Si/ <sup>28</sup> Si	0.45	0.31
<sup>36</sup> Ar/ <sup>40</sup> Ar	1.09	0.76
<sup>38</sup> Ar/ <sup>40</sup> Ar	0.64	0.43

The value without mixing is taken from the *Turcotte et al.* [1998] models, and the values with mixing are the same results corrected by the estimated effect of tachocline mixing as discussed in the work of *Brun et al.* [2000].

[24] As a result of the large mass difference between its isotopes, helium has the largest variation in its isotopic ratio. Although the variation of the isotopic ratio is by far the largest variation of all ratios either isotopic or elemental, the study of helium is compromised by the lack of accurate measurements of the isotopic ratio of helium at earlier times in the Sun's life, as has been touched upon in the introduction. For other elements, the isotopic ratios vary much less but not much more so than elemental ratios as seen in Table 2. Not surprisingly, the largest effect, after helium, was found for <sup>18</sup>O/<sup>16</sup>O and <sup>36</sup>Ar/<sup>40</sup>Ar, which have similar isotopic relative mass differences. As a general rule, as the mass of the element increases, the effect decreases gradually as the relative mass difference between isotopes decreases. Nonetheless, significant effects can be seen when comparing the more massive isotopes of Mg and Si with their major isotopes.

#### 4. Selecting Best Tracers of Solar Chemical Evolution

[25] The aim of this work is to identify elemental or isotopic abundance ratios that are especially susceptible to elemental migration effects, well determined in meteorites, and which can be precisely measured in the solar wind. In this section we consider possible biases and fractionation processes which need to be taken into account in both meteoritic and solar wind studies and then motivate our selection.

##### 4.1. Elemental Abundances From Meteorites

[26] Because meteorites can be analyzed in the laboratory, elemental abundance measurements performed on meteorites or terrestrial samples reach the highest possible precision. Measurement uncertainties are vanishingly small even for the application considered in this work. In Figure 5 we have plotted the Ca/Fe element abundance ratio versus the Mg/Fe ratio as derived by different authors (indicated next to the symbols and referenced in the caption). The actual measurement uncertainties are considerably smaller than the spread in all the data and also smaller than the spread in the data from the Mainz group, who publish abundance data for eight samples. Their uncertainty in the mean is about 1% for

Mg/Fe and larger for Ca/Fe. It is important to note that these uncertainties are not primarily due to the different authors of the studies, but rather to different (some subjective) choices of samples of meteoritic matter. Moreover, there are only five known CI chondrites, of which one has been studied extensively (Orgeuil), one was studied in some detail (Alais), and three are so small that obtaining samples from them must be considered a feat on its own [*Grady, 2000*]. Hence the observed variations in samples in Figure 5 must be considered a lower limit on the variability of these elemental abundance ratios in different separates of the most faithful samples of the presolar nebula. For comparison, we have also plotted a box with a diagonal which shows the maximum evolutionary change of the photospheric abundance ratios based on solar evolution models without mixing. Obviously, even if solar wind measurements were possible with much better precision than currently possible (for instance, with the Genesis samples), the effect of solar evolution cannot be determined by considering elemental abundance ratios. Uncertainties in meteoritic abundances will render futile any such endeavor.

##### 4.2. Isotopic Composition From Meteorites

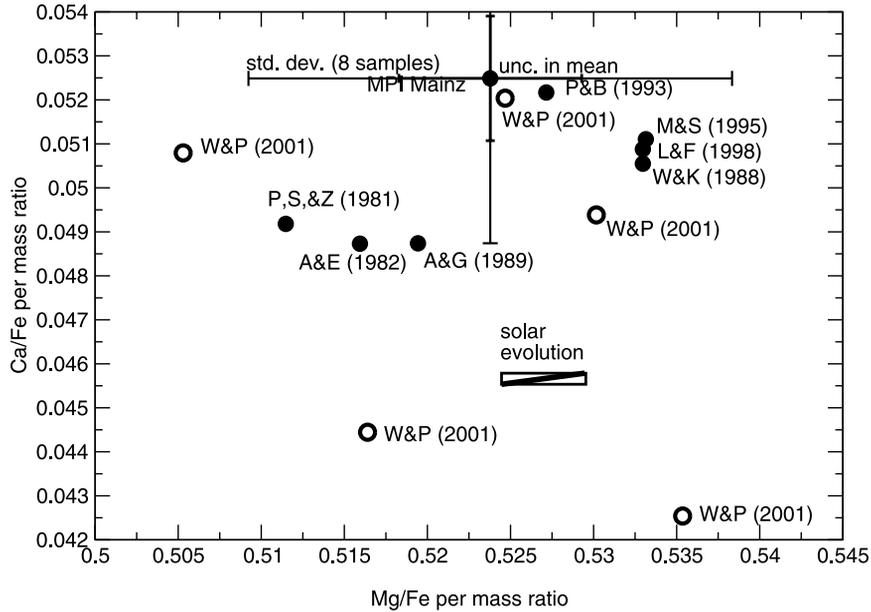
[27] It is well known from studies such as the one of *Anders and Grevesse* [1989] that there is little variation in the abundance ratios among the nonvolatile elements in different materials of the solar system. This homogeneity in elemental compositions of different solar system materials reflects the fact that the early condensates in the inner parts of the solar nebula did not undergo strong chemical fractionation. Isotopic fractionation (e.g., due to incomplete condensation) was limited to tiny effects [*Humayun and Clayton, 1995*]. Consequently, it is not surprising that there is also not much variation in the isotopic abundance of the refractory elements in the bulk of solar system samples.

[28] The small variation of solar system isotopic abundances in refractory elements is illustrated in Figure 6 for

**Table 2.** Some of the Highest Photospheric Abundance Ratios as Predicted by Solar Models for Elements of FIP < 10 eV and Absolute Values of the Difference in Mass and FIP as well as of the Relative Change in Abundance Ratios at the Solar Age

Order	A/B	$\Delta$ Mass, amu	$\Delta$ FIP, eV	$\Delta(X_A/X_B)$ , %	
				No Mixing	Mixing
2	Ca/Mg	15.8	1.53	1.19	0.84
4	Ca/Al	13.3	0.13	1.11	0.78
5	Ti/Mg	23.6	0.83	1.11	0.78
7	Fe/Ca	15.8	1.76	1.05	0.74
9	Ti/Al	21.1	0.83	1.03	0.72
11	Ca/Si	12.0	2.04	0.98	0.69
12	Fe/Ti	8.0	1.05	0.97	0.68
14	Ca/Na	17.1	0.97	0.92	0.65
16	Ti/Si	19.8	1.33	0.90	0.63
18	K/Mg	14.8	3.31	0.89	0.62
20	Cr/Mg	27.8	0.88	0.88	0.61
21	Mn/Ca	14.9	1.32	0.85	0.59
25	K/Al	12.3	1.65	0.81	0.57
29	Mn/Ti	7.1	0.62	0.77	0.54
31	Fe/K	16.7	3.53	0.76	0.53
36	Fe/Cr	3.9	1.10	0.74	0.52
51	Ni/Fe	2.8	0.24	0.58	0.41

The numeral in the leftmost column indicates the position in the list of all relative variations of the ratios in inverse numerical order.



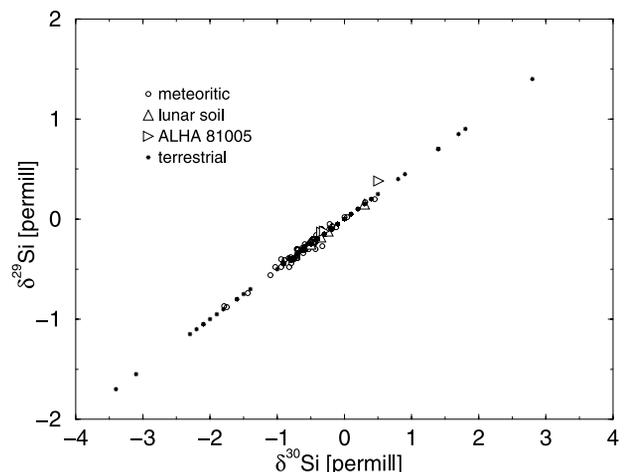
**Figure 5.** Ca/Fe versus Mg/Fe elemental mass abundance ratios for various studies of CI chondritic samples. The abbreviations next to the symbols refer to the authors of the corresponding studies: P,S,&Z (1981), *Palme et al.* [1981]; A&E (1982), *Anders and Ebihara* [1982]; A&G (1989), *Anders and Grevesse* [1989]; W&K (1988), *Wasson and Kallemeyn* [1988]; L&F (1998), *Lodders and Fegley* [1998]; M&S (1995), *McDonough and Sun* [1995]; P&B (1993), *Palme and Beer* [1993]; MPI Mainz, *Spettel et al.* [1993]; W&P (2001), *Wolf and Palme* [2001]. We have also plotted the standard deviation of Max-Planck-Institut measurements of eight samples as well as the uncertainty in the unrealistic mean. Single measurement errors are smaller than this uncertainty; the scatter reflects variability in different mineral separates of CI chondrites Orgeuil and Alais. The diagonal of the small box shows the effect of solar evolution on photospheric abundances. The absolute position of the box is unimportant; it describes the relative change of the two elemental abundance ratios.

the case of Si. The conventional  $\delta$  notation is used,  $\delta^{29}\text{Si} = 1000 \times [(n^{29}\text{Si}/n^{28}\text{Si})_{\text{sample}}/(n^{29}\text{Si}/n^{28}\text{Si})_{\text{ref}} - 1]$  in per mill. In this three-isotope diagram a variety of different solar system samples follow a straight line with slope 1/2 which is typical for chemical isotope fractionation. The entire variability is confined to a narrow range of a few per mill per mass unit and hence the uncertainty of the mean of the  $\sim 200$  samples is much smaller, about 0.15 per mill. This clearly reflects the efficient isotopic homogenization of the solar nebula. It also lends confidence to the assumption that there cannot be much difference between the bulk isotopic composition of Si and other refractory or weakly volatile elements in the Sun and the rest of the solar system samples, including terrestrial ones. It is for this reason that Si and Mg are often used as standards for isotopic fractionation in the solar wind (to within a few per mill per mass unit).

#### 4.3. Elemental Composition of the Solar Wind

[29] The composition of the solar corona is not the same as that of the photosphere, and the differences allow us to characterize various fractionation processes. There are several properties of an individual atom or ion that allow for fractionation. In the strong gravitational field of the Sun, fractionation according to mass would be extremely strong if there were no other forces acting on the particles. Simplistically assuming an isothermal atmosphere between the photosphere and the chromosphere, a barometric equa-

tion would tell us that we should not be observing any heavy elements in the corona or the solar wind at all. The exponential nature of this equation thoroughly depletes any mass but the lightest. Obviously, this is not the case, and



**Figure 6.** Compilation of the silicon isotopic composition of various sources in the solar system. See *Wimmer-Schweingruber et al.* [1998] for sources and detailed discussion.

other forces must be acting upon the ions and atoms already in the lowest layers of the solar atmosphere. Among the best known is the process that, in some still badly understood way, separates neutral and charged particles. Physically, it is probably based on a competition of two timescales, the first ionization time (FIT) and some timescale that characterizes the removal or supply of neutral material. Because FIT is a model-dependent quantity, it is more conventional to speak of this important fractionation effect as the first ionization potential (FIP) effect. The FIP is a well-determined atomic property for all important elements in the solar wind.

[30] In order to describe the FIP effect, it has become customary to use a double ratio of abundances. One normally determines the solar wind abundance ratio of element X with respect to oxygen, X/O, and normalizes this observed quantity with the corresponding photospheric value, X/O<sub>photo</sub>. The double ratio  $\Xi = (X/O)/(X/O_{\text{photo}})$  lies between 2 and 3 for low-FIP elements (FIP <10 V) in the slow wind and between 1 and 2 in the fast wind [e.g., von Steiger *et al.*, 2000]. Because volatility is generally correlated with FIP, this means that refractory elements (i.e., low FIP) are enhanced by a factor of about 2 in the average solar wind when compared with their photospheric abundance.

[31] Because of the magnitude of the FIP effect, only high-speed solar wind should be used for testing solar evolution models. However, even in this otherwise benign type of solar wind, elemental abundances are not necessarily fully determined by the FIP effect. Especially wave-particle interaction, widely believed to be the accelerating agent in this type of solar wind, is highly dependent on the ionization state of the ion and hence on its atomic structure. Given current uncertainties in atomic parameters, it appears unlikely that elemental abundances will be used in the near future for the purpose studied in this work.

#### 4.4. Isotopic Composition of the Solar Wind

[32] The strong fractionation observed for elements in the slow solar wind is mostly due to first ionization potential effect. Although this effect is of utmost importance for elemental fractionation, it is probably quite unimportant for isotopic fractionation. For instance, the elemental fractionation model of Marsch *et al.* [1995] can be understood as a competition between two timescales, diffusion and ionization. The authors derive the following expression for the mass-dependent part of elemental fractionation  $f_{ij}$  between two species  $i$  and  $j$ :

$$f_{ij} \propto \left( \frac{A_i + 1}{A_i} \right) \left( \frac{A_j}{A_j + 1} \right)^{1/4},$$

where  $A_{i,j}$  is the atomic mass number of species  $i$  and  $j$ . For the example of magnesium this expression evaluates to a depletion of the heavy isotopes of less than half a per mill per mass unit. In other words, FIP is unimportant for isotopic fractionation according to the Marsch *et al.* [1995] model. Note, however, that the model of Schwadron *et al.* [1999], which invokes resonant ion cyclotron heating of weakly ionized species to explain the FIP effect, could produce significantly stronger isotope effects. This is concluded from analogy with the severe isotope fractionation observed in energetic particles related with impulsive flare events.

[33] Inefficient Coulomb drag is most probably the most efficient isotopic fractionation process. Under the assumption of an isothermal solar atmosphere and neglecting wave acceleration, one may derive the following expression for the maximum fractionation between the two isotopes  $k$  and  $l$  of an element due to inefficient Coulomb drag [Bodmer, 1996; Bodmer and Bochsler, 1998, 2000]:

$$f_{kl} \propto \frac{2A_k - Q - 1}{2A_l - Q - 1} \sqrt{\frac{A_k + 1}{A_l + 1}}.$$

This evaluates to more than 5% per mass unit for the example of silicon. Thus for isotopic fractionation, inefficient Coulomb drag can be 2 orders of magnitude larger than the FIP effect. The fractionation of isotopes has been tested for in the solar wind. Combining measurements of Ne, Mg, and Si, Kallenbach *et al.* [1998] found a depletion of the heavier isotopes in the slow solar wind. However, the isotopic composition of the solar wind is consistent with meteoritic values in high-speed streams [Bochsler *et al.*, 1997, Kallenbach *et al.*, 1997]. This confirms theoretical expectations that isotopic fractionation should be very weak in high-speed streams [Bodmer and Bochsler, 1998, 2000]. Since the proton flux is high in the high-speed solar wind, Coulomb friction is probably unimportant in these streams, consistent with Ultraviolet Coronagraph Spectrometer (UVCS) measurements of high outflow velocities of heavy ions in coronal holes [e.g., Kohl *et al.*, 1997] which are the source regions of the high-speed streams [Krieger *et al.*, 1973]. Since these observations show oxygen out-flowing at higher speeds than protons [Cranmer *et al.*, 1999], it appears that Coulomb drag plays no role in carrying heavy species in the high-speed solar wind. If indeed wave-particle interaction succeeds to impart the momentum needed to move these species into the coronal hole-associated solar wind, as is generally believed, isotope effects are expected to be weak. This is also borne out by the observed constancy of the  $^3\text{He}/^4\text{He}$  isotopic abundance ratio in high-speed streams [Bodmer and Bochsler, 1998; Gloeckler and Geiss, 1998]. It is thus to be expected that the isotopic composition of the fast solar wind most accurately resembles that of the reservoir that it is being fed from. Hence it is measurements in high-speed streams which should be used to limit the amount of gravitational settling of the heavy isotopes toward the solar core during solar evolution.

#### 4.5. Selection

[34] In view of the variations in meteoritic elemental abundance ratios and in the expected magnitude of solar wind fractionation processes, it appears unrealistic to use elemental abundance ratios as a test for solar evolution models. Nevertheless, for the sake of completeness, we give a list in Table 2 of those elemental abundance ratios for low-FIP (<10 V) elements for which the effect of solar evolution exceeds 2.5 per mill. Of these, Ca/Mg is the top candidate from the evolution point of view but, as was already mentioned, is not determined with sufficient accuracy in CI chondrites. If some clear-cut criterion for sample selection could be found that would narrow down the sample variability, this could be the best compositional test of solar evolution models.

[35] On the other hand, the small variations in the isotopic composition of refractory elements (e.g., Mg, Si, ...), obvious from the already discussed Figure 6, should allow such a test. Current in situ mass spectrometers are not capable of measuring the isotopic composition of the solar wind to the precision necessary for this study. Linear time-of-flight mass spectrometers do not resolve isotopes of refractory elements, and isochronous mass spectrometers have systematic uncertainties which are about 2 orders of magnitude too large to detect the effect of solar evolution. However, the recently launched Genesis mission will collect and return to Earth samples of the solar wind in various solar wind regimes including the fast solar wind. These samples will be available for laboratory analysis. The Genesis mission has the aim of measuring the isotopic composition of oxygen to a relative precision of  $10^{-4}$ . The abundances of the rare isotopes of oxygen are low ( $^{17}\text{O}/^{16}\text{O} \sim 1/2625$ ,  $^{18}\text{O}/^{16}\text{O} \sim 1/499$ ) in solar system samples [Anders and Grevesse, 1989; Clayton, 1993] and in the solar wind [Collier et al., 1998; Wimmer-Schweingruber et al., 2001]. Because of the large abundance of the rare isotopes of Mg and Si isotopes, this measurement should be possible with these samples. The Genesis measurement precision for O isotopes translates to a similarly high precision for Mg and Si isotopes. Because the heavy and less abundant isotopes of Mg and Si are not nearly as rare as those of O, Genesis should return high-precision and statistically significant samples of the isotopic composition of Mg and Si in the solar wind.

[36] Mg and Si have other positive aspects to them that make them attractive for this study. They are the lightest refractive elements with three stable isotopes; moreover, their rare isotopes are still fairly abundant. In addition, as can be seen in Figure 3, they lie in a local minimum in the predicted photospheric abundance  $\Delta X_{\text{surface}}$ , i.e., a local maximum in the change. Because the isotopic effect is well approximated by  $\Delta X_{\text{surface}}$  times the relative mass difference of the isotopes, the isotopes of these two elements offer the best chance of measuring subtle changes in their composition due to solar evolution.

## 5. Discussion

[37] Today standard solar models include effects of elemental segregation. In this picture, all elements heavier than hydrogen are gradually depleted in the solar photosphere over the course of solar evolution. Their current photospheric abundances are about 8% lower than in the bulk Sun or in the presolar nebula. This depletion is primarily due to differences in the radiative and gravitational forces acting on the various elements. Modern solar models compare favorably with sound speed profiles of the Sun inferred from helioseismology. Nevertheless, the agreement is far from satisfactory; differences in inferred and model sound speeds are still very large in comparison with the modeled uncertainties on their magnitudes.

[38] In this paper we have investigated a more direct approach to obtain limits on the amount of element segregation throughout solar history. The smallness of the effect makes it very difficult to detect. There are two possibilities to check such a secular change in photospheric abundances. One can measure implanted

solar wind in lunar soils of various antiquity, or one can compare contemporary photospheric or solar wind abundances with bulk solar abundances inferred from (predominantly) meteoritic data. The first test has proven to remain ambiguous [Heber, 2002]. Uncertainties in photospheric abundance determinations are of the order of or exceed 25%–30%. These uncertainties are mainly due to badly known atomic properties [Del Zanna et al., 2001] but are also due to the badly understood physics of the photosphere and lower chromosphere [Holweger, 2001; Del Zanna et al., 2001]. Hence it is not to be expected that photospheric abundances will be measured in the near future with sufficient accuracy to measure the effect of element migration in the near future. Therefore we have investigated the possibility of detecting or at least putting limits on this effect by using in situ solar wind data.

[39] The use of in situ solar wind data immediately restricts the set of elements than may be considered. Because of the magnitude of the insufficiently understood FIP effect, only elements with low FIP (FIP < 10 V) should be considered for comparison. However, in this case, no comparison can be made with hydrogen, implying that the magnitude of the effect of element settling is decreased considerably. It amounts to only typically 0.5% for most element combinations. We give a list of the best candidate pairs in Table 2. The smallness now results in an additional difficulty, namely, that the normalizing meteoritic abundances (or element ratios) are not known with sufficient accuracy.

[40] We have shown that only isotopes of refractory elements offer any chance to measure the magnitude of the effect of elemental segregation in the solar convection zone. With Genesis it should be possible to determine the Mg and Si isotopes with an accuracy of about 1 per mill, good enough to detect this effect because in this case, meteoritic data are of comparable or better quality.

[41] Alternatively, high-precision measurements of solar wind noble gas isotopic abundances in lunar soils still have the potential to unravel solar chemical evolution if isotopic and elemental fractionation in the implantation process can be reliably modeled and if it can be understood in sufficient detail throughout the complex history of lunar soils and other archives for the solar wind.

[42] The alteration of the photospheric (and hence solar wind) isotope composition is especially important for oxygen which will be measured at a very high precision ( $\sim 0.01\%$ ) with Genesis. Here accurate measurements of isotope ratios of refractory elements such as Mg and Si will be important to “calibrate” the influence of solar evolution on more volatile and chemically reactive elements such as oxygen. Inclusion of element migration throughout solar history will be crucial to the interpretation of the measured values of  $^{16}\text{O}/^{18}\text{O}$  and  $^{16}\text{O}/^{17}\text{O}$ . Because solar isotopic evolution will tend to follow the traditional chemical fractionation line slope of  $\sim 1/2$  while alternative models for O isotopes in the solar system involve non-mass-fractionating processes, a precise knowledge of the solar effects is of utmost importance for the understanding of the history of the solar system.

[43] While it is doubtful that the required understanding of all fractionation processes in the solar wind exists at this

time for an accurate analysis of isotopic ratios in relation to physical processes in the Sun, we believe that the necessary knowledge is attainable.

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