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# Solar Wind and Solar System Matter After Mission Genesis

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## 1. Introduction

Elemental abundances in the Sun have been found to be generally consistent with those observed in carbonaceous meteorites (except volatiles), but the available solar system (SS) isotopic abundances are not uniform and studied objects in the inner and outer SS show variations in the isotopic abundances of some elements. Since the presolar cloud environment was dynamically evolving due to stellar additions of nucleosynthetic products and chemical reactions in a partially ionized medium, it is possible that matter was not uniform and not equilibrated at the time of SS formation. The isotopic abundances in the solar atmosphere and in the Sun cannot be accessed accurately by optical methods and it is necessary to rely on solar wind (SW) abundances. Some SW isotopic abundances (N, O and noble gases) have been determined in the form of implanted ions in catcher-foils returned by NASA's Apollo and Genesis missions, and also in some SW-exposed meteoritic matter, as well as in soils returned by lunar missions (see 4.).

The SS today is 4567 Ma old (Amelin et al., 2010) and is considered to have formed in a cluster of stars, embedded within a molecular cloud (Adams, 2010). The clouds have lifetimes of several tens of millions of years or less (Hartmann et al., 2001). Within the clouds, the clusters themselves live for tens of millions of years and protoplanetary disks of one solar mass typically have lifetimes of 3 Ma (Williams and Cieza, 2011). Even the long-lived open clusters dynamically evaporate over hundreds of millions of years. As a result, the birth environment of the Sun has long since been dissipated. Nonetheless, the statistics of protoplanetary disk evolutions (Williams and Cieza, 2011) and various properties of our SS (Adams, 2010), coupled with an emerging understanding of star and planet formation processes, allow some visions of the birthplace. A mechanism for the production of crystalline silicates was suggested (Vorobyov, 2011), associated with the formation and destruction of massive fragments in young protostellar disks at radial distances of 50–100

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AU, and the annealing of small amorphous grains when the gas temperature exceeds the crystallization threshold of  $\sim 800$  K.

Isotopic abundance studies in solar matter and in a variety of SS objects not only can provide information on where the elements were synthesized, but the same data are also important for the evaluation of current paradigms of star and planet formation. These issues have evolved over the years and today there exist rather detailed models for the origin of stars and planets. As discussed in Adams (2010) review, the properties of our SS are known in greater detail than those in other systems, and properties in our SS can be used to investigate initial birthplace conditions and to compare these to extrasolar environments that are being observed. The origin of the Oort cloud comets is being debated (Levison et al., 2010) and some models imply that accretion in the inner solar system was a protracted series of exchanges and probably not a single early event. However, even if some Oort cloud comets have been formed outside the solar system, they probably still formed from the same original cloud, and apart from some possible nucleosynthetic anomalies injected from rapidly evolving massive stars, their bulk composition will not be distinguishable from solar system matter. Nevertheless, the possible radial motion of Jupiter and Saturn (Walsh et al., 2011) implies a considerable redistribution of matter in the inner SS and exchanges with the outer parts at later times.

Isotopic composition studies of planetary bodies and meteorites have provided a powerful tool to unravel the history of the solar system. The chemical composition of the Sun with respect to refractory and moderately volatile elements seems well reflected in the so-called primitive meteorites. Whereas a very large body of data has been collected for the isotopic composition of meteorites, our knowledge of the isotopic composition of the Sun remains sketchy. Unfortunately, the isotopic composition of the solar atmosphere and the Sun cannot be accessed by optical methods. The only way to infer the solar isotopic composition is through analysis of solar particles, i.e., through investigations of the isotopic composition of the SW and of solar energetic particles. The Genesis mission of NASA has opened the window for extensive investigations of the SW nuclei and promises to solve some long-standing problems with respect to the isotopic composition of the Sun.

A quick look at the history of research on the elemental and isotopic abundances in SS matter shows that the agreement of solar spectroscopic data, and of abundances in other main sequence stars, with nonvolatile element abundances in carbonaceous chondritic meteorites has been interpreted to reflect a homogeneous SS environment (e.g. Arnold and Suess, 1969). These elemental and isotopic abundances (Suess and Urey, 1956) were used with much success (Burbidge et al., 1957; Cameron, 1957) in models of element synthesis. Although SS matter was taken to represent a well-mixed reservoir of nuclei that originated from several independent stellar sources, the research on isotopic abundances in meteorites from various sources and their precursor materials has shown that isotopic compositions of SS matter are non-uniform, and that this is especially true for the abundant light elements oxygen (O) and nitrogen (N). The recently determined isotopic abundances in the SW collected by Genesis (McKeegan et al., 2011; Marty et al., 2011) show that isotopic differences extend all the way to the center of our SS, the Sun itself. We will discuss the isotopic data for the Sun and some proposed models that may or may not account for the abundances observed in inner and outer SS matter and in planets. The isotopic make-ups of the heavy elements reflect largely differences in the mixing ratios of major nucleosynthetic

components, but the presence of several minor anomalous isotopic signatures in meteorites raises questions of origin, degree of homogenization of SS matter, and the timing of accretion in the nebular environment which gave birth to the Sun and the SS. There are also suggestions that late events have modified the SS objects, such as during a late bombardment (e.g. Willbold et al., 2011). It has become increasingly clear that a solar system reference standard is required for measured isotopic abundances. The preferred selection of solar data for this purpose appears reasonable, when we consider that the Sun accounts for 99.8% of matter in the solar system, but at present we have SW isotopic data for only a few elements and the procedures to convert SW data to solar abundances need improvements. If these efforts are successful, abundances now determined in foils returned by NASA's Genesis mission can be expected to help resolve fundamental questions of how the solar system formed and evolved, and in what type of environment.

## **2. Isotopic fractionation processes in the Interstellar Medium (ISM) and the SS**

Isotopic fractionation processes that are generating variabilities in the isotopic composition of solar system matter essentially originate from the differences in nuclear masses.

### **2.1 Isotope fractionation in chemical reactions**

The existence of a non-vanishing zero-point energy of quantum-physical oscillators leads to energetically lower lying vibration states of the heavy isotope compared to the levels of a light isotope in an otherwise identical molecule. Consequently, the heavier isotope is more strongly bound and the equilibrium of a chemical reaction is somewhat shifted in the direction where the heavy isotope is more strongly bound. Similarly, isotopic shifts are observed in reaction rates. For astrophysical applications it is important to note that, even when a medium is extremely cold and the chemical equilibria among neutral species cannot be achieved due to the sluggish reaction kinetics, strong isotopic fractionation effects are expected to occur in ion-molecule reactions, which can proceed even at very low temperatures.

Considering the formation of solids during the birth of the solar system, physical-chemical processes such as adsorption of gases on grain surfaces, or condensation, sublimation and evaporation, can produce isotope effects, in the sense of heavier isotopes being trapped more readily than light isotopes. Again, generally these effects are considered to be "mass-dependent", i.e., an isotope whose mass differs by two mass units from the principal isotope is approximately twice as much affected as an isotope which differs by only one mass unit.

### **2.2 Mass-independent isotope fractionation**

Strictly speaking, all isotopic fractionation effects discussed in this section are dependent on mass. However, in the literature the term "mass-independent" fractionation has been established for mechanisms, which do not discriminate between isotopes of a given element strictly according to their mass number.

Chemically identical molecules containing different isotopes are susceptible to different electromagnetic radiations, and consequently undergo chemical reactions with different time scales, depending on the flux of the corresponding frequency in the sensitive range.

Photo-dissociation of molecules is often a decisive first step in triggering chemical reactions in an astrophysical medium. In this context, molecules containing oxygen are of particular interest for mass-independent fractionation, because of the large variety of isotopic abundances. Whereas  $^{16}\text{O}$  makes 99.76 percent, only 0.20 percent of natural oxygen is  $^{18}\text{O}$ , and  $^{17}\text{O}$  constitutes only 0.04 percent. While an interstellar molecular cloud or a stellar accretion disk might be opaque to the radiation contributing to the photo-dissociation of a molecule containing  $^{16}\text{O}$ , it might be transparent to the equivalent radiation causing the dissociation of molecules containing the minor isotopes. Self-evidently, this can lead to a systematic isotopic discrimination of  $^{16}\text{O}$ , but not of  $^{17}\text{O}$  and  $^{18}\text{O}$  for subsequent chemical reactions. Ca-Al rich minerals in meteorites, the first ones to condense in a hot medium in an intensive radiation field, appear to be depleted in  $^{17}\text{O}$  and simultaneously in  $^{18}\text{O}$ , compared to ordinary meteoritic material; or putting it inversely: These refractory minerals contain excesses of  $^{16}\text{O}$ , indicating “mass-independent” fractionation of oxygen.

### 2.3 Isotope fractionations in the solar atmosphere, the solar corona, and the solar wind

Bochsler (2000) has investigated possible isotope effects related to secular gravitational settling of elements in the outer convective zone of the Sun. Despite the efficient vertical mixing of the outer convective zone, there is a tendency of heavier species to be slightly enriched at the bottom of the convective zone. This fractionation mechanism was extensively studied by Michaud and Vauclair (1991), and by Turcotte et al. (1998). Whereas the calculations of Bochsler (2000) are based on the modeled elemental depletions reported by Turcotte (1998), and were intended to be order-of-magnitude estimates, Turcotte and Wimmer (2002) used full-fledged solar models to compute the same effect. Although the effects turned out not to be very large, both studies clearly yielded isotopic fractionation factors, which deviate from the mass-dependent rule, in the sense that,  $^{17}\text{O}$  was depleted in the outer convective zone relative to  $^{16}\text{O}$  not by half the amount of  $^{18}\text{O}$ . Similar results were found for all other chemical species containing more than two isotopes. This is due to the fact that, in addition to gravitation, which acts on the mass of a species, also radiation pressure plays a role, which is independent of the mass of a particle, and depending on the relative importance of the two agents, a deviation from strictly mass-dependent fractionation occurs. Fig.1 shows in a three-isotope plot the expected modification, due to gravitational settling, of the O isotopic composition of bulk solar oxygen (star symbol) to O present in the convective outer zone of the Sun. As indicated before, the effects are small, nevertheless they are important and above the detection limit for Genesis isotopic abundance measurements.

In the solar atmosphere, in the acceleration region of the solar wind, apart from the gravitational attraction, other forces come into play, among them wave pressure, Coulomb drag, the electric field due to the local separation of electrons and positively charged particles. Many sophisticated models have been developed to investigate the acceleration of heavy particles in this region. Bodmer and Bochsler (2000) have carried out a detailed study to investigate isotope effects in steady state models of the solar wind. For instance, they provide the  $^{18}\text{O}/^{16}\text{O}$  fractionation effect in a typical coronal hole, and in a typical coronal streamer. These authors succeed in reproducing the typical elemental depletion of He/H as found in both streaming regimes. In the coronal streamer they find a depletion of  $^{18}\text{O}$  relative to  $^{16}\text{O}$  compared to the source, of 47 permil, and of 17 permil in a coronal hole associated solar wind.

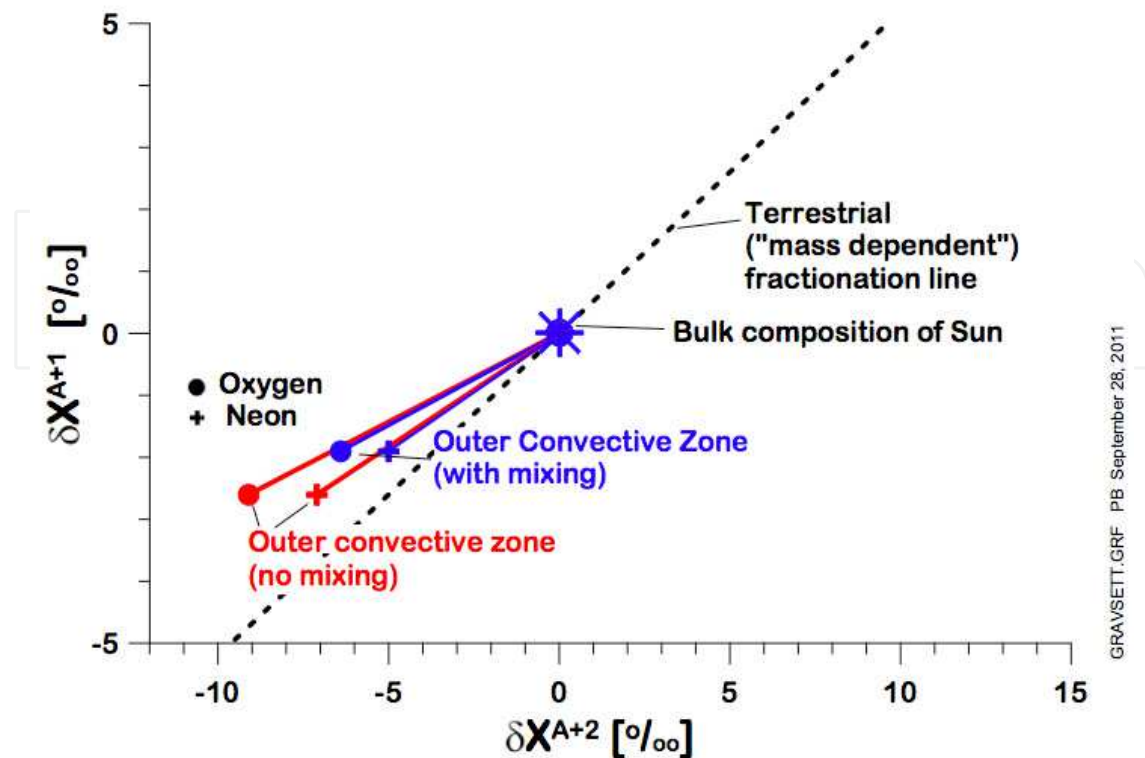


Fig. 1. Illustrates in a three-isotope plot the expected modification of the O isotopic composition, starting with bulk solar oxygen (star symbol) and comparing it to O in the convective outer zone (COZ) of the Sun, due to gravitational settling as modeled by Turcotte and Wimmer-Schweingruber (2002).

$^{16}\text{O}$ , the lightest isotope, may be enriched in the SW relative to the heavier isotopes in this non-linear mass-dependent process. In order to predict the concomitant depletion of heavier isotopes, one would have to produce a full-fledged model of the acceleration of the solar wind, which is beyond the goal of the present paper. However, it is possible to make some estimates with the guidance of the paper of Bodmer and Bochsler (2000).

The relevant quantity is the Coulomb drag factor

$$H_x = \frac{2A_x - Z_x - 1}{Z_x^2} \sqrt{\frac{A_x + 1}{A_x}}$$

of a species, where  $A_x$  is the atomic number and  $Z_x$  is its charge at the relevant location near the coronal temperature maximum. In the case of oxygen  $Z \approx 6$ .

Following Bodmer and Bochsler (2000), and based on flux conservation after the coronal base, one finds with some algebra the following approximation:

$$\frac{f_{17}}{f_{16}} = \frac{\frac{f_{18}}{f_{16}} (H_{18} - H_{16})}{\frac{f_{18}}{f_{16}} (H_{18} - H_{17}) + (H_{17} - H_{16})}$$

Although, with the quantities given above, the relation between the relative enrichment factors  $f_{17}/f_{16}$  and  $f_{18}/f_{16}$  is close to  $f_{17}/f_{16} = 0.5 f_{18}/f_{16}$ , it is clear from the above equation that this is not exactly true. As in the case of gravitational settling in the outer convective zone, several forces are involved in a rather complicated manner. Again, as a consequence of this non-linearity, the isotopic fractionation pattern in an element with three stable isotopes, exhibits some deviation from the simple 'mass-dependent' fractionation (e.g., parallel to a terrestrial fractionation line). An extrapolation of Genesis results to the isotopic composition of the outer convective zone, or even the solar bulk composition needs refined modeling. On the experimental side, since the solar isotopic Mg composition is presumably very close to the average SS composition, a determination of the isotopic composition of Mg in the solar wind in Genesis foils would provide important clues regarding the importance of isotopic fractionation. Unfortunately, in situ measurements of the Mg isotopic composition in the SW have not been possible with the necessary accuracy (e.g. Bochsler et al. 1995, Kallenbach et al. 1998).

### 3. Review of isotopic signatures in meteoritic matter

#### 3.1 Oxygen isotopes

The relative abundances of the three oxygen isotopes in SS matter vary, in particular the relative abundance of  $^{16}\text{O}$  from being like that of the Earth to being depleted or enriched compared to the other two isotopes. One popular explanation for this variation is that dust and gas in the SS began with the same  $^{16}\text{O}$ -rich composition, but that the solids evolved towards the terrestrial value. A study of the protosolar silicate dust from refractory CAI (Ca-Al-rich inclusions) concluded that primordial dust and gas differed in O isotopic compositions (Krot et al., 2010). In this interpretation dust had a different history than did gas before being incorporated into the SS. In another study the variable O isotopic compositions in SS matter was evaluated based on a random sampling hypothesis (Ozima et al., 2007). These authors inferred a common mean value of  $\Delta^{17}\text{O} = 0$  (terrestrial fractionation line, see Fig. 1) for all planetary objects and conclude, that solar O and planetary O should be the identical, but distinct from CAI-oxygen. Further, O in chondrules, the high temperature components of chondrites, which presumably accreted early in SS history, was studied in detail (Libourel and Chaussidon, 2010; Connolly and Huss, 2010). Libourel and Chaussidon (2010) identified metal-bearing Mg-rich olivine aggregates to be among the precursors of Mg-rich chondrules of type I, the origin of which they consider to be condensation-evaporation processes in the nebular gas or in a planetary settings. Their Mg-rich olivines of type I chondrules, as well as isolated olivines from unequilibrated ordinary chondrites and carbonaceous chondrites, revealed the existence of several modes in the distribution of the  $\Delta^{17}\text{O}$  values and the presence of a large range of mass fractionations. These authors conclude that oxygen isotopic compositions in Mg-rich olivines are unlikely of nebular origin (SS condensates) and suggest that such grains or aggregates might represent mm-sized fragments from disrupted first-generation differentiated objects, but Rudraswami et al. (2011) found no evidence in relict olivine grains to support a planetary origin. Connolly and Huss (2010) found significant variation in the O isotopic compositions in CR2 chondrite type II chondrules with no apparent relation to petrographic or geochemical data. These authors do not rule out that chondrules could have formed in different regions, but prefer an explanation that CR2 type II chondrules document changes in solid and gas compositions during formation. Liu et al. (2009) investigated the O records

in the same individual refractory hibonites that were studied for  $^{26}\text{Al}$ - and  $^{10}\text{Be}$ -records (see 5.2). They found that oxygen isotopic compositions are highly  $^{16}\text{O}$ -enriched, but are not derived from a homogeneous reservoir, as  $\Delta^{17}\text{O}$  values span a range of  $-28\%$  to  $-15\%$ .

Isotopic abundances implying extensive  $^{16}\text{O}$  isotope fractionation were found in fine-grained matrix of a carbonaceous chondrite (Sakamoto et al. (2007) and these authors suggest that fractionation mechanism of this magnitude are important in tracing the origin of O isotopic variations. They conclude that this matrix was formed by oxidation of Fe-Ni metal and sulfides by heavy water that must have existed in the early SS. Their O data expand the range of observed  $^{17,18}\text{O}/^{16}\text{O}$  variations to from  $-8\%$  to  $+18\%$ , relative to the terrestrial standard.

### 3.2 Nitrogen isotopes

Spectroscopic methods do not permit determinations of the N isotopic composition in the Sun with required accuracy. Most attempts have been indirect, based either on the analysis of the atmospheres of giant planets or of the SW nitrogen trapped in lunar soils. The recent determination of the N isotope ratio in SW, collected in concentrator foils during the Genesis mission (Marty et al. 2011), provides a SW reference. Busemann et al. (2006) found  $^{15}\text{N}$ -rich compounds in meteoritic insoluble organic matter (IOM) that exceed enrichments already known to exist in interplanetary dust. Organic matter shows N isotopic variations that survived in meteorites, despite extensive alterations in the SS and on the parent bodies. Known SS objects exhibit values of  $^{15}\text{N}/^{14}\text{N}$  ranging from  $1.9$  to  $5.9 \times 10^{-3}$ , inclusion of meteoritic material increases that range to  $22 \times 10^{-3}$ , and N implanted in the lunar surface reveals enigmatic variability in  $^{15}\text{N}/^{14}\text{N}$  between  $2.8$  and  $4.3 \times 10^{-3}$  (Marti and Kerridge, 2010). N in the terrestrial planets is found to be variable, but relatively uniform when compared to asteroidal, cometary sources and Jupiter's atmosphere. The possible radial dependence in the SS was investigated, as well as a possible relationship with the D/H isotopic signature (Marty et al., 2010), but N in comet Wild-2 particles is heterogeneous (McKeegan et al., 2006) and cometary water with terrestrial D/H ratios (Hartogh et al., 2011) does not fit such a trend. Since the SS was formed in the collapse of a presolar cloud, isotope data in N-containing molecules should be useful tracers. Gerin et al. (2009) measured  $^{15}\text{N}/^{14}\text{N}$  ratios in several dense cores of the interstellar medium (ISM) and found ratios in the range of  $1.3$  to  $2.8 \times 10^{-3}$ , which are low but overlap the range observed in meteorites.

### 3.3 Noble gas isotope abundances in SS reservoirs

For trapped heavy noble gases (Ar, Kr, Xe) uniform isotopic abundances are found in chondritic meteorites, while noble gas reservoirs in the inner planets atmospheres evolved and do not represent early trapped components. Heavy noble gas isotopic abundances in different meteorite classes are similar, although they were given different names: OC (ordinary chondritic; Lavielle and Marti, 1992), Q-type gases (Lewis et al., 1975) and Abee-type (Lee et al., 2009) in enstatite chondrites. Q-gases are located in carbonaceous carrier phases (Q), together with some interstellar grains (SiC, diamond) and are concentrated in acid-resistant residues (HF/HCl residues) (Lewis et al., 1975). Q-gases have a characteristic elemental pattern (Busemann et al., 2000) and show strong relative depletions of light gases when compared to solar abundances, for He by about seven orders of magnitude. The uniform isotopic abundances either indicate a common SS reservoir that differed from SW



abundances, or they reveal a uniform presolar carrier phase. The Ne isotopic abundances are less uniform, and in phase Q  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios are in a range 10.1 to 10.7, clearly lower than in solar Ne. The evidence that chondrites contain IOM compounds with large  $^{15}\text{N}$  excesses (see 3.2) may indicate a carrier and a presolar source. A presolar environment for Q-gas incorporation was also suggested by Huss and Alexander (1987) to account for the elemental fractionation pattern and the simultaneous presence of nucleosynthetic gas components. A similar elemental fractionation pattern without isotopic fractionations has been produced in the laboratory with gas trapping by carbon condensates (Niemeyer and Marti, 1981).

Enstatite chondrites (EC) show more variable elemental abundance patterns, with relatively high ratios Ar/Xe in some enstatite chondrites (Lee et al., 2009), as well as very low Ar/Xe ratios in an E3 chondrite (Nakashima et al., 2010). The Xe isotopic abundances in separated phases of EC's reveal the presence of small but variable components of solar Xe and of a nucleosynthetic component (HL-Xe, carried in diamonds). Lavielle and Marti (1992) suggested that also OC-Xe (or Q-Xe) data are consistent with mixtures of solar and HL-Xe components. Noble gas carriers in stardust were identified (e.g. Anders and Zinner, 1993) and include diamonds, SiC and graphite, containing different products of stellar synthesis.

### 3.4 Isotopic differences in Mg and Cr: Clues for extinct nuclides?

Magnesium and chromium isotopic data document decay products of  $^{26}\text{Al}$  and  $^{54}\text{Mn}$  (312 d half-life, an e-capture decay) and show that products from stellar synthesis were not well mixed in the presolar environment. Large  $^{54}\text{Cr}$  excesses are residues of stellar synthesis, but a relation to  $\Delta^{17}\text{O}$  (Trinquier et al., 2007) suggests that also ISM processes are documented, as well as a coupling to the s-process component in Mo (Dauphas et al., 2002). Extremely large  $^{54}\text{Cr}$  anomalies were found in the acid-resistant residue of the CI chondrite Orgueil (Qin et al., 2011). These workers found that  $^{54}\text{Cr}$ -rich regions are associated with sub-micron Cr oxide grains, likely spinels, and they suggest a Type II supernova origin and a heterogeneous distribution of the  $^{54}\text{Cr}$  carrier.

Schiller et al. (2010) reported Mg isotope data for most classes of basaltic meteorites, and with the exception of four angrites and one diogenite, which have young ages or have low Al/Mg ratios, all bulk basaltic meteorites have  $^{26}\text{Mg}$  excesses. The authors conclude that excesses record asteroidal formation of basaltic magmas with super-chondritic Al/Mg and confirm that radioactive decay of short-lived  $^{26}\text{Al}$  was the primary heat source of melted planetesimals.

Villeneuve et al. (2011) found variable  $^{26}\text{Mg}$  radiogenic enrichments and deficits, relative to terrestrial Mg, in separated refractory olivines from matrix samples and individual CAIs. These authors show that olivines formed in reservoirs enriched in  $^{26}\text{Mg}$  from the decay of extinct  $^{26}\text{Al}$ , while olivines in a pallasite show a deficit, and use the inferred crystallization ages to calculate the time of metal-silicate differentiation, which occurred only  $\sim 0.15$  Ma after CAI formation.

### 3.5 Stellar synthesis products in heavy elements

Isotopic heterogeneities were observed in primitive chondrites and in chondrite components for Ba, Sm, Nd, Mo, Ru, Hf, Ti and Os, sometimes with conflicting results and interpretations.

Van Acken et al. (2011) suggest that Os is an ideal synthesis tracer because its abundances are affected by p-, r-, and s-processes; and since Os is a refractory element, it documents records from the earliest stages of condensation. They found that Os in less evolved enstatite and Rumuruti chondrites, representing end-members in oxidation state, shows similar deficits of the s-process component as some primitive carbonaceous and unequilibrated ordinary chondrites, while enstatite chondrites of higher metamorphic grades have terrestrial isotopic compositions. These authors report that laboratory-digestion-resistant presolar grains, most likely SiC, are carriers of anomalous Os and that presolar grains disintegrated during parent body processing. The magnitude of the anomalies requires a few ppm of presolar SiC with an unusual isotopic composition, possibly produced in a different stellar environment and injected into the region of formation. In other work on Os isotopes, Yokoyama et al. (2011) found excesses of the s-process component in acid residues that were enriched in insoluble organic matter (IOM), while they found terrestrial Os isotope compositions in bulk chondrites. Nearly all IOM-rich residues were enriched in s-process Os, prompting these authors to conclude that s-process-rich presolar grains (presolar SiC) are found in presolar silicate hosts from either red giant branch (RGB) or asymptotic giant branch (AGB) stars. Since they also found that Os that dissolves by weak acid leaching of bulk chondrites is enriched in r-process nuclides, they suggest that a fine-grained presolar silicate carrier phase formed from supernovae ejecta. Nucleosynthetic isotope variations in Mo as observed in a wide range of meteorites, but not between planets Earth and Mars, were recently reported by Burkhardt et al. (2011). There is a clear message in these Os and Mo isotope data, since s- and r- process nuclides were produced in different locations: either the respective carriers were not equilibrated, or the carriers formed in heterogeneous environments.

The elements Ba, Nd and Sm, all with allotments of p-, s-, and r-process products, are equally good tracers of heterogeneous distributions of nucleosynthetic products. Ordinary chondrites were found to be uniform in Ba isotopic abundances, but variations were found in phases of carbonaceous chondrites (Carlton et al., 2007). These authors suggest that isotopic variability observed in Ba, Nd and Sm in carbonaceous chondrites reflect distinct stellar nucleosynthetic contributions to early SS matter. Further, by using the ratio  $^{148}\text{Nd}/^{144}\text{Nd}$  to correct for observed s-process deficiency, they found that the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  isochron (from alpha-decay of  $^{146}\text{Sm}$ ) is in agreement with earlier data, but that the  $^{142}\text{Nd}$  abundance is deficient in these chondrites, compared to terrestrial rocks. Qin et al. (2011) analyse in detail correlated nucleosynthetic isotopic variations in Sr, Ba, Nd and Hf in a carbonaceous and in an ordinary chondrite and conclude that these variabilities are best explained by variable additions of pure s-process nuclides to a nebular composition slightly enriched in r-process isotopes compared to average SS material. Andreasen and Sharma (2007) found excesses of  $^{135}\text{Ba}$  and  $^{137}\text{Ba}$  in carbonaceous chondrites, but no anomalies in  $^{130}\text{Ba}$ ,  $^{132}\text{Ba}$ ,  $^{138}\text{Ba}$  and in Sr isotopes. They conclude that carbonaceous chondrites have r-process excesses in  $^{135}\text{Ba}$  and  $^{137}\text{Ba}$  with respect to Earth, eucrite parent bodies and ordinary chondrites and suggest that the SS was heterogeneous beyond 2.7 AU, a region where carbonaceous chondrite parent bodies formed.

#### 4. The SW collection mission: Genesis

NASA's Genesis mission collected SW atoms for more than two years and returned these for laboratory analyses. Positioned at the Sun-Earth L1 Lagrange point about 1.5 million km

from Earth, the spacecraft was well beyond the Earth's atmosphere and magnetic field. Highest priorities of the mission were a determination of the abundances of the isotopes of oxygen and nitrogen in the SW (Burnett et al., 2003). On returning to Earth in 2004 with its payload, the capsule suffered an unplanned hard landing in Utah, shattering most of the collector materials and thereby greatly complicating the sample analysis. Isotopic abundances for noble gases, oxygen and nitrogen have now been published and studies on other elements are in progress.

The SW is the most relevant source of information on the isotopic composition of the Sun. In the pre-Genesis era a substantial amount of data has been obtained on the isotopic composition of the SW. Unfortunately, most of this data did not bring the required precision, i.e., a precision which enables distinction between the SW composition and the known SS isotopic signatures. The notable exception is the contribution of the Apollo-foil experiments, which sampled light noble gases during a similar phase of declining solar activity, and then analyzed these with laboratory mass spectrometers. Slightly, but significantly different data than Genesis were found, which still lack an explanation (Fig. 2). In situ measurements, in contrast to most foil experiments, are very valuable in providing high time resolution, allowing a good correlation with relevant solar wind parameters and, hence, a careful assessment of possible isotopic and elemental fractionation effects in the solar wind. Understanding these effects is crucial for the interpretation of most of the data, and difficult, if not impossible with any type of foil collection experiments.

#### 4.1 SW noble gases collected by Genesis and in exposed SS surfaces

Heber et al. (2009) reported elemental and isotopic abundances of noble gases in the SW at L1 as collected by foils in the NASA Genesis mission. He, Ne and Ar were analyzed in diamond-like carbon on a silicon substrate (DOS) and were quantitatively retained in DOS and, with exception of He, also in Si. SW data presented by Heber et al. (2009) have the following isotopic composition:

$${}^3\text{He}/{}^4\text{He} = 4.64 \times 10^{-4}, {}^{20}\text{Ne}/{}^{22}\text{Ne} = 13.78, {}^{21}\text{Ne}/{}^{22}\text{Ne} = 0.0329, {}^{36}\text{Ar}/{}^{38}\text{Ar} = 5.47.$$

Measured elemental ratios are  ${}^4\text{He}/{}^{20}\text{Ne} = 656$ , and  ${}^{20}\text{Ne}/{}^{36}\text{Ar} = 42.1$ .

The ratio  ${}^3\text{He}/{}^4\text{He}$  reported by these authors agrees within uncertainties with long-term averages (Coplan et al., 1984; Bodmer and Bochsler, 1998) and does not indicate variations.

Fig.2 compares the SW Genesis data for  ${}^4\text{He}/{}^3\text{He}$  and  ${}^4\text{He}/{}^{20}\text{Ne}$  (Grimberg et al.,2008; Heber et al.,2009) with those of the Apollo-SWC experiment (Geiss et al. 2004). The Apollo data have been gathered in the declining phase of solar cycle 20, those of Genesis were collected during the declining phase of cycle 23. The Genesis data represent an average over 2.3 years exposure and are representative for in-ecliptic SW, while despite of considerably shorter exposures the Apollo-SWC experiments have sampled a period of comparable length (1969 through 1972) and suggest an intrinsic variability of the SW. Whereas the value by Grimberg et al. (2008) is compatible with the average and the scatter of the Apollo measurements, the determination of Heber et al. (2009) is incompatible with the Apollo values. It is not clear, whether the difference between these results can be explained with a real (secular) variability of the solar wind composition.

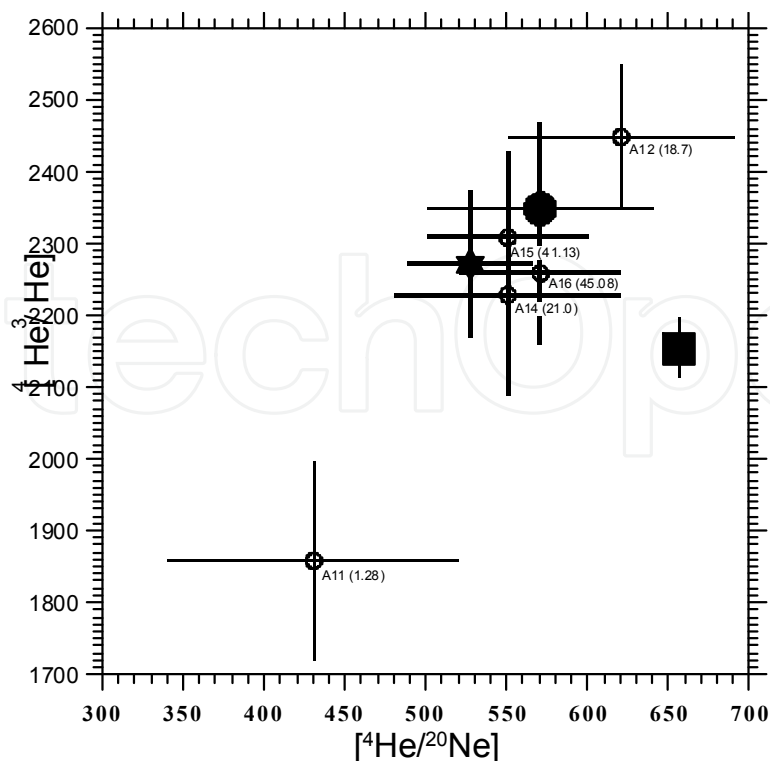


Fig. 2. Comparison of  $^4\text{He}/^3\text{He}$  and  $^4\text{He}/^{20}\text{Ne}$  ratios from the Apollo SW composition (circles) experiments and the Genesis mission. The exposed Genesis samples were bulk metallic glass (star symbol; Grimberg et al., 2008) and diamond-like carbon on silicate substrate (full square; Heber et al., 2009). The results from the Apollo missions are shown as circles with letters indicating the number of the mission and exposure times for the foils (in hours). The full circle shows the flux weighted average as given by Geiss et al. (2004).

The average  $^{36}\text{Ar}/^{84}\text{Kr}$  ratio obtained by Vogel et al. (2011) from 14 individual analyses is  $2390 \pm 120$  agrees with a preliminary ratio of 2030 measured by Meshik et al. (2009), while the preliminary upper limit (9.71) by these authors for the  $^{84}\text{Kr}/^{132}\text{Xe}$  ratio compares well with  $9.9 \pm 0.3$  given by Vogel et al. (2011). Vogel et al. (2011) reported an average ratio  $^{36}\text{Ar}/^{38}\text{Ar} = 5.50 \pm 0.01$  which also agrees well with a ratio  $5.501 \pm 0.005$  of Meshik et al. (2007). Reported ratios  $^{86}\text{Kr}/^{84}\text{Kr} = 0.303 \pm 0.001$  and  $^{129}\text{Xe}/^{132}\text{Xe} = 1.06 \pm 0.01$ , at this time the only values available from Genesis, are consistent with solar data as observed in early etch steps in lunar ilmenite samples (Wieler and Baur, 1994). Martian interior samples (SNC meteorites) also contain a solar type Xe-S component (Ott, 1988; Mathew and Marti, 2001), while SW-implanted Xe components were observed in gas-rich meteorites like Pesyanoe (Marti, 1969; Mathew and Marti, 2003). Minor solar components were observed in 'sub-solar' gases in E-chondrites (Crabb and Anders, 1981; Busemann et al., 2003).

The solar photospheric abundances of the heavy noble gases that were not well known (Anders and Grevesse, 1989; Asplund et al., 2009; Lodders et al., 2009), can be inferred from SW data in Genesis foils. These data (Vogel et al., 2011) are in good agreement with ratios measured in the gas-rich meteorite Pesyanoe (Marti et al, 1972) that also provided the first isotopic data on solar-type Xe. Apparently, ion implantation processes and losses in asteroidal surfaces did affect light noble gases (e.g. the ratio  $\text{Ne}/\text{Ar}$ ), while elemental abundance ratios of Ar, Kr and Xe were not much altered.

## 4.2 Oxygen in the SW and in the Sun

Oxygen isotopic abundances in the SW collected at L1 were measured in returned Genesis concentrator foils and corrected for fractionation according to radial position within the concentrator (McKeegan et al., 2011). The use of measured Ne isotopic data from adjacent samples for this correction is a good approximation, although the charge states for O and N are not identical (Bochsler, 2000), and the adopted mass-linear fractionation represents an approximation.

For  $\Delta^{17}\text{O}$  in the SW, the displacement of measured  $^{17}\text{O}$  data from the terrestrial fractionation line (see Fig. 1;  $\Delta^{17}\text{O} = 0$ ), McKeegan et al. (2011) determined a mean value  $\Delta^{17}\text{O} = -2.84\%$  for SW at L1, and after fractionation corrections they inferred an identical  $\Delta^{17}\text{O} = -2.84\%$  datum for the Sun, implying that the average required fractionation correction is mass-dependent. However, as discussed earlier (in 2.3), a correction for gravitational settling in the outer convective zone (OCZ) is not linear in mass. The approach of forcing the solar value onto the correlation line for oxygen in CAIs appears quite arbitrary. Since the origin of CAIs is not known, this raises the issue of whether the implied assumption of having only two primitive O isotopic reservoirs in the SS, is appropriate. In the O three-isotope system it is always possible to interpret observed ratios by invoking a mass-dependent fractionation acting on mixtures of two distinct reservoirs, at least as long as such fractionations are within acceptable limits.

Note that a significant  $\Delta^{17}\text{O}$  difference between the Sun on one hand, Earth, Moon and Mars on the other, contradicts the model of Ozima et al. (2007). It was discussed earlier that matter in the forming SS was recycled and mixed, at least in the inner parts, as is seen also from the close relationships in  $\Delta^{17}\text{O}$  values in inner planetary reservoirs. O is the third most abundant element in the SS and it is not easy to keep solar and planetary oxygen apart. Reworking the total inventory of planetary oxygen in a non-mass-dependent process (e.g., by photo-dissociation of O-bearing molecules) is not easy. One may wonder what happened in such a procedure to volatile isotopic anomalies, such as Ne-E ( $^{22}\text{Ne}$  from short-lived  $^{22}\text{Na}$ ) in meteoritic grains.

## 4.3 Nitrogen in Genesis foils

The N isotope ratio in the SW at L1, determined by ion probe in foils of the Genesis concentrator (Marty et al., 2011),  $^{15}\text{N}/^{14}\text{N} = 0.002178$  is much lower than that in the terrestrial atmosphere (0.00376). It differs from ratios observed in martian meteorites ALH84001 and Chassigny which, like the solar-type Xe isotopic abundances, were interpreted to represent primitive martian N (Mathew and Marti, 2001). The reported isotope ratio (0.002268) for the Sun (Marty et al., 2011) is obtained after corrections for an adopted fractionation for Coulomb drag (Bodmer and Bochsler, 1998), foil position in the concentrator, and gravitational settling. This value is close to that observed in osbornite of a meteoritic inclusion (Meibom et al., 2007), that the authors assume to represent an early SS condensate. Marty et al. (2011) suggest that the measured SW ratio characterizes nitrogen in the primitive SS, as a  $^{15}\text{N}$ -depleted component is required to account for N in osbornite and for N in the atmosphere of Jupiter (Owen et al, 2001), and more generally to explain isotope variations in SS objects. The sources of heavy N, as observed in the inner SS, are currently not known, although presolar phases, indicating a range of  $^{14}\text{N}/^{15}\text{N}$  ratios from  $\sim 50$  to  $\sim 20,000$  (Zinner et al., 2007), did make some contribution to N budgets in the SS.

## 5. Review of models of formation, origin and chronology

### 5.1 Time of formation of the Solar System (SS)

Determinations of the time of formation require the identification of solid objects that crystallized from homogeneous SS matter, and the recovery of undisturbed mineral isochron ages based on long-lived radionuclides. The most accurate determinations of absolute ages of the oldest SS objects currently are based on Pb-Pb ages, because of the precision in the half-lives of the progenitors  $^{235}\text{U}$  and  $^{238}\text{U}$  and the coupled age data of isotope pairs. The adopted most pristine solids for this purpose, chondrules and CAIs, were considered to have invariant SS abundance ratios of these two progenitors, which turned out to be an incorrect assumption (Brennecka et al., 2010). The first combined high-precision U and Pb isotopic data for a CAI, and U isotopic data for chondrules and whole rock fractions of the Allende meteorite (Amelin et al., 2010) show that the Allende meteorite bulk rock and chondrules data have distinctly lower ratios ( $^{238}\text{U}/^{235}\text{U}=137.747$ ) than the CAI. The difference in the  $^{238}\text{U}/^{235}\text{U}$  ratio of 0.129 between the CAI and chondrules and bulk meteorite document not only a difference in age, but shows that uncertainties in absolute ages of SS matter remain. The likely precursor,  $^{247}\text{Cm}$  is formed in *r*-process nucleosynthesis in supernovae, and decays with a half-life of 15.6 million years (Ma) to  $^{235}\text{U}$ . If it was present in the local ISM at the time of SS formation, and in a not completely homogenized environment, it can account for  $^{235}\text{U}$  abundance variations. More data are required on the abundances and distribution of  $^{235}\text{U}$  and  $^{247}\text{Cm}$  to provide constraints on the interval between the last *r*-process nucleosynthetic event and the formation of the SS.

### 5.2 Presence of now- extinct nuclides in ISM and in SS matter

We consider specific isotopic excesses observed in SS matter due to extinct radionuclides with <10 Ma half-lives (given in parentheses, units Ma):

$$^7\text{Be} (53.44 \text{ days}); ^{10}\text{Be} (1.39); ^{26}\text{Al} (0.717); ^{36}\text{Cl} (0.30); ^{41}\text{Ca} (0.10); \\ ^{53}\text{Mn} (3.74); ^{60}\text{Fe} (2.62); ^{107}\text{Pd} (6.5); ^{182}\text{Hf} (8.90).$$

These short-lived, now-extinct, radioactive species indicate that a rather short time (< 1 Ma) must have elapsed between their production and their subsequent incorporation into early SS matter.  $^7\text{Be}$  and  $^{10}\text{Be}$  nuclides are not produced in stars and the half-life of fully ionized  $^7\text{Be}$  may be much longer, because of delayed e-capture decay.  $^{60}\text{Fe}$  is synthesized through successive neutron captures on Fe isotopes in neutron-rich environments inside massive stars, before or during their final evolution to core collapse supernovae. It can be detected after supernova ejections into the interstellar medium, from  $\beta$ -decays and gamma emission, like other radioactive isotopes  $^{44}\text{Ti}$ ,  $^{56}\text{Co}$ ,  $^{26}\text{Al}$ . These nuclides provide evidence that nucleosynthesis is ongoing in the galaxy (The et al., 2006; Wang et al., 2007). Because of their short half-lives  $^{44}\text{Ti}$  and  $^{56}\text{Co}$  are detected as pointlike sources, e.g. in young type II supernova remnants (SNRs) Cas A and 1987A, respectively (Iyudin et al. 1994;). With its longer half-life  $^{26}\text{Al}$  may propagate over significant distances and accumulate in the interstellar medium from many supernovae, until production and  $\beta$ -decay are in balance in the ISM, giving rise to a diffuse and galaxywide glow (Mahoney et al. 1982; Wang et al. 2007).  $^{60}\text{Fe}$  from the same massive-star sources can be expected to follow  $^{26}\text{Al}$  and new measurements (Wang et al. 2007) confirmed this. Although the detections of these isotopes are in agreement with the broad outlines of nucleosynthesis theory, there are also discrepancies in details. For example,  $^{44}\text{Ti}$

lives long enough that it should have been detected from several recent galactic supernovae, if these occur at a rate of  $\sim 2$  per century. Also concentrations of  $^{26}\text{Al}$  were seen in very young OB associations where even the most massive stars are not expected to have exploded, which led to the suggestion that most  $^{26}\text{Al}$  production is associated with ejections in a pre-explosion phase of stellar evolution (Knödlseeder et al. 1999).

Liu et al. (2009) studied  $^{26}\text{Al}$  and  $^{10}\text{Be}$  records in individual refractory chondritic hibonites. Spinel-hibonite spherules bear evidence of in situ  $^{26}\text{Al}$  decay, whereas what the authors call PLATy-Crystals (PLACs) and Blue-aggregates either lack resolvable  $^{26}\text{Mg}$ -excesses or exhibit  $^{26}\text{Mg}$ -deficits by up to 4%. They also found that eight out of 11  $^{26}\text{Al}$ -free PLAC grains record  $^{10}\text{B}/^{11}\text{B}$  excesses that correlate with Be/B and the inferred initial  $^{10}\text{Be}/^9\text{Be}$  ratio was  $(5.1 \pm 1.4) \times 10^{-4}$ . These data demonstrate that  $^{10}\text{Be}$  cannot be used as a chronometer for these objects and that most of the  $^{10}\text{Be}$  observed in CAIs must be produced differently, possibly by irradiation of precursor solid. The lack of  $^{26}\text{Al}$  in PLAC hibonites indicates that  $^{26}\text{Al}$  was not formed in the same process as  $^{10}\text{Be}$  in PLAC, and Liu et al. (2009) conclude that these data indicate a very early formation of PLAC hibonites, prior to the incorporation of  $^{26}\text{Al}$ .

Possible sources of short-lived radionuclides were discussed (Wasserburg et al., 2006; Tachibana et al., 2006; Wadhwa et al., 2007) and include production by energetic particle irradiation, stellar nucleosynthesis and mass-loss winds from Wolf-Rayet stars. In explosive synthesis generally several options exist and may not require multiple sources to provide a satisfactory match with observed abundances. However, most supernova models imply that if a supernova provided  $^{26}\text{Al}$  and  $^{41}\text{Ca}$  into the solar system, it would also have supplied 10-100 times the estimated  $^{53}\text{Mn}$  abundance in the SS (e.g., Goswami and Vanhala 2000). The observed variability of abundances in meteorites raises questions regarding a widely accepted paradigm of SS formation, the gradual cooling of a collapsed molecular cloud and the sequential condensation of matter, growing from mineral grains to planets. Rather, the early solar nebula may have represented a dynamic assembly of domains, differentiating planetesimals and dust, which coexisted for a still poorly defined time. The time markers for these processes in principle are provided by abundances of short-lived isotopes as observed now as decay-products in SS matter.

### 5.3 Environment of formation

Adams (2010) has discussed the data for outer “edges” of the SS that provide further constraints on its dynamical past. The first edge is marked by the planet Neptune, which orbits with a semimajor axis  $a \approx 30$  AU, the range of planet formation. Beyond the last giant planet, the SS contains a large collection of smaller rocky bodies in the Kuiper Belt with orbits indicating much larger eccentricities and inclinations than the planetary orbits (Luu & Jewitt 2002). The Kuiper belt is dynamically excited and this property must be consistent with scenarios for SS birth, but these bodies contain relatively little of the total mass, which has been estimated to be 10-100 times less than Earth's (Bernstein et al. 2004). The outer boundary of the SS (inner boundary of the Kuiper belt) at 30 AU is thus significant and a drop-off is observed around 50 AU (Allen et al. 2000), the radial distance that roughly corresponds to the 2:1 mean motion resonance with Neptune. Because it is likely that additional bodies could have formed and survived beyond this radius, the existence of this edge at  $\sim 50$  AU is important. At still greater distances, the SS contains a large, nearly spherical collection of comets known as the Oort cloud, a structure that extends to about

60,000 AU. Because the comets in the Oort cloud are loosely bound, gravitational perturbations from passing stars can easily disturb the cloud.

The presence of synthesized radionuclides such as  $^{60}\text{Fe}$  (see 5.2) constrains the formation environment, since a moderately sized cluster of stars is required in order to contain a massive progenitor star for a supernova. Most models start with specific assumptions, like that Jupiter formed approximately at the current radial distance. There is information on one other Sun-like star with transient planets, Kepler-11, which has a closely packed six-member planetary system (Lissauer et al., 2011) and can provide useful information on dynamics and composition. In this case transient planets permit the determination of radii, and the inferred mass to size relations indicate substantial envelopes of light gases, but the largest planet (<300 earth masses) has a semi-major axis of only 0.46 AU. Lissauer et al. conclude that an in situ formation would require a massive protoplanetary disk of solids near the star and/or trapping of small solid bodies whose orbits were decaying towards the star as a result of gas drag. It would also require the accretion of significant amounts of gas by hot small rocky cores. Hydrodynamic calculations (Masset and Snellgrove, 2001; Walsh et al., 2011) have shown that giant planets can undergo a two-stage inward-then-outward migration. Further, it is not known whether matter from neighboring planetary systems in the star-forming cluster has been added to the SS, such as the Oort cloud of comets, as suggested by Levison et al. (2010).

#### 5.4 Effects from an active early Sun

When a SS disk is exposed to external or internal UV radiation, the gas can be heated to sufficiently high temperatures to trigger and to drive flows; strong radiation fields also produce chemical changes. For example, oxygen isotopic changes are produced if the SS formed in an environment of intense FUV radiation fluxes. In one scenario, UV radiation may have produced selective photo-dissociation of CO within the collapsing protostellar envelope of the forming SS (Lee et al., 2008), or in an alternative scenario, the isotope selective photo-dissociation may have occurred at the surface of the nebula (Lyons and Young, 2005). Effects due to intense UV-radiation and/or plasma during an active phase of the Sun may also have affected matter in the inner SS. Shu et al. (2001) and Shang et al. (2000) proposed detailed models for effects by the active Sun, specifically the transport of CAI and chondrules. Lee et al (2009) proposed a scenario for loading enstatite grains at elevated temperatures with solar plasma in the inner SS, in a way similar to the proposed incorporation of Ar now observed in the atmosphere of Venus (Wetherill, 1981).

It seems plausible that an intense X-type solar wind, as proposed by Shu et al. (2001) led to a strong recycling and redistribution of condensates in the inner SS. Furthermore, it seems likely that this wind has established chemical and isotopic gradients with radial and latitudinal dependences. Also, it seems likely that this wind had a strong influence in shaping the atmospheric composition of the inner planets.

#### 5.5 A look at the Interstellar Medium

It is not a purpose of this paper to discuss the literature of observations of molecules and of processes in the ISM. We refer the interested reader to a recent review of gas-phase processes and implications (Smith, 2011). However, since organic matter in the SS (primitive



meteorites, comets) show large isotopic variations, it is important to determine the origin of this organic matter. Hydrogen in the ISM is observed to have huge enrichments of deuterium, and efficient processes at very low temperature capable to achieve enrichments are ion-molecule reactions. Regarding the elements O and N, we note that CO is the second most abundant molecule in interstellar clouds after H<sub>2</sub>, with readily observable electronic transitions in the vacuum ultraviolet, vibrational bands in the infrared, and pure rotational lines in the millimeter-wave regime. The isotopic varieties of CO are used to constrain models of star formation, chemical networks, and stellar evolution. Isotopic O abundance measurements by high-resolution spectroscopy of X Persei with the Space Telescope Imaging Spectrograph (Sheffer et al., 2002) provided the first ultraviolet interstellar <sup>12</sup>O<sup>17</sup>O column density data. The measured isotopomeric ratio is <sup>12</sup>C<sup>16</sup>O/<sup>12</sup>C<sup>17</sup>O = 8700, while the detection of interstellar <sup>12</sup>C<sup>18</sup>O establishes its isotopomeric ratio <sup>12</sup>C<sup>16</sup>O/<sup>12</sup>C<sup>18</sup>O = 3000. These ratios are about five times higher than local ambient oxygen isotope ratios in the local ISM. The severe fractionation of rare species can be interpreted to show that both <sup>12</sup>C<sup>17</sup>O and <sup>12</sup>C<sup>18</sup>O are destroyed by photo-dissociation, whereas <sup>12</sup>C<sup>16</sup>O avoids destruction through self-shielding depending on column densities. These authors also explain the small effects in the ratio <sup>12</sup>C/<sup>13</sup>C by a balance between the photo-dissociation of <sup>13</sup>C<sup>16</sup>O and its preferential formation via the isotope exchange reaction between CO and C<sup>+</sup>.

Although large differences are observed between N isotopic abundances in different classes of meteorites, N is heavy when compared with the ratio in the SW, and the spectroscopic data on N in the ISM appear to be relevant. Also, N isotopic records in lunar surface samples which were exposed to the space environment at different times, including the recent exposure of South Ray samples (2 Ma ago), show that an influx of N into the inner SS has persisted to the present (Geiss and Bochsler, 1982; Marti and Kerridge, 2010). The observed abundances of C and N in implants of non-solar origin indicate low ratios C/N (Marti and Kerridge, 2010), distinct from ratios in carbonaceous chondrite matter. When looking for potential N-rich sources, we note that in Very Large Array observations of NH<sub>3</sub>, Ragan et al. (2011) found in six infrared Dark-clouds at distances from 2 to 5 kpc that ammonia can serve as an excellent tracer of dense gas, as it shows no evidence of depletion, and they report an average abundance in these clouds of  $8.1 \times 10^{-7}$  relative to H<sub>2</sub>. These authors found that although volume densities are on par with those in local star-formation regions of lower mass, they consist of much more mass, which induces very high internal pressures. Charnley & Rodgers (2002) showed that higher <sup>15</sup>N/<sup>14</sup>N ratios are generated in high-density cores, where CO is depleted onto dust grains and N<sub>2</sub> remains in the gas phase. For prestellar cold cloud environments, with NH<sub>3</sub> freeze-out onto dust grain surfaces, models predict an enhancement in the gas-phase abundance of <sup>15</sup>N-bearing molecules. Bizzocchi et al. (2010) confirmed that this is the case for the N<sub>2</sub>H<sup>+</sup> ion in a Taurus starless cloud, which is one of the best candidate sources for detection owing to its low central core temperature and high CO depletion. These authors infer a ratio <sup>15</sup>N/<sup>14</sup>N that is about twice as large as the ratio inferred from NH<sub>3</sub> measurements and show that significant fractionations are observed under these conditions. They suggest that observed N isotopic variations observed in SS matter may be considered as a remnant of interstellar chemistry in the protosolar nebula, but also a transport mechanism is required for matter in the inner SS. Kwok and Zhang (2011) suggest that unidentified infrared emission features in circumstellar environments and in the ISM may arise from amorphous organic solids, of a type similar to IOM observed in chondrites (see 3.2). If correct, there may be a direct connection between meteoritic matter and the ISM.

## 6. Discussion

### 6.1 Noble gases as tracers of origin and evolution

Noble gases, like organic molecules discussed earlier, are useful tracers in studies of origin and evolution, due to the volatility (He and Ne) and the chemical inertness, but it is not possible to treat them as gas-phase-only elements, because trapped noble gases (Q-gases) are located in carbonaceous carriers that represent solid phases of an environment in which matter formed. On the other hand, solar-type gases as observed in planetary regoliths (lunar surface and gas-rich meteorites) represent implanted ions. Further, solar-type gases were observed in martian meteorites and in the atmosphere of Jupiter. The observed atmospheric abundances on the inner planets demonstrate complexities first because of the very low noble gas abundances, but mainly because of differences in isotopic abundances.

Reynolds (1963) introduced the term “xenology” for studies involving the abundances of 9 stable isotopes of Xe in solar system matter, which he expected to provide important information. One example is found in an apparently close relationship between trapped gas Q-Xe (or OC-Xe, Abee-Xe; see 3.3) and the solar Xe-S signature. Some papers (Lavielle and Marti, 1992; Marti and Mathew, 1998) considered mixing models of Xe-S and HL-Xe (component observed in presolar diamond) that were successful in accounting for observed components in meteorites, except for Xe abundances in Earth’s atmosphere and Xe in chondritic metal (FVM-Xe; Marti et al., 1989). A model of an evolving environment such as one providing destruction of presolar diamonds (Huss, 1990) followed by processes of isotope homogenization is considered here. The lack of total homogenization of Xe in meteorites was documented in distinct isotopic abundances found in a ureilite (Wilkening and Marti, 1976), which indicates slightly variable mixing ratios of solar Xe-S and HL-Xe. The  $^{182}\text{Hf}$ - $^{182}\text{W}$  chronometric data for ureilites by Lee et al. (2009) provide a time-frame and show early differentiation of the ureilite parent body, shortly after the SS formed. Likewise, isotopic data for an environment where the Xe homogenization process had progressed even less is found in CB-carbonaceous chondrites (Nakashima et al., 2008; Nakashima and Nagao, 2009) with abundances somewhat closer to the solar Xe-S composition, specifically in a metal concentrate. Another longstanding xenology puzzle is found in monoisotopic excesses of  $^{134}\text{Xe}$  in chondritic metal (Marti et al., 1989). This so-called FVM-Xe appears to relate to the just discussed variable mixing ratios of Xe-S and HL-Xe. In this case the FVM-Xe data is consistent with a mixture of Xe-S and fission-Xe, the latter with the specific signature of neutron-induced fission of  $^{235}\text{U}$  (Marti et al., 1989). FVM-Xe was enriched in small grains, characteristics for surface locations, and may represent ions implanted together with fission Xe into metal grains. The neutron fluence required to produce the inferred amount of fission-Xe is high, however, and suggestive of an ISM environment (Hua et al., 2000). There is evidence for very early formation of chondritic metal (Lee and Halliday, 1996; Zolensky and Thomas, 1995).

Turning to planetary atmospheres, there are atmospheric data for the largest planet (Mahaffy et al., 2000), and the isotopic abundances of the larger isotopes are consistent with solar-type Xe, although the data have large uncertainties and their abundance relative to H is about 2.5 times larger. For the inner planets, there are atmospheric data for Mars and these are best compared to those in Earth’s atmosphere. Remarkably, the Xe isotopic abundances in the atmospheres of the two planets are similar (except fission-affected heavy Xe isotopes), but differ strongly from those in other SS reservoirs. There are two distinct Xe

components in the case of Mars (Mathew and Marti, 2001), solar-type Xe-S in its interior (in martian meteorites) and atmospheric Xe that is mass-fractionated (favoring the heavy isotopes) by 37.7 permil per amu, relative to Xe-S. Pepin (2006) favors a fractionation pattern based on hydrodynamic escape that fits the observed abundances well, without invoking a fission component in the martian atmosphere. For planet Earth Caffee et al. (1999) reported a very minor distinct Xe-S component in some well gases, but in this case the same hydrodynamic fractionation (Pepin, 2006) of solar Xe-S does not work. When considering isotopic fractionations in the gravity fields of these different size bodies, the option of a common origin can not be discarded. Lunar rocks that were never exposed to SW have shown that the composition of lunar Xe reveals an excellent match to the terrestrial atmosphere (Lightner and Marti, 1974). However, there is an unresolved question of whether Xe represents an indigenous component, or a contaminating phase with a terrestrial source (Niedermann and Eugster, 1990). The excellent agreement of lunar and terrestrial O isotopic abundances prompted Pahlevan and Stevenson (2007) to investigate the issue of isotopic exchanges between lunar and terrestrial matter by the giant impact and during the time required for the orbiting disk of magma and gas to condense into the moon. These calculations address oxygen isotopic exchanges, but also apply to exchanges of Xe. The time of formation of the moon was inferred from  $^{182}\text{Hf} - ^{182}\text{W}$  data, but depends on the initial W isotopic composition, but likely was 60 Ma after formation of the SS (Touboul et al., 2007), consistent with data from coupled  $^{146}, ^{147}\text{Sm} - ^{142}, ^{143}\text{Nd}$  systematics in lunar samples (Boyet and Carlson, 2007). Late collisions and accretion of matter by the moon remain options (Jutzi and Asphaug, 2011; Willbold et al., 2011). Also, if terrestrial  $\text{H}_2\text{O}$  was supplied by comets, as suggested by Hartogh et al. (2011), a supply of noble gases to the earth-moon system as well as to other inner planets can not be excluded.

## 6.2 Gas and condensed phase elements: Oxygen and nitrogen

In a self-shielding environment photons capable of dissociating  $^{12}\text{C}^{16}\text{O}$  are attenuated and as a result  $^{17}\text{O}$  and  $^{18}\text{O}$  are preferentially dissociated from CO molecules (see 2.3 and 5.4). These atoms can recombine into  $\text{H}_2\text{O}$  molecules and produce heavy water (Clayton, 2002; Yurimoto and Kuramoto, 2004). If a mechanism exists, capable of separating newly formed heavy water from the remaining oxygen, this heavy signature can be exported. If  $\text{H}_2\text{O}$  vapor freezes onto grains and forms ice mantles while  $^{16}\text{O}$  preferentially remains as CO in the gas, then a separation of solids from gas produces distinct isotope reservoirs. Yurimoto and Kuramoto (2004) discuss the observation of water ices in molecular clouds and suggest that heavy water in the SS probably was imported from its presolar molecular cloud and redistributed into the inner SS. Water ice and vapor was also observed in the disk around a young star (Hogerheijde et al., 2011). In the model of heavy water additions to SS matter, observed O isotopic signatures should plot on mixing-lines of the end-member components, the original presolar gas phase and the local water ices of the presolar molecular cloud. The O data reported for olivines of enstatite and carbonaceous chondrites (Weisberg et al., 2011; Ushikubo et al., 2011) determine a mixing line that is consistent with O data in Allende chondrules (Rudraswami et al., 2011) and also fits O in Earth's mantle, as well as O in the very heavy (presolar) water in a matrix sample (see 3.1).

Alternatively, Clayton (2002) suggests that self-shielding may have prevailed at the inner boundary of the solar nebula for intense UV radiation from the early active Sun, and that this radiation may have dissociated CO and also  $\text{N}_2$ . An effective separation and

redistribution of residual gas and condensed phases must then account for the O and also N isotopic variations. These requirements apparently are met in the environments of the ISM or the presolar molecular cloud, but restrictions apply in the environment of the inner boundary of the SS. In simple models the observed isotopic composition depends on a mixing ratio, and mixing models of two components with different isotope ratios have been considered ever since the discovery of anomalous  $^{17}\text{O}$  (Clayton et al., 1973). The large difference in the ratios  $^{15}\text{N}/^{14}\text{N}$  of inner planets, meteorites and the SW (Marty et al., 2011) are even more difficult to explain in a SS environment. Further, the large variations in implanted N in lunar regolith samples require distinct sources of N. On the moon the smaller fraction of N has its origin in SW implants. In meteorites, and specifically in phases of the carbonaceous matrix where elements reveal isotopic signatures of stellar nuclear processes, another source is indicated, an origin in the presolar molecular cloud. Maret et al. (2006) suggest that  $\text{N}_2$  abundances in the ISM are very small, because most N exists in atomic form (and in ices) and this would account for large fractionations, of a magnitude as observed in meteorites.

N concentrations observed in presolar grains of SiC, diamond and graphite range from permil to percent (Zinner et al., 2007), but these grains apparently are rare in chondrites. Busemann et al. (2006) working on phases of carbonaceous chondrites found very large isotopic anomalies in hydrogen and nitrogen, exceeding those found in interplanetary dust particles, and suggest an origin in the presolar molecular cloud or perhaps in the protoplanetary disk. The most extreme D/H values were found in IOM (Insoluble Organic Matter), and since these highly anomalous separates survived the chemical separations and of course all the parent body processing, IOM appears to represent robust matter that formed in special environments with properties as observed in the ISM. Remusat et al. (2007) found that the ratio D/H in IOM depends on the C-H bond dissociation energy, and they suggest that the observed correlation of D-enrichments does not indicate formations in the ISM, but rather equilibrium exchanges in a D-rich reservoir after IOM syntheses. However, since meteoritic D/H ratios are generally smaller than those observed in the ISM, it appears that a correlation with bond dissociation energies could also be due to hydrogen exchange reactions during reheating events. The inferred  $^{15}\text{N}$ -rich source with low C/N ratios in the lunar regolith is not known. The lack of a relation of N isotope ratios in SS matter with either D/H or  $\Delta^{17}\text{O}$  (Marty et al., 2011) do not indicate simple mixtures of a  $^{15}\text{N}$ -rich end-member (like IOM) and a solar ( $^{15}\text{N}$ -depleted) component. In the scenario of a delivery of  $\text{H}_2\text{O}$  with a terrestrial H/D ratio by comets (Hartogh et al., 2011) a supply of N also has to be expected. Mumma and Charnley (2011) review the chemical composition and isotopic abundances in comets that indicate a general enrichment in  $^{15}\text{N}$ . They conclude that an understanding of the nitrogen isotopic variations in volatile SS material demands more rigorous astronomical ground-truths, such as measurements of N isotope ratios in molecular clouds, and specifically in highly depleted cores that are forming low-mass protostars. In the previous discussion (6.1) an evolving environment (destruction of a pre-existing component) was considered, and a similar fate could affect N: a looked-after component does no longer exist, but the environment has changed by way of its destruction.

### 6.3 Origin of SS nucleosynthetic heterogeneities

Ti isotopic variations in matter of the inner SS permit some insight into the history of stellar products. Although the anomalies for isotopes  $^{46}\text{Ti}$  and  $^{50}\text{Ti}$  have different nucleosynthetic

origins, the observed variations (Trinquier et al., 2009) permit to follow an evolutionary path for correlated mass-independent variations of  $^{46}\text{Ti}$  and  $^{50}\text{Ti}$  in bulk solid analyses. These authors conclude that the observed correlations imply that the presolar dust, inherited from the protosolar molecular cloud, must have been well mixed when SS solids formed, but that a subsequent process was necessary that imparted isotopic variability at the planetary scale. This process could have been thermal processing of molecular cloud material, like volatile element depletions in the inner SS, including selective destruction of thermally unstable, isotopically anomalous presolar components. As discussed earlier (see 3.5), the Os isotope homogeneity in bulk chondrites contrasts with isotopic heterogeneities observed in various other elements (Cr, Mo, Ba, Sm, and Nd), at the same level of resolution, while Os isotopic abundances are not uniform in separates of carbonaceous chondrites. It is not clear, whether different carriers were involved in the transport, or differences existed in chemical compositions or thermal processing during imports of matter into the inner SS.

## 7. Conclusions

Several of the observed isotopic abundance variations in SS matter are due to incomplete mixing of products from different stellar sources. These components were injected into and processed in the presolar cloud before the formation of the SS, and grains that escaped homogenization processes exhibit substantial variations in their isotopic make-ups. Some stellar products were radioactive nuclei with about Ma half-lives ( $^{10}\text{Be}$ ,  $^{26}\text{Al}$ ,  $^{53}\text{Mn}$ ,  $^{60}\text{Fe}$ ) that are used in chronological applications that trace the sequence of events in the nebula. Multiple sources are indicated for these radionuclides, and the extent of homogenization is recorded in the decay products, which are often found to be variable, sometimes even missing. The early solar nebula may have represented a dynamic assembly of domains, differentiating planetesimals and dust, which coexisted for some time.

The paper first summarizes observed abundance variations for O, N, noble gases and some heavy elements (recorders of p-, s- and r-processes) and then assesses these abundances in the light of available SW abundance data as obtained by the Genesis and lunar missions. Some striking isotopic differences invite reevaluations of origin and paths of evolution, although some uncertainties remain between the measured SW data and real solar abundances that, although small, are nevertheless critical in some evaluations. The discussion focuses on large differences observed in isotopic data of O and N in different locations of the inner SS, in giant planets and in comets, and evaluates a model of changing mixing ratios of isotopically distinct forms of matter (gases and solids/ices). In this case the observed abundances in SS matter are determined by presolar nebular gas-phase data (presumably close to, but not identical to solar data) and the abundances in partially homogenized condensed phases (solids/ices). As discussed (see 6.2), water ices were also observed in the disk of a young star. The water ice signatures determine isotope ratios in mixtures, for O in a three-isotope diagram, and determine whether planetary and meteoritic O data plot on different mixing-lines. Reported O data in olivines of carbonaceous and enstatite chondrites define a mixing-line that is consistent with O data in chondrules and also fits oxygen ratios in the Earth's mantle and O in reported heavy (presolar nebula) water (see 3.1). Characteristic data for sources of today's observed, and also of some lost (by destruction) carriers of isotopically distinct components, characterize a presolar environment with incomplete equilibrations. Some authors suggest that carrier phases and

ISM reaction residues were initially located in the outer ranges of the solar nebula and then injected to the inner SS, possibly also at later times. An injection of ices would also have changed isotopic abundances of volatiles like N or heavy noble gases. A documentation of sources is not easy, as the local ISM has evolved over the 4567 Ma timeframe. If unidentified infrared emission features in circumstellar environments and in the ISM arise from amorphous organic solids (as observed in carbonaceous chondrites) as suggested, this data may provide a direct link between meteoritic matter and the ISM. Indications of coupled isotopic variations, like those for  $^{54}\text{Cr}$ , s-process Mo and  $\Delta^{17}\text{O}$ , require detailed documentation of carrier phases. The available data for SS matter also may be incomplete (e.g. one comet with terrestrial water, and one meteorite with very heavy oxygen). In summary, the SW abundance determinations in foils from the Genesis mission provide essential reference data for investigations of abundance variations in SS matter.

## 8. Acknowledgment

PB acknowledges support by NASA SR&T Grant NNX09AW32G

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## **Exploring the Solar Wind**

Edited by Dr. Marian Lazar

ISBN 978-953-51-0339-4

Hard cover, 462 pages

**Publisher** InTech

**Published online** 21, March, 2012

**Published in print edition** March, 2012

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Kurt Marti and Peter Bochsler (2012). Solar Wind and Solar System Matter After Mission Genesis, Exploring the Solar Wind, Dr. Marian Lazar (Ed.), ISBN: 978-953-51-0339-4, InTech, Available from:  
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