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# Processes of noble gas elemental and isotopic fractionations in plasma-produced organic solids: Cosmochemical implications

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**Abstract**

The main carrier of primordial heavy noble gases in chondrites is thought to be an organic phase, known as phase Q, whose precise characterization has resisted decades of investigation. The Q noble gas component shows elemental and isotopic fractionation relative to the Solar, in favor of heavy elements and isotopes. These noble gas characteristics were experimentally simulated using a plasma device called the "Nebulotron". In this study, we synthesized thirteen solid organic samples by electron-dissociation of CO, in which a noble gas mixture was added. The analysis of their heavy noble gas (Ar, Kr and Xe) contents and isotopic compositions reveals enrichment in the heavy noble gas isotopes and elements relative to the light ones. The isotope fractionation is mass-dependent and is consistent with a $m^n$-type law, where $n \geq 1$. Based on a plasma model, we propose that the ambipolar diffusion of ions in the ionized CO gas medium is at the origin of the noble gas isotopic fractionation. In addition, the elemental fractionation of experimental and chondritic samples can be accounted for by the Saha law of plasma equilibrium, which does not depend on the respective noble gas masses but rather on their ionization potentials. Our results suggest that the Q noble gases were trapped into growing organic particles starting from solar gases that were fractionated in an ionized medium by ambipolar diffusion and Saha processes. This would imply that both the formation of chondritic organic matter and the trapping of noble gases took place simultaneously in the ionized areas of the protoplanetary disk.


*Keywords:* Noble gases; Plasma; Isotopic fractionation; Meteorites; Phase Q

## 1. INTRODUCTION

Noble gases are powerful tools to investigate the origin and processing of Solar system objects and reservoirs. Three main primordial components having distinct elemental and isotopic compositions have been identified. Solar gases, analyzed in the lunar regolith and in targets on the Genesis spacecraft, both exposed to solar-wind irradiation, are representative of the composition of the protosolar nebula (Crowther and Gilmour, 2013; Meshik et al., 2007, 2014). Presolar noble gases from pre-solar refractory grains found in primitive meteorites give insights in nucleosynthetic production yields of these elements (Huss and Lewis, 1995; Huss et al., 2003). All types of primitive meteorites and some achondrite groups contain an ubiquitous noble gas component, labelled Q (where Q stands for quintessence) (Ott, 2002; Avice et al., 2015). This trapped component is concentrated in an ill-defined phase that resists HF-HCl acid attack of meteorites which destroyed silicates and metal but not organics, and is lost upon organics oxidation (Lewis et al., 1975). From this behavior and regardless of its debated nature (Lewis et al., 1975; Ott, 2002; Marrocchi et al., 2015), Phase Q appears to be closely

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associated with meteoritic organics (Busemann et al., 2000). Phase Q hosts most of the heavy noble gas (Ar, Kr and Xe) inventory of primitive meteorites. It shows well-defined fractionated elemental and isotopic patterns relative to the solar composition (taken as a reference), defining the so-called "planetary pattern" (e.g., Ott, 2002, 2014). Planetary noble gases are elementally enriched in the heavy ones relative to the light ones, and also enriched in the heavy isotopes relative to the light ones (Huss et al., 1996; Busemann et al., 2000). The Xe isotopic composition of Q-gases has been interpreted as a mixture of three components: radiogenic $^{129}$Xe from the decay of $^{129}$I, the so-called Xe-HL component identified in nanodiamonds, and solar Xe mass-dependently fractioned by 0.8%/u (Gilmour, 2010; Crowther and Gilmour, 2013; Meshik et al., 2014). As a matter of fact, Q-gases are undoubtedly related to the main solar reservoir, but the nature of this relationship, i.e., the mechanism by which solar gases were trapped and fractionated, is debated. Adsorption (Fanale and Cannon, 1972; Bernatowicz and Podosek, 1986; Huss et al., 1996; Marrocchi et al., 2005a,b; Wacker, 1989) has been advocated, but adsorption in neutral conditions is unable to yield significant isotopic fractionation (Marrocchi and Marty, 2013). In contrast, trapping experiments involving noble gas ions using electric discharge devices result in elemental and isotopic fractionations consistent with those of Q-noble gases relative to solar (Frick et al., 1979; Dziczkaniec et al., 1981; Bernatowicz and Fahey, 1986; Bernatowicz and Hagee, 1987; Ponganis et al., 1997; Hohenberg et al., 2002; Marrocchi et al., 2011; Kuga et al., 2015). This clearly suggests that noble gas ions are a key ingredient in the Q-component formation recipe (e.g., Ott, 2014). It is worth noting that the co-synthesis of carbonaceous material is unnecessary for producing noble gas fractionation (Bernatowicz and Fahey, 1986), but likely enhances the trapping yield of noble gases (Fukunaga and Matsuda, 1997; Kuga et al., 2015). Several important observations have also been made. (i) There exists a strong correlation between noble gas elemental "planetary" pattern and their ionization potentials (Göbel et al., 1978; Ott, 2002, 2014; Rai et al., 2003); (ii) noble gas ions are quantitatively trapped even at low energies (a few eV to tens of eV, Bernatowicz and Hagee, 1987; Ponganis et al., 1997; Kuga et al., 2015); (iii) Xe isotopic fractionation in such electric discharge experiments follows a $m^1$ mass dependence law (Bernatowicz and Fahey, 1986; Bernatowicz and Hagee, 1987). While plasma ion implantation appears able to trap noble gases with an isotopic fractionation reminiscent of the Q-gas component (Ott, 2014; Kuga et al., 2015), no proper model exists to explain both elemental and isotopic fractionations of noble gases in plasmas. In this work, we intend to formalize such a model, based on our noble gas trapping plasma experiments and inspired by the observations on other plasma experiment results (Frick et al., 1979; Dziczkaniec et al., 1981; Bernatowicz and Hagee, 1987; Matsuda et al., 1991; Fukunaga and Matsuda, 1997; Hohenberg et al., 2002; Marrocchi et al., 2011). For this purpose, thirteen new samples were synthesized using the Nebulotron setup under varying conditions in order to better understand the physical parameters that control the elemental and isotopic fractionations of noble gases in plasma-deposited organic samples. Our results are compared with meteoritic data to better understand the process of isotopic fractionation of Q-gases relative to solar.

## 2. MATERIAL AND METHODS

### 2.1. The Nebulotron experiment

The experimental plasma setup used to produce noble gas-rich organic solid is called the Nebulotron and was already presented in (Kuga et al., 2014, 2015). It consists of a quartz reactor (inner diameter of 8 mm) equipped with a microwave cavity and supplied in gas mixtures via a glass line (Fig. 1). In the present study, gas mixtures were composed of CO and traces of residual air components as shown in (Kuga et al., 2015), to which a noble gas mixture, hereafter NGM, composed of 75% He, 15% Ne, 5% Ar, 3% Kr and 2% Xe, was added (Fig. 1 and Table 1). CO was used as the main gas since it is the most abundant C-bearing species in a gas of solar composition (Lodders, 2003).

The gas flows (in sccm, for standard cubic centimeter per minute) and proportions were controlled by using two mass-flow controllers (Brooks Delta Smart II) placed in the upstream part of the reactor, one calibrated for CO (50 sccm full scale) and the second one calibrated for the NGM (10 sccm full scale) used in this study. The total pressure in the setup, measured downstream with a capacitance gauge (Pfeiffer®, CMR262, $10^{-2}$–100 mbar range), was ~1 mbar, with a background vacuum of $\sim10^{-2}$ mbar. The plasma was initiated in the quartz tube and continuously fed thanks to a microwave generator (Opthos Instruments®, 2.45 GHz, 0–100 W) connected to a resonance cavity surrounding the quartz reactor (McCarroll, 1970). The neutral temperature was estimated to be 1000 K for microwave plasma discharges at 1 mbar (Es-Sebbar et al., 2009). The mean electron energy is estimated to be in the range 1–2 eV (Fridman, 2008) and the electron density is of the order of $10^{12}$ cm$^{-3}$ (Guerra et al., 2002).

Three sets of experiments were carried out by varying (i) the Xe partial pressure in the starting gas mixture (that is, changing the NGM/CO ratio from 1/8 to 1/1, while keeping a total pressure in the setup around 1 mbar – hereafter $P_{Xe}$ set), (ii) the duration of the deposition experiment (2–7 h range – hereafter $t_{deposition}$ set), or (iii) the power input of the microwave discharge (from 30 W to 65 W – hereafter ⚡ set). While varying one of these three parameters, the two other parameters were kept constant at $7.5 \cdot 10^{-7}$ bar of $^{132}$Xe in the gas mixture, 2 h for the duration, and at 40 W for the power input. During a typical 2 h-long experiment at 30 W and with a CO-NGM gas flow ratio of 5/1, the residence time of gases in the reactor was about 30 ms. A blank experiment, produced with CO gas only, i.e., without the addition of noble gases in the starting gas mixture, was also performed (Table 1).

After completion of the experiment, orange to dark solids cover the quartz tube, along a length of about 4 cm. These deposits show heterogeneity in color (dark to