^{187}Re - ^{187}Os Systematics, Highly Siderophile Element and S-Se-Te Abundances
in the Components of Unequilibrated L Chondrites

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Abstract

The ^{187}Re - ^{187}Os systematics, abundances of highly siderophile elements (HSE: Re, platinum group elements and Au), Te, Se and S as well as major and minor elements were determined in separated components of two unequilibrated L chondrites QUE 97008 (L3.05) and Cenicerros (L3.7). The ^{187}Re - ^{187}Os systematics are disturbed in the components of both meteorites, most likely due to open system behaviour of Re during terrestrial weathering of QUE 97008 and alteration on the L chondrite parent body as indicated by an internal errorchron generated for components of Cenicerros. The HSE abundance patterns suggest that the bulk rock abundances were mainly controlled by two different end members. Non-magnetic fractions display lower Re/Os and HSE/Ir than CI chondrites. Chondrules, metal-troilite spherules and fine magnetic fractions, are depleted in refractory HSE and show higher Rh/Ir, Pd/Ir and Au/Ir than in CI chondrites. The different HSE compositions indicate the presence of unequilibrated alloys and loss of refractory HSE- rich carrier phases from the precursors of some L chondrite components. Gold is decoupled from other HSE in magnetic fractions and shows chalcophile affinities with a grain size dependent variation similar to S and Se, presumably inherited from preaccretionary processes. Tellurium is depleted in all components compared to other analysed siderophile elements, and its abundance was most likely controlled by fractional condensation and different geochemical affinities. The volatility dependent depletion of Te requires different physical and chemical conditions than typical for the canonical condensation sequence as represented by carbonaceous chondrites. Tellurium also shows variable geochemical behaviour, siderophile in Cenicerros, predominantly chalcophile in QUE 97008. These differences may have been inherited from element partitioning during chondrule formation. Selenium and S on the other hand are almost unfractionated from each other and only show complementary S/Se in a few components, presumably due to the effects of volatility or metal-silicate partitioning during chondrule formation. Terrestrial weathering had negligible effects on the S, Se and Te systematics.

1. Introduction

The unequilibrated ordinary chondrites (UOC) are some of the most primitive rocks in the solar system (Nagahara, 1984; Alexander et al., 1990). They are composed of components such as different sized chondrules, matrix, Fe-Ni metal and, more rarely, refractory inclusions (Scott and Krot, 2003). These components were formed in different chemical and physical environments in the solar nebula (Larimer and Anders, 1967, 1970; Huss et al., 2001). The components show a diversity in elemental and isotopic compositions suggesting that they underwent fractionation processes in the early solar system (Wasson, 1972; Gooding and Keil, 1980; McNaughton et al., 1981; King and King, 1981; McKinley et al., 1981; Scott et al., 1981; Hinton and Bischoff, 1984; Rambaldi and Wasson, 1984; Robert et al., 1987; Rosman and Laeter, 1988; Brearley et al., 1989; Alexander et al., 1990; Clayton et al., 1991; Fisenko et al., 1992; Brearley, 1993; Russell et al., 1997; McKeegan et al., 1998; Huss et al., 2001).

Osmium isotopic compositions, abundances of highly siderophile elements (HSEs: Re, Os, Ir, Ru, Pt, Rh, Pd and Au) and S, Se and Te in chondritic components are useful tracers for constraining the elemental fractionation processes that may have taken place under different physical and chemical conditions in the solar nebula, in the meteorite parent bodies or during terrestrial weathering (e.g., Rambaldi, 1976, 1977; Rambaldi et al., 1978; Dreibus et al., 1995; Walker et al., 2002; Horan et al., 2003, 2009; Fischer-Gödde et al., 2010). These elements cover a wide range of condensation temperatures (50% condensation temperatures are ranging from 1821K to 664 K, Lodders, 2003).

Previous studies of bulk chondrites show that all three ordinary chondrite groups (H, L, and LL) have distinct abundance patterns of HSE, S, Se and Te (Case et al., 1973; Binz et al., 1976; Chen et al., 1998; Horan et al., 2003, Fischer-Gödde et al., 2010). Some previous studies on the separated components of ordinary chondrites (Chou et al., 1973; Rambaldi, 1976, 1977; Rambaldi et al., 1978; Grossman and Wasson, 1985; Kong and Ebihara, 1997; Humayun and Campbell, 2002; Horan et al., 2009) show that the differences in HSE ratios amongst the bulk rocks are caused by different compositions of the HSE carriers in the magnetic components of ordinary chondrites. The magnetic

fractions are mainly comprised of kamacite, taenite and fine-grained plessitic inclusions, which formed due to the exsolution of Fe-Ni metal during cooling. Two different carrier phases with very different HSE patterns were observed in the non-magnetic and magnetic fractions of the H chondrites Dhajala and Ochansk (Horan et al., 2009). Horan et al. (2009) proposed that these carrier phases were formed separately in the solar nebula at different conditions and never equilibrated with each other.

Rambaldi et al. (1979) have shown that H chondrites did not lose a metal component before accretion, consistent with their CI chondrite like Fe/Mg (Wasson and Kallemeyn, 1988). In contrast, L and LL chondrites have lost a metal component, presumably in the solar nebula, because ratios of Fe and refractory siderophile elements, relative to Mg, are lower than in CI chondrites (Rambaldi et al., 1979; Wasson and Kallemeyn, 1988). The content of metal and siderophile elements in these three groups shows a continuous range (metal content $H > L > LL$), therefore these groups may have been affected by common processes of metal loss. Different HSE carriers, as observed in H chondrites, may also occur in the two other ordinary chondrite groups. L chondrites are intermediate in their degree of oxidation (Weisberg et al., 2006) and are important candidates for shedding light on the timing and the processes responsible for the origins of the different HSE carrier phases in ordinary chondrites, and to constrain HSE fractionation processes during the metal loss from the L and LL ordinary chondrites (Rambaldi, 1976, 1977; Rambaldi et al., 1978; Kong and Ebihara, 1997).

Another important common feature of ordinary chondrites is the depletion of Te relative to Se and S (Larimer and Anders, 1967; Case et al., 1973; Wai and Wasson, 1977), the origin of which is highly controversial. Tellurium is less volatile compared to Se and S (50% condensation temperatures of Te, Se and S in the solar nebula are 709 K, 697 K and 664 K, respectively) during condensation in the solar nebula (Lodders, 2003). Wai and Wasson (1977) explained the depletion of Te on the basis of different nebular conditions in the ordinary chondrite formation region compared to canonical solar nebula conditions. Heating experiments show that more Te than Se may be lost by diffusion-controlled processes during open-system heating of homogenized powders of ordinary chondrites (Ikramuddin et al., 1977a, b). However, the loss of Te relative to Se and S in ordinary chondrites does

not show any straightforward relationship with metamorphic grades (Ikramuddin et al., 1977a, b; Takahashi et al., 1978). The effect of terrestrial weathering on Te in chondrite finds is uncertain, because it has not been studied in a systematic way. Thus, a combined study of the HSE and S, Se and Te in the components of L chondrites may help to reveal how high and low temperature elemental fractionation processes have affected the composition of siderophile elements in the bulk rocks of L chondrites.

Here we present a study of the ^{187}Re - ^{187}Os systematics, HSE and S, Se and Te abundances and their mass balance in the components of QUE 97008 and Cenicerros. QUE 97008 is a meteorite find that has undergone minor weathering (weathering grade A). It was classified as type L3.05 based on induced thermoluminescence (ITL) data (Benoit et al., 2002; Grossman and Brearley, 2005). Cenicerros on the other hand is a meteorite fall. It was initially classified as H3 (Graham, 1990), but reclassified later to type L3.7 by Rochette et al. (2003), based on magnetic susceptibility, detailed petrographic examination and abundances of HSE, which were measured by Horan et al. (2003). These meteorites were selected for this study to compare the fractionations due to the difference in the metamorphic grade in unequilibrated chondrites from same group. We have also analyzed the major and minor elements Mg, Ca, Cr, Mn, Fe, Ni and Co in the same aliquots to identify the mineralogy of separates and major HSE carrier phases present in the components. The main objectives of the study are to identify and constrain the timing and conditions of the siderophile element fractionation processes in the context of nebular, parent body or terrestrial alteration processes in case of unequilibrated ordinary chondrites.

2. Samples and their preparation

Approximately one gram pieces of QUE 97008 (provided by the Smithsonian Institution National Museum of Natural History) and Cenicerros (off BM.1990, M6, provided by The Natural

History Museum, London) were broken into fragments. Separation of chondrite components such as chondrules, metal sulfide nodules and clasts were carried out on broken fragments by naked eye and under the optical microscope (Kruss optronic MSZ 5600) using plastic tweezers. The separation procedure was discussed in detail by Kadlag and Becker, (2015). Calcium-aluminum-rich inclusions (CAIs) were not observed in the rock pieces. The detailed separation procedure is shown in the flowchart in Fig. 1.

In the case of QUE 97008, spherical objects were separated into two different samples, coarse silicate- rich chondrules (C), having diameter >1.5 mm, and metal-troilite spherules (MTS), having diameters < 0.5 mm. A sulfide clast (SC), about 3 x 0.8 x 1 mm was found in Cenicerros, half of it was digested for this study.

The remaining material was separated into five different size fractions in the case of QUE-97008: less than 80 μm (0-80), 80-150 μm (80-150), 150-200 μm (150-200), 200-250 μm (200-250) and greater than 250 μm (>250). In the case of Cenicerros, remaining material was separated into three grain size fractions: less than 50 μm (0-50), 50-200 μm (50-200) and greater than 200 μm (>200). All size fractions were further divided into magnetic (M), slightly magnetic (SM) and non-magnetic (NM) components using a hand magnet. The slightly magnetic 80-150 fraction of QUE 97008 was divided into three fractions, a matrix-rich fraction (QUE-SM 80-150_MTX), a fraction that is rich in chondrule fragments (QUE-SM 80-150_CHD), and a mixture of chondrule and matrix material (QUE-SM 80-150_MIX).

A small fragment of QUE 97008 (~ 6 mm x 8mm x 2 mm) was embedded in epoxy resin and polished for petrographic inspection. Because of the highly unequilibrated nature of the meteorite and the substantial heterogeneity of the distribution and petrologic context of troilite and metal grains, key petrographic details of this section are given in Fig. 2. Chondrules of variable size (0.3 mm-2.5 mm) are present. Metal grains with sizes ranging from < 1 μm to 200 μm are dispersed in the matrix and more rarely occur as small grains in chondrules. Troilite is present in the matrix and also as rims

around some metal grains in matrix and in chondrules. Silicates in chondrules and in matrix are mostly comprised of olivine and pyroxenes. Some chondrules contain a concentric zone of metal spheres (some of them showing the exsolution of kamacite and taenite) near their rim, but no troilite inside the chondrule (Fig. 2b, d). The absence of troilite from this particular chondrule and in its metal inclusions indicate that either all S was evaporated during chondrule melting, or it was not yet condensed during the crystallization of minerals in this chondrule (Fig. 2b, d and e). Some dusty olivines are present in the core of the chondrule, which contain abundant small ($<1\ \mu\text{m}$) metal grains (Fig. 2e). Such metal grains do not occur in all olivines and are very rare in pyroxenes surrounding olivines. Other chondrules contain metal inclusions which are rimmed by troilite (Fig. 2c). The differences between the chondrules indicate variable degrees of oxidation or sulfur fugacity during the formation of different chondrules, and also probably during the secondary metamorphic events which mobilizes S (Swindle et al., 1991 a and b). The preservation of these differences between chondrules indicate the highly unequilibrated nature of this meteorite. The fine-grained nature and inhomogeneous distribution of sulfide rims around metal grains and chondrules indicate that most of these sulfide rims may represent a late product of the chondrule formation processes, rather than of metamorphic origin (Grossman and Wasson, 1982, 1987). Sulfide rims around metal grains included in chondrules, may reflect coeval melting of silicates, metal and sulfides during chondrule formation, and subsequent exsolution of troilite from metal during cooling. Oxidized rims and fractures around some metal grains in chondrules (Fig. 2b, d) likely formed during recent processes, such as terrestrial weathering.

3. Analytical Techniques

The separated samples were digested in 2 ml HNO_3 + 1 ml HCl (both acids were two times quartz distilled and two times teflon distilled) in an Anton Paar^{TM} High Pressure Asher System (HPA-S) for 16 hrs at 320°C and at 100 bar N_2 pressure. The isotope dilution method was used to obtain precise concentration and isotopic data of the HSE and S, Se and Te. Abundances of the monoisotopic

elements Rh and Au were calculated by internal calibration relative to Ru and Ir, respectively. Chemical separations of HSE, S and Se were carried out using cation exchange resin (Eichrom™ AG50 W-X8, 100-200 mesh) and Te separation was carried out using anion exchange resin (Eichrom™ AG1-X8, 100-200 mesh). The procedures of sample digestion, chemical separation of the HSE and S, Se and Te and measurement protocols were described in detail by Fischer-Gödde et.al. (2010), Wang et al. (2013), Kadlag and Becker (2015) and references therein.

For major element analysis of the samples, aliquots of digestion solutions were diluted by factors ranging from 4×10^3 to 2.6×10^5 . Magnesium, Ca, Cr, Mn, Fe, Co and Ni were analysed by the addition of Sc for drift correction of intensities, and concentrations were determined by using the known concentrations of a matrix matched standard. Different dilutions of the Smithsonian Institution Allende meteorite standard reference powder (USNM 3529, Split 18, position 1) were used as a calibration standard. Detailed analytical methods for major elements were described in Kadlag and Becker (2015). Concentrations of all elements (except Os) were measured on the Element XR™ ICP-MS (Inductively Coupled Plasma Mass Spectrometer) at Freie Universität Berlin. Typical precision of concentration measurements of all elements was better than 10% RSD, except non-magnetic fractions, which display 20% RSD for elements with concentrations less than 30 ng/g. Osmium isotopic and concentration measurements were carried out on a Triton N-TIMS (Negative Thermal Ionization Mass Spectrometer) at Freie Universität Berlin Osmium was measured as OsO_3^- at an oxygen pressure of $\sim 1 \times 10^{-7}$ bar and isotopic ratios were corrected for instrumental mass fractionation, spike contributions and interferences from interfering ^{17}O and ^{18}O bearing species. Details are described in Fischer-Gödde et al. (2010) and Kadlag and Becker (2015).

3.1 Analytical blanks

Total procedure blanks were determined for all elements with each set of digested samples. Average values for the full procedural blanks ($n = 12$) are $\text{Re} = 1.9 \pm 0.8$ pg, $\text{Os} = 1 \pm 1$ pg, $\text{Ir} = 2 \pm 1$

pg, Ru = 4 ± 7 pg, Pt = 40 ± 30 pg, Rh = 9 ± 7 pg, Pd = 40 ± 20 pg, Au = 2 ± 2 pg, Te = 30 ± 10 pg, Se = 2.8 ± 0.5 ng and S = 7.6 ± 0.8 µg. Total procedure blanks contribute less than 5% to the measured abundances for most of the components. QUE-SM >250 and QUE SM 80-150 CHD separates required slightly higher blank corrections of up to 10% for Ru, Rh and Pd. Non-magnetic coarse and fine (NMC and NMF) fractions of QUE 97008, Cenicerros chondrules and non-magnetic 0-50 fractions required blank corrections of up to 30% for some elements (Re, Ru, Rh and Pd), because of the small sample weights and low abundances of these elements.

3.2 Reproducibility of Standards

The 2σ precisions of isotopic ratio measurements of HSE and S, Se and Te of the in-house standard for ICP-MS measurements at Freie Universität Berlin over the period of this study were $^{185}\text{Re}/^{187}\text{Re} = 0.607 \pm 0.004$ (n = 19), $^{191}\text{Ir}/^{193}\text{Ir} = 0.592 \pm 0.003$ (n = 25), $^{99}\text{Ru}/^{101}\text{Ru} = 0.735 \pm 0.004$ (n = 25), $^{106}\text{Pd}/^{105}\text{Pd} = 1.229 \pm 0.005$ (n = 25), $^{194}\text{Pt}/^{195}\text{Pt} = 0.971 \pm 0.004$ (n = 25), $^{103}\text{Rh}/^{193}\text{Ir} = 0.42 \pm 0.03$ (n = 25), $^{197}\text{Au}/^{193}\text{Ir} = 0.31 \pm 0.07$ (n = 19), $^{77}\text{Se}/^{78}\text{Se} = 0.318 \pm 0.003$ (n = 15), $^{125}\text{Te}/^{126}\text{Te} = 0.375 \pm 0.005$ (n = 15) and $^{32}\text{S}/^{34}\text{S} = 21.5 \pm 0.3$ (n = 11). The precision (2σ) of major element ratios for different dilutions of the Allende Smithsonian standard was < 4% over the period of this study. The repeatability of the $^{187}\text{Os}/^{188}\text{Os}$ ratio of the University of Maryland Johnson-Matthey Os standard measured by N-TIMS is 0.11382 ± 0.00007 (n = 7, 2σ) for Faraday cup measurements and 0.1138 ± 0.0001 (n = 12, 2σ) for electron multiplier measurements over the period of a year. The uncertainty of the $^{187}\text{Os}/^{188}\text{Os}$ in Table 2 is the internal reproducibility, given as two standard deviations of the mean.

4. Results

4.1 Major element abundances in the separates

The abundances of the major elements are used to identify the dominant mineral phases in the separates. The major and minor element data of the separates, calculated bulk rock values from the mass balance of all analysed components, and the average bulk rock composition of L3 chondrites from the literature are displayed in Fig. 3 and in Table 1. The calculated bulk rock composition of QUE 97008 shows less than 20% differences for individual elements compared to the average of L3 data from the literature (sources mentioned in the caption of Table 1), except for Ni, which differs by 29%. Calculated bulk rock values for Cenicerros show deviations of up to 40% from the literature average of L3 chondrites, except Ni, which shows a 55% difference. The large difference for Cenicerros is mainly the result of significant contributions from a sulfide clast which increased the Fe and S concentration and reduced the abundances of other elements in the piece of rock studied here.

In Fig. 3, components of QUE 97008 show a weak inverse correlation between Mn and S, whereas in case of Cenicerros, there is no such systematic variation in the components (Fig. 3a). The data show insignificant variation in Mn concentration with large variation in S (Fig. 3a). Magnetic components of Cenicerros have a lower Mn/S ratio than other components (Fig. 3a). Manganese is weakly correlated with Cr (Fig. 3b) and also linearly correlated with Mg (Fig. 3c), indicating that most of the Mn resides in silicate phases that not surprisingly predominantly occur in non-magnetic and slightly magnetic fractions. Mn/Cr and Mn/Mg in calculated bulk rocks of both meteorites are close to the values for CI chondrites. Chondrules, non-magnetic and some slightly magnetic fractions in QUE 97008 show almost 50% variations in Mg, which displays a negative correlation with Fe (Fig. 3d). The behaviour in Cenicerros is completely different, in that Mg variations are limited (7-14 wt.%) and Fe varies independently of Mg between 8 and 78 wt.%, yet the calculated bulk rock has a Fe/Mg similar to CI chondrites. The Fe/Mg in the magnetic components and in the sulfide clast in Cenicerros are always higher than in CI chondrites and in all other components. Most components and the bulk rocks show lower Ca/Mg than CI chondrites (Fig. 3e), indicating that Ca was lost from the precursors of the components of L chondrites.

The magnetic components of both meteorites show higher Fe, Ni and Co abundances compared to other components (Fig. 3f and g), mainly because of the higher Fe-Ni metal content in these samples. Magnetic components, QUE SM 80-150 MTX and the MTS fractions have higher Ni/Fe than CI chondrites, and all other components have lower Ni/Fe than CI chondrites (Fig. 2f). Nickel and Co correlate with each other (Fig. 3g) and the Ni/Co ratio is nearly CI chondritic in most components. The exceptions are the magnetic components of Cenicerros, which show large deviations from Ni/Co in CI chondrites. The Ni/Co ratio in the magnetic components of Cenicerros display size-dependent variations (Fig. 3g, 9, and Table 1). The coarsest size fraction has a slightly lower Ni/Co compared to fine grained fractions (shown in the inset in Fig. 3g).

The large variations in the abundances of major and minor elements in magnetic and non-magnetic components indicate efficient separation of major silicate, metal and sulfide phases. The slightly magnetic components are mixtures of these phases in different proportions. The chondrule fractions of both meteorites show very similar chemical properties (Fig. 3). The sulfide clast in Cenicerros is strongly depleted in Mn, Cr, Ca, Ni and Co, and shows strong enrichment in Fe and S (Fig. 3, Table 1).

4.2 ^{187}Re - ^{187}Os systematics

$^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios and Δ_{Os} (the deviation of the Os isotopic composition from the 4.56 Ga IIIA iron meteorite isochron from Smoliar et al., (1996), a precise definition is given in the caption of Table 2) of the analyzed components are given in Table 2 and the measured $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ are plotted in Fig. 4. Most of the components show deviations beyond analytical uncertainties from the IIIA iron meteorite reference isochron (Fig. 4). Magnetic fractions of both meteorites show similar $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$, and lie on or near the 4.56 Ga reference isochron, with higher $^{187}\text{Os}/^{188}\text{Os}$ compared to CI chondrites. The MTS fraction of QUE 97008 is characterized by an unusually high $^{187}\text{Os}/^{188}\text{Os}$ value compared to the other components.

The components of Cenicerros show an apparent linear trend in the Re-Os isochron diagram, with systematic deviations from the reference isochron (Fig. 4). The chondrule fraction and magnetic components of Cenicerros have higher $^{187}\text{Re}/^{188}\text{Os}$ compared to the sulfide clast, slightly magnetic and non-magnetic fractions (Fig. 4). The $^{187}\text{Os}/^{188}\text{Os}$ in the components of Cenicerros varies systematically: $^{187}\text{Os}/^{188}\text{Os}_{\text{NM}} < ^{187}\text{Os}/^{188}\text{Os}_{\text{SM}} < ^{187}\text{Os}/^{188}\text{Os}_{\text{M}}$. Significant differences exist between both meteorites in the behaviour of slightly magnetic and non-magnetic fractions. Slightly magnetic components of QUE 97008 show higher $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ compared to SM components of Cenicerros and CI chondrites. In addition, the $^{187}\text{Re}/^{188}\text{Os}$ of the slightly magnetic components of QUE 97008 varies with the grain size. The smallest size fraction has a higher $^{187}\text{Re}/^{188}\text{Os}$ and shows a larger deviation from the isochron. The non-magnetic fractions display the lowest $^{187}\text{Os}/^{188}\text{Os}$ compared to all other components. Non-magnetic fractions of Cenicerros have lower $^{187}\text{Re}/^{188}\text{Os}$ compared to the non-magnetic fractions of QUE 97008 and CI chondrites, consistent with the variation in SM components.

The chondrule fractions of both meteorites show deviations from the reference isochron. The chondrules from QUE 97008 deviate from the isochron towards low $^{187}\text{Re}/^{188}\text{Os}$, whereas the chondrule fraction of Cenicerros lies at the high $^{187}\text{Re}/^{188}\text{Os}$ side of the isochron. The MTS fraction from QUE 97008 shows very high $^{187}\text{Os}/^{188}\text{Os}$ (0.1751 ± 0.0004) and $^{187}\text{Re}/^{188}\text{Os}$ (1.000 ± 0.003), and lies close to the isochron. The sulfide clast from Cenicerros also lies on the low $^{187}\text{Re}/^{188}\text{Os}$ side off the isochron (Fig. 4). Calculated bulk rock values of both chondrites also deviated from the isochron, however, in different directions (Fig. 4, Table 2). Calculated bulk rock values of Cenicerros show similar $^{187}\text{Re}/^{188}\text{Os}$ and slightly lower $^{187}\text{Os}/^{188}\text{Os}$ compared to literature bulk rock values of Cenicerros (Walker et al., 2002).

4.3 HSE abundances

The HSE abundances of the components, bulk rock values calculated from the mass balance of all analyzed components, average L3 bulk rock compositions, bulk rock data of Cenicerros and CI chondrite data from the literature (Ebihara, 1989; Kaczaral et al., 1989; Kallemeyn et al., 1989; Wasson et al., 1993; Ebihara and Ozaki, 1995; Kong and Ebihara, 1996; Bhandari et al., 2002; Horan et al., 2003 and Fischer-Gödde et al., 2010) are listed in Table 2 and are shown in CI chondrite normalized diagrams in Fig. 5. Calculated bulk rock values of the HSE in QUE 97008 are up to 25% lower than the average literature bulk rock values of L3 chondrites, whereas for Cenicerros the calculated bulk rock composition is about 40% lower than literature data (Horan et al., 2003). This difference is mainly caused by the presence of a HSE poor sulfide clast in this piece of Cenicerros.

The HSE are enriched in magnetic fractions and in the MTS fraction of QUE 97008 (Fig. 5). These components show 75-375 times higher HSE abundances compared to non-magnetic components (Fig. 5, Table 2). With the exception of Au, the HSE abundances in magnetic components of Cenicerros show an inverse relationship with the grain size similar to what has been observed in other unequilibrated ordinary chondrites (Rambaldi, 1976, 1977; Horan et al., 2009). On the other hand, Au abundances in the magnetic fractions of Cenicerros are higher in the intermediate size fraction and show a size dependent behavior that follows that of S and Se abundances (See Fig. 6). The HSE abundances in QUE 97008 are also enriched in the smallest (0-80 μm) and intermediate sized (200-250 μm) magnetic fractions compared to magnetic fractions of other sizes (Fig. 6). Gold behaves somewhat different from the other HSE, as it shows larger differences between the size fractions. Note that the size-dependent behavior of the HSE in the magnetic fractions differs fundamentally from the size-dependent variations of Ni, Co and Fe (Fig. 6c and g). It is clear from Fig. 6 that Au abundances in the magnetic components of both meteorites are decoupled from the other HSE and shows a behavior similar to S and Se.

Three different types of CI normalized HSE abundance patterns can be distinguished for the components (Fig. 5, 7). Some components display nearly CI chondritic HSE ratios (QUE chond C, QUE slightly magnetic 0-80 and 80-150 CHD and >250 fractions, SC and slightly magnetic

components of Cenicerros). Other components are depleted in the refractory HSE Os, Ir and Ru compared to the less refractory HSE Pt, Rh and Pd (most magnetic fractions, QUE chond S, slightly magnetic fractions of QUE 97008). A third type of pattern occurs in non-magnetic fractions and shows depletions in Pd with respect to all other HSE.

4.4 Abundances of S, Se and Te

The concentrations of S, Se and Te in the components and calculated bulk rocks, average L3 chondrites from the literature and CI chondrites are listed in Table 2 (Haramura et al., 1983; Jarosewich, 1984, 1990; Fredriksson et al., 1986; Hewins et al., 1988; Kaczaral et al., 1989; Kallemeyn et al., 1989; Graham, 1993; Wasson et al., 1993; Dreibus et al., 1995 ; Yanai et al., 1995; Kong and Ebihara, 1996; Bhandari et al., 2002 and Wang et al., 2013). Sulfur, Se and Te are depleted in all components compared to CI chondrites (Fig. 5 and 8), except in the sulfide clast from Cenicerros (Fig. 5 and 8). The abundances of these elements are higher in the magnetic and slightly magnetic components compared to chondrules, MTS and non-magnetic fractions. CI-normalized abundances in magnetic components are depleted in the order $Se < S < Te$.

Selenium and S are linearly correlated (Figs. 5, 8a). The Systematic complementarity of S/Se ratios is observed between the components (Fig. 8a). The non-magnetic fractions, chondrules and some SM fractions have higher S/Se, whereas M and some SM fractions have lower S/Se than CI chondrites. The calculated bulk rocks have slightly lower S/Se than CI chondrites. The average S/Se of both chondrites is 2334 ± 49 and average CI chondrite S/Se is 2745 ± 2 (Lodders et al., 2003).

A characteristic feature in the CI-normalized abundance patterns of L chondrites is the depletion of Te relative to the neighbouring elements Au, Se and S, and CI chondrites (Fig. 5). With the exception of the M 0-50 fraction of Cenicerros, which has nearly CI chondritic ratios of Se and Te, the depletion of Te occurs in all components of the analysed L chondrites. In the case of QUE 97008,

Te is more depleted than Se and S, but shows a correlation with these elements (Fig. 8a and b). Accordingly, the total variation of Se/Te (23 ± 3) in components of QUE 97008 is limited, whereas in case of Cenicerros, Te is decoupled from Se and S (Fig. 8b). The magnetic components of Cenicerros have CI-like to moderately high Se/Te, whereas the non-magnetic and slightly magnetic fractions of Cenicerros have very high Se/Te.

5. Discussion

5.1 Mineral proportions and their influence on the composition of the components

The abundances of major elements were used to identify the relative fractions of silicate, sulfide and metal phases in the separated components. The abundances of Mn and S show a weak inverse correlation with each other (Fig. 3a), indicating that Mn is mainly present in silicate phases (Lodders, 2003), which is consistent with the positive correlation between Mn and Mg (Fig. 2c). The variation of Fe/Mg in magnetic and non-magnetic components mainly stems from differences in metal, sulfide and silicate contents in these separates (Fig. 3d). The outlier is the magnetic 0-50 fraction of Cenicerros. This fraction is enriched in Fe-Ni metal (see insets of Figs. 3f and g), which shows higher Cr and Fe content compared to all other magnetic components (Fig. 3b and d). This difference is probably due to the presence of fine grained chromite (FeCr_2O_4). A predominance of silicates in the non-magnetic components, compared to the magnetic components, is indicated by higher abundances of Ca, Mn, Cr, Mg and lower S/Mn and Ni/Fe (Fig. 3).

The magnetic components have higher Ni/Fe and Ni/Co (except for the M >200 fraction of Cenicerros) compared to the non-magnetic components (Fig. 3f and g). There are several possible explanations for these variations. Iron is present in silicates, sulfides and metal phases, whereas Ni is mainly present in metal phases (Larimer and Anders, 1970). Higher Ni/Fe and Ni/Co than in CI chondrites in the MTS fraction of QUE 97008 and in magnetic fractions indicate a predominance of

metal phases over silicates and sulfides in these components. The higher $D^{\text{metal/silicate}}$ of Ni compared to Co and Fe at low pressures and moderate temperatures (Schmitt et al., 1989) provides the most likely explanation of the higher Ni/Co in magnetic fractions compared to non-magnetic fractions. Thus, the variation in Ni/Co in different mineral phases would be due to metal-silicate partitioning before the accretion of the components, probably during chondrule formation. Alternatively, large variations of Ni/Co in the magnetic components of Cenicerros may represent exsolution of Ni-poor kamacite and Ni-rich taenite during cooling of metal grains. The fine grained fraction is mostly enriched in taenite and shows a higher Ni/Co ratio (Fig. 3g). Note that not all the magnetic fractions have higher Ni/Co compared to the non-magnetic fractions. The magnetic >200 fraction of Cenicerros have low Ni/Co compared to CI chondrites and all other components (Fig. 3g), which show complementary lower Ni/Co ratio compared to fine grains fractions. It indicates the higher taenite/kamacite ratio in fine grained magnetic fraction compared to coarse grained fraction.

The non-magnetic fractions of both meteorites show almost two fold variations in the abundances of Ca, Mg, Mn, Cr and S without comparable variations in Fe, Ni and Co (Fig. 3). Considering that troilite is the main sulfide phase in ordinary chondrites (Kong et al., 2000), differences in Fe and S behavior indicate that Fe abundances in the silicate phases of the non-magnetic fractions must be variable (Fig. 5). The variation of Fe is mainly controlled by different proportions of pyroxene and olivine in the non-magnetic and chondrule fractions of the meteorites (Fig. 5). The presence of minor amounts of sulfides has negligible effect on the Fe abundances of these fractions. Higher Ca, Mn, Cr and Mg in the non-magnetic components of QUE 97008 compared to the non-magnetic components of Cenicerros (Fig. 3) indicates that the non-magnetic fraction in QUE 97008 contains more pyroxenes, whereas in the non-magnetic fraction of Cenicerros, olivine and sulfides are more abundant (Fig. 3a and e). Chondrule fractions of both chondrites are depleted in the siderophile elements (HSE, Fe, Ni and Co), consistent with the results of Gooding et al., (1980).

5.2 ^{187}Re - ^{187}Os constraints on early and late fractionation processes

Significant variations in $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ are observed among the components (Fig. 4). Only the magnetic components lie close to the 4.56 Ga IIIA iron meteorite reference isochron (Smoliar et al., 1996). All other components show significant deviations from the reference isochron (Fig. 4). The magnetic components have higher Re^*/Os compared to the slightly magnetic and non-magnetic fractions (Fig. 9). Re^* is the initial undisturbed Re concentration calculated from the measured $^{187}\text{Os}/^{188}\text{Os}$, assuming that, i) the Os isotopic composition was not disturbed by later processes, ii) the initial $^{187}\text{Os}/^{188}\text{Os}$ of the solar system is 0.09524 at 4.56 Ga (Smoliar et al., 1996), and iii) $\lambda(^{187}\text{Re}) = 1.666 \times 10^{-11} \text{ year}^{-1}$ (Shirey and Walker, 1998). Re^*/Os ratios vary significantly among the components (0.06-0.213). The components of Cenicerros show a systematic increase in Re^*/Os and Pd/Ir (the time-integrated Re concentration Re^* was used here, assuming that only Re was significantly disturbed compared to other HSE during oxidation processes (Palme et al., 1998) from non-magnetic to magnetic components (Fig. 9), indicating that either fractional condensation, evaporation or another partitioning processes occurred at 4.56 Ga (the details of the processes will be discussed further below).

The deviation of components from the isochron may have been caused by irradiation in the solar nebula (Qin et al., 2015). Large variations in the neutron capture cross sections of ^{187}Os , ^{188}Os and ^{187}Re (320, 4.7 and 76 barns respectively, Mughabghab, 2003) suggest that this process could produce lower $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ than the initial isotopic composition of the Re-Os carriers. However, such a large deviation in $^{187}\text{Os}/^{188}\text{Os}$ isotopic composition due to neutron capture seems to be unlikely because similar effects have not been observed for other Os isotopes or $^{187}\text{Os}/^{188}\text{Os}$ in CAIs, which are most prone to irradiation effects compared to other chondrite components (Archer et al., 2014; Brandon et al., 2005).

Osmium isotopic homogenization during recent processes is also very unlikely, because then all components should have similar $^{187}\text{Os}/^{188}\text{Os}$ ratios, which is not the case (Fig. 4, Table 2). If partial

equilibration occurred, then complementary deviations from the isochron should be observed in the components. Yet most Cenicerros components lie on the low $^{187}\text{Re}/^{188}\text{Os}$ side of the isochron, and mass balance does not indicate a complementarity of Os isotopes in the components.

Disturbed ^{187}Re - ^{187}Os systematics in Cenicerros implies that processes other than terrestrial weathering may have played a role in the disturbance of the ^{187}Re - ^{187}Os systematics of the components of L chondrites. If interpreted as an internal errorchron, the positive correlation of the Cenicerros components yields an age of 1388 ± 670 Ma (Fig. A2), suggesting a role of late processes on the L chondrite parent body (see also Becker et al., 2001 who reported an 1.6 Ga internal errorchron for a CAI from the Allende meteorite).

Rhenium is the most refractory element under solar conditions, but also the most volatile HSE under oxidizing conditions (Palme et al., 1998), therefore redistribution of Re is the most likely reason for the resetting of the Re-Os systematics. A late exposure of the L chondrite parent body to oxidizing conditions might be the reason for local Re mobilization and partial resetting of the ^{187}Re - ^{187}Os systematics, although it is difficult to assess what the causes of these changes may have been. Despite of the similar mineralogy of slightly magnetic fractions of both meteorites (Table 1 and 2), opposite trends are observed for the measured $^{187}\text{Re}/^{188}\text{Os}$ ratios. In QUE 97008, terrestrial weathering and aqueous alteration are the likely causes of the partial disturbance of the ^{187}Re - ^{187}Os system (Dobrică and Brearley, 2011).

5.3 Origin of HSE variations in the components – volatility control or igneous processes?

The metal-rich fractions (magnetic and MTS) show enrichments in HSE compared to other components and CI chondrites (Fig. 5), consistent with the high metal-silicate partition coefficients of these elements at low pressures (O'Neill et al., 1995). The variation in Re/Os among the components (Figs. 4, 5 and 9) were discussed in the previous section.

The abundances of Ir, Ru, Pt and Rh are correlated with each other in all components and show CI chondritic relative abundances in most components (See Fig. 10). On the other hand, components such as the slightly magnetic fractions of QUE 97008, have lower CI normalized Ir, Ru and Pt abundances compared to Rh, Pd and Au (Fig. 5), suggesting a slight loss of refractory HSE compared to moderately volatile HSE. This depletion may reflect a loss of early formed refractory condensates by fractional condensation before the condensation of Fe-Ni metal, a feature that is known from enstatite chondrites (e. g., Horan et al., 2003; Fischer-Gödde et al., 2010 and Kadlag and Becker, 2015).

Lower Ni/Ir, Pd/Ir, Ru/Ir, Re/Ir and Pt/Ir ratios in the sulfide clast, non-magnetic and slightly magnetic fractions than in magnetic fractions and in CI chondrites (Fig. 10) indicate preferred partitioning of Ir into the HSE host phases of the non-magnetic components. Previous studies of L chondrite components (Rambaldi, 1976, 1977a) show similar behaviour of Ir and Os in non-magnetic fractions. Rambaldi (1976, 1977a) explained this behavior by the presence of Ir and Os enriched fine metal fractions in the non-magnetic components. Fractionations between HSE in non-magnetic and slightly magnetic fractions in the present study can be explained similarly. By contrast, lower Os/Ir and higher Re/Ir, Au/Ir, Ru/Ir, Rh/Ir, Pt/Ir/ Ni/Ir and Pd/Ir than in CI chondrites in the fine grained magnetic fractions (Fig. 10) and the MTS fraction of QUE 97008 require another explanation. Partitioning of trace elements during kamacite-taenite exsolution of the metal represents a feasible process. Nickel, Ru, Rh, Pd and Au have higher $D^{\text{taenite/kamacite}}$ compared to Os, Ir, Pt and Co (Rasmussen et al., 1988; Hsu et al., 1998; Campbell and Humayun, 2003; Ash et al., 2007). The depletion of Os and Ir compared to all other HSE (Fig. 10) in the fine grained magnetic component of Cenicerros can be explained by this process, if $D^{\text{taenite/kamacite}}$ of Pt is less than that of Os and Ir.

Solid -liquid metal partitioning processes can fractionate HSE as refractory HSE have higher $D^{\text{solid metal/ liquid metal}}$ compared to Pd and Au (e.g. $D^{\text{solid metal/ liquid metal}}$ (refractory HSE) / $D^{\text{solid metal/ liquid metal}}$ (Pd and Au) are ranging from 1.1-8, depending on the amount of non-metals such as C, S and P present in the metallic liquid, Chabot et al., 2003, 2011; Brennan and Bennett, 2010). Lower Pd/HSE in

the non-magnetic fractions can be explained on the basis of the solid metal composition which is depleted in Pd compared to refractory HSE. However, Re, Os and Ir are unfractionated and behave similarly during solid metal- liquid metal partitioning processes (Chabot et al., 2003, 2011; Brenan and Bennett, 2010). The linear variation between Re*/Os and Pd/Ir in most components (Fig. 9) is inconsistent with this fractionation process. It is more likely that the variation in HSE/Ir and HSE/Os ratios in different components are the result of the presence of Re-Os-Ir-rich alloys in the non-magnetic and slightly magnetic components.

The non-systematic variations in Au abundances with the HSE and Fe in the magnetic components of both meteorites (Fig. 7) may reflect secondary hydrothermal alteration on the parent body. Evidence of aqueous alteration on unequilibrated L chondrites has been noted in previous studies (Alexander et al., 1989; Wasson and Krot, 1994; Dobrică and Brearley, 2011). The high mobility of Au and S during hydrothermal alteration inevitably leads to changes in S/Se and Au/S (Ebihara et al., 1982; Dreibus et al., 1995). However, the correlation between S and Se (Fig. 8a) and S/Se close to CI chondrites indicate that distributions of these elements were not affected by alteration. Sulfur is decoupled from refractory HSE (e.g. Ir, Fig. 8c) and shows binary mixing relations with Au and Se abundances (Fig. 8d and 9a). Therefore, it is more likely that high-temperature processes, mixing and dilution likely control the distribution of Au, S and Se abundances. Partitioning of Au in-to sulfide phases could explain the correlations between S and Au (Fig. 8d) and decoupling of Au from Fe and Pd (Fig. 7).

5.4 Origin of variations in S, Se and Te

A first-order observation is that the calculated bulk rock abundances of Te, Se and S in L3 chondrites are depleted compared to other analyzed elements and CI chondrites (Figs. 5 and 8). An igneous processes involving sulfide-metal-silicate partitioning would strongly fractionate not only S and Se, but also the HSE (Helmy et al., 2010; Brenan, 2008; Mungall and Brenan, 2014). It is not

observed at the bulk rock scale. Therefore the higher volatility of these elements (Lodders, 2003) compared to other analyzed elements is likely the main cause of these depletions. Therefore, volatility controlled processes like partial condensation or evaporation likely have played a key role in the overall depletion of the S, Se and Te. Tellurium is predicted to be more refractory than Se and S (Lodders, 2003). Yet, almost all components display lower CI-normalized Te abundances than normalized Se and S abundances (except the Cenicerros magnetic 0-50 fraction). Either the volatility dependent loss of these elements did not occur under canonical nebular conditions, or the calculated condensation temperature for Te is incorrect. In detail, the variation of S/Se in the L chondrite components is much more simple and straightforward to explain, compared to S/Te and Se/Te (Fig. 8a and b). Clearly, Te is the element with the complex behavior. Therefore, in the next sections we will discuss the fractionation of S-Se and Te separately.

5.4.1 S-Se variations

Sulfur and Se in components of both chondrites show a linear correlation, with a S/Se slope that is close to CI chondrites (Fig. 8a). Except for the sulfide clast in Cenicerros (27.4% S and 118.7 $\mu\text{g/g}$ Se), concentrations of S and Se in the components are lower than in CI chondrites (Figs. 5 and 8a), consistent with the volatile depletion in L chondrites compared to CI chondrites. QUE 97008 is an Antarctic find and Cenicerros is a fall. However, there is no difference in the S-Se systematics in the components of the two meteorites (Fig. 8a). Slightly higher calculated bulk rock S and Se concentrations in Cenicerros compared to QUE 97008 are due to the presence of the large sulfide clast in this piece of Cenicerros. Therefore, we conclude that the effect of minor weathering (weathering grade A, Grossman, 1999) on S and Se concentrations in the QUE 97008 components and on the bulk rock of the analyzed sample is negligible. This behavior is in contrast to the Re-Os systematics, which suggests substantial internal redistribution of Re, notably in SM and chondrule fractions (Fig. 4). The difference between Re-Os and S-Se, suggests that most of the limited alteration in QUE 97008 affected metal and not troilite (evidence for the late-stage alteration of metal along fractures and at metal-silicate grain boundaries is shown in Fig. 2b, d).

Calculated bulk rock values have slightly lower S/Se compared to CI chondrites (Fig. 8a). All components of Cenicerros show slightly lower than CI chondritic S/Se, whereas components of QUE 97008 show complementary S/Se variations, with higher than CI chondritic S/Se in the non-magnetic material and slightly lower S/Se in the magnetic fractions (Fig. 8a). Two processes may be responsible for the S-Se fractionation between the components of L chondrites. The lower than CI chondritic S/Se in the components may reflect volatilization and S loss to the gas phase. However, the MTS, chondrules and non-magnetic fractions of QUE 97008 have higher S/Se and also higher S/HSE compared to the metal-rich magnetic fractions, suggesting more complicated processes. The differences of S/Se between non-magnetic ($S/Se \geq$ CI chondrite) and magnetic ($S/Se <$ CI chondrite) components in QUE 97008 are suggestive of control by metal-silicate-sulfide partitioning, as such processes also control the ratios of other moderately siderophile elements (e.g., Ni/Co, Ni/Fe, Fig. 3). The complementary variations of S/Se and Se/Te in magnetic and non-magnetic components (Fig. 8a and b) are consistent with the large differences in partition coefficients of S, Se and Te during metal-sulfide-silicate partitioning (Rose-Weston et al., 2009). Sulfide rims around silicate-rich chondrules may reflect late condensation of sulfides around chondrules (Fig. 2). Thus, these partitioning processes likely have occurred during melting, segregation and evaporation/condensation of metal, sulfide and silicates during chondrule formation, and perhaps also during diffusion of S and Se during metamorphic processes in case of secondary sulfides.

The MTS fraction of QUE 97008 shows higher S/Se than CI chondrites, and also has higher abundances of Ni, Co, HSE than CI chondrites (Figs. 3, 5, 8a). Notably, this component also shows higher lithophile element abundances compared to the magnetic fractions (Fig. 3). This unusual combination of properties is consistent with a larger proportion of high temperature condensates in this component. Because of the relatively high concentration of volatile elements (e. g., Mn, Au, S), we suggest that the MTS in QUE 97008 formed by late condensation of moderately siderophile volatile elements around refractory phase assemblages. The sulfide clast in Cenicerros has a very similar S/Se (2303) as other components and the bulk rocks of L chondrites. It may have formed by

fragmentation and melting of an earlier generation of genetically related differentiated objects. Collision with or impact on such differentiated planetesimals, might be responsible for melting and higher evaporative losses of S compared to Se.

In summary, the behavior of S and Se and other siderophile elements in the different components, along with textural evidence (Fig. 2a-d) suggests that partitioning between metal-sulfide- and silicate melts (likely during chondrule formation) was the main controlling factor in producing differences in abundances and in S/Se between different components. The distributions likely were established during chondrule formation and subsequent cooling. The data yields no evidence that terrestrial weathering had a significant influence on the bulk rock scale abundances of these elements as QUE 97008 and Cenicerros display similar behavior for S and Se. The slightly lower than CI chondritic concentrations and S/Se of both bulk rocks suggests preferred evaporative loss of S. In the bulk rock of Cenicerros, the budget of S and Se is affected by the sulfide clast, which suggests that metamorphic heating had little influence on the abundances of these volatile elements in unequilibrated L chondrites.

5.4.2 Origin of the depletion of Te in L chondrites

One of the important features in the abundance patterns is the depletion of Te compared to all other elements (Fig. 5). Only the magnetic 0-50 fraction of Cenicerros shows a Se/Te that is similar to CI chondrites (Fig. 5 and 7b). In all other components and in calculated bulk rocks, Se/Te ratios are substantially higher than in CI chondrites (Fig. 5 and 8b). The behavior of Te in the two L chondrites is different. In QUE 97008, it correlates well with Se and S and shows predominantly chalcophile behavior in all components (Fig. 8a and b). By contrast, in Cenicerros Te is decoupled from S and Se in the magnetic components compared to other components. The non-magnetic and slightly magnetic components of Cenicerros form a linear array with high Se/Te, indicating that troilite in Cenicerros contains little Te, whereas Se/Te in the three metal fractions is lower and highly variable (Fig. 8b). The variations in Se/Te among the components of Cenicerros indicate that Te preferentially partitioned

into metal (Fig. 8b, 6a, b). Results from heating experiments at low pressures on homogenized powder of Krymka (L3) and chemical equilibrium calculations suggest that in the ordinary chondrite environment, Te should be highly mobile and more volatile compared to Au, Se and S when temperature exceeds 600 °C (Ikramuddin et al., 1977a, b; Schaefer and Fegley, 2009). From these considerations, it follows that the depletion of Te compared to Se and S may be explained by volatilization during metamorphic heating. However, these are unequilibrated meteorites hence, they never experienced high temperature metamorphism. In Ceniceros, Te shows a very similar size dependent behaviour to the HSE (Fig. 6), which suggests that the predominantly siderophile behaviour of Te, acquired before accretion, has been preserved. Evaporation of Te would have resulted in random variations of Te in all components, not only in the magnetic fractions of Ceniceros. There is no systematic decrease in Te abundances were observed in the higher grade equilibrated chondrites (Freidrich et al., 2003 and 2004). The linear correlation of Te and Se defined by components and different grain size fractions in QUE 97008 (Fig. 8b) likely would not have survived substantial late element losses by evaporation. These observations and the S-Se systematics discussed in the previous section are difficult to reconcile with the notion that significant amounts of Te were lost during parent body metamorphism.

More significantly, evaporative loss of Te compared to Au, Se and S during metamorphic heating would also imply that ordinary chondrites of higher petrologic type should be more depleted in Te than highly unequilibrated chondrites. There is no evidence for greater Te depletions in the ordinary chondrites of higher metamorphic grades (Takahashi et al., 1978). In this study, the bulk rock of QUE 97008 (L3.05) shows 2.5 x higher Te abundances compared to Ceniceros (L3.7), however, if we exclude the sulfide clast from Ceniceros, then QUE 97008 has higher abundances of *all* volatile elements than Ceniceros. This difference may simply reflect sample heterogeneity or intrinsically higher abundances of volatile elements in components of the former. Similar Te-HSE systematics in the components also indicates that Te loss during terrestrial weathering is not a likely scenario (Fig. 8e).

The element systematics suggests that the Te depletion in the components of both meteorites is independent of the different geochemical behavior in the rocks and that the depletion of Te must have occurred before accretion of the components. Several different models and processes may explain the depletion of Te, from the precursors of L chondrite components before accretion.

(1) Te depletion may simply reflect fractional condensation and the loss of a Te-rich component from the region where L chondrite precursors were formed. This seems unlikely to be the case for all ordinary chondrites, because if Te was mostly siderophile, loss of Te must have occurred together with the loss of Fe metal from L and LL chondrite precursors. However, H chondrites also show Te depletions compared to S and Se (Case et al., 1973; Binz et al., 1976; Wai and Wasson, 1977). Therefore loss of Te by a simple fractional condensation process does not provide a universal explanation for Te loss from the ordinary chondrite formation region. The HSE carriers in the non-magnetic fractions are depleted in Pd compared to other HSE. Formation of Pd, Te and Bi alloys and separation of these alloys due to fractional condensation could be envisioned as has been observed in R chondrites by Bischoff et al., (2011). However, to date no evidence for the existence of telluride phases in UOC matrix has been reported, and it is unknown if such phases would have been stable in the relevant range of condensation temperatures.

(2) The depletion of Te relative to S and Se may indicate that the nebular conditions where the L chondrite precursors formed were different from the canonical solar nebula. Tellurium may have been more volatile than S and Se and thus remained in the gas phase when most of the sulfide and metal condensed and may have been lost with remaining gas (Wai and Wasson, 1977). If Te was more volatile than Se and S, it should have condensed at a lower temperature than Se and S, and should be mainly hosted by sulfides (Schaefer and Fegley, 2009), which may be the case in QUE 97008, but not in Cenicerros (Fig. 8b). In Cenicerros, most Te is present in metal. The higher condensation temperature of Fe-Ni metal (Lodders, 2003) than FeS and the siderophile to partly siderophile behavior of Te are inconsistent with the notion that Te may be more volatile than S and Se. Changes in the volatility of Te can only be reconciled with its behavior in the L chondrites if the siderophility

of Te was inherited from melting, evaporation and recondensation processes during chondrule formation. In any case, the data shows that the chemical affinity and condensation temperature of Te is highly variable and may be affected by the composition of residual gas from condensation or evaporation processes.

6. Summary and conclusions

Inverse relationships between HSE abundances and grain size suggest that the HSE (and most Te in Cenicerros) preferentially partitioned into Fe-Ni metal in magnetic components. Metal-sulfide-silicate partitioning likely occurred before accretion of the components. Solid metal-liquid metal partitioning is of limited importance as it cannot explain the observed HSE systematics among the components.

The variation of $^{187}\text{Os}/^{188}\text{Os}$ in the components of Cenicerros follows the order $^{187}\text{Os}/^{188}\text{Os}_{\text{SNM}} < ^{187}\text{Os}/^{188}\text{Os}_{\text{SSM}} < ^{187}\text{Os}/^{188}\text{Os}_{\text{SM}}$ (also Pd/Ir show similar behavior). This systematic difference likely reflect slight differences in the partitioning of Re, Pd, Os and Ir in different components or the volatility-controlled loss of Re and Pd compared to other HSE from the HSE carriers in non-magnetic components. As in H chondrites (Horan et al., 2009), unequilibrated HSE carriers (Fe-Ni metal) with different HSE patterns are observed in L chondrite components. One carrier is characterized by CI chondritic ratios of refractory HSE and slightly higher Rh/Ir, Pd/Ir and Au/Ir. The smooth depletion of Pd, Au and Te with respect to Ir in the second HSE carrier phase may have formed by fractional condensation. The latter carrier is more refractory and condensed before the full condensation of moderately volatile elements. The depletion of refractory elements ($T_{\text{condensation}} > 1400 \text{ K}$) compared to moderately volatile elements such as Mn ($T_{\text{condensation}} < 1400 \text{ K}$) is the effect of fractional condensation and loss of earlier formed refractory phases.

The loss of tellurium was inherited from precursor dust (because it is mostly contained in metal and depleted in all components) and may have occurred due to melting of the metal grains and subsequent changes in the volatility of Te relative to Se and S. Loss of Fe in the form of low temperature metal may also explain the Te depletion compared to HSE in magnetic components, but it is less likely, because H chondrites also show similar Te depletion (Case et al., 1973; Binz et al., 1976; Wai and Wasson, 1977). Tellurium and to some extent Se are more siderophile than sulfur (Rose-Weston et al., 2009), indicating incorporation of these elements into S bearing metal melt during high-temperature processing before accretion of the components.

The depletion of Se and S may have occurred either during melting and evaporation in the process of chondrule formation or from precursor gas due to incomplete condensation of volatiles or both. Tellurium is less volatile than Se and S under canonical solar nebula conditions (Lodders, 2003). The depletion of Te compared to S and Se by volatility-controlled processes requires that Te was more volatile than S and Se at some stage of the formation of L chondrites. The observed depletion suggests that condensation or evaporation of Te occurred significantly below 600 K and thus most Te should have condensed into FeS, which is not observed in Cenicerros. If Te is more refractory than S and Se (Lodders, 2003), then it must have been lost with metal due to melting and evaporation of metal grains. Similar siderophility and the size dependent behaviour of Te and the HSE (Fig. 6) support this scenario. Tellurium abundances in L3 bulk rocks vary by a factor of 7 or more (Keays et al., 1971; Case et al., 1973, Binz et al., 1976; Kaczaral et al., 1989) indicate that heterogeneous recondensation of evaporated Te on metal grains might be the reason for Te depletion in the ordinary chondrites. The observed depletion requires that Te should be either significantly more refractory or more volatile than the conditions of troilite recondensation. The depletion of Te can be explained if re-condensation of Te on metal was inhibited by condensed troilite rims around metal and thereby the loss of remaining volatile siderophiles either in gas phase or dust alloys. The sulfide rims around the metal grains in matrix may represent such scenario.

The studied L chondrite aliquots show little evidence for an influence of terrestrial weathering on the S-Se-Te systematics of the components and bulk rocks. On the other hand, measured Re/Os show large random variations in QUE 97008, indicating that terrestrial weathering may partially reset the ^{187}Re - ^{187}Os systematics of metal bearing components in chondrites. Rhenium is most strongly affected by terrestrial weathering of Fe-Ni metal.

The existence of components with distinct Re*/Os, Pd/Ir and Au/Ir in unequilibrated chondrites from different chondrite classes (this work, Horan et al., 2009; Kadlag and Becker, 2015) indicates heterogeneous sampling of nebular material. These HSE carriers have undergone siderophile element fractionation processes before accretion and never equilibrated after accretion. The different origin of such components in unequilibrated chondrites should be considered in chronological studies using short-lived nuclides and in studies of isotopic variations of nucleosynthetic origin.

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Fig.1. A flowchart representing the temporal sequence of mechanical and magnetic separation procedure of the separates of the QUE 97008 and Cenicerros.

Metal grains in matrix having sulfide rims shown by red dashed circles

Alteration veins

Sulfide rim

Metal grains with sulfide rims

Fig.2 Backscattered electron images of QUE 97008. a) Overview. b) Spherical chondrule with discontinuous zone of metal droplets near the chondrule margin and continuous sulfide rim outside the chondrule. No sulfide phases are present inside this chondrule. Secondary veins occur in the chondrule. c) Irregular shaped chondrule with sulfide rim. d) Metal grains from the chondrule shown in b) display taenite-kamacite exsolution, T= taenite and K= kamacite. The taenite grains are smaller compared to kamacite, and may represent the Ni rich metal in the smallest size fractions. e) Enlarged image of a part of the chondrule from b), Ol = olivine, Py = pyroxene and M = metal. Pyroxene rims around sub- to euhedral olivine likely were formed from the interaction of olivine with remaining silicate melt and gas.

Fig.3 a) Mn-S, b) Mn-Cr, c) Mn-Mg, d) Mg-Fe, e) Ca-Mg, f) Ni-Fe and g) Ni-Co. Triangles: Cenicerros, diamonds: QUE 97008. M: magnetic, SM: slightly magnetic, NM: nonmagnetic, MTS: metal-troilite spherules. CI chondrite data (Lodders, 2003) are shown as the red circles. Black symbols show the calculated bulk rock values from the mass balance of all analyzed components. Gray symbols shows literature bulk rock data for L3 chondrites (sources are mentioned in the caption of Table 1). The dotted and dashed areas in a), b) and d) indicate the grouped variation of the components of Cenicerros and QUE 97008, respectively. Mn, Mg and Ca abundances are controlled by silicate phases. Lower than CI chondritic Ca/Mg in most components indicates the loss of refractory lithophile elements. Fe and S abundances are mainly controlled by variable proportions of sulfide and metal in the components. Most components have CI chondritic Ni/Co. Magnetic components of Cenicerros show large variations in Ni/Co ratio from CI chondrites. Higher Ni/Co in some magnetic fractions results from preferred sampling of exsolved taenite.

Fig.4 ^{187}Re - ^{187}Os isochron diagram of analyzed components of a) QUE 97008 and b) Ceniceros. Reference line is the 4.56 Ma IIIA iron meteorite isochron (Smoliar et al., 1996). CI chondrite data and bulk rock data of Ceniceros from Fischer-Gödde et al. (2010) and Walker et al. (2002), respectively. The components of Ceniceros show a linear trend, whereas components of QUE 97008 show random variations, likely caused by redistribution of Re during terrestrial weathering.

Fig.5 HSE, chalcophile elements, Ni, Co and Fe concentrations in the components of the QUE 97008 and Cenicerros normalized to CI chondrites. Elements are ordered from left to right in increasing order of volatility, assuming the 50% condensation temperature in the solar nebula by Lodders (2003). Differences in the symbol size of some components indicate different grain size fractions (numbers given in the legend represent size fractions). CI chondrite values from Dreibus et al. (1995), Horan et al. (2003), Fischer-Gödde et al. (2010) and Wang et al. (2013, 2014). Bulk rock HSE data for Cenicerros from Horan et al. (2003). Bulk rock chalcogen element and Ni, Co and Fe data for both meteorites are L3 chondrites average values (Yasinskaya and Osadchij, 1973; Kirova et al., 1975; Graham et al., 1976; Fitzgerald, 1979; Haramura et al., 1983; Jarosewich, 1984, 1990; Fulton and Rhodes, 1984; Fredriksson et al., 1986; Hewins et al., 1988; Ebihara, 1989; Kaczaral et al., 1989; Kallemeyn et al., 1989; Graham, 1993; Wasson et al., 1993; Ebihara and Ozaki, 1995; Yanai et al., 1995; Kong and Ebihara, 1996; Bhandari et al., 2002; Horan et al., 2003).

Fig.6 CI-normalized abundances of a) S, Se and Te, b) HSE, c) Fe, Ni and Co, d) Cr, Ca, Mg, Mn and Fe of magnetic components of Cenicerros are shown as a function of grain size fraction. Gold is decoupled from the HSE and shows a similar size dependent behavior to S and Se. All other HSE and Ni show similar size dependent behaviors. The decoupled behavior of Fe, Co and Ni in the magnetic fractions of Cenicerros is likely the result of kamacite-taenite exsolution. The abundance variations in the magnetic components of QUE 97008 between grain size fractions are shown in the e) S, Se and Te, f) HSE, g) Fe, Ni and Co, h) Cr, Ca, Mg, Mn and Fe. All HSE, except Au, show similar size dependent behaviors in the magnetic components and are decoupled from Fe, Co and Ni (b and c). These variations indicate that either HSE carrier phases other than Fe-Ni metal alloys exist in the magnetic components, or the HSE carriers were not completely equilibrated with Fe-Ni metal.

Fig.7 a) Pd-Au and b) Au-Fe variation among the components of QUE 97008 and Cenicerros. The Au abundances in the magnetic components are decoupled from Fe and Pd, indicating that the process that caused the variation of Au in the magnetic fractions is independent of the fractionations of other HSE.

Fig.8 a) S-Se variations showing a linear relationship between S and Se for all components of both chondrites. Sources of the bulk rock data are given in the caption of Table 1. In the case of QUE 97008, two components with complementary S/Se exist, whereas in case of Ceniceros all components have lower than CI chondritic S/Se. b) Te-Se variations among the components of QUE 97008 and Ceniceros. QUE 97008 components show a linear relationship (indicated by dashed field) between Te and Se indicating the chalcophile nature of Te. In contrast, $Te/Se_M \gg Te/Se_{NM}$ in the components of Ceniceros suggesting a predominantly siderophile behavior of Te in this meteorite. c) S-Ir, d) S-Au and e) Te-Ir variations among the components indicate that the SM and NM components have nearly CI chondritic S/Au, S/Ir and Te/Ir ratios. S-HSE variations in the components indicate two-component mixing of CI chondritic material in NM and some SM components, and volatile depleted material in M components. The S/Ir variations are more complex and involve mixing of at least two different carriers which have lower than CI chondritic S/Ir (shown by dashed lines) with CI chondritic S/Ir. The data also indicates that the S loss with respect to HSE may have occurred during the thermal processing of magnetic components.

Fig.9 a) Re^*/Os - Pd/Ir variation in the components of QUE 97008 and Cenicerros. Re^* is the calculated Re concentration from the measured Os isotopic composition. Components of Cenicerros show a correlation between Re/Os and Pd/Ir (dashed field indicates the variation in the components of Cenicerros). The NM and SM components have lower Re^*/Os and Pd/Ir compared to the M components and the chondrule fraction of Cenicerros. No systematic variation is observed in the case of QUE 97008.

Fig.10 a) Re-Ir, b) Au-Ir, c) Rh-Ir, d) Ni-Ir, e) Os-Ir, f) Ru-Ir, g) Pt-Ir and h) Pd-Ir variation in the components of QUE 97008 and Cenicerros. Components with higher Ni/Co (< 50 fraction of Cenicerros and MTS fraction of QUE 97008, see Fig.2g) show higher HSE/Ir (except Os/Ir), likely due to their preferred partitioning into taenite compared to Ir (see text).

Fig.A1 An internal errorchron defined by components of Cenicerros, calculated by using Isoplot 4 (Ludwig, 2008), yields an age of 1388 ± 670 Ma, presumably indicating late alteration on the L chondrite parent body.