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MINOR AND TRACE ELEMENT CONCENTRATIONS IN ADJACENT KAMACITE AND TAENITE IN THE KRYMKA CHONDRITE.

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Abstract

We report in situ NanoSIMS siderophile minor and trace element abundances in individual Fe-Ni metal grains in the unequilibrated chondrite Krymka (LL3.2). Associated kamacite and taenite of 10 metal grains in four chondrules and one matrix metal were analyzed for elemental concentrations of Fe, Ni, Co, Cu, Rh, Ir and Pt. The results show large elemental variations among the metal grains. However, complementary and correlative variations exist between adjacent kamacite-taenite. This is consistent with the unequilibrated character of the chondrite and corroborates an attainment of chemical equilibrium between the metal phases. The calculated equilibrium temperature is 446 ± 9 °C. This is concordant with the range given by Kimura et al. (2008) for the Krymka post-accretion thermal metamorphism. Based on Ni diffusivity in taenite, a slow cooling rate is estimated of the Krymka parent body that does not exceed $\sim 1 \text{K/Myr}$, which is consistent with cooling rates inferred by other workers for unequilibrated ordinary chondrites. Elemental ionic radii might have played a role in controlling elemental partitioning between kamacite and taenite. The bulk compositions of the Krymka metal grains have non-solar (mostly subsolar) element/Ni ratios suggesting the Fe-Ni grains could have formed from distinct precursors of non-solar compositions or had their compositions modified subsequent to chondrule formation events.

1. INTRODUCTION

Metal is one of the major constituents in most chondritic meteorites, and iron and nickel alloys are among the products to condense in the solar nebula (Grossman 1972; Grossman and Olsen 1994). Studies of individual metal grains in several primitive chondrite classes have shown that processes such as chondrule formation and parent body metamorphism were determinant in fixing the final chemical compositions of phases like kamacite and taenite. These studies have been conducted on major and minor elements like Ni and Co, mineral inclusions-forming elements like Si, Cr, P, and C in kamacite and taenite (Afiatallab and Wasson 1981; Rambaldi and Wasson 1981 & 1984; Perron et al. 1992; Lee et al. 1992; Zanda et al. 1994; Mostefaoui et al. 2000; Connolly et al. 2001; Kimura et al. 2008; Wasson and Rubin 2010), or on trace metals like platinum-group-elements PGEs of bulk individual metal grains (Rambaldi 1977; Ikramuddin and Binz 1977; Kong and Ebihara 1997; Campbell and Humayun 2003 & 2004; Jacquet et al. 2013).

As to the origin and evolution of the metal and their mineral phases in primitive chondrites, a number of questions have been raised, in particular the following two: 1- What process (es) fixed the metal composition? More precisely, when the metal became a closed system, i.e. chemically separated from its surrounding environment? 2- When and how its main phases, kamacite and taenite, have ceased to exchange chemically with each other to acquire their final compositions? To answer the first question, two hypotheses have been proposed. The first considers the metal as an unmodified condensate from the gas of the nebula (Olsen et al. 1973; Grossman and Olsen 1974; Grossman et al. 1979; Rambaldi et al. 1980). The second advocated elemental reduction in metal during chondrule formation (Scott and Taylor 1983; Zanda et al. 1994; Lauretta et al. 2001). Arguments exist for each of these two hypotheses.

The second question addresses the issue of the formation of kamacite and taenite in primitive chondrites, which remains poorly understood: When they have formed and what phase formed first? The Fe-Ni phase diagram tells us that taenite is the stable phase at high temperature, and then with decreasing temperature kamacite starts to form at the expense of the taenite (Reuter et al. 1989). However, if this happened during the brief chondrule formation events, fast cooling would first form martensite (Kaufman and Cohen, 1956), which is incoherent with major observations of metal in primitive chondrites (Afiatallab and Wasson 1981; Rambaldi and Wasson 1981 & 1984). Following this reasoning, the kamacite and taenite would have formed, or maybe completed their formation, during thermal metamorphism, and only then after some stage of cooling would the phases cease their mutual chemical exchange.

The study of individual metal grains in primitive chondrites for their minor and trace element compositions in adjacent kamacite/taenite is a key to test this hypothesis. Assessing minor and trace element concentrations in chondritic metal as well as their fractionation behavior between the constitutive metallic phases enables understanding the mechanisms controlling their distribution and thermal history. Although PGE concentrations in adjacent kamacite and taenite have been determined in a number of iron meteorites using techniques such as INAA, ICPMS and SIMS (Rasmussen et al. 1988; Hirata and Nesbitt 1997; Campbell and Humayun 1999; Hsu et al. 2000), they have remained inaccessible in chondrites due to the technical difficulties of measuring low concentration elements in small metallic phases.

The high sensitivity and spatial resolution of the NanoSIMS have made possible the measurement of trace elements in situ in individual kamacite and taenite grains in the Krymka unequilibrated chondrite. We report the first systematic siderophile trace element study of

adjacent kamacite/teanite in a chondrite. Our data allow us to shed some light on the conditions under which the Fe-Ni metal in Krymka is formed and evolved throughout its thermal history.

2. EXPRIMENTAL

2.1. Sample preparation

A one-inch epoxy-mounted polished thin section of the Krymka (LL3.2) unequilibrated ordinary chondrite sample MNHN-3440 was examined by optical microscopy and by a JEOL JSM-840A Scanning electron microscope (SEM) at the Muséum National d'Histoire Naturelle MNHN for locating suitable Fe-Ni metal grains with adjacent kamacite and taenite phases (Fig. 1). Depending on whether we opted for SE/BSE imaging or qualitative analysis of elemental concentrations, the working distance was set either to 8 or to 39 mm. The EDX analyses were carried out at an accelerating voltage of 20kV and a beam current of about 10 nA. A second, higher performance, Tescan VEGA II LSU SEM at the MNHN was used as well in order to acquire semi-quantitative X-ray maps of the elements Fe, Ni, Cr, P and S using a SD³ Bruker Energy Dispersive Spectrometer detector. Using an accelerating voltage of 15kV and working distance of 15.7mm, the image acquisition time was set to about two hours to produce maps of 1024x1024 pixels.

Quantitative analyses of metal (Fe, Co, Ni and Cu) were carried out with the CAMECA SX-100 electron microprobe (EPMA) equipped with wavelength dispersive spectrometers at UPMC in Paris. Measurements were performed at 15 kV accelerating voltage, using a beam current of 10 nA for Fe and Ni, and 300 nA for Co and Cu. In addition, two spectrometers were used simultaneously for both Co and Cu in order to improve statistics for these relatively low concentration elements. Fe-Ni alloys (0, 9.6, 17 and 30% Ni) were analyzed in order to

improve the background correction to Co (for the contribution of $Fe_{K\beta}$) and Cu (for the

contribution of Ni_K $_{\beta}$) (see Afiattalab and Wasson 1980). Under these conditions, the detection limits are 0.1 % (Fe), 0.14 % (Ni), 50 ppm (Co) and 60 ppm (Cu). The 2 σ error on both Co and Cu is 20 ppm. A polished section of Coahuila iron meteorite was analyzed repeatedly during the analytical sessions.

Because the electron microprobe was used after the NanoSIMS measurements, we had difficulties to find zones in Krymka metal not bombarded with the ion beam. Some grains have taenite almost completely consumed during the bombardment. Considering that clean and flat surface is a necessary sample condition for a reliable EPMA analysis, to avoid experimental artifacts our measurements were only limited to three grains (kamacite and taenite in two grains and kamacite in one grain). Besides, the interpretation of the data should not overlook such a context.

2.2. NanoSIMS analytical procedure

Analysis of major (Fe and Ni), minor (Co and Cu) and trace (Ir, Pt, Rh and Ag) elements was performed by using the MNHN Cameca NanoSIMS-50 ion microprobe. A 16 keV Cs⁺ primary ion beam with a spot diameter of $\sim 2\mu m$ and an intensity of $\sim 1nA$ through D1-2

diaphragm was used to sputter negative secondary ions of ⁵⁶Fe, ⁶²Ni, ⁶⁵Cu, ⁵⁹Co, ¹⁹⁸Pt, ¹⁹³Ir, ¹⁰³Rh and ¹⁰⁹Ag. A combined mode of two magnetic fields was applied using five electron multiplier EM detectors (Table 1). The metal grains were measured by ion image scanning over areas $15x15\mu m^2$ of 128x128 pixels with a total number of 10 cycles. In order to remove coating, initial surface contamination and to reach a steady-state regime, sample presputtering was performed for 14 minutes under conditions similar to those used for analysis. The limited size of the primary beam permitted us to measure some taenite grains in Krymka without the contribution of the coexisting generally larger kamacite. A high mass resolving power of ~9000 (Cameca definition) was used in order to resolve secondary ion beams from various molecular interferences. Fig. 2 shows typical peak shapes and interferences around the measured masses. For ⁵⁶Fe, ⁶²Ni and ⁶⁵Cu the Fe-Ni matrix does not show significant isobaric interferences. For ⁵⁹Co, care is required because of close molecular interferences such as 58 NiH (Fig. 2). We thus systematically controlled the peak shape and positioned the deflector voltage in the leftmost flat top part of the ⁵⁹Co peak. ¹⁹³Ir and ¹⁹⁸Pt, for which we expect small signals because of their low concentrations, do not exhibit significant isobaric interferences and can be resolutely measured (Fig. 2). Despite the high mass resolution we had strong interference problems for ¹⁰⁹Ag and to a lesser extent for ¹⁰³Rh. The former shows extremely low signals and is positioned at the shoulder of a large unidentified interference peak. ¹⁰³Rh has also an interfering peak at the low-mass side that can be significant at low count rates.

As reference materials, we first used pure native element minerals and high elemental concentration standards in order to identify the desired high mass range trace elements peaks. These were extremely helpful in order to confirm the respective positions of the masses from isotopic signals. NIST standard reference materials SRM-661 and SRM-663, and the Gibeon iron meteorite (Table 2), containing 1.99 wt%, 0.32 wt% and 7.93 wt% of nickel, respectively, were used as reference materials to calibrate data in kamacite and a synthetic 51.5%Ni Fe-Ni metal alloy was used to calibrate data for taenite. Because only Fe and Ni concentrations are known in the Ni-rich synthetic standard, it was used for calibrating Ni in the taenite. Due to the scarcity of standards with known homogenous PGE concentrations, both minor and trace elements in taenite are calibrated with the NIST and Gibeon metal standards, assuming the effect of Ni on iron yields for these elements are minor. In this context, Hsu et al. (2000) noted that Ni matrix effect serves to lower ion yield in high Niphase. Their results were based on the measurement of a standard with 99% Ni, which is an entirely different matrix from the taenite. The authors could not resolve a dependence of ion yields over the range of Ni content, which certainly affects the accuracy for extrapolating the calibration to 50% Ni. We assume the Ni matrix effect for taenite do not affect much the calibration of minor and trace elements. Anyway, in no case would it lower the minor and trace element concentrations by more than 20%.

Despite the prolonged pre-sputtering time for Cs^+ implantation, the ion yields, defined as counts per second/nA/ppm remained unstable. This is clearly seen in the standards we measured (Fig. 3) in which the ion yields varied from spot to spot, in some cases by more than one order of magnitude. Since ion yields for the elements correlate with those for Fe (Fig. 3), we adopted the same method applied by Hsu et al. (2000) for iron meteorites to quantify ion signals-to-elemental abundances. The method consists in converting the Fe ion signal to ion yield knowing the ion current and Fe concentration (see Table 3), then deducing the elemental concentration of the desired element from its NanoSIMS measured signal and the corresponding correlation in Fig. 3. For ¹⁰⁹Ag, we unfortunately cannot apply this method

because of the lack of any correlation with Fe ion yield (Fig. 3). This is probably due to the contribution of unresolved intricate interferences on the ¹⁰⁹Ag peak. So, for this element no concentrations were determined.

The NanoSIMS ion images were processed with the L'IMAGE Software. To get the integrated signal of analyzed elements from the ion images we defined regions of interest (ROIs) for each kamacite and taenite in the Krymka metal grains. The generally small size of the analyzed taenite grains together with the relatively large Cs^+ ion beam on the sample surface restricted our ROIs for this phase. The ROIs must be small to avoid contribution from the surrounding kamacite but not too small in order to ensure reasonable counting statistics. This limitation made the contribution of kamacite unavoidable for some taenite grains with a small surface area. From the Ni measured in "mix" taenite/kamacite ROIs and the Ni concentration determined by SEM on the taenite alone (Table 3) we evaluated the fractional contribution of the surrounding kamacite (Table 4). We found that half of the analyzed taenites have more than 10% contribution from surrounding kamacite, with the highest being 84% for 1ch1c. Such a contribution, if not corrected for, would led to calculated concentrations of elements in taenite farther from their actual values. This is particularly pertinent for elements highly partitioning in favor of kamacite like Co, or whenever the kamacite contribution is too high (Table 4). Knowing the NanoSIMS elemental concentrations of the surrounding kamacite, we recalculated by mass balance correlated elemental concentrations in taenite (see Appendix A). This was done for all the taenite grains we measured in Krymka. As expected, the highest correction was on 1ch1c taenite for which Co corrected concentration is diminished by more than 70% and Cu and Rh augmented by about a factor of two. For Ir and Pt, the correction in most cases does not exceed 30%, which can be understood from their generally close kamacite and taenite concentrations.

Evaluating the precision and accuracy of the NanoSIMS results requires knowing the source of the errors and their propagation through the data. The two main sources of uncertainties are the counting statistics and the reproducibility of the standards. The counting statistics are the major source of uncertainty for the elements Ir, Pt and Rh as they contribute on average of more than 90% of the total uncertainty. This is also valid, to a lesser extent, for Co in taenite and for Cu in kamacite. As the ion yields of analyzed elements are variable, a precise determination of the reproducibility by comparing the standard measurements cannot be obtained. Yet from the ion yield correlations (Fig. 3) one can evaluate uncertainties on the slope and on the intercept. They range up to about 2% (2σ) (with averages about 0.8%) for all elements except for Rh, for which 3.4% and 6.3% uncertainties are calculated for the slope and the intercept, respectively. In the taenite, to this uncertainties will be added uncertainties due to the correction from the contribution of kamacite (see Appendix A). These are estimated to range from 1% to 1.7% for all corrected taenite grains except for 1ch1c for which the uncertainties are considered for the final data output.

3. PETROGRAPHIC CONTEXT

Previous studies of Krymka showed it is composed of shocked and unshocked lithologies (Semenenko et al. 1987; Semenenko and Perron 2005). The Krymka specimen MNHN-3440 used for this study (Fig. 1) is from material without any visible effects of shock. It is thus appropriate for the study of secondary events such as thermal metamorphism. The total area of 310 mm² of the sample was searched for metal grains with associated kamacite-taenite. These grains were selected upon two criteria: 1- The kamacite and taenite phases must be in

direct contact with each other without any intermediate oxidation boundary or other phase separating them. This is important to ensure that predictable elemental diffusion between the two phases should not be subjected to any factor except for temperature drop. 2- With the nominal NanoSIMS Cs⁺ beam size of ~2 μ m, the analyzed kamacite and taenite areas must be large enough to allow elemental measurements of the individual phase by limiting mutual contributions. Using these two criteria, a total of 10 metal grains (9 in four chondrules and one large matrix metal-troilite assemblage) were successfully measured with the NanoSIMS. The chondrules are typical type I and type II (Fig. 4) with textures ranging from porphyritic to micro-porphyritic. Chondrule 1ch1 is a micro porphyritic olivine (PO) with groundmass glass. Its metal grains are mostly situated in the outer part of the chondrule. The other three chondrules are porphyritic olivine and pyroxene (POP). Dusty olivine is present in 1ch1 and 7ch5, indicating olivine reduction and formation of dusty metal during chondrule formation. Chondrule 8ch4 is a type II with minor glass. Table 5 summarizes the textures and the Fo-En contents of the silicates in the chondrules and their variations.

Most of the metal grains in the investigated chondrules exhibit round shapes (see Fig. 5a,b,c,d,f,g). They range in size from 18 to 110 μ m (Table 3). Eight of them are composed exclusively of associated kamacite and taenite. The Ni content of the taenite indicate that tertataenite (an ordered structure with 48-57 wt% Ni; Clarke and Scott, 1980) is probably dominant (Table 3). In two grains kamacite is associated with more than one taenite crystal (1ch1a and 8ch4a, Fig. 5a,e). One metal grain (11ch1b, Fig. 5g) contains also troilite. The kamacite in this grain is polycrystalline. At least five differently orientated crystals can be seen according to their distinct BSE image contrasts (outlines in white dashed lines in Fig. 5g). This effect comes from the difference in density of the exposed orientations, not from compositional differences.

An elemental SEM X-ray map of the metal grain 11ch1b is shown in Fig. 6. The Fe-Ni phases are homogeneous in composition. Profiles of Fe and Ni concentrations across kamacite-taenite-kamacite interfaces are shown (Fig. 6) from spots measured every 0.5 micrometers. There is no zoning at the level of the defined steps. Cr is present in and around the metal as micrometer to sub-micrometer sized inclusions of chromite. Also, P forms visible Caphosphate crystals along the border of the grain. Such inclusions are typical of unequilibrated ordinary chondrites and are known to result from diffusion followed by oxidation during mild thermal metamorphism of previously dissolved Cr and P in metal, presumably during high temperature chondrule formation events (Zanda et al. 1994; Perron and Denise, 1992; Perron et al. 1992; Mostefaoui 1996). The homogeneity issue is corroborated more quantitatively for the kamacite in grain 11ch1a using electron microprobe. Thirteen measurements spreading over the phase and far away from the NanoSIMS scanned zone gave variations of 0.2%, 6% and 2% for Fe, Ni and Co, respectively (Table 3). The large variation for Cu (33%) is quite reasonable as the concentration values are close to detection limit.

Metallic assemblages are rare in the Krymka matrix (Fig. 1). Most of them are fine-grained and exclusively consistent of individual kamacite with minor tetrataenite (Rambaldi and Wasson 1984). The kamacite occurs in assemblages described by Rambaldi and Wasson (1984) as metal-sulfide nodules. Those with adjacent kamacite-taenite phases are extremely rare. Only one grain satisfying our criteria was found. It is composed of a complex association of kamacite, taenite, troilite, and silicate, surrounded by a thin rim of fine-grained silicates and Fe-oxide (Fig. 5h). A small taenite crystal in kamacite is visible in the lower right side of the image. Its Ni content indicates it is probably tetrataenite (Table 3).

4. NANOSIMS RESULTS

Table 4 summarizes our NanoSIMS results for the 10 investigated metal grains. While the large size of taenite in grain 11ch1b allowed measuring the kamacite and taenite in separate $15x15 \ \mu\text{m}^2$ scans, the phases in the nine others have been measured in single scans. ROIs delimiting these phases, for which the pixels are added up, permit to determine elemental concentrations. Fig. 7 shows ion images of grain 1ch1a and its kamacite and taenite ROIs. Since Ni was used to calculate the contribution of kamacite to the taenite ROIs (see Section 2), the values of Ni in taenite in Table 4 are those measured by SEM. Thus all taenite results but Ni are the NanoSIMS values corrected for kamacite contributions.

The results (Table 4) show that there are large variations in elemental concentrations among the kamacite and taenite grains, including metal grains within the same chondrules. The Ni and Co values are consistent with typical compositions of Krymka metal (Rambaldi and Wasson 1984). The Ni and Co concentrations in the extrachondrule kamacite grain are 3.5 wt% and 1.07 wt% respectively (Co is up to 4x higher than that in chondrule kamacite). These observations, and Ni and Co concentrations in taenite, are in agreement with the observations of Rambaldi and Wasson (1984) with respect to the occurrence of the metal (i.e. in chondrules and extrachondrules). We note that the EPMA/SEM-EDX Ni concentration values (see Table 3) are systematically higher than that from NanoSIMS, even though they are not drastically different. Also, the Co and Cu electron microprobe concentrations in the three grains 11ch1a, 11chab and 1ch1a (Table 3) are coherent with the corresponding NanoSIMS results. All taenite grains exhibit higher abundances of Cu than the adjacent kamacite grains with differences of up to 50 times in 11ch1b. There is no minor or trace element compositional peculiarity between taenite and tetrataenite. For the trace elements Rh, Ir, and Pt, the differences between kamacite and taenite are much less pronounced. Nevertheless, in chondrule metal there is a tendency for Ir to be higher in kamacite than in taenite. In the extrachondrule metal grain the tendency seems to be reversed, with Ir about an order of magnitude lower than that in chondrule metal. Extrachondrule metal seems so distinctive not only by its high Co, but also by its extremely low Ir (0.01 wt% and 0.03 wt% in kamacite and taenite, respectively; Table 4). The concentration of Pt in the metal is systematically higher than that of Ir, with a subtle affinity to taenite in most chondrule metal grains. The metal in the type II 8ch4 chondrule shows the highest Ir and Pt concentrations in kamacite (1.14 ppm and 11.28 ppm, respectively) and in taenite (5.89 ppm and 10.08 ppm, respectively). These Ir and Pt concentrations differ significantly from those of type I chondrules and the extrachondrule metal grains. These compositional discrepancies corroborate the hypothesis of a genetic difference between extrachondrule, type I chondrule and type II chondrule metal.

5. DISCUSSION

In contrast to previous studies of minor and trace elements in kamacite and taenite, which focus on comparisons between various types of meteorites, including irons and chondrites, our study is the first devoted to the measurement of these elements in associated kamacite-taenite grains in a chondrite. Our results can provide a better understanding of the chemical behavior of these elements in metal phases in chondrites. We will address a number of questions related to the formation conditions of the metal grains in Krymka and attempt to shed some light on the thermal events through which the metal might have gone.

5.1. Origin of metal and the final chemical composition of kamacite and taenite

The results described above show a large range of chemical variations among the metal particles in Krymka, which is consistent with the unequilibrated nature of this chondrite (Rambaldi and Wasson, 1984). The variances in elemental concentrations of the associated kamacite-taenite pairs are likely to reflect initially distinct bulk compositions and/or changes due to the thermal histories of the metal particles. To understand the origin of these variations it is essential to understand the conditions experiences by the grains in order to evaluate their effects on the chemical compositions of the metal particles.

Before their accretion into a chondritic parent body, the metal particles are either solar nebula condensates, reduction products of chondrule formation, grains from fine matrix whose origin is controversial, or mixtures of all or parts of these components. Studies of bulk minor and trace element contents of individual metal particles in the least equilibrated chondrites indicate that metal can be the result of reprocessed precursors during chondrule formation events (Campbell and Humayun 2004; Kong and Ebihara, 1997). In the carbonaceous CR chondrites, which have presumably escaped thermal metamorphism, metal shows a solar Co/Ni ratio, interpreted as condensation from a gas of solar composition (Weisberg et al., 1993; Weisberg 1995). More recent studies of minor and trace elements including PGEs in Renazzo metal have stressed more quantitatively the role of oxidation/reduction during chondrule formation in producing the observed correlative trends (Connolly et al. 2001; Humayun et al. 2002; Campbell et al. 2005; Jacquet et al. 2013). In ordinary chondrites, Fe reduction during chondrule formation has also been suggested (Kong and Ehibara 1997) as well as interaction of different, FeS-bearing, precursor materials with gas during chondrule formation, and processes like evaporation, recondensation and sulfidization (Hewins et al. 1997; Yu et al. 1996; Zanda et al. 1996).

The compositions of the metal particles in Krymka could have been established prior to accretion. In such a scenario, the metal grains would not have necessarily evolved under the same conditions and therefore their bulk chemical compositions would not be expected to be the same. To test this hypothesis we need to assess the bulk chemical compositions of the individual metal particles we studied which is a difficult task because we only have compositions of kamacite and taenite of the exposed surfaces of the grains. Nevertheless, some constraints are available from the taenite and kamacite measurements. In Fig. 8 we plotted Co, Cu, Ir, Pt and Rh vs Ni in kamacite and taenite. Except for Co, the elements show subsolar element-to-nickel ratios in both kamacite and taenite (we do not give much weight to Rh because of potential analytical difficulties, see analytical part). Therefore, from mass balance considerations the bulk Ir/Ni, Pt/Ni, and Cu/Ni ratios in these grains must also be subsolar. For Co, the Co/Ni ratios of kamacite and taenite are opposed to each other relative to solar ratio (see Fig. 8). Whether the bulk Co/Ni ratios of the grains are solar depends on the taenite/kamacite volume fractions. Table 6 shows our calculated taenite volume fraction $X_{\rm T}$ and the corresponding bulk elemental concentrations and element/Ni ratios based on a solar Co/Ni ratio of the grains. The calculated Ir/Ni, Pt/Ni and Cu/Ni ratios are essentially subsolar (the ratios for Ir and Pt in grain 8ch4a are supersolar) suggesting that the grains are presumably reflecting non-solar ratios. It can be argued that the calculated X_T fractions of the grains are not accurate because Co and Ni are perhaps not siderophile enough to be used for the test. Ir and Pt are highly siderophile (they are 3000x more concentrated in metal than in silicates); their concentration ratios in metal are more likely to remain unaffected by reduction during chondrule formation. Fig. 9 is a plot of Ir vs. Pt concentrations of the grains in which the kamacite follows quite well the trend of solar ratio, except for slightly lower, but significant, Ir/Pt ratios in chondrule 1ch1. By mass balance with taenite, the calculation of X_T in chondrules 11ch1, 7ch5 and 8ch4 metal lead to bulk Co/Ni ratios in the grains from 0.025 to 0.042, which are 1.1x to 1.8x lower than solar. Bulk metal compositions in LL chondrites also give subsolar ratios (Kong and Ibihara, 1997) indicating that we were sampling similar metal types. To sum up, the metal grains we analyzed in Krymka seem to have different bulk chemical compositions, with mostly subsolar element/Ni ratios suggesting the metal grains either formed from distinct precursors of non-solar compositions or had their compositions modified subsequent to chondrule formation events. Processes like metal sulfurization and Feoxidation, which are more likely to occur during metamorphism, may have played a role in such modifications. However, they cannot completely explain the trends observed because siderophile elements considered here do not enter, or only a little, sulfides and Fe-oxides. The supersolar ratios for Ir and Pt in grain 8ch4a are accredited to the anomalously high concentrations of these elements in taenite and kamacite (see Table 4). Such anomalies have already been reported for CR chondrites metal, and they could either be inherited from chondrule precursor material condensed from a gas of solar composition but did not equilibrate with it or be the result of a partial melting of host chondrule with some loss of Fe, Ni and Co (Connolly et al. 2001). Intriguingly, the anomalies by Connolly et al. (2001) were found in type I chondrules while ours are in a type II (8ch4 in Table 4). In a series of INAA analysis of bulk chondrules in unequilibrated ordinary chondrites, Grossman and Wasson (1982; 1985) reported the presence of metal with high Ir/Ni ratio in Ni-poor chondrules. The chondrules are metal-poor PO and POP with little mesostasis. The olivine composition of the Krymka chondrule 8ch4 (Fig. 4, Table 5) looks very similar to their Ni-poor chondrules. They interpreted the enrichment in Ir to indicate a precursor component originally formed as a metal condensate rich in siderophile elements. Another observation that deserves attention, is the low Ir (and also Pt, with a lesser extent) in kamacite and taenite of the extrachondrule 11gr5 grain (Table 4), which is also reflected in the calculated bulk Ir of 0.018 ppm (Table 6, Fig. 9). If the metal grain had gone through chondrule formation events (Lauretta et al. 2001; Zanda et al. 1994; Rambaldi and Wasson, 1984), one would expect that reduced Fe had partially diluted its original composition, which results in lowering Ir. Yet, such a scenario remains implausible, as it is difficult to reconcile with the high Co in this grain unless the chondrule silicates were originally enriched in Co (Grossman and Wasson, 1985).

Despite the primitive nature of Krymka suggested by the wide ranges of chemical compositions of its metal grains (Rambaldi and Wasson 1984; Rubin 1990), different lines of evidence indicate that the final compositions of kamacite and taenite were fixed during the mild parent body thermal metamorphism experienced by this meteorite, and not earlier. 1-Experimental studies of Fe-Ni alloys conducted at low temperatures (i.e. within the range of unequilibrated chondrites metamorphism) show that the microstructures and chemical compositions of the metallic phases are sensitive to temperature changes and continue to evolve even under low temperature regimes (Yang and Goldstein 1996). The presence in many primitive chondrites, including in the least equilibrated Semarkona LL3.0, of mineral inclusions in metal known to have formed during thermal metamorphism from dissolved elements in the metal (Perron et al. 1992; Zanda et al. 1994; Mostefaoui 1996) indicates that elemental diffusion in metal remains active at low temperature. Kong and Ebihara (1996) studied the characteristics of the bulk metal by INAA and concluded that kamacite and taenite in L chondrites are low temperature diffusion products of parent body metamorphism. 2- The presence of tetrataenite in Krymka indicates that the metal evolved via solid-state diffusive exsolution under a low temperature regime (Reuter et al. 1989; Albertsen and Knudsen 1980; Paulevé et al., 1962). 3- The absence of zoning in Krymka metal would argue for a long cooling period in order to erase any previous compositional gradients. This would establish partitioning of the elements between kamacite and taenite with coefficients prone to the "blocking" temperature (defined as the limit at which diffusion ceased to produce further

chemical changes, see Wasson and Hoppe 2012). This demonstrates that even though successive thermal events the metal particles in Krymka might have gone through could have markedly contributed to their bulk compositions, the final equilibrium compositions of adjacent kamacite and taenite are likely to have been fixed during the last thermal event, i.e. metamorphism. The subsolar bulk compositions of the metal grains result in low elemental concentrations in adjacent kamacite and taenite.

5.2. Partitioning of elements between kamacite and taenite and influence of their ionic radii

In Fig. 10 we plotted our data on the partitioning of elements between taenite and kamacite in Krymka, $D_{T/K}(E) = [element]_T/[element]_K$, as a function of decreasing affinity to taenite in the order Cu<Ni<Rh<Pt<Ir<Co. All elements but Co, and possibly also Ir, partition in favor of taenite; this is concordant, except for Ir, with SIMS results by Hsu et al. (2000) and with INAA and LA-ICP-MS results of Rasmussen et al. (1988) and Campbell and Humayun (1999), respectively, on iron meteorites. In contrast with our results on Pt and with those of Hsu et al. (2000) on Ir, Hirata and Nesbitt (1997) made in-situ laser-ablation ICPMS measurements of metal in iron meteorites and found that both elements, Ir and Pt, were rather concentrated strongly in kamacite. The distribution of minor and trace elements between coexisting phases depends on various parameters. One of these is the ability for a given element to fit in the crystalline structure. Elements with higher affinity to kamacite, like Co. fit better in its lattice than that of taenite. Hirata and Nesbitt (1997) suggested that the controlling mechanism of the distribution of platinum group elements between metallic phases in iron meteorites is the ionic size. Watson et al. (2008) observed that the partitioning of siderophile elements in iron meteorites correlates negatively with atomic numbers for period 4 elements and positively for period 5 and 6 elements, but did not provide any interpretation to these correlations. In contrast to these studies, Hsu et al. (2000) interpreted the partition of minor and trace elements in iron meteorites to be controlled by the interplay of the size and electron configuration of the elements and the crystal structure of kamacite and taenite.

The chemical behavior of minor and trace elements in a mineral depends also on the ability of these elements to substitute for a major element (Fe and Ni in the case of kamacite and taenite). The substitution mechanism is governed by electron chemistry in which parameters like elemental ionic radius and valence can play a significant role. In metallic alloys, the dominant type of chemical bond of the atoms is the metallic bond (Colombié 2012). This type of bond ensures the cohesion of the crystal structure by the electrostatic attractive force between the positively charged ionic lattice (ionic atoms) and its surrounding electron cloud of the conductive band. As the outer electrons of the metallic atoms are in the conduction band (delocalized), the substitution rule for the substituting atoms will apply to the ionic radius (positively charged atoms) and not to the atomic radius (neutral atoms). As a given oxidation degree corresponds a specific ionic radius (Table 7), what finally favors the substitution are the respective oxidation states of the substituting pairs. In Fig. 11 we plotted the partition coefficients of elements between taenite and kamacite as a function of ionic radii of the main oxidation states of the elements sixfold coordination (Shannon 1976). The diagram shows a clear positive correlation between the partition coefficients and the ionic radius suggesting that atoms with higher main oxidation state ion radii partition preferentially into taenite. Cobalt plots fairly short of the correlation. It would better fit if the 3^+ oxidation state is considered (filled triangle in Fig. 11) instead of the 2^+ main oxidation state. We

assume Co for some reason substituted as 3^+ , which is also a common oxidation state of the element, rather than 2^+ .

The correlation in Fig. 11 is consistent with the fact that the major elements in metal, i.e. Fe and Ni in taenite and kamacite, with which the minor and trace elements substitute, have distinctly different ion radii of main oxidation state, 0.55 and 0.69, respectively (Table 7). Thus, elemental partitioning in kamacite and taenite in Krymka is controlled primarily with the main oxidation state ionic radius. This is consistent with results in iron meteorites by Hirata and Nesbitt (1997) who suggested that the controlling mechanism of PGE partitioning between metal phases is ionic size.

5.3. Compositional correlations of associated kamacite and taenite and their relationship to temperature

Quantifying the extent of chemical homogenization of silicates and Fe-Ni metal is the basis for the classification of chondrites according to their metamorphic grade (Dodd et al. 1967; Van Schmus and Wood 1967; Afiatallab and Wasson 1980; Rubin 1990; Kimura et al. 2008). Equilibrated chondrites owe their uniform Ni and Co concentrations in kamacite and taenite to temperatures high enough to allow equilibrium between the metal grains (Afiatallab and Wasson 1980). In this context, Wood (1967) evoked diffusion of Ni and Fe between the metal grains through the silicates as a mechanism to ensure equilibrium attainment. In unequilibrated chondrites, the low temperature of metamorphism renders elemental diffusion too sluggish for the mineral grains to equilibrate with each other. In the highly unequilibrated ones, the grains retain their pre-accretionary chemical compositions, resulting in a maximum scatter of chondritic metal compositions.

In the previous section, we argued that elemental diffusivity in Fe-Ni metal could stay active at the low temperature regime corresponding to metamorphism experienced by the least equilibrated chondrites. We thus argue that in these chondrites even though grain-to-grain diffusion is ineffective, diffusion can still be ensured within single grains between kamacite and taenite. If different metal grains are brought to the same temperature for a long time (i.e. thermal metamorphism in the parent body) chemical equilibrium can be reached between kamacite and taenite within individual grains. In such a case, one should expect compositional correlations between kamacite and taenite pointing to the blocking temperature of the phases.

This correlation was tested in previous investigations. Based on the experimental results of Widge and Goldstein (1977), Afiattalab and Wasson (1980) first used kamacite/taenite Co concentration ratios to determine the metamorphic equilibrium temperatures for several chondrites. Similarly, Mostefaoui (1996) found positively correlated Co between kamacite and taenite in different metal grains in Bishunpur (Type 3.1). The slope of the correlation was used to determine the equilibrium temperature of these grains. Recently, Wasson and Hoppe (2012) used Co/Ni ratios of kamacite and taenite (abbreviated as $R\alpha\gamma$) in iron meteorites to determine their equilibrium temperatures and cooling rates. While the use of the experimental results on iron meteorites are subject to some caution (Goldstein et al. 2012), their application succeeded in attributing the high ratio of Co/Ni in kamacite to taenite in mesosiderites to post-shock annealing (Wasson and Hoppe 2014).

From these studies, it seems plausible that the slope of the correlating Co/Ni ratios between kamacite and taenite is a sensitive parameter able to reflect equilibrium between metal phases and subsequently constrain thermal conditions of the meteorites parent asteroids. However, if

true for Co, this should also apply to other siderophile elements for which correlations exist. In Fig. 12 we plotted the elemental ratios between kamacite and taenite in Krymka. Positive correlations are clearly evident for cobalt, copper, iridium and platinum. The much weaker trend for Rhodium is misleading because of the probably unrealistically large values of measured Rh in two taenites in chondrule 7ch5 (it is more than 1 order of magnitude higher than average in 7ch5f taenite, see Table 4) which are more likely resulting from the contribution of an interfering element that is not present in the standards.

The correlations in Fig. 12 show unambiguously that chemical equilibrium was reached between associated kamacite-taenite in Krymka. This equilibrium more likely happened for all metal grains during a common thermal event. The Co/Ni trend gives a slope of 28.5 with a χ^2 value of 1.7. After Widge and Goldstein (1977), we calculate an equilibrium temperature between kamacite and taenite of 446 ± 9°C. This temperature is consistent with post-accretion thermal metamorphism and is within the range given by Kimura et al. (2008) for Krymka metamorphism. Constraining the temperature by elements other than Co (e.g. iridium, which has an even better correlation) would be a nice confirmation but unfortunately, there are no experimental results on their temperature-dependent partitioning between alpha and gamma phases.

Our observation of the absence of compositional zoning in metal indicates that the thermal event was sufficiently long for chemical homogenization within the grains. Knowing the temperature dependence of the diffusivity of Ni in metal one can give a rough estimate of the cooling rate of the Krymka parent body from the closure temperature and size of the metal phase to be homogenized. This can be done following Jacquet et al. (2012) after Dodson (1973):

$$\frac{dT}{dt} = -2\frac{\mathrm{D}(\mathrm{T})\mathrm{R}T^2}{a^2 E_a}$$

where T is temperature, D(T) the temperature dependent diffusion coefficient, a is a characteristic diffusion distance, R the gas constant, and E_a the activation energy of diffusion. Because Ni diffusion is slower in taenite than in kamacite, the criterion is calculated for taenite characteristic size of 10µm. For temperatures within the range of the Krymka metamorphic grade and an activation energy of 320 kJ.mol⁻¹, the Ni diffusivity from the experimental results of Goldstein et al. (1965) is in the order of 10^{-26} m² s⁻¹. Estimates from other studies give similar diffusivities, differing by no more than one order of magnitude in the most extreme cases. We obtain a slow cooling rate not in excess to about 1K/Myr, which is in agreement with the value reported by Taylor et al. (1987) for Krymka. This also agrees with metallographic cooling rates of other unequilibrated chondrites (Scott and Rajan 1981; Taylor et al. 1987) supporting conjectures that unequilibrated chondrites cooled slower than the equilibrated ones.

6. CONCLUSIONS

We have reported NanoSIMS measurements of *in situ* siderophile minor and trace element abundances in individual Fe-Ni metal grains in the unequilibrated chondrite Krymka (LL3.2). This is the first study of siderophile trace elements in adjacent kamacite/taenite in a chondrite. Associated kamacite and taenite of 10 metal grains in four chondrules and one matrix metal

were investigated for elemental concentrations of Fe, Ni, Co, Cu, Rh, Ir, Pt and Ag. The results show large elemental variations among the metal grains, which is consistent with the unequilibrated character of the chondrite. Taken individually, the associated kamacite and taenite of the grains show correlated elemental concentrations suggesting chemical equilibrium between the metal phases; this equilibrium was established during a common thermal event. Elemental taenite /kamacite partition coefficients correlate positively with the elements ionic radii of main oxidation states, with atoms of larger ion radii partition preferentially into taenite. This indicates that the main oxidation state ionic radius might have played a significant role in controlling elemental partitioning in kamacite and taenite in Krymka. Estimates of the bulk element-to-Ni ratios for minor and trace elements in the metal grains show they are non-solar (mostly subsolar). The ratios are variable, indicating that the grains retained their pre-accretionary bulk chemical compositions. This suggests the metal grains could have formed from distinct precursors of non-solar compositions or had their compositions modified subsequent to chondrule formation events. The calculated equilibrium temperature between kamacite and taenite of the grains is 446 ± 9 °C; fairly consistent with post-accretion thermal metamorphism and concordant with the range given by Kimura et al. (2008) for Krymka. Using the Ni diffusivity in taenite we estimate that the Krykma parent body cooled at a slow rate that did not exceed $\sim 1 \text{K/Myr}$, which is concordant with literature values for unequilibrated ordinary chondrites.

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Appendix A

Calculation of elemental concentrations in taenite from kamacite-taenite ROIs mixture.

Elemental concentrations in ROIs of pure taenite are calculated from NanoSIMS count rates of the considered elements and Fe ion yields via the correlations in Fig. 3. However, when a taenite-kamacite ROI mixture is considered, using the count rate of the element and the Fe yield can give a wrong concentration value because not only the abundances of the element may be different in the two phases but also ionization efficiencies. To assess intrinsic elemental concentrations of pure taenite in the mixture the calculation method must take into account these considerations. One of the parameters required for this calculation is the fraction of the contributing phases.

Let us call *f* the taenite fraction in the mixture and let also define the following parameters:

Fe^m, Ni^m: count rates of Fe and Ni in the mixture.

 Fe^k , Fe^T , Ni^K , Ni^T : count rates of Fe and Ni in kamacite and taenite

Using mass-balance, the following equations can be written:

$$\begin{cases} Fe^{m} = fFe^{T} + Fe^{K} (1 - f) & (1) \\ Ni^{m} = fNi^{T} + Ni^{K} (1 - f) & (2) \end{cases}$$

As the count rates of Fe and Ni in the mixture are known from NanoSIMS measurements, we will deal with two equations of three variables, which are f and the count rates of Fe and Ni in taenite.

Let us call Y_{Fe}^{T} and Y_{Ni}^{T} the ion yields of Fe and Ni in taenite. These can be related by the formula:

$$Y_{Ni}{}^{T} = \alpha_1 Y_{Fe}{}^{T} + \alpha_2 \qquad (3)$$

in which α_1 and α_2 are the regression coefficients in the taenite correlation diagram of Fig. 3.

The yields can also be written as follows:

$$Y_{Ni}^{T} = \frac{Ni^{T}}{A_{Ni}^{T}} \quad (4)$$

and

$$Y_{Fe}^{T} = \frac{Fe^{T}}{A_{Fe}^{T}} \quad (5)$$

where A_{Fe}^{T} and A_{Ni}^{T} are, from the ion yield definition itself, the NanoSIMS ion current intensity (A) x concentration (ppm) of iron and nickel, respectively. Fe and Ni concentrations are known (see Table 3).

Combining (3), (4) and (5) one can write:

$$Ni^T = A_{Ni}^T \frac{\alpha_1}{A_{Fe}^T} F e^T + A_{Ni}^T \alpha_2 \quad (6)$$

Injecting (6) in (2) gives:

$$Ni^{m} = f(A_{Ni}^{T} \frac{\alpha_{1}}{A_{Fe}^{T}} Fe^{T} + A_{Ni}^{T} \alpha_{2}) + Ni^{K} (1 - f)$$
(7)

We end up with two equations (1) and (7) of two variables in which f can be calculated as follows:

$$f = \frac{Ni^m + \frac{A_{Ni}^T}{A_{Fe}^T} \alpha_1 F e^K - \frac{A_{Ni}^T}{A_{Fe}^T} \alpha_1 F e^m - Ni^K}{\frac{A_{Ni}^T}{A_{Fe}^T} \alpha_1 F e^K + A_{Ni}^T \alpha_2 - Ni^K}$$

Since f is in the form $\frac{U}{V}$, its uncertainty can be expressed as: $\Delta f = f \sqrt{\left(\frac{\Delta U}{U}\right)^2 + \left(\frac{\Delta V}{V}\right)^2}$ with

$$\left(\frac{\Delta U}{U}\right)^{2} = \frac{\left(\Delta Ni^{m}\right)^{2} + \left(\frac{A_{Ni}^{T}}{A_{Fe}^{T}}\alpha_{1}Fe^{K}\right)^{2}\left[\left(\frac{\Delta\alpha_{1}}{\alpha_{1}}\right)^{2} + \left(\frac{\Delta Fe^{K}}{Fe^{K}}\right)^{2}\right] + \left(\frac{A_{Ni}^{T}}{A_{Fe}^{T}}\alpha_{1}Fe^{K}\right)^{2}\left[\left(\frac{\Delta\alpha_{1}}{\alpha_{1}}\right)^{2} + \left(\frac{\Delta Fe^{m}}{Fe^{m}}\right)^{2}\right] + (\Delta Ni^{K})^{2}}{\left(Ni^{m} + \frac{A_{Fe}^{T}}{A_{Fe}^{T}}\alpha_{1}Fe^{K} - \frac{A_{Ni}^{T}}{A_{Fe}^{T}}\alpha_{1}Fe^{m} - Ni^{K}\right)^{2}}$$

and

$$\left(\frac{\Delta V}{V}\right)^{2} = \frac{\left(\frac{A_{Ni}^{T}}{A_{Fe}^{T}}\alpha_{1}Fe^{K}\right)^{2}\left[\left(\frac{\Delta\alpha_{1}}{\alpha_{1}}\right)^{2} + \left(\frac{\Delta Fe^{K}}{Fe^{K}}\right)^{2}\right] + (A_{Ni}^{T})^{2}(\Delta\alpha_{2})^{2} + (\Delta Ni^{K})^{2}}{\left(\frac{A_{Ni}^{T}}{A_{Fe}^{T}}\alpha_{1}Fe^{K} + A_{Ni}^{T}\alpha_{2} - Ni^{K}\right)^{2}}$$

The percent kamacite fraction F in Table 4 is:

$$F = 100(1-f)$$

Ones *f* and its uncertainty are known, elemental count rates in taenite are recalculated the same manner as in formula (1) and Y_{Fe}^{T} deduced from Fe^{T} (formula 5). Elemental concentrations including their uncertainty propagation are determined from the respective ion yields of the elements (Fig. 3).

Figure captions:

Fig. 1: Back-scattered electron (BSE) image of the Krymka section showing the four chondrules and the matrix metal investigated.

Fig. 2: NanoSIMS mass scans on Krymka metal around ⁵⁶Fe, ⁶²Ni, ⁵⁹Co, ⁶⁵Cu, ¹⁰³Rh, ¹⁰⁹Ag, ¹⁹³Ir and ¹⁹⁸Pt peaks. The scans are acquired by varying the deflector voltages in front of the detector exit slits. The vertical lines are the positions where the measurements are made.

Fig. 3: Diagrams showing ion yields (counts per second/nA/ppm) of the elements (vertical axis) plotted against the ion yield of Fe (horizontal axis) for the standards NBS661, NBS663, Fe-Ni (51.5%) and Gibeon. The slopes of the lines are used to infer element concentrations in Krymka kamacite and taenite using the method of Hsu et al. (2000). Notice the distinct slopes for Ni between the Fe-Ni (51.5%) and NBS661, NBS663 and Gibeon standards showing that ionization efficiency differ significantly between Ni-rich and Ni-poor phases. These slopes are used to correct Ni data respectively in taenite and kamacite.

Fig. 4: BSE images of Krymka chondrules. 1ch1, 7ch5 and 11ch1 are typical type I chondrules. 1ch1 is micro porphyritic (PO) with groundmass glass. Its metal is in the outer part of the chondrule. 7ch5 and 11ch1 are porphyritic (POP). Dusty olivine is present in 1ch1 and 7ch5, indicating olivine reduction and formation of dusty metal during chondrule formation. 8ch4 is a type II (POP) with minor glass and scarce metal of irregular shapes.

Fig. 5: BSE images of single metal grains in Krymka. All grains, but 8ch4a and 11gr5, are round in shape. They are mostly kamacite in contact with taenite either existent as single crystals or dispersed within the kamacite (e). Troilite is visible in grains 11ch1b and 11gr5. In 11ch1b, the kamacite has five distinct grey levels (outlines in while dashed lines) indicating different crystal orientations. T: taenite, Tr: troilite and K: kamacite.

Fig. 6: SEM X-ray map of Fe, Ni, Cr, P and S in the metal grain 11ch1b. The NanoSIMS scans on kamacite and taenite are visible in the images. The black patch in the Ni and Fe images are edge of disorientation damage of NanoSIMS sputtering. Also are shown Fe and Ni concentration profiles along a kamacite-taenite-kamacite line (blue arrow).

Fig. 7: BSE image and NanoSIMS element/Fe ion ratio images of grain 1ch1a. The sizes of the ion images are $15x15\mu m^2 128x128px$.

Fig. 8: Plots of elemental concentrations against Ni of Krymka kamacite and taenite. Solid lines represent the solar ratios (data from Anders and Grevesse 1989).

Fig. 9: Diagram of Ir vs Pt concentrations in Krymka kamacite and taenite. The solid line represents the solar Ir/Pt ratio (data from Anders and Grevesse 1989).

Fig. 10: Partition coefficients of the elements between kamacite and taenite in Krymka as a function of decreasing affinity to taenite in the order Cu<Ni<Rh<Pt<Ir<Co. Individual values are plotted on the top and average values on the bottom. Errors on the average values are 1-sigma standard deviations.

Fig. 11: Partition coefficients of elements between taenite and kamacite (average values) as a function of ionic radii (in picometer) of the main oxidation states of the elements in sixfold coordination. Errors are 1-sigma standard deviations.

Fig. 12: Diagrams of elemental/Ni ratios between kamacite and taenite of Krymka metal. The slope values, intercepts, and reduced χ^2 of the lines in the diagrams are parameters of the weighted least-square fitting regression through the data points.

Table 1. The combined mode disposition of the NanoSIM	S-50 configuration.
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ined mode dispo	sition of	the Nar	IOSIMS-	-50 cont	iguratio
Detectors (EMs) /B-Field	Det-1	Det-2	Det-3	Det-4	Det-5
B1	⁵⁶ Fe ⁻	⁶² Ni⁻	¹⁰³ Rh ⁻	¹⁹³ lr ⁻	¹⁹⁸ Pt ⁻
B2	⁵⁹ Co ⁻	⁶⁵ Cu⁻	¹⁰⁹ Ag ⁻		

Table 2. Chemic	cal compositions of reference	e materials used as standar	ds for the NanoSIMS.

Concentration	Fe	Ni	Со	Cu	Rh	Ag	lr	Pt
Gibeon		7.93 [*]	0.39 [*]	0.0155 [*]	1.20 ^{**}		2.71 ^{**}	6.91 ^{**}
SRM 661 [§]	95.6	1.99±0.01	0.032±0.001	0.042±0.001		4±1		
SRM 663 [§]	94.4	0.32±0.01	0.048±0.001	0.098±0.005		38		
Fe-Ni (51.5%Ni) [£]	48.5	51.5						

The values reported are for Fe, Ni, Co, and Cu in wt% and Rh, Ag, Ir and Pt in ppm. ^{*} Rasmussen et al. (1988). ^{**} Petaev and Jacobsen (2004). [§] Standard Reference Material from NIST. ^f Standard from BRGM (Bureau de recherches Géologiques et Minières).

Metal	φ (μm)	Phase	Fe	Ni	n	Fe	std	Ni	std	Со	std	Cu	std
			SEM/E	DX					EPM	А			
11ch1a		т	45.2	54.2									
IICIIIa	50	К	96.0	3.1	13	96.42	0.19	3.14	0.19	0.326	0.009	0.006	0.002
11ch1h		т	48.9	50.8	1	47.75		52.03		0.092		0.161	
TICHID	110	К	94.7	3.7	4	96.29	0.43	3.28	0.44	0.322	0.003	0.003	0.005
1ch1a		т	57.0	42.4	3	49.12	2.8	46.93	2.8	0.081	0.009	0.075	0.025
ICHIA	35	К	94.2	3.8	3	95.35	0.55	4.11	0.56	0.426	0.024	0.010	0.010
1ch1h		т	49.3	50.1									
	18	К	93.4	4.9									
1ch1c		т	48.3	50.9									
	25	К	94.0	4.0									
1ch1d		т	48.3	50.9									
ICHIU	18	К	94.0	3.9									
7ch5o		т	51.1	47.9									
70136	22	К	94.1	3.52									
ZchEf		т	47.6	51.7									
70151	20	К	93.6	3.6									
8ch/a		т	53.9	44.4									
0CI14a	35	К	94.2	2.8									
11 or 5		т	48.8	49.1									
TTRID	200	К	91.7	5.0									

Table 3. Metal grain sizes (longest dimension), and EPMA/SEM-EDX concentrations of Fe, Ni, Co, and Cu (wt%) in kamacite and taenite of Krymka.

n: number of electron microprobe measurements. Std: 2-sigma standard deviation.

Chond.	#	Phase	F	Ni	er	Со	er	Cu	er	Rh	er	lr	er	Pt	er
	2	Т	3	54.2 [*]		0.041(0.059)	0.017	0.12525(0.10263)	0.01189	17.13 (16.55)	2.52	0.17 (0.16)	0.15	2.35(1.96)	0.42
11ch1	a	К		2.73	0.02	0.305	0.002	0.00411	0.00012	28.76	1.80	0.25	0.03	0.35	0.04
11011	h	Т	0	50.8*		0.039	0.009	0.15137	0.00862	14.86	1.38	0.08	0.03	1.24	0.09
	D	К		3.11	0.02	0.270	0.001	0.00318	0.00003	19.82	1.23	0.24	0.01	0.40	0.02
	2	Т	0	42.4		0.120	0.009	0.08630	0.00250	2.37	0.16	0.27	0.03	2.88	0.13
	a	К		3.74	0.03	0.478	0.003	0.00328	0.00013	0.71	0.05	0.50	0.03	1.57	0.05
	b	Т	35	50.1*		0.095(0.111)	0.015	0.11554(0.06041)	0.00662	1.65(1.74)	0.22	0.13(0.16)	0.07	3.93(2.44)	0.39
1ch1		К		2.88	0.02	0.258	0.004	0.00337	0.00023	3.45	0.22	0.36	0.02	1.59	0.07
		Т	84	50.9 [*]		0.038(0.137)	0.041	0.05482(0.01529)	0.00984	6.01 (2.11)	1.06	0.25(0.16)	0.28	1.54 (0.99)	0.70
	C	К		2.88	0.02	0.345	0.005	0.00226	0.00021	1.45	0.10	0.27	0.02	1.58	0.07
	Ь	Т	22	52.5*		0.090(0.110)	0.012	0.13927(0.09742)	0.00677	3.77(4.55)	0.40	0.31(0.27)	0.07	2.25 (1.88)	0.27
	u	К		2.73	0.02	0.329	0.006	0.00417	0.00034	12.80	0.81	0.38	0.03	2.08	0.10
	•	Т	4	47.9 [*]		0.050(0.068)	0.012	0.09038(0.07723)	0.00441	22.52(19.57)	1.74	0.30 (0.31)	0.07	2.85(2.52)	0.21
ZchE	C	К		2.70	0.02	0.316	0.003	0.00255	0.00015	2.91	0.18	0.71	0.03	1.08	0.05
7015	f	Т	15	51.7 [*]		0.303(0.311)	0.037	0.10615(0.06416)	0.00827	170.13(105.83)	14.05	0.40 (0.55)	0.18	3.28(2.43)	0.48
	•	К		3.13	0.02	0.644	0.006	0.00256	0.00018	5.80	0.37	1.54	0.05	2.24	0.08
8ch4	а	Т	27	44.4		0.112(0.139)	0.014	0.06814(0.04154)	0.00379	13.79(13.74)	1.14	1.39 (2.16)	0.25	11.28(9.07)	0.75
	u	К		3.20	0.03	0.320	0.005	0.00330	0.00025	23.63	1.48	5.89	0.18	10.08	0.30
11gr5		т	0	49.1		0.418	0.016	0.08586	0.00271	6.98	0.53	0.03	0.02	0.24	0.08
J		к		3.54	0.03	1.074	0.005	0.00372	0.00010	1.46	0.10	0.01	0.01	0.44	0.04

Table 4. NanoSIMS measured concentrations of minor and trace elements in Krymka metal.

The values reported are for Ni, Co, and Cu in wt% and Rh, Ir and Pt in ppm by weight. F: The fraction (in %) of contributing kamacite to taenite and for which the correction of the elements concentrations in the taenite are recalculated. In brackets are taenite NanoSIMS results uncorrected from kamacite contribution (their uncertainties are from 2 to 10x less than those of the corrected values). *: Results from SEM EDX measurements. Errors are 2σ .

Fa

Phase

En

Fs

Wo

11ch1	Ol#1	99.3	0.7	Px#1	98.1	0.8	1.1
РОР	Ol#2	96.5	3.5	Px#2	98.9	0.5	0.6
type l	Ol#3	97.5	2.5	Px#3	98.8	0.6	0.6
	Ol#4	99.4	0.6	Px#4	98.9	0.5	0.6
	OI#5	99.3	0.7	Px#5	98.7	0.7	0.6
	1σ	1.3	1.3	Px#6	96.5	3.0	0.5
				Px#7	98.6	0.9	0.5
				1σ	0.9	0.9	0.2
1ch1	Ol#1	99.6	0.4				
РО	OI#2	99.7	0.3				
type I	OI#3	99.5	0.5				
	OI#4	99.5	0.5				
	OI#5	99.2	0.8				
	Ol#6	99.5	0.5				
	Ol#7	99.5	0.5				
	OI#8	99.5	0.5				
	OI#9	99.5	0.5				
	Ol#10	99.5	0.5				
	Ol#11	99.6	0.4				
	Ol#12	98.3	1.7				
	1σ	0.4	0.4				
7ch5	Ol#1	98.2	1.8	Px#1	98.5	0.9	0.6
РОР	Ol#2	98.9	1.1	Px#2	98.5	0.8	0.6
type I	Ol#3	98.3	1.7	Px#3	97.3	2.1	0.6
	Ol#4	98.1	1.9	Px#4	98.4	0.9	0.6
	Ol#5	94.1	5.9	Px#5	98.6	0.9	0.5
	Ol#6	98.4	1.6	Px#6	98.1	1.0	0.9
	Ol#7	76.5	23.5	Px#7	97.0	2.0	1.0
	Ol#8	97.2	2.8	Px#8	97.0	2.4	0.5
	Ol#9	95.1	4.9	1σ	0.7	0.7	0.2
	Ol#10	96.7	3.3				
	1σ	6.7	6.7				
8ch4	Ol#1	89.9	10.1	Px#1	87.8	8.8	3.4
РОР	OI#2	90.0	10.0	Px#2	63.1	7.5	29.5
type II	OI#3	89.3	10.7	Px#3	85.4	9.9	4.7
	Ol#4	87.5	12.5	Px#4	87.4	9.1	3.5
	Ol#5	89.7	10.3	Px#5	60.4	37.3	2.3
	Ol#6	90.6	9.4	1σ	13.8	12.8	11.7
	Ol#7	89.8	10.2				
	1σ	1.0	1.0				

Table 5. SEM-EDX chemical compositions of chondrules olivine and pyroxene.

Fo

Chondrule Phase

Metal	X _T	Ni	Со	Cu	Rh	lr	Pt	Cu/Ni	Rh/Ni [*]	Ir/Ni [*]	Pt/Ni [*]
11ch1a	6.9	6.3	0.29	0.0124	27.96	0.247	0.487	0.0020	4.46	0.039	0.078
11ch1b	5.3	5.6	0.26	0.0110	19.56	0.228	0.445	0.0020	3.48	0.041	0.079
1ch1a	14.4	9.3	0.43	0.0152	0.95	0.467	1.758	0.0016	0.10	0.050	0.189
1ch1b	5.4	5.4	0.25	0.0095	3.35	0.343	1.713	0.0017	0.62	0.063	0.315
1ch1d	8.1	6.8	0.31	0.0151	12.07	0.372	2.093	0.0022	1.79	0.055	0.310
1ch1c	8.5	7.0	0.32	0.0067	1.83	0.265	1.580	0.0010	0.26	0.038	0.227
7ch5e	8.2	6.4	0.29	0.0098	4.53	0.674	1.226	0.0015	0.71	0.105	0.191
7ch5f	19.5	12.6	0.58	0.0228	37.85	1.317	2.442	0.0018	3.00	0.105	0.194
8ch4a	8.3	6.6	0.30	0.0087	22.82	5.516	10.181	0.0013	3.46	0.835	1.542
11gr5	33.2	18.7	0.86	0.0310	3.29	0.018	0.373	0.0017	0.18	0.001	0.020

Table 6. Calculated taenite volume fraction X_T and corresponding bulk elemental concentrations and element/Ni ratios in metal.

The values reported are for Ni, Co, and Cu in wt% and Rh, Ir and Pt in ppm. *: values to be multiplied by 10⁴

Element	At. N°	IR (1+)	IR (2+)	IR (3+)	IR (4+)	IR (5+)	IR _m	Main ox. Stat.
Fe	26		61	<u>55</u>	58.5		55	3
Cu	29	77	<u>73</u>	54			73	2
Ni	28		<u>69</u>	56	48		69	2
Rh	45			<u>66.5</u>	60	0.55	66.5	3
Pt	78		80		<u>62.5</u>	0.57	63	4
Ir	77			68	<u>62.5</u>	0.57	62.5	4
Co	27		65	54.5	53		54.5	2

Table 7. Oxidation states and corresponding ionic radii of the elements.

IR: lonic radius (in picometer); data taken from the revised values of Shannon (1976). IR_m : lonic radius of the main oxidation state. ^{*} For Co, the 3⁺ radius is used instead of the mean oxidation state.







































