HETEROGENEOUS AND FRACTIONATED METAL IN CANYON DIABLO (IA) GRAPHITE – METAL ROCK.

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Introduction: Iron meteorites are widely believed to be igneous rocks derived from cores or impact melt pools of planetesimals. In any case, iron meteorites allegedly formed by crystallization from a metal melt [e.g., 1-4]. On the other hand, it is known for a long time that iron meteorites are very old and carry abundant signs of primitiveness, like daughter nuclei of short-lived radioactive parents [5-11]. Inclusions of minerals and rocks in iron meteorites are common and clearly indicate that metal and inclusions (silicates, sulfides, oxides, phosphides, carbides, etc.) must have been brought together in the solid state. A liquid metal - solid xenocryst/xenolith mixing would not have worked as surface tension of the liquid metal and any gravity field would have quickly separated these phases [e.g., 12]. In addition, the fractionation trends exhibited by the chemical groups require different solid metal/liquid metal distribution coefficients [e.g., 3]. In order to overcome these problems, complex fractional crystallization - mixing models have been proposed [e.g., 4,13,14]. Recently, very clear evidence was found for a sub-solidus formation of IAB iron meteorites [e.g., 15-17]. Previous findings of inhomogeneous distribution of Ir in some iron meteorites [18-20] already gave a strong signal in favor of a low temperature origin of at least some iron meteorites. Here we report on the investigation of metal present in a graphite – metal rock from the Canyon Diablo (IA) iron meteorite. The results extend those obtained previously on a similar graphite nodule [21] and show that metals with highly different trace element contents co-exist on a sub-mm scale.

Sample and Methods: A large (8.5 cm diameter) graphite – metal inclusion from the Canyon Diablo iron meteorite was cut and investigated by optical microscopy, analytical scanning electron microscopy and analyzed by electron microprobe. Samples of metal, graphite – metal veins and graphite matrix were separated manually for instrumental neutron activation analysis (INAA). Analysis were done at the university of Cologne following procedures of [22]. Typical analytical errors are < 5 % for Fe, Co, Ni, Cu, Ga, Ir, Au, 5-10 % for Ge, W, Re, and 10-20 % for Mo, Os, Ru, Pt and Pd. Selected metal was analyzed for Co, Ni, Fe, P, Si and Cr with the electron microprobe in Vienna against artificial standard alloys and under standard conditions. The abundances of platinum group elements (PGEs), Re, W, Au, Cu, Ga, Ge and Co were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Analyses were made on 50 µm wide spots using an ultraviolet (266 nm) Nd-YAG laser coupled to a VG Fisons PQ2S ICP-MS instrument at St. John's. Absolute element contents were derived by comparison with Hoba (IVB) metal (with Ni as internal standard). Typical analytical errors for the contents of Co, W, Ir, Pt and Au are 1-4 %, 5-25 %, 3-6 %, 3-10 % and 3-8 %, respectively.

Results: The Canyon Diablo graphite-metal rock consists of a porous aggregation of platy, spherulitic, vermicular and botryoidal graphite (cliftonite – related). The pore space is mostly filled by kamacite, occasionally also by silicates (enstatite or forsterite or albite)) or schreibersite or rust. Small pores (1 - 4 µm) at the center of the spherulites (cliftonites) are open. The rock is cut by several systems of veins of different age. Thick veins (1 - 3 mm, Fig, 1) consist of granular kamacite (~ 100 – 200 µm grain size) with variable contents of cliftonite which is distributed in clouds and bands. Rarely, graphic schreibersite and taenite are present. The thick veins are mostly the origin of platy graphite – metal veins of medium dimension (0.2 – 0.4 mm). They consist of plates and spindles of graphite which are oriented perpendicular to the vein wall (Fig. 1, center). Graphite is dense near the wall but forms large, elongated voids in the center of the vein which are filled by kamacite. Thin veins (< 0.2 mm) consist either of graphite – metal intergrowths similar to those in the medium – sized veins or they consist of rust (with relic metal) which in places contains high amounts of Cl. Freshly polished surfaces of the Canyon Diablo graphite – metal rock develop abundant acidic droplets mainly along thin veins when exposed to air. The Cl content therefore, could stem from lawrencite.

Kamacite composition varies somewhat: 5.2 – 6.4 wt% Ni and 0.43 – 0.53 % Co within thick metal veins, 5.6 % Ni and 0.58 % Co in platy graphite – metal veins and 4.9 – 5.7 % Ni and 0.58 % Co in interstitial metal. Trace element contents of metal determined by INAA and LA ICP-MS agree very well but vary widely from point to point and between different metal occurrences (Fig. 2). Refractory siderophile elements (RSEs: W, Re, Os, Ru, Pt, Rh) have abundances between 2 and 20 times CI abundances, the common metals Co and Ni and the volatile siderophile elements (VSEs) Pd, Au, Ga and Ge between 7 and 15xCI. Copper is strongly depleted to about 0.2xCI. Compared to Canyon Diablo bulk metal, metals in the graphite – metal rock show similar fractionation patterns but are either depleted (thick veins) or enriched (medium = thin veins and interstitial metal) in RSEs. Rhodium, Co and Pd are enriched and Cu is depleted in all metals of the graphite – metal rock and Ga and Ge normalized abundances are high and indistinguishable.

Discussion and conclusion: Nickel and Co contents of metal in the graphite – metal rock vary only slightly from vein to vein and are similar to that of the kamacite in the Canyon Diablo host. However, trace element contents vary over a wide range (Fig. 2) and metals rich in refractory PGEs coexist with those depleted in these elements. This inhomogeneity on a sub-mm scale indicates that metals were deposited under a variety of conditions. These metals are recrystallized and show an equigranular texture, however, grain size is small indicating a brief and moderate thermal event. Persistence of chemical inhomogeneity on a microscopic scale strongly suggests that this rock never has experienced a high temperature event. Consequently, the host metal must have been deposited around the graphite – metal rock also at low temperature, as is also demanded by rare gas and N isotope data [15-17]. Therefore, the Canyon Diablo graphite – metal rock and the Canyon Diablo iron itself could not have been formed from a metal melt as suggested by [21], because such high temperatures in conjunction with the slow cooling rates found for iron meteorites would have homogenized the metal. We have to conclude, that Canyon Diablo (and very likely many other iron meteorites) must have been formed by a non - igneous process, very likely by chemical vapor deposition (CVD). The overall CI – normalized abundance pattern is remarkable as it does not reveal any obvious volatility dependence and RSEs and VSEs have approximately similar abundances, except for Cu. The pronounced fractionation trends are independent of elemental volatilities but apparently reflect volatilities of certain chemical carrier phases of the elements in the region of the formation of the Canyon Diablo iron. Co – precipitation of metal and graphite strongly suggests that carbonyls could have been one of the major carrier phases. Formation of metals from carbonyls is a widely used industrial technique [e.g., 23] and has been suggested for the formation of iron meteorites a long time ago [24]. Typical reactions could have been:

$$Fe(CO)_5 \rightarrow Fe^0 + 5CO$$

and

$$2CO \rightarrow C + CO_2$$

The presence of lawrencite supports this suggestion as many metals form halogen carbonyls and/or volatile halogenides. Also, the constant depletion of Cu with respect to all other siderophile elements supports that view as Cu does not form carbonyls and halogenides comparable to those formed by the other elements. Interestingly, abundance patterns similar to those reported here have been found in fremdlinge located in the rim of Efremovka CAI EF2 [25]. Is there a link?

References: [1] Scott E.R.D. and Wasson J.T. (1975) Rev. Geophys. Space Phys. 13, 527-546. [2] Wasson J.T. et al. (1980) Z. Naturforsch. 35a, 781-795. [3] Wasson, J.T. (1985) Meteorites. Freeman, N.Y.[4] Choi B.G. et al. (1995) GCA 59, 593-612. [5] Alexander E.C. and Manuel O.K. (1968) EPSL 4, 113-117. [6] Bogard D.D. et al. (1971) GCA 35, 1231-1254. [7] Niemeyer S. (1979) GCA 43, 843-860. [8] Kaiser T. and Wasserburg G.J. (1983) GCA 47, 43-58. [9] Luck J.-M. and Allegre C.-J. (1983) Nature 302, 130-132. [10] Göpel C. et al. (1985) GCA 49, 1681-1695. [11] Jentsch O. and Schultz L. (1987) Meteoritics 22, 418-419. [12] Fish R.A. et al. (1960) Astrophys. J. 132, 243-258. [13] Scott E.R.D. et al. (1996) GCA 60, 1615-1631. [14] Chabot N.L. and Drake M.J. (1999) MAPS 34, 235-246. [15] Maruoka T. et al.(1998) MAPS 33, Suppl.,A97-A98. [16] Asame K.S. et al. (1999) 24th Symp. Antarct. Met. NIPR, Tokyo, 1-3. [17] Matsuda J. (1999) pers. comm.. [18] Jochum K.P. et al. (1980) Z. Naturforsch. 35a, 57-63. [19] Wasson J.T. (1990) LPSC XXI, 1301. [20] Kurat G. et al. (1991) LPSC XXII, 767-768. [21] Hirata T. and Nesbitt R.W. (1997) EPSL 147, 11-24. [22] Kong P. et al. (1996) Anal. Chem. 68, 4130-4134. [23] Kodas T. and Hampden-Smith (1994) The Chemistry of Metal CVD. VCH, Weinheim, 530 pp. [24] Bloch M.R. and Müller O. (1971) EPSL 12, 134-136. [25] Campbell A.J. et al. (1999) LPSC XXXX, #1609. [26] Anders E. and Grevesse N. (1989) GCA 53, 197-214.

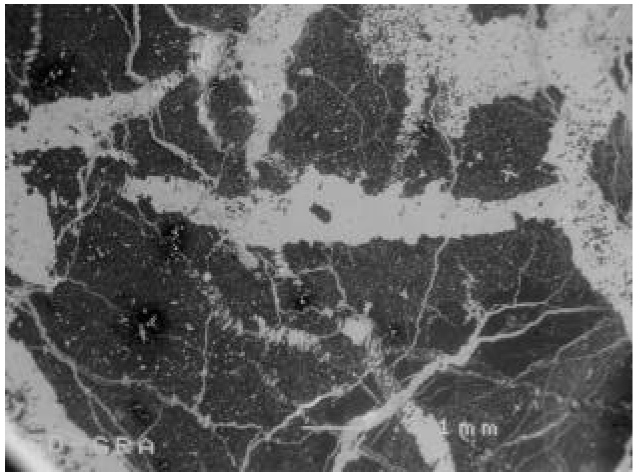

Fig. 1: BSE image of graphite – metal rock from Canyon Diablo.

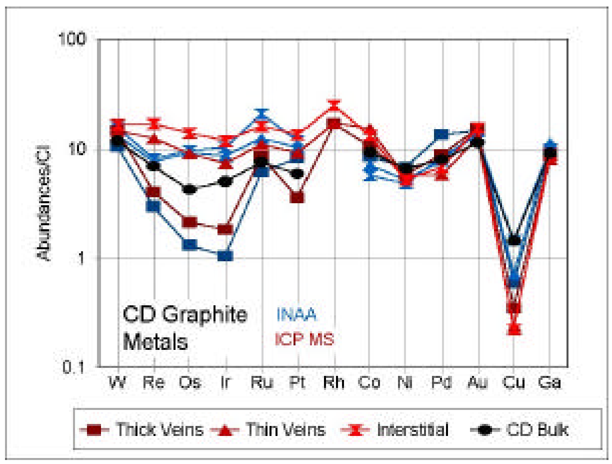

Fig. 2: CI – normalized [26] abundances of trace elements and Ni in metals of a graphite – metal rock from Canyon Diablo as determined by INAA and LA ICP MS compared to bulk Canyon Diablo metal [4].