PARTITIONING OF Cr, Mn, V AND Ni BETWEEN Fe MELT, MAGNESIOWUESTITE AND OLIVINE AT HIGH PRESSURES AND TEMPERATURES.

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The abundances of Mn, Cr, V, and Ni in the Earth's mantle and crust, the Moon and the eucrite parent body normalized to Si and C 1 are shown in Fig. 1. Compared to C 1 chondrites these four and, of course, all siderophile elements are depleted in the Earth's mantle and the Moon (1). These elements may reside now, at least for the case of the Earth, in an Fe,Ni-core. In order to partition Cr, Mn, and V into the metal or sulphide phase oxygen fugacities must be quite low and in fact to such a degree that practically no Ni is retained in the upper mantle. This is not the case and the dilemma of plausible explanations exists.

Two main possibilities are offered today:
1) A two stage model with highly reduced material accreting first, accompanied later and followed by more oxidized material which is not in equilibrium anymore with an already separated core (2,3). The light element in the core could be either Si, S or C or any combination of these elements.

2) Basically a single stage model whereby the core was in equilibrium with the whole mantle (4). In order to preserve the present abundances of the above elements in the mantle the partition coefficients have to be changed accordingly from what we know up to date mainly from experiments at 1 atm between metal and silicate melts. It has been suggested (5,6) that this can be achieved by dissolving oxygen in the metal, and the light element in the core to be oxygen.

In order to really test any model for core separation it is important to know partition coefficients at high pressures and this not only between metal and silicate melts, but also and probably more important between metal melt and solid silicates like olivine and pyroxene and especially the very high pressure analogues like the spinel structure (olivine), the perovskite structure (pyroxene) and the rocksalt structure (magnesiowuestite). In order to study the later structures pressures up to 250 kbar are required. So far we can reach 60kbar and 2000°C with our belt apparatus which limits the field of investigation. Nevertheless it is possible to study partition coefficients between metal/pyroxene, metal/olivine, and metal/magnesiowuestite. We have investigated the later two simultaneously by choosing the appropriate chemical system at 1550°C and 1700°C and from 20 - 50 kbar.

A big problem in this kind of investigation is the loss of metal to the sample container. We avoid this by using cylindrically drilled olivines (4 mm in diameter) from San Carlos with a central hole (2 mm in diameter) to take up the sample and with an olivine lid. The whole assemblage is placed in a Pt-capsule which is welded shut. In this way Fe-loss only occurs from the olivine capsule over about 100 microns, whereas no Fe is lost from the actual sample. A typical profile of Fo content of an olivine capsule is shown in Fig. 2. The starting material consisted of 49.41 wt-% olivine from a spinel Iherzolite from Mongolia (Fo75 with 0.39 % NiO) and 49.41 wt-% Fe98Ni2 alloy with 3000 ppm Cr203, 2000 ppm Mn, and 750 ppm V2O5 added. All material was finely crushed and sieved to grain sizes less than 20 microns.

Fig. 2: Compositional profile through one wall of an olivine capsule. Each dot represents a microprobe analysis. Run conditions: 30 kbar, 1550°C, 150 mins.
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The run products are olivines of Fe$_2$O$_4$ with about 0.5 % MnO and 0.2 % CrO (Ni and V are below the detection limit of the Li-drifted Si-detector of our microprobe), metal melt (Fe$_3$Ni) with 0.1 % Mn and 0.3 % Cr and newly grown magnesiowuestites (100Mg/Mg+Fe 49.5) with 8 % CrO, 1 % MnO, 0.45 % VO and Ni just at the detection limit (±100 ppm). The later phase grows due to the reaction

$$\text{Mg}_2\text{Si}_4 \text{O}_7 + 2\text{Fe} + \text{O}_2 \rightarrow \text{Fe}_2\text{Si}_4 \text{O}_8 + 2\text{MgO}$$

This reaction is given by Williams (7) as an oxygen buffer reaction. Therefore we can calculate the oxygen fugacities which prevailed during the experiments. Taking the activities of the components of the various phases into account we find that the oxygen fugacity was about two log units below the iron-wuestite buffer.

Apparent partition coefficients for Mn and Cr as a function of pressure and temperature under these oxygen fugacities are shown in Fig. 3. It appears that increasing pressure and temperature bring the partition coefficients closer to unity (Fig.3). The magnesiowuestite takes in 25 - 40 times as much Cr as olivine and 15 - 20 times more than the metal melt. Chromium is about twice as much in the metal melt than in the olivine. Manganese is about 2.5 times as high in magnesiowuestite than in olivine and about 10 and 5 times more in magnesiowuestite and in olivine, respectively, than in the metal melt. Nickel is below the detection limit in the olivine. The partition coefficient between metal and olivine must therefore be greater than 50. Since the Ni content in magnesiowuestite is at the detection limit, the partition coefficient of the metal-magnesiowuestite must be about 30.

A number of authors believe that the earth was heated up very strongly during accretion (e.g. 8) and that consequently core separation took place almost immediately. The metal melt was then in equilibrium with silicates at shallow depths and metal melt-olivine partition coefficients as determined here at oxygen fugacities below the IW-buffer may be applicable. Chromium and much more nickel would then be strongly partitioned to the metal phase, whereas manganese stays in the olivine. The consequence from this would be that the present day upper mantle is too high in Cr and Ni (by a factor of 2 and at least 5, resp. - see Fig. 1) and too low in Mn by a factor of 2.7 (Fig.1).

If core separation was delayed (i.e. the accretion energy was somehow dissipated off to a large extent), then the metal melt may have been in equilibrium with the high pressure phases of the deeper mantle. For the purpose of discussion one can assume that the mantle consists entirely of magnesiowuestite. The mantle would then appear to be too low in Mn (by a factor of 3) and too high in Ni (by a factor of 3, see Fig.1). We do not know the partition coefficients for the perovskite structure, but if they were similar to metal-olivine, one could find appropriate mixtures of magnesiowuestite and perovskite to satisfy the requirement of chondritic abundances for Cr. Nickel would still be overabundant in the earth’s mantle but not to such a high degree as implied by the presently available partition coefficients. The low abundance of Mn cannot be explained with the observed partition coefficients and a single stage model.

At present it seems that no single stage model is able to explain the abundances of Mn, Cr, V, and the siderophile elements in the earth’s mantle. High pressure equilibria may also have been of importance in two stage models since it could well be that after separation of the metallic FeNi during accretion additional amounts of Fe and other elements are gradually expelled from the mantle and transferred to the core (2,6,9).