

UTILIZATION OF ICP-MS ANALYTICAL TECHNIQUES FOR DETERMINATION OF SIDEROPHILE-ELEMENT ABUNDANCES: POTENTIAL USES FOR THE PLANETARY GEOCHEMIST.

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Differentiation of the terrestrial planets into a zoned entity composed of a crust, mantle, and core requires a total re-organization of the chemical budget. The mantle will be deficient in those elements which are concentrated in the crust and the core. While the timing of such differentiation events occurred shortly after accretion [1], the exact nature and timing of the processes involved remain enigmatic [2]. On Earth, no rocks older than ≈ 3.8 Ga have survived so in order to examine the differentiation this planet, chemical signatures must be used. Critical in tracing core formation are the siderophile-element abundances, which would be preferentially partitioned into the FeS/Fe-metal core. Indeed, the Earth's mantle is depleted in these elements relative to primordial CI chondrites (e.g., [3-6]). It is the magnitude of these depletions which is used to model core formation producing the following models: 1) Heterogeneous Accretion - multiple accretion and core formation stages (e.g., [7,8]); 2) Inefficient Core Formation - retention of Fe-metal + sulphides in the mantle during core formation (e.g., [9,10]). These depletions produce siderophile element abundances (W, Mo, Ru, Rh, Pd, Ir, Pt, Au, Sn, Sb) in a primitive mantle of 0.5 to 20 ppb [4,11]. Siderophile element abundances from lunar rocks indicate they are depleted by a factor of 27 ± 20 [12] relative to the Earth's mantle. Accurate determination of these elements at such low abundances is critical for the development of the models briefly outlined above. Previously, siderophile element abundances have been determined by neutron activation techniques (e.g., [11]), nickel assay ICP-MS (e.g., [13]), and isotope dilution spark-source mass spectrometry [14]. Neutron activation requires irradiation and several weeks for completion of the counting procedures, nickel assay ICP-MS requires a pre-concentration stages prior to dissolution, and ID-SSMS requires a lot of sample preparation and can only analyze for a limited number of elements at any one time

The purpose of this paper is to report an initial study using ICP-MS analytical techniques as a fast and accurate method for siderophile element determination. The ultimate goal is to be able to accurately determine the abundances of a number of siderophile elements in silicates without pre-concentration.

ICP-MS TECHNIQUE: The initial study utilized a VG PQIISTE quadrupole ICP-MS fitted with a de Galan "V-groove" nebulizer. This was coupled with standard liquid sample introduction apparatus. The spray chamber was cooled to 5°C and the aspirated liquid sample was taken into a plasma of high purity (99.999% Ar) dry argon, where it was ionized. The machine was first tuned using a 10 ppb solution of Be, Co, In, Ce, Pb, Bi, and U. The signal was optimized at In and Pb in order to give the strongest signal over the desired mass range. The ion beam was detected in pulse counting mode and each sample was analyzed for 40 seconds in scanning mode.

Samples were prepared from a stock solution of SPEX standard containing 10 ppm Ru, Rh, Pd, Sn, Sb, Te, Hf, Ir, Pt, and Au. Samples and standards were prepared at 1 ppb, 750 ppt, 500 ppt, 250 ppt, 200 ppt, 150 ppt, 100 ppt, and 50 ppt in a matrix of 10% HCl. Three internal standards (all at 10 ppb) were used to cover the mass range and these were Sr, Sm, and Pb. One standard and five sample analyses were undertaken at each concentration.

RESULTS: Results for 50 ppt, 500 ppt and 1 ppb samples are presented in Fig. 1 along with 1 sigma error bars. These results are not directly blank subtracted and the method of standardization attempts to remove such background effects. For example, standard samples are plotted on a graph of concentration (entered by the user) against counts per second detected by the machine. At zero concentration, all standards intersect the cps axis beneath the 50 ppt standard, but above zero cps. This appears to be successful at removing blank effects at higher concentrations, but blank contributions may be raising the 50 ppt samples above the 50 ppt level (Fig. 1a). Blank levels were calculated by twice analyzing a 10% HCl solution spiked with the

internal standards. NOTE: the HCl was only single distilled and blank levels calculated using the standards from this study are as follows: 55 ppt Ru; 15 ppt Rh; 24 ppt Pd; 46 ppt Sn; 20 ppt Sb; 16 ppt Hf; 25 ppt Ir; 20 ppt Pt; and 2 ppt Au. Further interpolation of the standard data is required to totally remove the effects of blank contributions. It is envisaged that double-distilled acids will allow a further reduction of these blank levels to allow lower concentrations to be analyzed (see below).

It is evident that characterization of siderophile element concentrations down to 50 ppt is possible using the ICP-MS set-up outlined above, although analysis of the raw data indicates that the detection limit is approached at 50 ppt. There are many factors which can account for the error bars associated with some of these analyses (i.e., Pd and Sn), such as high ionization potential, blank levels (see above), machine stability, etc. Optimizing the ion beam in order to sample the area in the plasma which is most efficiently ionizing the siderophile elements can be carried out by adjustment of the torch position. Machine short-term stability is generally better than 5% across the mass range, but can be improved by use of the USN which allows increased stability and sensitivity. It is essential at such low concentrations that the aerosol is desolvated as high solvent loadings lead to high levels of interference ions [15]. Detection limits are usually improved by an order of magnitude by use of the USN [16]. The ICP-MS facility at Notre Dame is in the process of installing an USN.

PROBLEMS: The above discussion demonstrates that the ICP-MS can be used to analyze for siderophile-element abundances. Application to "real rocks" is currently underway and blank levels in HF, HNO₃, and HClO₄ acids (all double distilled) will be closely monitored. Problems of dissolution of refractory phases is a potential problem, but for the siderophile elements Totland et al. [17] suggested that microwave digestion is adequate to ensure that phases containing these elements are fully dissolved. Such a set-up is available at Notre Dame. Another problem is detection limit coupled with reproducibility. While we have analyzed the standard solutions five times using the somewhat crude technique outlined above, the reproducibility, especially at 50 ppt, needs to be substantiated. Furthermore, the ICP-MS requires dilution of solid samples to $\leq 2\%$ total dissolved solids (TDS). This translates to extremely low siderophile element concentrations, especially as abundances are generally low to begin with. For example, an elemental concentration of 5 ppb translates to 100 ppt at 2% TDS. While such a concentration is within the detection limits of the technique described above, an initial concentration of 0.5 ppb will require the use of the USN.

CONCLUSIONS: The ICP-MS can analyze siderophile element abundances down to 50 ppt concentrations (after dilution to $\leq 2\%$ TDS). Extending these detection limits to lower values requires reduction of blank levels in reagents, as well as use of an ultrasonic nebulizer to increase machine stability. Work is currently underway to fully quantify this analytical technique and its application to rock samples.

REFS: [1] Solomon et al. (1981) BVSP, 1129-1234; [2] Newsom (1990) Origin of the Earth, 273-288; [3] Chou et al. (1983) PLPSC 13th, A507-A518; [4] Wänke et al. (1984) Archean Geochemistry, 1-24; [5] Drake et al. (1989) GCA 53, 2101-2111; [6] Newsom et al. (1986) EPSL 80, 299-313; [7] Chou (1978) PLPSC 9th, 219-230; [8] Wänke (1981) Phil. Trans. Roy. Soc. London A303, 287-302; [9] Arculus and Delano (1981) GCA 45, 1331-1343; [10] Jones and Drake (1986) Nature 322, 221-228; [11] Sims et al. (1990) Origin of the Earth, 291-317; [12] Newsom (1986) Origin of the Moon, 203-229; [13] Jackson et al. (1990) Chem. Geol. 83, 119-132; [14] Jochum et al. (1988) Fresenius Z. Anal. Chem. 331, 104-110; [15] Williams (1992) Hdbk. of ICP-MS, 58-80; [16] Tingfa et al. (1990) J. Anal. Atom. Spectrom.; [17] Totland et al. (1992) Chem. Geol. 95, 35-62.

