SELENIUM DURING STEPWISE DISSOLUTION OF ALLENDE – AN EXPLORATORY STUDY.

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Summary: Abundance and isotopic composition of Se have been determined during stepwise dissolution of the Allende meteorite. From preliminary results we conclude that there is no evidence for mass-independent isotopic effects larger than an (at this stage still rather imprecise) upper limit of ~1 ‰.

Introduction: A so far unique class of isotope abundance anomaly is that observed in chromium during stepwise dissolution of the most primitive carbonaceous chondrites [1,2]. The largest effects have been seen in CI Orgueil, with relative overabundances of ^{54}Cr up to 2.5 % in HCl leaches of subfractions [3,4]. No effects have been found in the same leach fractions for other elements of the solar system abundance peak around Fe [1,5]. As far as the possible origin of excess ^{54}Cr is concerned, this has mostly been considered in connection with the overabundances of the neutron-rich isotopes of the Fe peak elements found in Ca-Al-rich inclusions (CAIs; e.g., [6]). One explanation for the pattern observed there is a multizone mixing (MZM) model of neutron-rich nuclear statistical equilibrium [7], but there exists the alternative of a neutron capture process such as the r-process [8] or a neutron burst [9].

If excess ^{54}Cr in the leaches [1,2] were due to such a neutron capture effect, effects in other elements accompanying it might more easily be found in the heavy elements that quite generally owe their existence to neutron capture reactions. Hence, selenium should be a good element to have a closer look at: a) it is not too far removed from Cr; b) it is located on the first of the r-process abundance peaks in the solar system abundance distribution (associated with magic neutron number N=50); c) and – maybe most crucially – while mostly occurring in association with sulfur [10] - selenium, like chromium, can occur in a variety of valence states. This property may be crucial in finding an existing effect by the stepwise dissolution technique.

Experimental: First trial experiments reported here were performed on the Allende C3V carbonaceous chondrite. Dissolution steps were identical to those used by [2], up to dissolution by HF/HCl. The solutions were slowly dried down, taken up with 3 ml of HCl and then exposed to cotton pretreated with thioglycolic acid for quantitative adsorption of selenium [11,12]. Selenium was released from the cotton using 200 µl of 6 N HNO$_3$, again transferred into HCl (in order to have Se in the +4 valence state) and then distilled and reduced to Se^{-2} using NaBH$_4$ [13]. Overall yields for this rather complex procedure were on the order of 50 %, but we hope to improve them as we gain more experience. Small amounts of almost pure (~99 %) ^{74}Se were added in order to determine the amounts of Se dissolved by isotope dilution.

Thermally Se does not readily form positive ions, and ICP-MS under standard conditions leads to serious interferences in the Se region such as ^{40}Ar$_2$ at mass 80. Hence, isotopic compositions were measured by N-TIMS on a single-collector Finnigan MAT 261. Samples after collection from the distillation in HNO$_3$ were dried and taken up again in aqueous solution immediately prior to loading on single Re filaments. Ba(OH)$_2$ as emitter and colloidal graphite (Aquadag) were added following procedures described by [14]. Measured ratios were internally normalized to ^{78}Se/^{80}Se = 0.479207 [15]. Analysis times ranged from 4 to 12 hours corresponding to 20 to 50 blocks of data each containing 9 complete sets of isotopic ratios. Most data were taken by electron multiplier in the analog mode.

Results: Results have been obtained so far up to the HCl 80°C solution step; they are summarized in Table 1 and Figs. 1 and 2. Table 1 shows the amounts of Se (normalized to bulk meteorite). Those dissolved by acetic acid, nitric acid and hydrochloric acid at room temperature are all rather similar, each corresponding to ~2 ppm concentrations in bulk Allende. Much less is dissolved by the subsequent higher temperature HCl treatments. Taken a total Se content for Allende of 9 ppm [10], it seems – not unexpected - that most Se occurs in sulfates and sulfides susceptible to these acids and that only a small fraction is associated with silicate and/or more acid-resistant phases.

acetic acid	nitric acid	HCl RT	HCl 40°C	HCl 80°C
2.0 ppm	1.9 ppm	2.2 ppm	0.3 ppm	0.1 ppm

Table 1: Amounts of Se dissolved (relative to bulk). RT= room temperature.

Isotopic compositions are compared to measurements of terrestrial standards in Fig.1. Here we concentrate on the ^{82}Se/^{80}Se ratio, because in all likelihood an isotopic effect related to that in ^{54}Cr would show up as an overabundance of the most neutron-rich (r-only) isotope ^{82}Se. For the 40°C HCl leach fraction we were not able to obtain meaningful data on the unspiked sample. The data point shown instead is from a spiked sample, where the amount of spike added was low

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enough to be negligible at all isotopes except [74,76]Se. Obviously precision is not yet at the level we would like to achieve, but taken at face value any deviations in internally (to $^{78}Se/^{80}Se$) normalized $^{82}Se/^{80}Se$ ratios from normal are < 3 ‰, and hence there are clearly no effects comparable in size to what has been observed for [54]Cr in Orgueil [3].
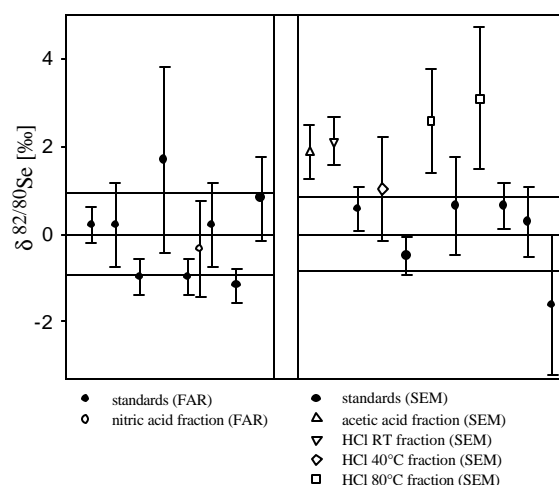

Fig. 1. $^{82}Se/^{80}Se$ ratios during stepwise dissolution of Allende. Data have been internally corrected for mass dependent fractionation using $^{78}Se/^{80}Se = 0.479207$ [15]. Shown are deviations from the mean of standards in ‰. Errors are 2σ. The lines indicate the variability of the standards (standard deviation around the mean). Left: Faraday measurements; right: multiplier.

Closer inspection shows that while the composition of the nitric acid fraction, which could be measured on the Faraday collector, plots right on the average for standards (Fig. 1, left), the samples measured on the multiplier all show somewhat enhanced $^{82}Se/^{80}Se$, by about 2-3 ‰ (Fig. 1, right). We believe this to be an artifact. This is based on the normality of the nitric acid fraction, and the apparently correlated enhancement of ^{77}Se (Fig. 2). While more exotic explanations cannot be ruled out at this stage, a likely explanation is the presence of unidentified intereferences, of about equal size at masses 77 and 82. This is also supported by the fact that we sometimes in case of very small samples clearly observed interferences at masses 74 and 76. Remaining non-mass dependent isotopic effects at ^{82}Se after correction based on the correlation with mass 77 (Fig. 2; and assuming normal ^{77}Se) are at most ~1 ‰.

This is, in fact, not surprising. Taking our clues from chromium again, the large ^{54}Cr excesses during stepwise dissolution have only been seen in C1 meteorites, with effects much subdued in C2s and essentially absent from thermally more metamorphosed meteorites

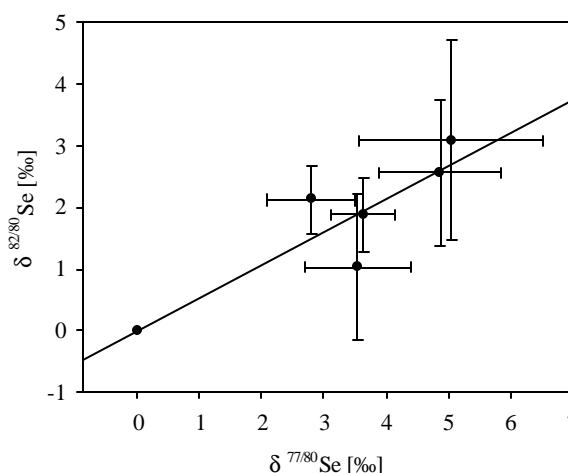such as C3V Allende [1], presumably due to redistribution and homogenization.

Fig. 2. Correlation of d $^{82}Se/^{80}Se$ and d $^{77}Se/^{80}Se$ for leaching steps measured with multiplier. Errors are 2σ.

Perspectives: Our preliminary data obtained show that the project should be feasible in principle. Higher precision data will be obtained due to improvements in chemistry and changeover from the single collector mass spectrometer used in this exploratory study to one with multiple Faraday collectors and/or ion counting system. When this has been demonstrated, we will apply the techniques to the more interesting case of C2 and C1 meteorites.

Another potential application of Se isotopes in meteorites as a tracer of chemical reactions is suggested by the large mass-dependent effects observed during chemical transformation [14,12].

References: [1] Rotaru M. et al. (1992) *Nature 358*, 465-470. [2] Podosek F.A. et al. (1997) *Meteorit. Planet. Sci. 32*, 617-627. [3] Nichols R.H.Jr. et al. (1998) *Lunar Planet. Sci. XXIX*, #1748 (CD-ROM). [4] Alexander C.M.O'D. (2002) *Lunar Planet. Sci. XXXIII, #1872.* [5] Podosek F.A. et al. (1997) *Lunar Planet. Sci. XXVIII*, 1121-1122. [6] Loss R.D. and Lugmair G.W. (1990) *Ap. J. 360*, L59-L62. [7] Hartmann D. et al. (1985) *Ap. J. 297*, 837-845. [8] Kratz K.-L. et al. (2001) *Mem. S.A. It. 72*, 453-466. [9] Meyer B.S. et al. (2000) *Ap. J. 540*, L49-L52. [10] Dreibus G. et al. (1995) *Meteoritics 30*, 439-445. [11] Yu M. Q. et al. (1983) *Talanta 30*, 265-270. [12] Rouxel O. et al. (2002) *Geochim. Cosmochim. Acta 66*, 3191-3199. [13] Tanzer D. and Heumann K. G (1991) *Anal. Chem. 63*, 1984-1989. [14] Johnson T.M. et al. (1999) *Geochim. Cosmochim. Acta 63*, 2775-2783. [15] Wachsmann M. and Heumann K.G. (1992) *Int. J. Mass Spectr. Ion Proc. 114*, 209-220.