VOLATILE ELEMENT ENRICHMENTS IN INTERPLANETARY DUST DUE TO NEBULAR PROCESSES? T. Stephan, D. Rost and E. K. Jessberger, Institut für Planetologie, Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany; stephan@nwz.uni-muenster.de.

Introduction. Interplanetary dust particles (IDPs) potentially allow to investigate the most pristine solar system bodies, comets and asteroids. Therefore, they should be predestined to provide information on nebular processes. Many stratospheric IDPs are richer in volatile elements than CI chondrites (cf. compilation by Arndt *et al.* [1]) while the abundances of major elements usually are chondritic. Attempts to explain the enrichments range from postulating a new type of volatile rich chondrite-like matter [2] to invoking atmospheric contamination processes [3]. Before far reaching conclusions on nebular processes can be drawn, stratospheric processes, contamination during capture and handling, artifacts from various selection effects or from analytical techniques and even from numerical data treatment have to be excluded.

Contamination. After the probable importance of stratospheric contamination processes was emphasized based on plausibility reasoning [3], the first direct experimental evidence for contamination – at least for Br, the element with the highest enrichment, up to $10^3\times$CI – were Br-salt nano-crystals attached to IDP W7029E5 [4] and a halogen rich exterior rim of IDP L2006G1 found with TOF-SIMS (time-of-flight secondary ion mass spectrometry) [5]. The distributions of secondary halogen ions emitted from a section of this IDP upon sputtering with primary Ga^+ ions (Fig. 1) reveal an outer ring structure for F, Cl, and also Br, though the latter image is disturbed by rather high background. Assuming a spherical particle, 20 µm in diameter, and a continuous 1.5 µm thick surface layer, this layer represents ≈28 vol.-% of the IDP. This estimate is an upper limit but illustrates the influence that surface contamination might have on bulk chemistry.

To test more directly for surface contamination, we analyzed the *original* surfaces of stratospheric particles with TOF-SIMS. A major analytical problem results from residual silicone oil from IDP collection and handling that often cannot be completely removed, even not by extensive hexane rinsing. Nevertheless, we unequivocally detected F, Cl, and Br on the very surfaces of six particles – one Fe,NiS-rich IDP (U2071H9), four Al_2O_3 spheres (rocket exhaust), and one Ca-rich particle of unknown origin. Extensive sputtering reduced and finally removed the halogens from the Al_2O_3 surfaces, an unambiguous proof of a contamination surface layer.

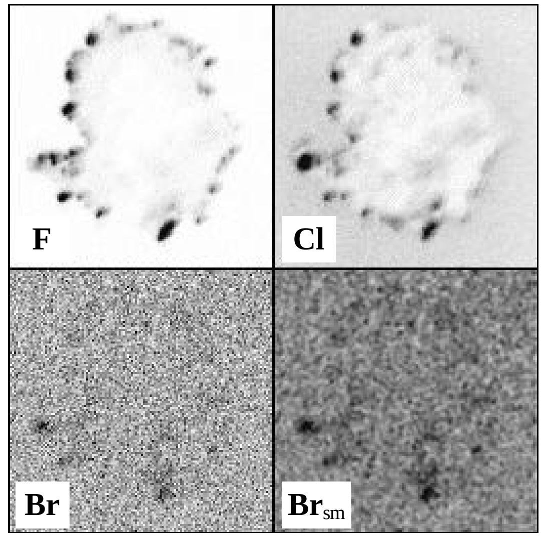

Fig. 1: Lateral distribution of negatively charged secondary F, Cl, and Br ions, respectively, from IDP L2006G1. The three elements are clearly correlated. Field of view is 30×30 µm^2, high intensity is shown as black. Since the background of Br is relatively high, we also show a smoothed Br image (Br$_{sm}$). In this section the halogens occur in a 1.5 µm thick rim surrounding the 20 µm (diameter) sized particle.

Arndt *et al.* [6,7] studied experimentally the question *when* contamination occurred by exposing to the stratosphere IDP analogues on a capture flag. Br was measured with PIXE before and after flight. Br concentrations before were below detection limit, while after significant Br signals were detected. The stratospheric air column passed by the collector even quantitatively accounts for the Br contamination.

Another source of contamination observed in our TOF-SIMS study was surface correlated Be resulting from SEM EDS analysis performed on Be substrates. After such analyses some particles tend to stick to the substrate and carry Be after they were removed.

For other elements no unambiguous evidence for or against contamination is available so far.

Selection effects. Stratospheric IDPs are subject to selection processes. Thus, the collected particles only roughly represent the near Earth dust population. The first and maybe most severe selection is caused by the stratosphere itself, more precisely by atmospheric entry heating. Large and high-velocity particles do not survive entry into the atmosphere and thus smaller and slower particles are over-represented [8].

Another *human* selection occurs, prevailing in most studies, in that mostly only "chondritic looking" (black and fluffy) particles are picked from the collector flags [9] and only particles pre-classified from SEM EDS analysis as "cosmic" are further investigated. The latter classification is mainly based on major element composition. This strong bias might be the main reason for the observation that *cosmic particles* are usually *chondritic***.**

Analytical techniques and data treatment. To measure trace element concentrations in IDPs very often approaches the limits of detection of most analytical techniques. Therefore, the *average* concentrations of trace elements are prone to be overestimated since element abundances below detection limits are typically not considered.

To calculate averages itself is also a problem. The general question is: What does an average tell us if individual IDPs have individual and different parent bodies? Certainly, one does this exercise in order to search for large scale similarities. But *strictu sensu* only the mean composition of particles that demonstrably – by whatever means – are related to each other provides information on the chemical composition of their precursor. However, no criteria to demonstrate a relation have so far been developed.

Most trace element abundances are only known as element ratios relative to a major element, Fe [1]. Low Fe can therefore feign high trace element contents and elements anti-correlated with Fe are overestimated. However, by discussing element *groups* as done by Arndt *et al.* [1] this effect is minimized.

Another question is: Which *type* of average, e.g., geometric or arithmetic, most reliably reproduces the original the parent body composition? If all particles had the same mass and Fe-concentration, the arithmetic average would be the best choice. If absolute atom numbers were available for all individual IDPs and if all selection effects were neglected, then the *summed* atom numbers would represent the parent body composition [10]. However, in the doable case, i.e., with the existing limited data set, the geometric averages are appropriate [1]. One also has to keep in mind that within individual IDPs the trace element distributions are largely variable and reflect chemical inhomogeneity on a micron scale [1,11].

Discussion. Since trace element abundances are available for only 89 stratospheric particles the reliability of any conclusion from *average* compositions has to be closely scrutinized [1]. If not all IDPs have the same parent body, averaging can be instrumental to detect features common to *all* IDPs like contamination or to define groups of IDPs that reflect large scale chemical differences of the source regions.

Cl and Br enrichments already have been attributed to atmospheric contamination processes. As, Rb, and Zr were detected only in a few IDPs since their limits of detection are close to the chondritic values. Thus, the significance of the enrichments remains questionable [1]. The other elements that are enriched at least in chemically defined subgroups of the whole IDP set – P, Cu, Ga, Ge, Se, and Zn – show distributions over about one or two orders of magnitude that include the respective chondritic values. Geometric averages yield enrichment factors of about 2 for these elements that appear to be significant, questionable possibly for Ge.

S and Ca, on the other hand, are significantly depleted in almost all IDPs and only a few particles with enrichments have been found [1]. S depletion by atmospheric entry heating has been proposed [12]. In CI chondrites, the best available analogue to chondritic IDP parent bodies, Ca occurs as carbonate. Therefore, Ca depletion may result from two effects: First, during disruption of the parent bodies carbonate-rich grains are released that might be too large to survive atmospheric entry. Second, if individual carbonates survive they would probably be discarded as terrestrial contamination since their composition is far from CI-like. Similar selection effects can produce apparent enrichments as well as depletions also for other elements.

Conclusions. Since only little is known about the actual host phase of most trace elements even in CI chondrites, far reaching conclusions on enrichments in IDPs cannot be drawn. Selection effects during brake-up of the parent body, capture by the Earth and by the collector, as well as particle picking in the laboratory may strongly bias the sample assemblage. Nevertheless, since most IDPs chemically are remarkably similar to CI chondrites they most probably represent an adequate sample of primitive solar system material and even the only available sample of comets.

References. [1] Arndt P. et al. (1996) Meteorit. Planet. Sci. 31, 817–833. [2] Flynn G. J. and Sutton S. R. (1992) LPS 23, 373–374. [3] Jessberger E. K. et al. (1992) EPSL 112, 91–99. [4] Rietmeijer F. J. M. (1993) JGR 98, E7409–E7414. [5] Stephan T. et al. (1994) LPS 25, 1341–1342. [6] Arndt P. et al. (1996) Meteorit. Planet. Sci. 31, A8. [7] Arndt P., pers. comm. [8] Love S. G. and Brownlee D. E. (1994) Meteoritics 29, 69-70. [9] Warren J. L., pers. comm. [10] Jessberger E. K. et al. (1988) Nature 332, 691–695. [11] Stephan T. et al. (1994) EPSL 128, 453–467. [12] Flynn G. J. et al. (1993) LPS 24, 497-498.