**INTRODUCTION**: The library of extraterrestrial organic compounds in carbonaceous chondrites has mostly been elucidated by analytical techniques that require the destruction of the sample for their extraction [1 and references therein]. This methodology is acceptable for purely qualitative or quantitative research objectives i.e. to determine what organic species are present or the concentration of individual organic species, respectively. However these do not consider the inorganic mineral phase of the sample which is, in many instances, destroyed in order to liberate the organic component. This means that any information regarding the spatial relationship between the mineral types and the organic species is lost. There have been many in situ analyses attempted with varying degrees of effectiveness and reliability involving molecular labelling [2, 3], fluorimetry [4-6], or combining microscopy and various spectroscopies [7, 8]. We will describe progress towards developing a non-reactive, easily produced, fluorescent sensor that may be a solution to resolving spatial discrimination.

**Rationale**: The lanthanide (Ln) elements europium (Eu) and terbium (Tb) are atoms which produce very well defined and indicative fluorescent spectral emissions which are narrow, line-like, sharp, high intensity and very long lived [9]. Since fluorescent emissions are governed by electronic transitions, any external interactions that may energetically perturb or affect the system can likewise perturb the luminescent emission characteristics. Any organic molecules that interact could alter the known spectra [10, 11]. Therefore, theoretically, the spectra will be uniquely altered depending upon the specific interaction afforded by each individual analyte. This could allow direct molecular identification, in situ or within solution. In order to make use of these fluorescent properties, the elements need to be rendered chemically inert but at the same time must remain susceptible to electronic interactions. To achieve this, an organic ligand must be employed to yield a stable complex. LnDOTA complexes are already used in imaging applications, biomedical research and biological assays [12, 13] so it was logical to investigate their applicability to fluorimetric analysis of extraterrestrial organics. DOTA (1,4,7,10-tetraazacyclododecanetetracetic acid), a tetra-substituted cyclen ring, was chosen as a plausible organic ligand because its structure, ability to chelate and its co-ordination sphere are well characterised. DOTA is also commercially available and easy to prepare.

DOTA complexes are known to be very stable [10, 14], because the Ln is entirely enveloped within the DOTA structure. This is advantageous because, once prepared, the complex can be stored over time with little degradation and, once in solution, is unlikely to dissociate. The disadvantage of this is that the Ln is entirely shielded from any analyte, resulting in little or no analyte/Ln interaction. Experimental procedures were designed to investigate these theoretical advantages and disadvantages.

**Methodology**: Sources of intrinsic fluorescence (organic and inorganic) have been identified according to the criteria that: i) their excitation and/or emission wavelengths are similar to that of the LnDOTA complex, ii) they interact with the sensor altering the fluorescent properties of one or other or both or iii) there is a chemical reaction between the mineral or organic molecule which destroys the LnDOTA complex entirely. Design of an inert and very stable sensor molecule should prevent the latter, but the former two criteria would need to be back-ground corrected for so that any LnDOTA/analyte interaction can be characterised and data collected.

DOTA (abcr GmbH, Germany) was chelated with Eu3+ and Tb3+ respectively. DOTA was combined with hydrated chloride salts of Eu and Tb, separately, in 18.2 Ω water, with a stoichiometry such that the DOTA was in slight excess. The reaction mixture was maintained at 80°C and stirred for 24 hours under a nitrogen atmosphere. The reaction mixture was freeze dried and the resulting precipitate washed under vacuum with 0°C diethyl ether.

Approximately 50 compounds of a range of chemical classes were chosen as analytes to give a good representation of the organics previously identified in extraterrestrial samples. These compounds were chosen depending on their structural and electronic properties and whether these may give them a propensity to interact electrostatically, perturb the electronic state of the Ln metal ion and affect any fluorescent spectral emission.

An EuDOTA baseline fluorescent spectrum was obtained and compared against EuDOTA/analyte mixtures of a range of concentrations resembling those present in extraterrestrial samples. Upon collation and
analysis of results (discussed vide infra) a much reduced set of analytes were chosen for experimentation with TbDOTA.

**Results & Discussion:** Initial results for EuDOTA/analyte showed no change in fluorescent intensity or emission spectrum for any of the analytes at the concentrations found in extraterrestrial samples (μM to nM) with this particular sensor. Two possible hypotheses were suggested; 1) there is no interaction at all at any concentration of analyte with the sensor or 2) there is an intrinsic limit of detection.

In order to rule out 2) and confirm 1) the EuDOTA and TbDOTA experiments were carried out at equimolar concentration with a reduced suite of analytes. There was a detectable increase in fluorescent intensity for some analytes (e.g. adenine, Figure 1A), and decrease for others (e.g. ornithine, Figure 1B). However there was no discernable trend in behaviour according to analyte structure or how they might interact as a result.

It is probable that any increase in intensity of the fluorescent emission was due to displacement of water molecules from the complex coordination sphere. Any reduction of fluorescent emission could be as a result of quenching by the analyte. Neither scenario necessarily indicates a direct analyte/Ln interaction; further investigation would help elucidate this. The first coordination sphere geometry for Ln is square antiprismatic, i.e. eight-coordination. It is, therefore, most likely that the four nitrogen atoms of the cyclen ring and the four ethanoate pendant arms of the DOTA molecule occupy all eight coordination points. This prohibits, or at least reduces, the ease with which the analyte can approach the Eu or Tb atom thereby minimising any subsequent changes in fluorescent signal.

Attention has now turned to the tris-substituted cyclen ring, DO3A, which has one less ethanoate pendant arm than DOTA. Although this reduces the stability of the Ln complex, it has the advantage of increasing ease of access for the analyte thereby facilitating ability to directly couple with the Ln atom.

**Conclusion:** It is clear that DOTA is, as expected, an unsuitable ligand to use for further development of the sensor. Experimentation has shown that neither the EuDOTA nor the TbDOTA complex exhibited a change in fluorescent spectrum, so it is the ligand that requires modification not the choice of Ln. We will present results from the development and preliminary testing of the DO3A sensor.


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Figure 1. Fluorescent emission spectra of EuDOTA and EuDOTA/adenine, A), and EuDOTA/ornithine, B), at equimolar concentrations of 1 mM for comparison.