

HALOGEN CONCENTRATION AND DISTRIBUTION IN ALLAN HILLS 84001 MEASURED BY TIME-OF-FLIGHT SECONDARY ION MASS SPECTROMETRY. G. Holland¹, I. C. Lyon¹, B. Cliff², N. P. Lockyer², and J. C. Vickerman², ¹Department of Earth Sciences, University of Manchester, Manchester, M13 9PL, UK (gholland@fs1.ge.man.ac.uk), ²Department of Chemistry, University of Manchester, Institute of Science and Technology, Manchester, M60 1QD, UK.

Introduction: The study of halogens in ALH 84001, particularly I, may be important as a possible biomarker [1] for assessing the claims of [2] that evidence of ancient martian life is present in ALH 84001 carbonates. Time of flight secondary ionisation mass spectrometry (TOF-SIMS) was performed on two small (4–8 mg) polished grains from ALH 84001, 287 in an attempt to determine halogen concentrations and distribution between phases.

Experimental: Analyses were obtained using the BIO-TOF instrument at UMIST [3]. Data were acquired using a Ga⁺ primary beam with a current of 4nA and an accelerating voltage of 13kV. A ~5 µm spatial resolution was used to obtain high count rates whilst still providing sufficient spatial resolution to investigate possible relationships between halogen concentration and mineral phase. Accompanying electron probe analyses of carbonates were performed using the Manchester Cameca SX100 EPMA with an accelerating voltage of 15 kV and a beam current of 10nA defocused onto a ~7 µm diameter spot.

Results: Electron probe microanalyses of ALH 84001 carbonate rosette suggests an average chlorine concentration of 1000 ppm varying between ~700 ppm and ~1200 ppm but with no clear zonation. These concentrations are consistent with the bulk value in ALH 84001 of 1.9–5.1 ppm [4].

Chlorine was observed in the carbonate by TOF-SIMS that correlates well with chlorine distribution from EPMA analyses. Therefore by comparing the chlorine concentrations from EPMA analyses and integrated counts of ³⁵Cl and ³⁷Cl peaks in the carbonate spectra, a TOF-SIMS chlorine sensitivity calibration can be made. Bromine and I were not detected. Assuming identical sensitivities for chlorine, bromine and I [5], a 500 ppb upper limit for bromine and I in the carbonate can be estimated. This is equal to the average I concentration in ALH 84001 carbonate estimated by [1]. Inhomogeneous distribution of I due to zoning might be expected to have produced an observable I signal above our detection limit in parts of the carbonate. In its absence we tentatively infer that there is no large heterogeneity in I within the carbonate. This is heavily dependant on sensitivity. If sensitivity depends on electron affinity, I detection limits would be higher, implying >500 ppb I.

Chlorine, bromine and I were observed in two different regions of chromite neighbouring the carbonate. The

bromine and I signals from chromite are five times greater than from an equivalent area of epoxy so contamination is not thought to be a problem. If halogen sensitivities are assumed to be the same in chromite as they are in carbonate, this yields bromine and I concentrations of ~8.5 ppm and ~1.5 ppm respectively. If all the I in ALH 84001 were present solely in similar chromite with a modal abundance of 1% [6], the bulk I concentration in ALH 84001 would be ~15 ppb. This is within the 10–40 ppb bulk value estimated by [1]. The possibility of reduced sensitivity for bromine and I would increase these concentrations.

Discussion: Chlorine concentrations of 1000 ppm in the carbonate are significantly greater than typical values of ~150 ppm in terrestrial carbonate [7]. This could reflect a concentration of salts in the source fluid as suggested in evaporite models [e.g., 8].

Chromite is assumed to be igneous in origin [6]. It is unclear how a primary igneous mineral now contains sufficient amounts of bromine and I to be detectable using TOF-SIMS. Unfortunately with no electron probe chlorine concentrations for chromite, the estimated concentrations are speculative. Further electron probe analyses for chlorine are planned that will aid calibration of TOF-SIMS halogen peaks in chromite. However, even if the calibrations are in error, the presence of bromine and I in chromite is real. It is possible that terrestrial chlorine (and other halogens) may have contaminated ALH 84001 as is observed in Antarctic shergottites [9], although release of I with martian atmosphere in bulk ALH 84001 makes this unlikely [1]. Contamination during sample preparation is also unlikely.

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