C, N, O abundances and isotopic compositions in the Sun

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For most elements, their solar (=cosmic) abundance and primordial isotopic composition have historically been determined via precise laboratory measurements of primitive meteorites. However, this approach is not possible for highly volatile elements which are strongly depleted, relative to the solar photosphere, even in CI chondrites. Similarly, isotopic compositions, especially for N and O, are so variable among planetary bodies and components of meteorites that distinguishing an average starting composition for the solar nebula was impossible prior to the Genesis mission [1]. By analyzing solar wind (SW) captured in high purity targets, the Genesis science team established that the nitrogen [2] and oxygen [3] isotopic compositions of the Sun are grossly different than those of Earth and almost all planetary materials of the inner solar system. The mechanisms to establish isotopic fractionations of ~40% (N) and ~7% (non-mass-dependent for O) from the average solar nebula starting composition are still being investigated and it is interesting to consider the isotopic shifts in the light of elemental depletions in planetary matter. For this and other purposes, it is necessary to know the solar elemental composition of elements heavier than He.

Photospheric determinations of the solar abundances of the most significant volatile elements (C, N, O) have recently undergone serious revision downward by factors of 1.7 (O), 1.7 (N) and 1.3 (C), thus reducing the solar "metallicity" from 0.0201 to 0.0134 [4]. While solving some long-standing astronomical problems related to the Sun's composition and age, the new results are at odds with models of the solar interior based on helioseismology [see 4]. This discrepancy remains unresolved. We analyzed Genesis Si and SiC targets to determine the fluences of C, N, and O in captured SW. These data can be related to absolute abundances in the Sun when considered with H fluence and a model of ion fractionation in formation and acceleration of the SW.

Fluences of C, N, and O were obtained by back-side depth profiling of passive (Si) collectors that had been mechanically thinned [5]. Even with this approach, background corrections were relatively high: ~4 % for ¹²C, ~20% for ¹⁶O and ~6% for ¹⁴N. The O fluence can be measured with lower background on the SiC target of the SW Concentrator by utilizing the known concentration factor as a function of radius determined from ²⁰Ne data [6]. Preliminary results for the inter-element ratios C/O and N/O agree within uncertainty with the new photospheric compositions, suggesting that high first ionization potential elements are not fractionated relative to each other and lending confidence to the new photospheric abundances.

References: [1] Burnett et al. (2011) *PNAS* **108**, 19147-19151. [2] Marty et al. (2011) *Science* **332**, 1533-1536. [3] McKeegan et al. (2011) *Science* **332**, 1528-1532. [4] Asplund et al. (2009) *Ann. Rev. Astron. Astrophys.* **47**, 481-522. [5] Heber et al. (2011) *LPSC* 42, #2642. [6] Heber et al. (2011) *MAPS* **46**, 493-512.

Ion specific effects at the calcite(104) – water interface

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In this study the influence of Li⁺-, Na⁺-, K⁺-, Rb⁺-, and Cs⁺-chloride solutions on the calcite zeta-potential is investigated and surface diffraction data that can be used to relate the observed ion specific effects to the calcite(104) – water interface structure is presented. Specular and off-specular resonant surface diffraction data are used to locate and quantify Rb^+ ions at the calcite(104) – water interface. In a 0.01 molar RbCl solution equilibrated with atmospheric CO₂ and calcite (pH = 8.2), we observe the main Rb^+ species (~0.17) mono layers (ML)) 3.2 Å above the surface, associated with the second well ordered water layer at the interface, a position that might mark the upper end of a Stern layer at the calcite(104) surface [1]. An unexpected result is that there seems to be inner-sphere adsorbed Rb^+ (< 0.1 ML) closely associated with the surface carbonate groups. Additionally there are outer-sphere Rb⁺ species at \sim 5 and \sim 11 Å above the surface, likely associated with Rb⁺ in the diffuse layer above the calcite surface. In order to test to what extent these results are specific for Rb⁺ or whether they can be transferred to the other alkali-metal cations we measured specular surface diffraction data on calcite(104) in contact with equilibrated 0.01 molar alkali chloride solutions across the whole series from Li⁺ to Cs⁺, and indeed certain trends are observable. The analyses of these data is still ongoing and it is not yet clear if changes are due to the increasing number of electrons in the series $Li^+ - Cs^+$ or due to actual changes in interface structure.

Streaming potential measurements performed on an Anton Paar SurPASS electrokinetic analyzer show that, if we successively add Ca²⁺ to a solution containing 0.01 mol/L of an alkali metal chloride as background electrolyte at fixed pH (~9), remarkable changes in the behavior of the calcite zetapotential are observed across the series of 0.01 molar alkali chloride solutions: the Ca²⁺ concentration at which zero zetapotential is measured is 0.5 mmol/L in CsCl solution and increases continuously across the series of alkali metals, up to 2.5 mmol/L in LiCl solution. For Ca²⁺ concentrations >5 mmol/L the calcite zetapotential reaches a plateau. The plateau zetapotential value lies at 5 mV in the LiCl system and at 20 mV in the CsCl system. These two effects clearly demonstrate the ion specific effect of the alkali metal cations on the affinity of Ca2+ ions to the calcite(104) surface. The calcite zetapotential measured as a function of pH in the absence of added Ca²⁺ is the same in 0.01 molar solutions of all alkali metal chlorides investigated. These results may have important implications e.g. for calcite growth-, adsorption-, or surface complexation models.

[1] Heberling et al. (2011) *Journal of Colloid and Interface Science* **354**, 843-857.