Ryugu Samples: Promising Potential Proxies For Solar System Elemental Abundances

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Potential: The discovery that Ryugu samples have kinship to CI-chondrites makes them potential proxies for refining solar system elemental abundances of elements more refractory than water ice at the time of solar system formation. The Sun with most of the solar system's mass is the best candidate to obtain solar system abundances, but not all elements can be quantified in the solar photosphere, and those that can often still have large uncertainties (> 25%) [1]. Thus there is the need for additional proxies to obtain a full set of solar system abundances for the 83 stable and long-lived elements in the periodic table. One reason was and still is that CI- chondrites are the best match to solar photospheric abundances for elements where the comparison can be made [1]. Since the 1960s, the main reason for using CI-chondrites as solar system abundance proxies is that they contain the largest relative amounts of volatile elements among chondrites. We can extend this argument: Both CI-chondrites and Ryugu underwent aqueous alteration on their parent bodies which requires accretion of water ice. Condensation of water ice occurs below the 50% condensation temperatures of the halogens, In, Tl, Hg, Cd, and other highly volatile elements; see updates in [2]. Thus, CI-chondrites and Ryugu samples are primitive (unfractionated) in terms of abundances for elements more refractory than water ice, even though these rocks are certainly not primitive chemically or mineralogically.

Promising: What makes Ryugu samples especially promising is that they are more pristine than CI-chondrites with regard to terrestrial oxidation. Ryugu samples were not exposed to open atmospheric passage, and careful curation prevents their "contamination in the museum", and limits oxidation by air and humidity. This is important for potential loss and/or redistribution of elements (see below). Of course both the Ryugu and CI-parent bodies could have been contaminated on their surfaces by impacts of asteroidal debris.

Problems: Aqueous alteration on the parent asteroids very likely altered (or erased) the "primordial" mineralogy of the original accreting materials. The key questions are whether the alteration was isochemical (closed system without mass loss), and what was the size of such a "closed system". These are old questions, and variations in major and trace element contents in the different CI-chondrites are long known, and cm to km-scale variations might exist on the CI-parent asteroid(s) [3]. Related to widespread ancient fluid circulation is salt precipitation as the free water has disappeared from Ryugu by now. Either all available water from accreted ice ultimately ended up in hydrous silicates, or evaporated from the asteroid, or both. The original rock/ice ratio may have affected the oxidation state if water was involved as an oxidizer (see below). It also affects sample heterogeneity. If evaporation is involved, salts deposit preferentially at the surface-gas (or vacuum) interfaces, and in pore spaces and veins. In that case, halide, carbonate, phosphate, borate, sulfide, and sulfate deposits control elemental abundances of salt-forming elements such as alkalis, alkaline earths, B, C, P, S, halogens, but also e.g., As, Sb, Bi, S, Se, Te, Mn, Sc, Zr, Hf, Nb, Ta, Ag, Au, U, Th, REE. Deposits could be over-abundant (relative to solar elemental abundances) in surface samples unless the regolith was overturned to "rehomogenize" the asteroid. This may also explain some of the known elemental variations among CI-chondrites.

Evidence of salt deposition during water loss is the efflorescence rapidly forming in and on CI-chondrites in museums [4,5]. Here the source of water for mineral transport is from the hygroscopic Mg-sulfates formed by sulfide oxidation with O_2 from the air. This causes acidification, and attack of phyllosilicates and possibly unaltered Mg-silicates to get the Mg for the Mg-sulfates with varying crystal water ($MgSO_4 \cdot (0-7)H_2O$). Efflorescence forms if the water-bearing rocks are stored in vacuum or under dry inert gases because the wet rock will mobilize water (and bring solubles along) to the surfaces to equilibrate the humidity with its surroundings. This is a problem for CIs, but minimized for Ryugu samples although Ryugu samples exposed to air do change [6,7].

Heterogeneity in elemental concentrations can be caused during primary aqueous alteration/serpentinization, where trace elements can be intercalated into layer silicates and/or are selectively dissolved; and during secondary alteration when the water is either used up or evaporated and salts precipitate from a brine. The CIs are more oxidized than Ryugu [e.g., 8], and in stark contrast to Ryugu, the CIs contain ferrihydrite, sulfates, and elemental sulfur (disproportionation product), likely from terrestrial oxidation [4,5]. This tertiary alteration affected the distributions of e.g., Na, K, Ni, and S in CI-chondrites but there is generally not much known about which other elements are affected by this. Differences in bulk sample elemental concentration distributions between Ryugu and CIs will inform which elements could be affected by alteration in humid air. As for sampling issues, white efflorescence forming on the top of the rock means that there is a deficit somewhere else in the rock. Often obviously "veined" or "white" samples were deliberately excluded from bulk analyses of CIs, and "fresh interior"

samples were preferred also because of their lower contamination potential. Chances of local element loss to efflorescence within CIs is rarely discussed. However, with larger number of analyses available, bias from redistribution and sampling on concentrations can also be identified using geochemical and statistical tools [9].

Salt dissolution and (re-)deposition depend on what anions are present as these control the host phases that are present now. A key controlling factor is the oxidizer. It is generally assumed that hydrous minerals formed on the parent bodies from "dry" Mg,Fe silicates, FeNi metal, troilite, and accreted water ice. During aqueous processing, halide salts - the major expected condensates of halogens [10]- dissolve. Accretion of CO_2-ice could account for carbonate formation. But what was the *oxidizer* to make magnetite, phosphates, and Ca-sulfates in Ryugu and CIs? Anoxic alkaline solutions will not lead to magnetite formation, and we still have to explain the phosphates and sulfates.

In [5,11 and references therein] we describe the pathway of magnetite formation which occurs via the Schikorr reaction and with so-called green rust (general formula $[Fe^{II}_{6-x}Fe^{III}_x(OH)_{12}]^{x+} [(A^{n-})_{x/n} \cdot \cdot yH_2O]^{x-}$) as intermediaries, where Fe^{II} also can be replaced by Mg. These phases form on Fe metal in anoxic waters, and contain $(Fe^{II})(OH)_2$ layers with intercalated anions ("A" in the formula) such as hydroxide, chloride, bromide, iodide, carbonate, sulfate, and phosphate. Exposed to air, these isolated phases can be pyrophoric during rapid oxidation of Fe^{2+} in $Fe(OH)_2$ to Fe^{3+}. In solution, depending on availability of dissolved oxygen and pH, oxidation leads to magnetite, or ferrihydrite instead. Thus, meteoritic metal exposed to anoxic solutions containing hydroxide and halogens can form green rusts. But carbonate from organics, phosphate from metallic phases, and sulfate from sulfide require a direct oxidizer or some driving redox reaction(s). One source of an oxidizer on early parent bodies is H_2O dissociation by photolysis or radiolysis by (galactic) cosmic rays which would gradually increase oxidation and magnetite formation. This is where the initial ice/rock ratio comes in which controls the duration/availability of water and oxidation state on the parent bodies. Anions trapped in green rusts are freed during oxidation, which would explain frequent associations of magnetite with carbonates and phosphates, and the origin of iodine in magnetite in CI-chondrites. If green rust phases were still present when CI-chondrites fell, some ferrihydrite with fine intergrown salts may have developed on Earth, consistent with earliest observations of a "caloric behavior" of Orgueil, and possibly with Mössbauer findings of a super-paramagnetic phase in CI-chondrites [8] which is also a property known in green rusts [12].

Proxies: The determination of abundances of the mobile elements such as listed above are affected by sampling and sample sizes because these elements are highly sequestered in halides, carbonates, phosphates, sulfides, and sulfates. Active formation of hygroscopic sulfates in CI-chondrites may contribute to heterogeneous elemental distribution and in the worst case, losses of elements into efflorescence. These effects are traceable in larger samples (50-1000 mg) of CI-chondrites when enough measurements are available for an element to evaluate the concentration distributions. The careful curation of the Ryugu samples essentially remove issues with terrestrial alterations, but the problems remain to obtain representative bulk compositions from small samples when trace element enriched accessory phases such as phosphates are present [e.g., 13]. However, the analyses of multiple elements in smaller bulk samples, knowledge about the trace element composition in accessory phases – both in Ryugu and CI-chondrites- together with geochemical principles will clearly improve our knowledge on solar system abundances of the elements.

References

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