

**FORMATION OF SULFATES ON PARENT BODIES OF CARBONACEOUS CHONDRITES, CERES, EUROPA, AND OTHER ICY BODIES.** M. Yu. Zolotov, School of Earth and Space Exploration, Arizona State University, Tempe AZ 85287-1404, USA, E-mail: zolotov@asu.edu.

**Introduction:** Chemical compounds of  $S^{6+}$ , sulfates and/or  $SO_3$ , occur on Earth, Venus, Mars, parent bodies of carbonaceous chondrites, and icy surfaces of Europa and Ganymede. On the terrestrial planets, formation of  $S^{6+}$  species is related to atmospheric photochemical processes that produce  $O_2$  and other O-rich oxidants. Here we explain the formation of sulfates within chondritic bodies through aqueous oxidation of sulfides by  $O_2$  and  $H_2O_2$  released from irradiated water ices and through accretion of  $S^{6+}$ -bearing ices formed via radiolysis of more reduced sulfur species.

**Chondrites:** Petrographic and chemical studies of CM/CI carbonaceous chondrites indicate the occurrence of Ca, Mg, and Na sulfates and suggest their aqueous deposition on parent bodies [e.g. 1]. Although a low  $H_2$  fugacity ( $f$ ) and  $H_2$  escape favor stability of sulfates,  $H_2$  gas may not separate and escape from low- $fH_2$  solutions on parent bodies. Our models show that a gas phase may not exist at the low  $fH_2$  values needed to stabilize sulfates below  $\sim 70^\circ C$ . The presence of unaltered Fe-Ni metal in CM chondrites implies that  $fH_2$  was not low enough to stabilize sulfates. An elevated  $Fe^{3+}/Fe^{2+}$  ratio in less altered CM and some other chondrites [2,3] is inconsistent with progressive alteration through  $H_2$  escape. Low  $fH_2$  values needed to stabilize chondritic  $Fe^{3+}$  hydroxides/oxyhydroxides (e.g. ferrihydrite) could not be achieved through  $H_2$  escape. The occurrence of sulfates in mildly altered CM and other chondrites (Tagish Lake, Miller Range 07687 [4,5]) and a coexistence of sulfates with ferrihydrite are inconsistent with a  $H_2$  escape scenario. Strong oxidants (e.g.  $H_2O_2$ ) could be needed to explain apparent low-temperature oxidation of aliphatic groups in the insoluble organic matter in carbonaceous chondrites [6]. Although the stability of sulfates in the S-O-H system increases with temperature, mineralogy of metamorphosed chondrites suggests reduction of earlier formed sulfates. Finally, oxidation of sulfides by liquid water (e.g.  $HS^- + 4H_2O \rightarrow SO_4^{2-} + H^+ + 4H_2$ ) is inhibited below  $\sim 150\text{--}200^\circ C$  [7]. These inferences imply an action of strong oxidants at the early low-temperature stages of parent body alteration.

**Plausible formation scenario:** Chondritic sulfates could have formed through rapid low-temperature ( $< 0\text{--}30^\circ C$ ) aqueous oxidation of sulfides by strong oxidants ( $O_2$ ,  $H_2O_2$ ,  $O_3$ ,  $OH^\cdot$ ,  $HO_2$ , etc.) [8,9], which are produced through radiolysis and photolysis of water ice before accretion. Numerous data demonstrate the formation the O-rich compounds through UV [10], electron, proton, ion, and X-ray irradiation of water ice. A

majority of oxidants could have accreted with irradiated ices, consistent with the abundant (1-10%)  $O_2$  in the Jupiter family comet 67/P Churyumov-Gerasimenko [11]. In the presence of  $^{26}Al$ , additional oxidants could have formed through radiolysis of water within bodies [6]. In addition to the parent body oxidation of sulfides,  $H_2SO_4 \cdot nH_2O$  and  $SO_3$  could have formed through irradiation of  $SO_2$ ,  $H_2S$ , and  $S_n$  in water ices [12,13] followed by accretion on parent bodies.

In parent bodies, early acidic fluids formed through aqueous dissociation of  $H_2SO_4$  and  $H^+$  formation in reactions of strong oxidants with reduced S and Fe species. Subsequent dissolution of silicates and oxidation of kamacite led to mineral deposition in increasingly alkaline and  $H_2$ -rich conditions. Although  $SO_4^{2-}$  ions were unaffected by  $H_2$  by kinetic reasons, sulfates precipitated at different stages of aqueous alteration. Low-solubility gypsum formed at early stages while Mg/Na sulfates precipitated from late alkaline and saline fluids. On some bodies, subsequent thermal metamorphism led to reduction of sulfates by organic compounds and  $H_2$ .

Ferrohydrite, some  $CO_2$ , and carbonates could have formed through analogous early rapid oxidation of  $Fe^{2+}$  and organic compounds, though some  $Fe^{3+}$  and  $C^{4+}$  species could be products of pre-accretionary radiolysis.

**Ceres:** Ceres has spectral and density affinities to carbonaceous chondrites which escaped a major thermal metamorphism, and sulfates are expected. The optical spectroscopy of bright spots within Occator crater tentatively suggests a presence of Mg sulfates [14]. However, an aqueous accumulation is not possible at low surface pressures. Abundant salts could only accumulate at depth through boiling of post-impact fluids [15]. Elevated temperatures favored sulfate trapping to low-solubility  $CaSO_4$  and reduction to Fe sulfides [15]. If Ceres' sulfates are genuine, they may not indicate the body's origin among KBO objects.

**Mars:** The formation of martian sulfates is attributed to oxidation of volcanic and impact-generated  $SO_2$ ,  $H_2S$ , and  $S_n$  by  $O_2$  formed via atmospheric photochemistry and impacts [16]. A fraction of sulfates could be from irradiation of water ice-sulfide mixtures at the surface and from oxidation of sulfides by  $O_2$  and  $H_2O_2$  released through melting of irradiated surface ices.

**Europa and Ganymede:** Mg, Na, and H sulfates have been anticipated on the icy surface of Europa based on near infrared spectra. Galileo data suggest sulfates in colored endogenic materials [17,18], while ground data do not [19,20]. Some  $S^{6+}$  species

( $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ , metal sulfates,  $\text{SO}_3$ ) could form through implantation of iogenic S-bearing plasma [17,19] and through radiolytic oxidation of  $\text{SO}_2$ ,  $\text{S}_n$ , and sulfides in water ice [12,13]. On Ganymede, surface sulfates are reported away from younger grooved terrains [21].

Both the gas starved models for formation of Jupiter [22] and the Grand Tack model for planetesimal migration [23] imply accretion of ices and carbonaceous solids together with reduced anhydrous materials formed from both sides of Jupiter. The migration of carbonaceous and/or icy planetesimals toward the asteroid belt [23] could have delivered sulfates and irradiated ices to Galilean satellites. Some sulfates could have formed during and after accretion through oxidation of sulfides by  $\text{O}_2$  and  $\text{H}_2\text{O}_2$  released from irradiated ices. Low-solubility Mg and Na sulfates and chlorides were leached to primordial oceans [24]. The rest of sulfates were trapped in  $\text{CaSO}_4$  phases and reduced to Fe sulfides during post-accretional warming of the moons' rocky cores. Hydrothermal fluids formed through dehydration of rocks and subsequent silicate melts delivered sulfide compounds ( $\text{FeS}$ ,  $\text{H}_2\text{S}$ ,  $\text{HS}^-$ ) toward water(ocean)-rocky core interfaces. On Europa, subsequent hydrothermal circulation of oceanic water in reduced suboceanic rocks caused trapping of oceanic  $\text{SO}_4^{2-}$  to low-solubility Ca sulfates and Fe sulfides. As on parent bodies of chondrites,  $\text{H}_2$  escape could have not been sufficient to make sulfates stable in aqueous systems. A prolonged and/or extensive hydrothermal circulation could have consumed oceanic sulfates. In turn, a limited supply of igneous rocks and a low permeability of suboceanic materials favored the preservation of sulfates in the ocean throughout history. A delivery of surface radiolytic  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ , and  $\text{H}_2\text{SO}_4$  [17] to the ocean resupplied the inventory of sulfates through oxidation of sulfides in the water and rocks [25]. Sulfates and sulfides could have coexisted metastably throughout the ocean's history, though sulfate reduction could be bio-mediated and an excess of  $\text{SO}_4^{2-}$  could be consumed to Ca sulfates. On Ganymede, a post-accretional water-rock separation could have led to a Mg-Na-sulfate-chloride water ocean separated from rocks by high-pressure ices. Surface sulfates [21] may not be related to the ocean.

**Bodies beyond Jupiter:** There are no observational signs for sulfates on satellites of Saturn and other bodies beyond Jupiter. Sulfates have not been detected in solid plume emissions at Enceladus or in cometary materials, though the detection of  $\text{O}_2$  in the comet 67P [11] does not exclude a delivery of  $\text{O}_2$ -bearing ices beyond Jupiter. The apparent lack of sulfates at Enceladus is more consistent with radiolysis of ices in the solar system (at  $\sim 5$  AU) than with delivery of  $\text{O}_2$ -bearing ices from a parent molecular cloud [11,26].

**Summary:** Sulfates in chondritic materials could not form without invoking photochemical and radiolytic processes that produce O-rich oxidants. Escape of  $\text{H}_2$  from chondritic bodies is not a major driving force for oxidation of sulfides. A plausible scenario includes irradiation of water ice in the vicinity of the nebula's snow line and formation of  $\text{O}_2$  and other strong oxidants imbedded in ice. Some  $\text{S}^{6+}$  species ( $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ ,  $\text{SO}_3$ ) formed through irradiation of  $\text{H}_2\text{S}$ ,  $\text{S}_n$ , and  $\text{SO}_2$  in water ice before accretion. A majority of sulfates in chondritic materials formed after accretion within parent bodies of carbonaceous chondrites, carbonaceous asteroids, and Galilean icy moons through rapid low-temperature ( $<0^\circ\text{C}$ ) oxidation of sulfides by strong oxidants accreted with irradiated ices. The oxidation occurred within carbonaceous asteroids and Jovian moons immediately after melting of accreted ice. Beyond Jupiter, lesser irradiation of ices accounted for lesser or no sulfates formed within icy moons and trans-Neptunian objects.

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