

ANTARCTIC WEATHERING OF THE CK CHONDRITES EET90004, 90007, AND 90022: NICKEL AND SULFUR MOBILITY; C.S. Romanek, R.A. Socki[†], E.K. Gibson Jr. and J. H. Allton[†], Planetary Science Branch/SN4 and LESC[†], JSC/NASA, Houston, TX 77058

CK chondrites are a relatively new class of carbonaceous chondrite that have been described in the literature [1]. Most meteorites that comprise the CK group are restricted to Antarctic finds; therefore terrestrial weathering processes can influence the geochemical records contained within these chondrites. The paired CK chondrites EET90004, 90007, and 90022 share not only a common heritage but similar weathering histories since all three meteorites were found on Antarctic ice covered with thick evaporative coatings. Additional material has grown on these samples during curation at the Antarctic Meteorite Lab at JSC, NASA. At present, efflorescence up to a millimeter thick coats the surface of EET90004 and 90022, with less material coating EET90007. The chemistry, mineralogy and isotopic composition of efflorescence on EET90004 and 90022, described here, provide valuable information regarding the fate of meteoritic components in the Antarctic environment.

SEM photo-micrographs of grain mounts from EET90004 and 90022 surface coatings show that the efflorescence is composed of crystal aggregates up to 500 μm in length. Individual grains are composed of columnar to bladed crystals ~ 10 to 100 μm long with prismatic or pyramidal terminations. Crystal faces commonly contain desiccation cracks. Qualitative energy-dispersive x-ray analyses with a thin window detector show that the solid is composed solely of Ni, S and O, \pm minor Mg and Ca.

The mineralogy of the efflorescence is the hydrated nickel sulfate retgersite ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) on EET90022 and retgersite plus nickel hexahydrite (both $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) on EET90004, determined by standard x-ray diffraction techniques. All diffractogram lattice spacings from each sample can be attributed to one of these two minerals.

Differential scanning calorimetry (DSC) heat flow curves were taken of the samples and reagent grade synthetic analogs to confirm the mineralogy and determine the temperature release of structural water within the meteoritic efflorescence. Gas speciation from the effluent of synthetic analogs was determined using a quadrupole mass spectrometer. Mass scans were recorded for mass/charge ratios of 18, 32, 33, 34, and 64, to monitor for H_2O , S, HS, H_2S , and SO_2 release. All five species were detected during the heating of synthetic retgersite from $\sim 60^\circ\text{C}$ to 720°C , with only trace quantities of S-bearing gas species being detected. Reaction kinetics probably inhibit significant S-volatilization over the time interval of a single run. Observed total mass loss (45% by wt.) was in slight excess of the theoretical value for dehydration (41% by wt.), supporting the observation of minor gaseous sulfur release. Weight loss for EET90022 (45%) was identical to that for synthetic retgersite while that for EET90004 was slightly less (41%). Since EET90004 contains a significant proportion of nickel hexahydrite, perhaps the differences in weight loss can be attributed to mineral-specific reaction kinetics associated with S-volatilization.

DSC heat flow curves of efflorescence on EET90004 and 90022 are similar despite their distinct mineralogies. Curves display three common peak interval ranges that occur at 60° to 130°C , 130° to 240°C , and 300° to 450°C . Peak positions are similar to those from synthetic retgersite although peak shapes and areas differ. Since little to no S-bearing gases were generated during the runs, peaks probably represent the loss of water at different structural sites within the crystal framework. Previous work has shown that water in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is principally bound to the Ni cation [2]. Upon heating, five water molecules

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are lost at $\sim 100^\circ\text{C}$ and the sixth is lost at 280°C . The second two peaks observed in the DSC heat flow curves of the meteoritic efflorescence probably represent the release of these six structural water molecules, albeit shifted to slightly higher temperatures than those reported in the literature. The low-temperature peak observed in the meteoritic efflorescence and synthetic retdgersite is probably related to a highly mobile seventh water molecule that forms a hydrogen bond with SO_4 . DSC curves for the synthetic analog $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ display an intense peak that occurs precisely over this temperature interval. The shape and area of peaks from curves of EET90004 and 90022 are intermediary between synthetic retdgersite and $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, suggesting that some water is hydrogen-bonded to SO_4 in the efflorescence. These results place constraints on the interpretation of the H-isotopic composition of efflorescence reported below.

Hydrogen isotope analysis of the efflorescence was determined by pyrolysis of the solid at 625°C . All evolved gas was trapped in a cold finger held at -197°C . After 4 hours the temperature of the trap was raised to -80°C and evolved gas was isolated for chemical speciation on a quadrupole mass spectrometer. SO_2 was the only gas trapped at this temperature suggesting that, unlike other meteoritic efflorescence [e.g., 3], carbonates did not form. The remaining H_2O was sealed in a Pyrex tube containing Zn for reduction to H_2 at 450°C and analysis on an isotope ratio mass spectrometer. The δD for EET90022 efflorescence was -25‰ (SMOW) while that for 90004 was $+25\text{‰}$ (SMOW). Efflorescence is significantly enriched in deuterium compared with the ambient Antarctic water from which it precipitated (i.e., -425‰), suggesting that evaporative processes strongly influence isotopic composition. Mass balance calculations reveal this to be a reasonable scenario. Isotopic exchange of SO_4 -bonded water with local water vapor ($\sim 80\text{‰}$ SMOW) may have increased the δD of the solid but it could not have produced the excessive enrichments observed in the efflorescence.

The mobility of Ni and S play active roles in the terrestrial weathering of these CK chondrites. The most probable source for Ni and S is pentlandite $[(\text{Fe},\text{Ni})_9\text{S}_8]$ which occurs as small 10 to 20 μm grains that are dispersed throughout these meteorites. Freeze-thaw action of water could promote the migration of oxidizing fluids into the meteorite during sunny periods on the ice sheet [4]. Reduced solid phases that border fractures, such as pentlandite, would be highly soluble under these conditions and could contribute aqueous nickel and sulfur to the migrating fluid during mineral dissolution. The absence of Fe in efflorescence is explained by the formation of goethite pseudomorphs replacing pentlandite along meteorite fractures. Aqueous nickel and sulfur are deposited on the surface of the meteorite in the soluble phases, retdgersite and nickel hexahydrate, during periods of extreme evaporation. The hydrogen isotopic signature of the efflorescence records the extreme levels of evaporation required to enrich the hydrate in deuterium by 400‰ . The chemical, mineralogical and isotopic signature of evaporative weathering products can provide valuable clues about the processes responsible for the alteration of the pre-terrestrial record contained within CK chondrites.

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