

Structural and spectroscopic study of the kieserite-dwornikite solid-solution series, (Mg,Ni)SO₄·H₂O, at ambient and low temperatures, with cosmochemical implications for icy moons and Mars

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ABSTRACT

The investigation of the presence and role of sulfates in our solar system receives growing attention because these compounds play a crucial role in the water budget of planets such as Mars and significantly influence melting equilibria on the icy moons of Saturn and Jupiter, leading to the formation of subsurface oceans and even cryovolcanism. Despite the dominant presence of higher sulfate hydrates such as epsomite, MgSO₄·7H₂O, and mirabilite, Na₂SO₄·10H₂O, on these moons' surfaces, it is not excluded that lower-hydrated sulfates, such as kieserite, MgSO₄·H₂O, are also present, forming from higher hydrates under pressures relevant to the mantle of the icy moons. Given the composition of the soluble fraction in C1 and C2 chondritic meteorites, which are high in Ni content and also considered to represent the composition of the rocky cores of the Jovian icy moons, the actual compositions of potentially present monohydrate sulfates likely lie at intermediate values along the solid-solution series between kieserite and transition-metal kieserite-group end-members, incorporating Ni in particular. Moderate Ni contents are also probable in kieserite on Mars due to the planet's long-term accumulation of meteoritic nickel, although likely to a much lesser extent than Fe.

Structural and spectroscopic differences between the pure Mg- and Ni-end-members have been previously documented in the literature, but no detailed crystal chemical and spectroscopic investigation along the Mg-Ni solid solution has been done yet. The present work proves the existence of a continuous (Mg,Ni)SO₄·H₂O solid-solution series for the first time. It provides a detailed insight into the changes in lattice parameters, structural details, and positions of prominent bands in infrared (transmission, attenuated total reflectance, diffuse reflectance) and Raman spectra in synthetic samples as the Ni/Mg ratio progresses, at both ambient as well as low temperatures relevant for the icy moons and Mars. UV-Vis-NIR crystal field spectra of the Ni end-member also help to elucidate the influence of Ni²⁺-related bands on the overtone- and combination modes.

The (Mg,Ni)SO₄·H₂O solid-solution series shows Vegard-type behavior, i.e., lattice parameters as well as spectral band positions, change along linear trends with increasing Ni content. Infrared spectra reveal significant changes in the wavenumber positions of prominent bands, depending on the Ni/Mg ratio. We show that the temperature during measurement also has an influence on band position, mainly in the case of H₂O-related bands. The changes observed for several absorption features in the IR spectra enable rough estimation of the Ni/Mg ratio in the monohydrate sulfate, which is applicable to present and future remote sensing data, as well as in situ measurements on Mars or the icy moons. The spectral features most diagnostic of composition are the vibrational stretching modes of the H₂O molecule and a band unique to kieserite-group compounds at around 900 cm⁻¹ in the IR spectra, as well as the pronounced ν₃ and ν₁ sulfate stretching modes visible in Raman spectra.

Keywords: Kieserite-dwornikite solid solution, icy satellites, Mars, crystal chemistry, FTIR spectroscopy, Raman spectroscopy, UV-Vis-NIR spectroscopy; Volatile Elements in Differentiated Planetary Interiors