Stability field of the Cl-rich scapolite marialite

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Scapolites are widespread rock-forming aluminosilicates, appearing in metasomatic and igneous environments, and metamorphic terrains. Marialite (Na₄Al₂Si₉O₂₄Cl) is the Cl-rich end-member of the group. Even though Cl-rich scapolite is presumably stable over a wide range of pressure and temperature, little is known about its stability field. Understanding Cl-rich scapolite paragenesis is important since it can help identify subsurface fluid flow, metamorphic, and isotopic equilibration. Due to its metasomatic nature Cl-rich scapolite is commonly reported in economic ore deposits, hence it is of critical interest to the mineral resource industries who seek to better understand processes contributing to mineralization. In this experimental study two reactions were investigated. (1) The anhydrous reaction of albite + halite to form marialite [3NaAlSi₉O₂₄Cl + NaCl = Na₄Al₂Si₉O₂₄Cl]. (2) The hydrothermal equivalent described by H₂O + Na₄Al₂Si₉O₂₄Cl + liquid, where the liquid is assumed to be a saline-rich hydrous-silicate melt. Experiments were performed using a piston-cylinder press and internally heated gas vessels. The temperature and pressure conditions range from 700–1050 °C and 0.5–2.0 GPa, respectively. The starting materials were synthetic phases including end-member marialite, high-albite, and halite. For reaction 1, marialite was found to be stable above 920 to 990 °C over a pressure range of 0.65 to 2.0 GPa, but unstable between 800 and 950 °C at pressures of 0.5 GPa and lower. For reaction 2, marialite was found to be very intolerant of water, requiring a minimum bulk brine salinity of approximately 0.8 mole fraction of NaCl at 1050 and 1000 °C at pressures of 2.0 and 1.5 GPa, respectively. From the location of reaction 1 in pressure-temperature space, thermochemical data for marialite were extracted. Values for the enthalpy of formation (ΔH°) and third-law entropy (S°) for marialite at 298 K and 1 atm have been calculated as −12 167.5 ± 1.5 kJ/mol and 0.7579 ± 0.002 kJ/K mol, respectively, based on existing thermochemical data for high-albite and halite. The main implication of this study is that end-member marialite is only stable at temperatures greater than 920 °C and pressures equivalent to a minimum depth of 18 km under extremely dry conditions. These conditions are not generally realized in typical scapolite-bearing rocks, which occur at shallower-levels and in hydrothermal settings, which may be why pure marialite is rarely observed. This study is the first experimentally determined stability for end-member marialite and provides an important reference for quantifying the stability of Cl-rich scapolites found in nature.

Keywords: Scapolite, marialite, marialite stability, chlorine, chloride brine, albite

INTRODUCTION

Scapolites are widespread rock-forming aluminosilicates that display an extended range of solid solution. The scapolite mineral group can be thought of as the result of combining 3 mol of plagioclase with a salt (i.e., NaCl, CaCO₃, CaSO₄) (e.g., Evans et al. 1969; Goldsmith 1976; Hassan and Buseck 1988; Teertstra and Sherriff 1997). They can be compositionally illustrated as a solid solution of four end-members: a sodium chloride end-member, marialite (Na₄Al₂Si₉O₂₄Cl), two calcium carbonate end-members, meionite (Ca₃Al₂Si₉O₂₄CO₃) and mizzonite (NaCa₃Al₂Si₉O₂₄CO₃ = albite-2 anorthite CaCO₃), and a calcium sulfate end-member, sulfate meionite, or silvialite (Ca₃Al₂Si₉O₂₄SO₄) (Newton and Goldsmith 1976; Teertstra et al. 1999). Unlike other chloride-bearing minerals (such as amphiboles, apatites, and micas), scapolite usually contains little OH (Teertstra and Sherriff 1997), hence its composition can be used as a tracer of the Cl and CO₂ contents of the fluid responsible for its formation, independent of the fugacity of H₂O (fH₂O) (Ellis 1978; Rebbert and Rice 1996; Filiberto et al. 2014).

Scapolites are commonly reported in nature over a wide range of temperature and pressure, and it is regarded as a typical metamorphic mineral, so long as the fluids necessary for its stability are present (Boivin and Camus 1981; Teertstra and Sherriff 1997). Even though Cl-rich scapolite is thought to be stable over a wide range of pressure and temperature, little is known about its stability field and scapolites approaching end-member marialite are rare or perhaps nonexistent (e.g., Teertstra and Sherriff 1997). It is of interest to note that scapolite has been identified in chondritic meteorites (Teertstra and Sherriff 1997), and has been detected in SNC meteorites and on the surface of Mars via high-resolution reflectance spectra (Clark et al. 1990; Filiberto et al. 2014).