Heat capacity and entropy of stoichiometric jarosite compounds

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The goal of our project is to determine thermodynamic properties of the end-member stoichiometric jarosite compounds. For this purpose, we have synthesized natrojarosite, $NaFe_3(SO_4)_2(OH)_6$ and jarosite, $KFe_3(SO_4)_2(OH)_6$ by oxidizing metallic iron in acidic solutions [1]. These jarosite samples consist of euhedral rhombohedral (pseudocubic) crystals up to 0.05 mm large. The structure of jarosite minerals can be indexed in the space group R-3m. The lattice parameters were determined by Rietveld refinement; those of our natrojarosite sample are a = 7.312(2) and c = 16.588(2) Å, those for the jarosite a = 7.288(1) and c = 17.203(4)Å, with $\square^2$ of those refinements being 1.48, and 1.87 respectively. No impurities were detected either by powder X-ray diffraction or infrared spectroscopy. To determine the heat capacity (C_p) of natrojarosite, we have used a commercial (PPMS) quasi-adiabatic low-temperature calorimeter that does not require a large amount of sample (used 25 mg) as the adiabatic calorimeter does (min. 5 g). The C_p-data measured on natrojarosite were measured between 2 and -300K and the C_p at 298.15 K is 385.4±1.8 $J.mol^{-1}.K^{-1}$. The para-/antiferro-magnetic transition is visible as a C_p anomaly at 60.4 K and S(298.15 K) = 413.8±0.34 $J.mol^{-1}.K^{-1}$ from integrating the C_p/T data. Stoffregen [2] estimated the standard entropy of natrojarosite as 382.4 $J.mol^{-1}.K^{-1}$. Heat capacity and entropy measurements on a stoichiometric jarosite sample by adiabatic calorimetry are in progress and these results will be reported.

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Selective vs. bulk assimilation and the restricted chemical variability of igneous rocks

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Since the advent of widespread isotopic analyses of igneous rocks it is clear that many or most igneous systems incorporate foreign material into the magma. However, the exact mechanisms of incorporation are not well known. There are two end-member cases; one in which magmas ingest xenoliths whole (bulk assimilation) and one in which magmas extract and ingest a broadly rhyolitic liquid (selective assimilation), leaving behind a refractory metamorphic residue.

Bulk assimilation is commonly invoked as a way to make space for plutons and to dispose of the abundant xenoliths that should be present in plutons if stoping is a significant emplacement mechanism [1, 2]. However, bulk assimilation is inconsistent with the limited chemical variability of igneous rocks, the vast majority of which fall along a line in compositional space from basalt to rhyolite. For example, the principal eigenvector of the major-element variance-covariance matrix of 25,000 Cenozoic igneous rock analyses from NAVDAT accounts for 96% of the dataset's variance. In contrast, sedimentary processes yield far larger geochemical variability than igneous processes, commonly producing rocks that are near 100% SiO_2 or $CaCO_3$. Significant bulk incorporation of (meta)sedimentary rocks drives the contaminated magma's composition off of the igneous trend, but such excursions are rarely seen in data. In contrast, selective assimilation of silicic partial melt drives magmas along the igneous trend toward rhyolite and is consistent with available large-scale geochemical data, with case studies of magma-wall rock interaction [e.g., 3, 4], and with the presence of restitic, refractory xenoliths in many lavas and plutons. Selective assimilation also reduces the great thermal and rheological difficulties involved in bulk assimilation [5]. We conclude that bulk assimilation is at most a minor process in magma contamination.

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