MINERALOGICAL IN-SITU INVESTIGATION OF ACID-SULFATE SAMPLES FROM THE RIO TINTO RIVER, SPAIN, WITH A PORTABLE XRD/XRF INSTRUMENT. P. Sarrazin1, D.W. Ming2, R.V. Morris3, D. Fernández-Remolar4, R. Amils5, R.E. Arvidson6, D. Blake7, D. L. Bish8, 1inXitu Inc., 2551 Casey Ave Ste A, Mountain View, CA 94043 psarrazin@inxitu.com; 2 NASA Johnson Space Center, Mail Code KX3, Houston, TX 77058; 3 Centro de Astrobiología (CSIC/INTA) 28850 Torrejón de Ardoz, Madrid, Spain; 4 Earth and Planetary Sciences, Washington University, St. Louis, MO 63130; 5 NASA Ames Research Center, Moffett Field, CA 94035; 6Dept. of Geological Sciences, Indiana Univ., Bloomington, IN 47405-1405.

Introduction: A field campaign was organized in September 2006 by Centro de Astobiologica (Spain) and Washington University (St Louis, USA) for the geological study of the Rio Tinto river bed sediments using a suite of in-situ instruments comprising an ASD reflectance spectrometer, an emission spectrometer, panoramic and close-up color imaging cameras, a life detection system and NASA’s CheMin 4 XRD/XRF prototype [1]. The primary objectives of the field campaign were to study the geology of the site and test the potential of the instrument suite in an astrobiological investigation context for future Mars surface robotic missions. The results of the overall campaign will be presented elsewhere. This paper focuses on the results of the XRD/XRF instrument deployment.

The specific objectives of the CheMin 4 prototype in Rio Tinto were to 1) characterize the mineralogy of efflorescent salts in their native environments; 2) analyze the mineralogy of salts and oxides from the modern environment to terraces formed earlier as part of the Rio Tinto evaporative system; and 3) map the transition from hematite-dominated terraces to the mixed goethite/salt-bearing terraces where biosignatures are best preserved.

Deployment site: Rio Tinto is a river in the Sierra Morena mountains of southwestern Spain. The river water is characterized by high acidity (pH 1.5) and deep red color (Rio Tinto = tinted river) resulting from chemolithotrophic activity consuming iron and sulfide minerals of the subsurface rocks. These extreme conditions make Rio Tinto a possible Mars analog of astrobiological interest [2].

XRD/XRF instrument: The CheMin 4 instrument shown in Figure 1 is a portable XRD/XRF prototype developed to demonstrate the capabilities of the CheMin instrument that will be deployed on Mars as part of the science payload of MSL [3]. It can operate autonomously in the field, powered by internal Li-ion batteries that give over 6 hrs of operation. The complete instrument including batteries weighs 30kg and requires about 100W during operation.

X-rays are generated by a microfocus X-ray tube combined with a pinhole collimator to produce a fine X-ray beam that includes both Kα and Kβ characteristic radiation from the cobalt target as well as Bremsstrahlung radiation.

Figure 1. CheMin 4 instrument in Rio Tinto river bed with optional laptop computer for graphic user interface.

The material to be analyzed is loaded in a vertical cell composed of two thin polymer windows separated by 175µm. The cell is placed in the X-ray beam and vibrated to generate granular motion for improved statistics [4].

A CCD detector placed behind the sample perpendicular to the beam collects the X-ray signal over an angular range of 1.5-57°2θ. The CCD operates in direct detection (i.e., no phosphor is used for conversion of the X-ray signal to visible light) in a single-photon counting mode to allow measurement of the energy of incoming photons as well as their location on the detector. Practically, this is obtained by exposing the CCD for 30s, reading the collected signal, and repeating this a sufficient number of times to obtain adequate statistics. The CCD is cooled to -60°C with a 4-stage Peltier cooler to limit dark current. The CCD/cooler assembly is placed in a sealed vacuum camera head fitted with a thin beryllium window.

The raw CCD data are stored in an internal drive and later processed to extract XRD and XRF data. XRF data are obtained from an energy histogram of the CCD data, and XRD data are obtained from the spatial distribution of Co photons on the CCD. The
instrument can either be controlled by an embedded computer or through an external laptop computer when a graphic interface is desired.

**Experimental:** Due to the hot climate of southern Spain during the field campaign, with temperatures reaching 35-40°C at noon, the instrument was only deployed outdoors in the morning to allow sufficient cooling of the CCD.

Samples for analysis were selected after imaging and reflectance spectroscopy were used to identify key targets for in-situ analyses, much the way studies will proceed with a rover-based mission. After collection and drying, when required, samples were crushed and sieved to <150µm before loading in sample cells. Kapton film sample cells produced a diffraction peak near the 001 smectite peak, so an older sample stage with thin Mylar windows was used whenever smectite was expected in the sample.

Although typical instrument operation in the laboratory involves collection of 1000 frames, field operation in Rio Tinto had to be much faster. Samples were analyzed using 25 to 50 frames, providing sufficient counting statistics for phase identification. The diffraction resolution of CheMin 4, nominally 0.3°/θ, was degraded to 0.4-0.5°/θ by technical issues with the sample stages. This did not result in substantial loss in the instrument capabilities for mineral identification.

**Results:** Eighteen samples were collected and analyzed during the 2006 field campaign. Copiapite, a hydrated Fe-Mg sulfate hydroxide, was the major efflorescent salt found in evaporation pools on the river bed (Figure 2). Figure 3 shows the 2D diffraction pattern collected with this sample and the diffractogram resulting from the circumferential integration of this image. Line markers show copiapite peak positions and intensities.

Other acid-sulfate phases identified by the XRD/XRF instrument included jarosite, gypsum, hematite, and goethite. Quartz and illite were detrital phases in the river bed sediments that likely originated from the surrounding country rock. Smectite was identified in several sediment samples, however, it was not clear whether the smectite formed in situ or was transported from another source.

**Conclusions:** CheMin 4 was successfully deployed in Rio Tinto during a one-week geological and astrobiological investigation with a suite of in-situ instruments. Samples were collected and analyzed on the site. Although typical mineralogical field studies involve collection and storage of large numbers of samples for later analyses by laboratory XRD instruments, the approach taken here was to rapidly analyze the samples on site to determine the selection of the next samples. This approach is similar to that used on Mars with remote mineralogical tools.

**References:**
2. Fernández-Remolar et al. (2005), *EPSL, 240, 149-167.*