DEFINITIVE MINERALOGY OF ROCKY AND ICY PLANETS AND PLANETESIMALS USING POWDER X-RAY DIFFRACTION. D.F. Blake[1] and P. Sarrazin[2], [1]Exobiology Branch, MS 239-4, NASA Ames Research Center, Moffett Field, CA 94035 (david.blake@nasa.gov), [2]SETI Institute, Mountain View, CA 94043.

Introduction: More than simple compositional analysis, definitive mineralogical analysis can provide information about habitability: T, P conditions of formation, present/past climate, water activity, the activity of biologically significant elements and the like.

Powder X-ray diffraction is a general purpose mineralogical technique that can provide definitive, quantitative mineralogical analysis of nearly any conceivable mineral assemblage without recourse to or dependence on other data or measurements. Definitive mineralogical analysis through the determination of crystal structure (i.e., powder XRD) is the standard to which all other techniques are compared. If an unknown phase (or an inorganic compound not classified as a mineral on Earth) is identified by itself or in a simple association, it can be fully characterized by structural (XRD) analysis without recourse to other data, because XRD relies on principles of atomic arrangement for its determinations. Chemical, optical, calorimetric or oxidation state data are seldom definitive because chemical compositions, optical emission/absorption features, calorimetric data or valence information can represent a range of substances or mineral assemblages.

Minerals are uniquely defined by their structure, and, as a result, cation valence states, site occupancies and bonding types (which are a consequence of structure and symmetry) can often be unequivocally determined. Redox-sensitive elements such as Fe and Mn can also often be quantitatively measured, independent of compositional data. Likewise, minerals that can have a variety of hydration states and are difficult or impossible to identify by other methods, have unique and easily distinguished XRD patterns (e.g., the $CaSO_4.nH_2O$ series anhydrite, bassanite, gypsum or the $MgSO_4.nH_2O$ series keiserite, sanderite, starkeyite, pentahydrite, hexahydrite, epsomite). Minerals that exhibit a solid solution between compositional end-members (such as the olivine series forsterite-fayalite ($MgSiO_4$-$FeSiO_4$)) can be identified and the degree of cation substitution established using diffraction data. Polymorphism such as occurs in the SiO_2 system and order-disorder relationships such as occur in the potassium feldspar series can be identified and quantified. These structural and compositional variants, once identified, can be related to environments of formation that can be used to assess present or past habitability.

On icy planetesimals and the Ocean Worlds such as Europa, XRD can uniquely identify type I and II water ice clathrates [1], amorphous, cubic and hexagonal water ice [2] in addition to simple gas hydrates.

Modern XRD methods are able to quantify the abundances of all minerals in a complex mixture using full-pattern fitting methods such as Rietveld refinement [3]. When X-ray amorphous material is present, other full-pattern fitting methods such as FullPat [4] can be used to quantify the relative amount of amorphous material. When combined with XRF data, these types of analyses will yield as complete a characterization as is possible, by any spacecraft-capable technique.

The CheMin instrument on MSL: CheMin, the first XRD instrument flown in space, has been operating on Mars for more than 4 years as one of MSL's laboratory instruments. CheMin data were used to establish the quantitative mineralogy of the Mars global soil [5,6], to discover and characterize the first habitable environment on another planet [7,8], and to provide the first in situ evidence of silicic volcanism on Mars [9]. The instrument is now being used to systematically sample and characterize the depositional and diagenetic environments associated with the mudstone sediments that comprise the lower strata of Mt. Sharp.

Sample preparation for X-ray Diffraction: Conventional powder XRD requires a sample comprised of a myriad of small grains (ideally $>10^6$ grains with a grain size <10 μm) presented in random orientations to the X-ray beam. In CheMin, sample cells are vibrated at sonic frequencies that cause loose powder held between two X-ray transparent windows to pass through a 50 μm diameter X-ray beam in random orientations over time. This turbulent grain motion relaxes the requirement for a large sample because individual grains can pass through the beam many times in different orientations, and allows powders ≤150 μm to be analyzed. Nevertheless, a CheMin geometry instrument still requires mechanisms to collect, crush and sieve samples before analysis. However, other diffraction geometries are possible and have been designed to require little to no sample preparation prior to analysis.

Alternative XRD geometries: In the early days of X-ray diffraction when only film methods were available, a large number of camera designs were developed with special geometries for particular purposes. Many of these geometries can be realized using the same three basic elements present in CheMin – X-ray source, sample holder and CCD imaging detector.

Guinier XRD. A high-resolution, high-throughput XRD instrument based on a Guinier camera design using parafocusing geometry is being prototyped (fig. 1). As shown in fig. 2, the instrument can be built for

both reflection and transmission geometries. While sample preparation is still required, the advantages of this geometry are improved XRD resolution from the focusing of the diffracted signal on the cylindrical detector and rapid data collection because a larger sample area can be analyzed without directly affecting 2-theta resolution. The main challenge in the development of this geometry is the requirement for a cylindrical 2D X-ray detector. Several designs are currently being investigated based on bent CCDs or X-ray optics.

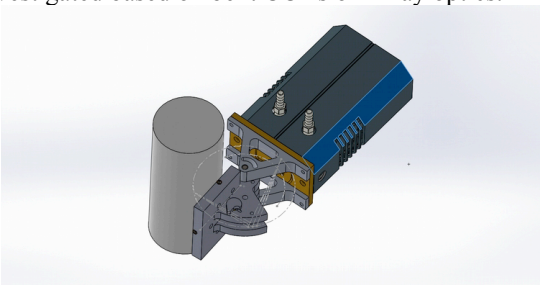

Fig. 1. Prototype Guinier XRD instrument built with COTS parts.

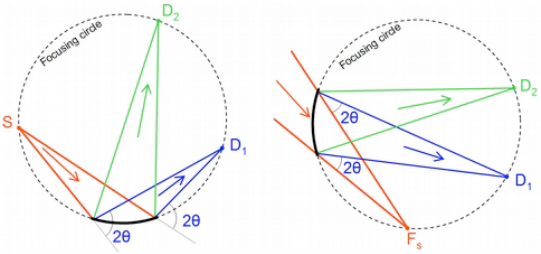

Fig. 2. Reflection and transmission geometries of a Guinier XRD.

XTRA (Extraterrestrial Regolith Analyzer): XTRA [10] (fig. 3) is designed to analyze fines in surface regolith without sample preparation. Fine-grained regolith coats the surfaces of most airless bodies in the solar system, and because this fraction is typically comminuted from the rocky regolith, it can often be used as a proxy for the surface as a whole.

Hybrid XRD. The hybrid instrument is designed to be placed on a rock or soil without a requirement for sample preparation. CCDs placed in a hemispherical arrangement collect diffracted photons (fig. 4). If the material is fine-grained enough, a powder XRD pattern is obtained, similar to CheMin or XTRA. With coarse grained crystals, the bremsstrahlung radiation striking the sample is diffracted into Laue patterns. The Laue spot energies are measured by the CCD and dedicated crystallographic software allows identification the minerals responsible for the diffraction (fig. 5).

Toward a high TRL tool-kit: the various geometries presented above all rely on similar basic components arranged and used in different fashions: a micro-focused X-ray tube and its high voltage power supply, a collimator or X-ray optics, a cooled CCD detector and its low noise driving electronics, and the software to extract crystallographic data from raw CCD frames. All basic sub-systems have been, or are being developed in partnership with the space systems and X-ray analytical industries. This approach enables quick turn-around and reduced cost in the development of future space-deployed XRD instruments.

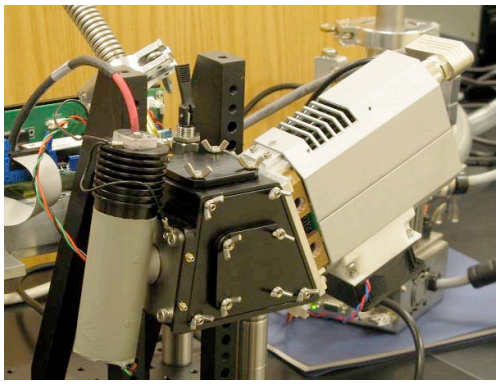

Fig. 3. Reflection geometry XTRA prototype instrument for use with unprepared regolith samples on airless bodies.

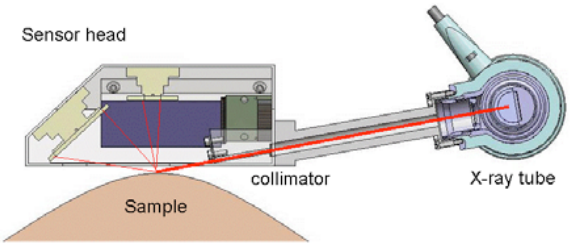

Fig. 4. Arm-mounted contact Hybrid XRD.

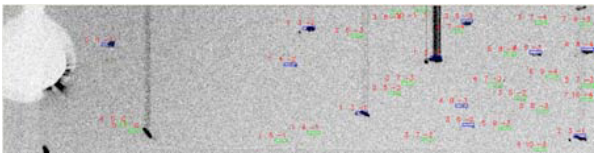

Fig. 5. Laue image of olivine marked with Miller indices found by the analytical software. Vertical lines result from spreading of X-ray signal during CCD readout at positions of intense diffraction.

References:

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