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# AN INTEGRATED EXPERIMENTAL SYSTEM FOR SOLID-GAS-LIQUID ENVIRONMENTAL CELLS

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**Abstract**—The geochemistry of minerals in intermediate to deep sedimentary rocks (2−10 km depth) is not known sufficiently well to predict accurately the effect of human activities, such as carbon dioxide sequestration or fracking. To carry out real-time experiments, a high-pressure environmental chamber (HPEC) was constructed for *in situ* X-ray diffraction (XRD) studies to 1000 bars and to 200ºC. In the HPEC, a liquid, *e.g*. a brine, plus sample in suspension, is pressurized by gas, *e.g*. $CH_4$ or $CO_2$, or liquid, *e.g*. supercritical $CO_2$. The unique aspect of this chamber is that the sample + liquid (~2 mL) form a dynamic system, and particles can move freely in the liquid while being illuminated by the X-ray beam. Several HPECs were constructed of Ti alloy, stainless steel, or carbon-fiber polyether ketone to be resistant to corrosion under basic or acidic conditions. These HPECs are compatible with standard transmission-mode diffractometers with sealed-tube X-ray sources (Mo radiation is being used at the University of Illinois at Chicago − UIC) or with brilliant X-ray sources. In addition, to allow long-duration studies or, for example, to study the effect of micro-organisms on these mineral reactions, a large-bore (~25 mL) reaction vessel system was devised that could be examined regularly at appropriate *P/T* conditions or off-line. Calibration of the HPEC and XRD pattern processing is discussed and illustrated. The potential significance of these devices goes beyond understanding the deep sedimentary environment, because materials and reactions can be studied while using nearly any liquid as an immersion agent. As an example, experimental results are given for the $d_{001}$ values of montmorillonite clay *vs*. temperatures to 150ºC at $P(CO_2)$ = 500 bars in a NaCl-rich brine.

**Key Words**—Experimental Clay Studies, Reaction Vessels, XRD.

## INTRODUCTION

The mineralogy, mineral kinetics, and the interactions of minerals and fluids in intermediate to deep sedimentary rocks (2−10 km depth) are, in general, not sufficiently known to predict the effect of human activities, such as carbon dioxide sequestration or oil and gas production, including fracking. To study this environment at the appropriate natural conditions, experimental techniques are required which allow the direct observation and monitoring of mineral changes at elevated temperatures and pressures in solid-fluid-gas systems. Cells for the analysis of solids in contact with a liquid for studies at elevated temperatures and pressures have been available since the 1960s (*e.g*. Van Valkenburg, 1962; Bassett and Takahashi, 1965; Hazen and Finger, 1982). Cells developed more recently consist of potentially harmful materials (*e.g*. Be in the case of Mauron *et al*., 2011) or require complex and sophisticated high-pressure anvils, image plates, microfocus X-ray sources, *etc*. (*e.g*. Toulemonde *et al*., 2014). Most of these environmental cells are not optimized to simulate the conditions of sedimentary basins at moderate pressures (<1−2 kbar) and temperatures (<200ºC), and these cells do not allow studies that characterize the changes in the physical and chemical properties of the solid phase as well as of the coexisting liquid and gas phases. In addition to a system allowing for the direct observation and monitoring of reactants at elevated temperatures and pressures, a system is needed that also allows small amounts of sample to be removed at the pressure and temperature of the experiment for *ex situ* analysis without ending the experiment. Such an environmental cell should be easy to use for in-house experiments, including loading of samples, assembly of the cell, and repair.

Because sedimentary basins contain clay minerals that may affect porosity and permeability, expansion (layer-to-layer distances), interlayer cation and molecular composition, and interlayer structure are important parameters. These structural and chemical parameters are believed to vary rapidly with changes in temperature and pressure. Clay minerals, therefore, are expected to back-react quickly when experiments are brought to ambient conditions. Thus, clay-mineral studies require

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an environmental cell that allows the properties of the phases to be monitored *in situ*, which commonly involves the use of an analytical tool such as X-rays or another electromagnetic radiation. These types of reactions and kinetics are rapid and require that, for example, the environmental cell can be mounted for a relatively short period of time, several hours or days, on analytical instrumentation, such as an X-ray diffractometer. Previously, Koster van Groos *et al*. (2002) described a chamber for gas–solid interactions at low temperatures (less than ambient temperature) and elevated pressures (<100 bar). This chamber utilizes reflection-mode XRD methods that are compatible with studies on rapidly evolving reactions. For example, the stability range of clay–hydrate complexes could be determined (Guggenheim and Koster van Groos, 2003; Koster van Groos and Guggenheim, 2009) by using this chamber to explore the stability of phases in the montmorillonite–methane and nontronite–methane systems.

Maintaining an environmental cell on an X-ray diffractometer to investigate physical and chemical processes over much longer durations (weeks or months) may be impractical or cumbersome. For example, in a study of carbon dioxide sequestration in deep sedimentary reservoirs, the $CO_2$ may be stored in the reservoir principally as interstitial gas without significant reaction or by carbonate formation through reactions of $CO_2$ with the mineral constituents. The latter reaction rates would be expected to be much slower than clay-mineral intercalation reactions. In such a study, a gas-pressurized reaction vessel heated in an oven may be more suitable than heating in an environmental chamber on a diffractometer, provided that samples (liquid, powder) can be routinely extracted periodically from the vessel without terminating the experiment. The extracted samples may then be examined by *ex situ* methods.

In this paper, an integrated experimental system is described. For real-time experiments, a high-pressure environmental chamber (HPEC) was constructed for use with *in situ* XRD in studies to 1000 bars and to 200ºC. In the HPEC, a liquid, *e.g*. a brine, plus sample in suspension, is pressurized by gas, *e.g*. $CH_4$ or $CO_2$, or liquid, *e.g*. supercritical $CO_2$. The unique aspect of this chamber is that the sample + liquid (~2 mL) form a dynamic system, and particles can move freely in the liquid while being illuminated by the X-ray beam. The dynamic aspects of the HPEC allow the study of clay minerals in fluids, even if flocculation occurs. In addition, to allow studies of long duration or the effect of micro-organisms on these mineral reactions, a large-bore (~25 mL), high-pressure reaction vessel and sampling system were devised. Experiments could then be examined regularly *via* injection at appropriate *P/T* conditions into the HPEC. The potential significance of these devices goes beyond deep sedimentary environments because materials and reactions can be studied while using nearly any liquid as an immersion agent.

## EQUIPMENT

### *High-pressure environmental chamber (HPEC) system*

The HPEC system is a closed-circuit channel that may contain a fluid (liquid, liquid-gas mixture) suspension of fine particles that is mobilized by an internal circulation pump. The fluid may be pressurized by a gas (*e.g*. $CH_4$ ) or a liquid (*e.g*. pressurized $CO_2$) using an external high-pressure pump. The HPEC has two high-pressure windows (Figure 1) to allow the suspension to be analyzed continuously using XRD. A transmission-mode X-ray diffractometer is used to minimize the path length of the X-ray beam to reduce absorption by the suspension. The dynamic nature of the system provides sufficient flow so that the particles can move freely while being illuminated by the X-ray beam, even if flocculation of the particles occurs. The HPEC may be heated using a series of cartridge heaters placed in appropriately spaced drill holes in the HPEC. Combined with the moving suspension, the temperature gradient in the chamber, therefore, is minimized. The system may be cooled instead by circulating a cooling fluid through these drill holes and a set of containment covers. A thermocouple, positioned within 2 mm of the sample flow near the X-ray windows, is used to measure and control temperature.

*HPEC*. Three different versions of the HPEC are available. A Ti alloy (6AL-4V ELI, ASTM Grade 5) HPEC is suitable for studies with neutral and acidic

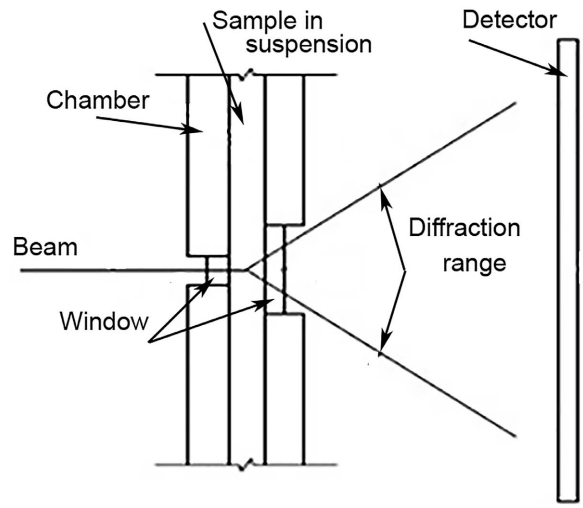



Figure 1. A schematic (not to scale) view of the diffraction component for the HPEC design. The HPEC, mounted on a Bruker 3-circle diffractometer, employs (graphite monochromatized) Mo radiation in a transmission-mode arrangement with a sample-to-detector distance of 12 cm. The single-crystal, (100) plane, vapor-deposited synthetic diamond windows are 1.0 mm thick, with the incident window of 3.0 mm diameter and the exit window of 6.0 mm diameter. The diffraction range is $2\theta = 70^{o}$. The detector in use is a CCD Bruker APEX.

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fluids. This version eliminates contamination that may occur with the stainless steel version using acidic fluids. At the UIC, this version has become the 'workhorse'. A stainless steel (#316) unit performed well with various brines/seawater pressurized with Ar or He, but it exhibited significant corrosion in the presence of $CO_2$ + $H_2O$ (*i.e.* carbonic acid) at elevated pressures. A third unit is made from black PEEK (carbon-fiber-reinforced polyether ether ketone) for studies with corrosive basic fluids. This unit is not being used currently.

The HPEC has two parts (Figure 2): the upper-body section (Figure 2A) contains the main portion of the closed-circuit channel. This section accommodates the diamond high-pressure window assembly, the (internal) circulation pump, and two ports, one located at the top and the other at the side of the unit. The lower-body section (Figure 2B) has a U-shaped channel that completes the closed circuit. This section has two ports. All ports are for access to the experiment as inlet or outlet ports, using appropriate valves. In addition, the ports are useful clean-outs that facilitate easy maintenance after a completed experiment. The channels in the lower and upper bodies are connected through two hollow cylinders and sealed using O-rings (Buna-N). Four assembly bolts hold the two components together.

The assembled HPEC (Figure 3) is mounted onto a dove-tail sled assembly and placed on a specially designed track on the diffractometer. The HPEC unit is aligned using adjustment screws. The (internal) circulation pump consists of an electromagnetic driven piston (sealed PEEK rod with an iron core) and a check valve

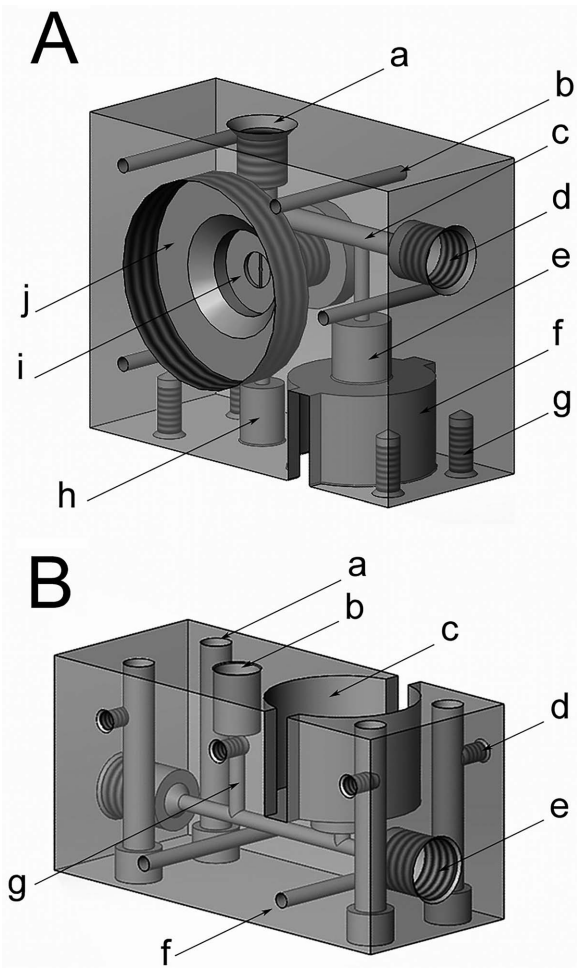



Figure 2. The 'transparent' drawing of the HPEC. Part A shows the upper section and B the lower part. Part A includes: (a) pressure port; (b) hole for insertion of cartridge heater element (or for cooling liquid); (c) portion of the closed-circuit channel; (d) access port; (e) well for connecting (large) hollow cylinder; (f) well for (electromagnetic pump) solenoid; (g) threaded assembly-bolt hole; (h) well for connecting (small) hollow cylinder; (i) well for exit window and PEEK-compression seal; and (j) well for a cone-shaped nut to compress the exit window assembly (see Figure 3). Part B includes: (a) assembly-bolt hole, see A(g); (b) well for connecting (small) hollow cylinder, see A(h); (c) well for (electromagnetic pump) solenoid, see A(f); (d) mounting hole for cooling plate, (e) access port; (f) hole for insertion of cartridge heater element (or for cooling liquid); and (g) portion of the closed-circuit channel.

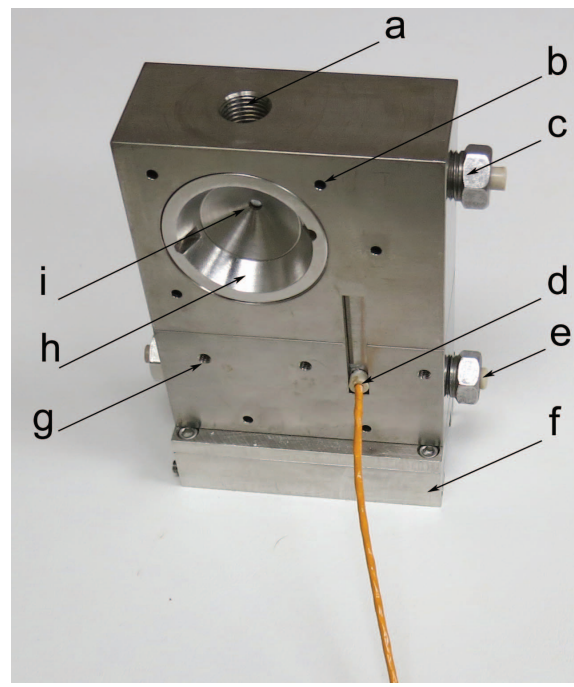



Figure 3. An assembled Ti-alloy HPEC: (a) pressure port, see Figure 2A(a); (b) hole for cartridge heater element, see 2A(b); (c) access port, see Figure 2A(d); (d) electrical lead controlling electromagnetic pump solenoid; (e) access port, see Figure 2B(e); (f) dove-tail sled assembly for placement on the diffractometer; (g) threaded mounting hole for cooling plate; (h) cone-shaped nut for exit-window assembly, see 2A(j); and (i) diamond exit window.

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(PEEK tube with a ceramic sealing ball) assembly in the large-diameter cylinder (see above). The ball mechanism of the check valve reduces back flow and is self-cleaning of fine particles. The two solenoids, used for the reversing action of the electromagnetic pump drive, are placed around this cylinder. The entrance X-ray window is a synthetic diamond plate (chemical vapor deposition, 3 mm diameter, 1 mm thick), as is the exit diamond window (6 mm diameter, 1 mm thick). The exit window allows 2θ measurement to 70º (Mo radiation, 0.7107 Å). Both windows are sealed using PEEK compression seals. The suspension flows between the windows through a 1.2 mm channel, where it is illuminated by the X-ray beam. The total X-ray path in the HPEC, therefore, is 5.2 mm.

*Diffractometer*. The Bruker (Bruker-AXS Inc., 5465 East Cheryl Parkway, Madison, Wisconsin, USA) three-circle, single-crystal diffractometer used with the HPEC requires only a minimal modification, thereby allowing rapid conversion (~10 min, including the alignment) to and from single-crystal mode. This diffractometer is commonly available in chemistry departments, single-crystal service departments, and most synchrotron facilities. The diffractometer is equipped with an APEX area detector and *SMART* and *GADDS* software.

A Nonius (now part of Bruker) short-style, micro-capillary (MonoCap) collimator, modified with a sleeve to allow mounting on the Bruker collimator track, is used to direct and intensify the incident X-ray beam. A curved incident-beam monochromator assembly is currently available (from Bruker) and may provide greater intensity, but this monochromator has not been tested at UIC. For the conversion to accommodate the HPEC, the omega and phi circles are fixed at 0.0º, and the diffractometer base plate is replaced with a thick base plate with a cam lock to engage the HPEC position in a repeatable location. This base plate has a mounted dove-tail base track for the HPEC and a beam stop.

*Control Cabinet*. To operate the HPEC, all necessary equipment is housed in an adjacent control cabinet. The cabinet includes a pressure-generating unit consisting of a high-pressure pump (SC Hydraulic Engineering, 1130 Columbia St, Brea, California, USA, with 180:1 pump ratio, that was modified at UIC to pressurize gases), a manifold with a supply valve to the HPEC and an exhaust valve, and a low-pressure air-control system (filter, regulator, 0–100 psi gauge, shut-off valve). The control cabinet also contains the electronics for the (internal) circulation-pump power supply with adjustable timers, panel meters for temperature measurement/control and pressure measurement, and appropriate switches, panel lights, draws, *etc*.

*High-pressure reaction vessel and sampling system*

A corrosion-resistant, high-pressure system to study reactions at pressures to 1000 bars and temperatures to 200ºC was developed that allows sampling of the material at pressure. The Ti alloy (6AL- 4V ELI, ASTM Grade 5) hydrothermal pressure reaction vessel (Figure 4) is 150 mm long with a 44 mm OD and a 1.9 mm bore. The internal volume is ~36.5 mL. The entrance of the bore is cone-shaped with a width of 25 mm and an angle of 45º. The vessel is sealed using a 50 mm-wide screw cap that presses a 'mushroom'-shaped, 50 mm-long Ti tube against the pressure vessel, using a cone-shaped PEEK ring seal. Up to six vessels, with the shut-off valve attached, may be mounted in a rotating holder (1 rpm) that is located in an oven. When the vessel is charged with solid-liquid sample, several ceramic balls (*e.g.* 6 mm radius) may be added to the sample to prevent clumping of the solid grains by agitating the mixture during rotation and to remove any reaction-product coatings from grains, thus facilitating reaction.

The shut-off valve is designed to allow sampling of the vessel contents, including the solid phase, without damage to the valve. Commercially available high-pressure needle valves are not suitable for extraction of suspended particles, because these particles are likely to damage the valve needle or valve seat. In addition, these valves are not sufficiently corrosion-resistant when using $CO_2$-$H_2O$ fluids, and result in Fe-contamination of the sample. To address these problems, a corrosion-resistant valve was developed.

The sample may be transferred from the vessel to a sample-holder tube (Figures 4, 5) with only a small loss (~2%) of pressure in the reaction vessel and sampling tube. The transferred sample may be used for further analysis (*e.g.* X-ray or chemical analysis), using a 1 mL

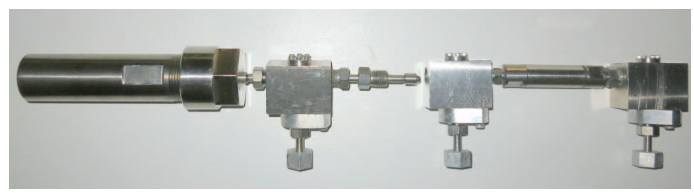


Figure 4. High-pressure Ti-alloy reaction vessel (left) and sampling system (right). This vessel is shown with a Ti-alloy shut-off valve so that suspended particulates may be extracted at pressure along with the fluid phase. The width of the valve body is 5 cm. The sampling system is shown with a hollow 1 mL sampling tube. The sampling tube is bound on either side by a shut-off valve. A connecting tube (shown) may be used to allow the transfer of material from the reaction vessel.

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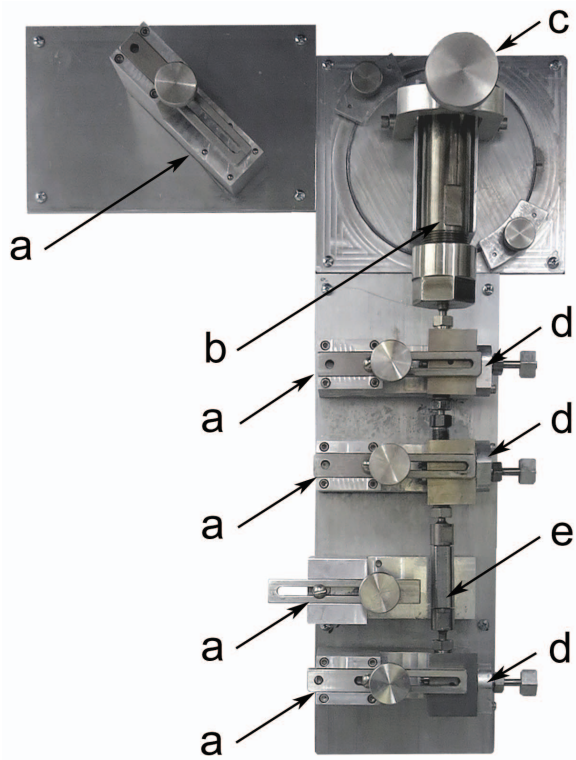



Figure 5. Wall-mounted holder assembly for pressurizing the reaction vessel or for the transfer of sample from a reaction vessel to a sampling tube. Parts of the wall-mounted holder assembly are: (a) clamp, (b) reaction vessel, (c) clamp for reaction vessel, (d) shut-off valve, and (e) sampling tube. The exchange of sample is accomplished in the vertical position so that the sample suspension is located at the bottom of the reaction vessel. The holder assembly may also be used to pressurize the reaction vessel, but pressurization requires the reaction vessel shut-off valve to be higher than the horizontal to avoid fluid from entering the pressure-intensifier assembly (not shown). For this application, the reaction vessel is rotated (note circular portion at the top of the assembly) so that the shut-off valve is positioned at clamp (a) on the far left of the figure. One clamp not in use adjacent to the hollow tube of the sampling system is present to accommodate the HPEC so that material from the reaction vessel may be injected directly into the HPEC.

size sampling tube or loaded into the HPEC (2.5 mL size) to allow the study of non-quenchable products. During sample transfer, neither the temperature of the reaction vessel nor the transfer sample-holder tube is maintained at the run temperature. The mass of each, however, is significant and temperature-loss can be minimized by a rapid transfer. Sample exchange is facilitated by a wall-mounted holder assembly (Figure 5). Because the sampling tube can be used to remove portions of the products sequentially, the rate of reactions may be monitored without having to re-start the experiment from the beginning. The reaction vessel can also be used as an incubation chamber for micro-organisms, which allows the study of the effect of organisms on mineral reactions.

## CALIBRATION AND PATTERN PROCESSING

### *HPEC calibration*

The HPEC pressure is measured using an inline pressure transducer. The temperatures are measured using a sheathed K-type thermocouple that is located in a well within 2 mm of the irradiated sample. As the HPEC is thermally conductive and the sample fluid is circulating relatively rapidly, the measured temperatures are assumed to be uniform throughout the chamber.

### *Pattern processing*

Pattern calibration of the APEX detector position with respect to the sample (HPEC) is required. Three parameters define the detector position: *dist* is the (refined) distance between the HPEC (window-to-window) center and the detector window (in mm), *x(center)* is the (refined) horizontal position of the detector window (in pixels), and *y(center)* is the (refined) vertical position of the detector window (in pixels). To obtain a broad range of 2θ values, *e.g.* using Mo radiation, the detector is placed at three 2θ positions, at 0, 20, and 35º, and the detector distance is set to near 120 mm. A single set of *x(center)*, *y(center)*, and *dist* values is obtained by taking the average from the three 2θ positions. If a single detector position is of greater importance, the 2θ value is fixed and average values are not used. For example, because the $d_{001}$ value of smectite is of greatest interest in clay mineralogy, the *x(center)*, *y(center)* and *dist* values at only one detector position (2θ = 0º, near 120 mm) are obtained by using chlorite [$d_{001}$ = 14.2 Å] for calibration. Where all three 2θ detector positions are useful, $LaB_6$ powder is used for calibration and the respective *x(center)*, *y(center)*, and *dist* values are averaged from each 2θ position. Bruker provides software (*GADDS*, Bruker-AXS, 2003) for calibration, for merging frames of various detector positions, and for the conversion of Debye rings (Figure 6) to a standard diffraction pattern (Intensity *vs*. 2θ pattern). In cases where there is high background, and the pattern of interest is reduced in intensity or obscured by background, a Bruker utility program is available to subtract frames. Thus, a frame involving only pure water may be subtracted from a frame obtained from a sample in water to obtain a frame with minimal background. Then, after conversion to a standard diffraction pattern from a frame, the pattern can be used as input to a data pattern analysis program (*e.g. MDI JADE*, Materials Data Inc., 1224 Concannon Blvd., Livermore, California, USA) for phase identification, cell-parameter refinement, or other analysis. Procedures for obtaining and processing powder diffraction patterns on the Bruker single-crystal diffractometer were presented in abstract form (Guggenheim, 2004) and as a Bruker application note (Guggenheim, 2005).

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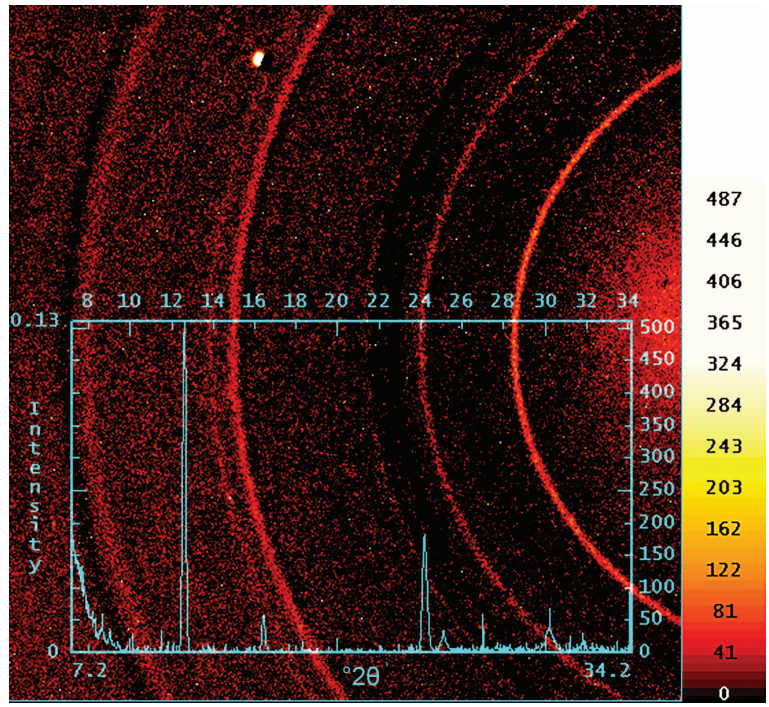



Figure 6. Frame of $TiO_2$ (NIST Standard Reference Material 674a) with the rutile structure, illustrating GADDS (Bruker) software that allows the conversion of Debye rings to a 'standard' powder diffraction pattern (Intensity *vs*. 2θ pattern), which is superimposed over the frame. A water suspension of ~150 mg of $TiO_2$ was used. The illustrated frame was produced by a (pixel-to-pixel) subtraction of a frame involving the diffraction of (pure) water from a frame involving the diffraction of $TiO_2$ + water. Both initial frames were for 20 min at 2θ = 20º at a detector distance of 12 cm, Mo radiation at 45 kV, 25 mA, and using a graphite monochromator and a MonoCap collimator under ambient conditions. Six Debye rings were obtained to produce a determined cell refinement of $a$ = 4.602(7), $c$ = 2.960(7) Å.

*High-pressure reaction vessel*

The pressure of the high-pressure reaction vessel is determined initially using a pressure transducer. By weighing the pressure vessel before and after an experiment, any loss of the pressurizing gas will be accompanied by a weight-loss. Because an oven is used as an external heat source, temperature within the oven is monitored with a standard thermometer or by using a thermocouple/temperature recorder.

## APPLICATIONS AND PERFORMANCE

The design of the HPEC allows studies at ocean-floor or bore-hole conditions in aqueous liquids that may be saturated with various gases (*e.g*. $CH_4$, $CO_2$, $O_2$). Mixing these gases with inert gases (*e.g*. He, Ar) allows control of the fugacity. An example of an application of the HPEC is the work of Giesting *et al*. (2012a,b), which used a prototype HPEC to study the effect of $CO_2$ (gas and supercritical fluid) on the XRD patterns of Na-, K-, or Ca-exchanged montmorillonite to pressures of 640 bars and temperatures to ~50ºC.

To illustrate the utility of the current system, the observed $d_{001}$ values *vs*. $T$ in a series of experiments (Figure 7) are given for ~200 mg of montmorillonite (The Clay Minerals Society Source Clay, SWy-2, from Wyoming) in ~2 mL of brine (NaCl at 250% content of sea water, or 100 g/L), under $CO_2$ pressure of ~500 bars. After pressure was attained at 500 ± 10 bars, a valve

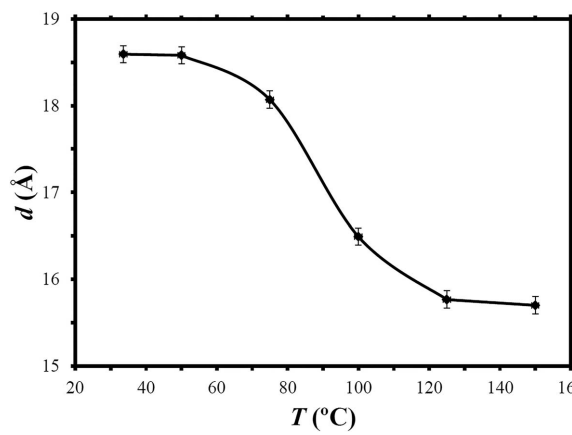



Figure 7. A $d_{001}$ *vs*. $T$ plot illustrating the change in $d$ value as a function of temperature in a brine at $P(CO_2)$ = 500 bars. Pressure was not corrected for the increase in temperature above ambient because the HPEC remained closed during heating. See text for details.

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located adjacent to the pressure port was closed. X-ray patterns [$d_{001}$] were obtained at 33.6, 50, 75, 100, 125, and 150ºC. Samples were allowed to rest for 30 min at each temperature prior to exposure, which was for 20 min. The closed valve prevented loss of fluids over the course of the heating experiments, but the temperature increase above 33.6ºC increased pressure accordingly. The $d_{001}$ values ranged from 18.6 to 15.7 Å. A more detailed account of the experiments will be provided elsewhere.

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