A flexible Au-Ir cell with quick assembly for hydrothermal experiments

ROBERT J. ROSENBAUER, JAMES L. BISCHOFF

U.S. Geological Survey, 345 Middlefield Road, Menlo Park, California 94025, U.S.A.

JARED M. POTTER

Coretest Systems Inc., 110 Pioneer Way, Unit L, Mountain View, California 94041, U.S.A.

ABSTRACT

We describe a new flexible reaction cell for high-temperature and high-pressure experiments in hydrothermal apparatus. The interior of the cell is all Au, except for two inert Ir gaskets. The design features an all Au cap that can be easily and rapidly assembled and disassembled. The capacity of the cell is approximately 240 mL, with a height of 20 cm and an o.d. of 6 cm.

INTRODUCTION

Flexible reaction cells have been used with hydrothermal experimental equipment to study high-temperature rock-H_2O interactions (e.g., Bischoff and Dickson, 1975; Seyfried, 1987; Rosenbauer and Bischoff, 1983; Berndt et al., 1989). This apparatus, pioneered by Dickson et al. (1963), circumvents many of the quenching problems associated with fixed volume autoclaves by allowing the isobaric and isothermal sampling of reacted fluid during the course of the experiment.

The technology of this type of experimental equipment has evolved slowly over the last 20 yr, and the search for universally applicable noncorrosive materials has met with only limited success. Table 1 lists the materials commonly used in the construction of flexible reaction cells and their critical characteristics in various reaction environments. The choice of material depends upon the specific application and goals of the experiment. Teflon[1] (E. I. duPont de Nemours and Company, Inc., Wilmington, Delaware) is generally inert but is limited to temperatures <290 °C and is permeable to H_2O, dissolved gases, and silica. Thus, the salinity and redox state of enclosed fluids are partially controlled by differences in chemical potentials on either side of the cell.

The Pt group of transition metals is chemically inert relative to other materials, but either material cost or other physical properties have precluded them from general use. Pt, however, has been widely used for capsules in high-temperature fluid-inclusion studies because it is stable under oxidizing conditions (Bodnar and Sterner, 1987) and permeable by H_2 (Chou, 1986). Ag is less permeable than Pt to H_2 and has been used for some studies but only in the absence of chloride-bearing fluids.

Au is inert under most experimental hydrothermal conditions, except in the presence of a strong oxidizing agent and a favorable complexing ligand (Puddephatt, 1978). But widespread use of all Au cells is limited, however, because cells must be fabricated by welding and cut open at the end of the experiment to access the reaction products. This procedure not only is time consuming but also reduces the volume of the cell and thus limits its lifetime. Another major problem with the all Au cell is that the integrity of the welded closure is highly dependent on the skill of the goldsmith.

A Au cell with a detachable Ti cap (Seyfried et al., 1979) combines most of the advantages of the all Au cell with the convenience of a mechanical closure. Ti owes its passive nature to its tendency to form an impermeable oxide on its surface, which prevents further oxidation. Its resistance to corrosion thus depends upon the permeability, reactivity, and solubility of this oxide layer in the corrosive fluid. This surface coating is adequately resistant to corrosion for most hydrothermal applications that involve complex and concentrated solutions. The all Ti cell (Seyfried et al., 1987) is a further variation on this design, but because Ti is less ductile than Au and tends to work harden, its application is limited. We found, moreover, that under some experimental conditions and with repeated use, Ti can be a contaminating factor, influencing H^+ activity and affecting the redox state of dilute unbuffered solutions.

This contamination became evident during experiments with dilute NaCl solutions to which HCl was added to adjust the pH. Repeated addition of acid resulted in an initial decrease in pH to that predicted by mass-balance calculation, but that was followed by an unexpected, gradual rise in both pH and dissolved Ca (Table 2). Significant dissolved Fe was also detected. Apparently, the cap had earlier taken up some Ca from previous experiments containing rock powder that was not readily removed during our rigorous cleaning procedures. The Fe may also be residual from previous experiments or primary as a trace component of commercial grade II Ti (Tico Inc., Farmington Hills, Minnesota) typically used

---

[1] Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

TABLE 1. Critical characteristics of reaction-cell material under various conditions

	Reaction environment				Other factors	
Material	Salt	Oxid	Red	Acid	Imp	Mal
Au	exc	fair*	exc	exc	exc	exc
Ti	good**	good†	good†	fair‡	exc	poor
Pt	exc	fair*§	good§	exc	fair	exc
Teflon‖	exc	exc	exc	exc	poor	good

Note: abbreviations are defined as follows: Oxid = oxidizing, Red = reducing, Acid = acidity, Imp = impermeability, Mal = malleability, exc = excellent.
* Dissolves only in the presence of complexing ligand.
** Adsorbs Ca (this study).
† Relies on oxide coating for inertness.
‡ Affects pH in unbuffered solutions.
§ Tendency to take up H_2 (Ebisuzaki et al., 1968).
‖ Temperature limited to 290 °C.

TABLE 2. Changes in pH and dissolved Ca and Fe with time when 2% NaCl is heated to 350 °C and pressurized to 500 bars in an Au-Ti reaction cell

t (h)	Ca (ppm)	Fe (ppm)	pH
Start	<0.1	<0.1	5.2
72	9.0	0.6	6.3
			acid added
96	10.0	2.2	2.9
120	11.7	1.0	5.3
			acid added
144	12.2	1.5	3.2
264	15.5	0.2	7.5
288	14.4	0.2	8.3

Note: acid (HCl) was added during the course of the experiment to adjust the pH to 3.0.

in cell fabrication. Therefore, we have extended the removable cap idea but have replaced the Ti with a newly designed Au cap.

Au-Ir CELL

Materials

Under prolonged and constant pressure at high temperatures Au will alloy to itself; this property precludes the use of any mechanical seal with Au-to-Au contact. Our approach therefore was to fabricate a Au cap but separate it from the deformable cell with a gasket of another compatible material to allow for disassembly. This material must be equally inert and not alloy with the Au.

We tried a variety of materials as candidates for gaskets before settling on Ir. At first, we tried no gasket at all and confirmed the self-alloying property of Au. Next, thin gaskets (0.025 cm) were made from Pt and Pt-group alloys. These provided excellent seals that alloyed easily with the Au and became permanent, apparently because of the relatively high solubility of Pt in Au. We considered double Pt gaskets, but Pt probably has self-alloying properties similar to Au. We tried also a commercial ceramic product, hexoloy SA silicon carbide (the Carborundum Company, Niagara Falls, New York), highly touted by the manufacturer for its corrosion resistance, but two different-sized gaskets of this material fractured during cell assembly. Another commercial product, graphaloy (Union Carbide, Chicago, Illinois) provided an adequate removable seal but gradually deteriorated with increasing time and temperature, contributing high levels of CO_2 to the system in the process.

Ir has a very low solubility in Au and, like Au, can be oxidized into various oxidation states (McBryde, 1968). Ir is a member of the Pt group of metals, and of all metallic elements it has the greatest resistance to corrosion (Burns et al., 1981), being insoluble even in aqua regia (Westland, 1981). It is also remarkable for its great mechanical strength at high temperatures and for the very high value of its elastic modulus (Westland, 1981). The material is typically ground instead of machined because

of its hardness. Ir is available commercially from precious metal suppliers, and its cost is very similar to the price of Au. These properties combine to make Ir an ideal material for use as a gasket between the Au top and the Au bag.

Design and fabrication

A new removable Au closure was designed around the existing geometry of the Au-Ti reaction cell within the tolerances of existing autoclaves. A schematic of this design is shown in Figure 1. The top edge of a standard-size Au tube (17.8 cm long × 4.44 cm diameter × 0.025 cm thick) is folded over at a 90° angle to create a flange. The bottom of the tube can be hemispherically closed and spot welded or folded over thrice and welded. A flat Au disk (5.5 cm in diameter, 0.10 cm thick) with a center hole (0.20 cm in diameter) serves as a top for the Au bag, replacing the Ti cap. For sampling purposes a Au exit tube (0.20 cm o.d. × 0.064 cm i.d. × 40 cm long) is passed through the center hole of the Au disk and welded to it. An additional mass of Au is accumulated around this weld to create a region for a filter; a cavity is then excavated in this mound of Au and packed with Au filings. A stainless steel backup plate adds rigidity to the Au disk and also houses a 0.635-cm stainless steel tube to hold the Au exit tube. The 0.635-cm tube is Tig welded to the top plate. The Au exit tube is flared over the outer end of the 0.635-cm tube and terminates in a Ti valve block for sampling. Reactivity within the valve block is considered negligible because it is at room temperature, but an Ir insert could be fabricated to replace the Ti insert within the valve block if desired.

The top Au disk is sealed to the Au bag with a simple flat seal incorporating two Ir rings (5.5 cm o.d. × 4.6 cm i.d. × 0.25 cm thick). Preliminary experiments had shown that, although Ir has a low solubility in Au, some alloying still occurred at sustained high temperature. However, Ir does not easily bond to itself. Therefore, a double Ir gasket was designed and sandwiched between the two Au flanges. A small counter bore was cut by grinding an angle into the outside edge of each Ir ring. This alteration decreases the sealing area and creates a region where a small
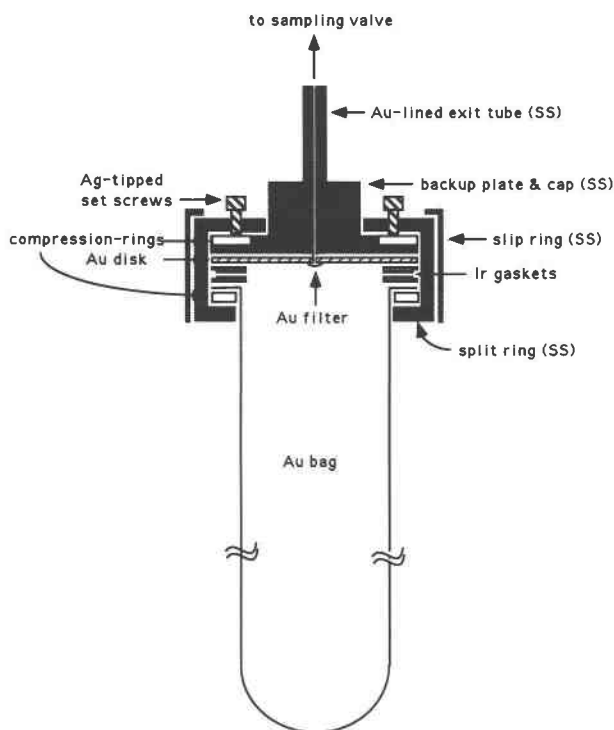
Fig. 1. Schematic diagram of a new Au-Ir reaction cell for hydrothermal experiments. SS = 316 stainless steel.

tool can be inserted to wedge the Ir rings apart if needed, although our experience is that these rings come apart very easily after an experiment. The entire sandwich of the Au disk and backup plate, two Ir rings, and the upper-folded flange of the Au bag is held together by two stainless steel split rings. A narrow stainless steel slip-ring holds the split rings in place while force is applied with six hex head set screws 10-32 × 1.59 cm long. These set screws are then individually replaced with Au-tipped set screws (Berg, Inc., East Rockaway, New York) to accommodate compression of the sandwich and to prevent extrusion of the Au due to thermal expansion of the materials. Ir does not easily deform and is almost impossible to machine, and so it is important to obtain polished Ir rings with parallel and flat surfaces to ensure a proper seal. A sacrificial thin Au washer (<0.025 cm) could be added between the Ir gaskets to aid in sealing.

TEST EXPERIMENTS

Several short preliminary experiments were performed with a dry and empty cell to test the temperature response of the closure. The entire closure was assembled and heated in a muffle furnace to various temperatures. Some expansion of the Au disk was noted above 400 °C, but the Ir rings came apart easily after cooling to room temperature. Originally, the Ir rings were oxidized at 800 °C to lessen the potential for alloying, but this oxide layer was neither durable nor necessary.

We repeated the control experiments over a wide sa-

linity range (0–20% NaCl), using a prototype reaction cell with a slightly different design and were able to achieve stable and predictable pH values. We used the cell also to investigate the possible hydrolysis of NaCl in the presence of quartz at 400 °C, from 500 to 40 bars. These experiments lasted one month and demonstrated clearly the importance of hydrolysis in the dry steam region. All components, including pH, which ranged from 5.5 to 2.5, followed a predictable and reproducible pattern without any evidence of corrosion of the reaction cell.

A long-term test of the current design was performed during our recent study of the equilibration of simple organic phases in the presence of a H_2 buffer. We heated 0.5 M acetic acid in the presence of quartz, fayalite, and magnetite (QFM) at 240 °C and 500 bars. Over a six-month period, we monitored and adjusted several components, including pH, which all responded in a predictable manner. The pH of this system started and remained at 3.5 for three months. Then we titrated the acetic acid with exactly the amount necessary to achieve a neutral pH. The system then remained neutral for three more months, when the experiment was terminated, and the reaction cell was disassembled. The Ir gaskets separated easily, and the closure came apart readily. There was no visible evidence of corrosion.

SUMMARY

The Au-Ir reaction cell for flexible hydrothermal apparatus offers a new level of corrosion-resistant and contamination-free environment for experimental investigations at high temperatures and pressures. It features a removable cap that can be easily assembled and disassembled, and the new cell is compatible with most existing high-pressure autoclaves commonly used today.

ACKNOWLEDGMENTS

REFERENCES CITED

Berndt, M.E., Seyfried, W.E., Jr., and Janecky, D.R. (1989) Plagioclase and epidote buffering of cation ratios in mid-ocean ridge hydrothermal fluids: Experimental results in and near the supercritical region. Geochimica et Cosmochimica Acta, 53, 2283–2300.
Bischoff, J.L., and Dickson, F.W. (1975) Seawater-basalt interaction at 200°C and 500 bars: Implications for origin of sea-floor heavy-metal deposits and regulation of seawater chemistry. Earth and Planetary Science Letters, 25, 385–397.
Bodnar, R.J., and Sterner, S.M. (1987) Synthetic fluid inclusions. In G.C. Ulmer and H.L. Barnes, Eds., Hydrothermal experimental techniques, p. 423–457. Wiley, New York.
Burns, D.T., Townshend, A., and Carter, A.H. (1981) Iridium. In R.A. Chalmers and M.R. Masson, Eds., Inorganic reaction chemistry, vol. 2. Reactions of the elements and their compounds, part A: Alkali metals to nitrogen, p. 211–215. Wiley, New York.
Chou, I-Ming (1986) Permeability of precious metals to hydrogen at 2 KB total pressure and elevated temperatures. American Journal of Science, 286, 638–658.

Dickson, F.W., Blount, C.W., and Tunell, G. (1963) Use of hydrothermal solution equipment to determine the solubility of anhydrite in water from 100° to 275°C and from 1 to 1,000 bars pressure. American Journal of Science, 261, 61–78.

Ebisuzaki, Y., Kass, W.J., and O'Keefe, M. (1968) Solubility and diffusion of hydrogen and deuterium in platinum. Journal of Chemical Physics, 49, 3329–3332.

McBryde, W.A.E. (1968) Iridium. In C.A. Hampel, Ed., The encyclopedia of the chemical elements, p. 299–305. Reinhold, New York.

Puddephatt, R.J. (1978) The chemistry of gold. In R.J.H. Clark, Ed., Monograph 16: Topics in inorganic and general chemistry, 274 p. Elsevier, New York.

Rosenbauer, R.J., and Bischoff, J.L. (1983) Uptake and transport of heavy metals by heated seawater: A summary of the experimental results. In P.A. Rona, K. Bostrom, L. Laubier, and K.L. Smith, Eds., Hydrothermal processes at seafloor spreading centers, p. 177–197. Plenum, New York.

Seyfried, W.E., Jr. (1987) Experimental and theoretical constraints on hydrothermal alteration processes at mid-ocean ridges. Annual Review Earth and Planetary Sciences, 15, 317–335.

Seyfried, W.E., Jr., Gordon, P.C., and Dickson, F.W. (1979) A new reaction cell for hydrothermal solution equipment. American Mineralogist, 64, 646–649.

Seyfried, W.E., Jr., Janecky, D.R., and Berndt, M.E. (1987) Rocking autoclaves for hydrothermal experiments. II. The flexible reaction-cell system. In G.C. Ulmer and H.L. Barnes, Eds., Hydrothermal experimental techniques, p. 216–239. Wiley, New York.

Westland, A.D. (1981) Inorganic chemistry of the platinum-group elements. In L.J. Cabri, Ed., Platinum-group elements: Mineralogy, geology, recovery. The Canadian Institute of Mining and Mineralogy, 23, 5–18.