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Applicability of electrochemical oxygen fugacity measurements to geothermometry

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Abstract

Reliability testing of the double-cell ZrO_2-electrolyte oxygen-fugacity sensors and selected geologic applications are discussed for oxygen-fugacity geothermometry. New data extending the use of single-cell ZrO_2 oxygen-fugacity sensors to 34 kbar total pressure are presented for a study comparing the Ni–NiO buffer with the hematite–magnetite buffer.

Specific geothermometric studies are reviewed to illustrate the application of the technique to the Bushveld Complex (Flynn *et al.*, in press), to the Stillwater Complex (Sato, 1972), and to the Oka Carbonatite (Friel and Ulmer, 1974). New fO_2–T data for diamondiferous kimberlite from the Premier Mine, South Africa, can be summarized by the equation: (atms)

$$\log fO_2 = 14.3 - \frac{3.17 \times 10^4}{T(\mathrm{K}^\circ)}$$

which is valid from 770°–990° C. The activation temperature for the oxidation of gem diamond oxidized in an argon-oxygen atmosphere similar to such a kimberlite matrix is 960° ± 15°C.

Introduction

The concept of applying electrochemical techniques to geothermometry was first theoretically proposed in 1965 by Sato who applied the thermodynamically-oriented solid-electrolyte studies of Kiukkola and Wagner (1957) to many geologic problems. In the ensuing decade this theoretical prediction of oxygen fugacity geothermometry has been substantiated. Sato (1970, 1971, and 1972) in a series of papers has excellently presented the theory, techniques, and necessary hardware to perform oxygen-fugacity geothermometric studies. The main goal of this discussion is therefore to present reliability testing data and geological applications which substantiate the use of electrochemically-measured oxygen-fugacity data to geothermometry.

General background and theory

Since Darken and Gurry (1945) first quantified redox equilibria in their study of the Fe–O system by the use of gas mixing, geologic interest in the role of fO_2 in petrology has continued to grow. With this in mind Sato (1970, 1971, and 1972) began using a double-cell design to measure intrinsic oxygen fugacities of mineral assemblages. In the double-cell design the first cell is used to read the emf generated between a known fO_2 buffer and the ambient furnace atmosphere. The second cell is used to read the emf generated between the same ambient furnace atmosphere and the unknown sample. The advantage to this double-cell design is that one can prejudice the ambient furnace atmosphere to be very close in its fO_2 value to the fO_2 of the unknown, thereby eliminating errors from leakage into the unknown. Leakage into the known cell of course is not desirable, but is not as critical since the known buffer can indeed "buffer" any small leaks. In the ultimate form of this double-cell design, the emf generated by the second cell can be amplified and used to drive a motorized valve to make the fO_2 of the ambient furnace atmosphere "track" the fO_2 of the unknown. In other words, by opening or shutting a H_2 valve, the ambient fO_2 can be brought within ± 0.10 log unit or less of the unknown fO_2. When the entire assembly is at equilibrium, in order to read the unknown fO_2, one must read and sum the emf from the two cells, thereby comparing the known buffer to the unknown sample via the media or "bridge" of the furnace atmosphere. Using this design concept, many of Sato's predicted (1965) geolotic applications could be successfully undertaken.

Data and results

Reliability tests

The reliability of the ZrO_2 electrolytic double-cell design has been intensively studied at one atmosphere pressure in at least six geologic laboratories. Comparisons of fO_2–T values have been done between the double-cell design and each of five different types of materials:

(1) known solid buffers
(2) known redox gas mixtures
(3) known synthetic single phases
(4) natural single phases
(5) multicomponent natural assemblages.

Electrochemically-measured oxygen-fugacity data taken at one atmosphere on solid buffer assemblages such as Ni-NiO, wüstite–iron, and hematite–magnetite, typically agree for these buffers to within ±0.10 log units of the fO_2 value published for the given buffer at a given temperature (Huebner, 1971). The high stability and excellent precision of the electrometers employed in data-taking preclude any instrumentation contribution to these deviations. However, an uncertainty in temperature control of ±3° C is typical at petrologic temperatures, and this ±3° C can contribute as much as ±0.04 log units uncertainty in determined fO_2 values. The remainder of the deviation can be attributed to systematic errors, such as thermal gradients. This precision and accuracy obtainable on invariant buffered assemblages has led many workers to use the ZrO_2 electrolytic double-cell technique as a primary investigative technique for redox equilibria. For example, Pehlke *et al.* (1975) have compared thoria- and zirconia-cell data for the Cr–Cr_2O_3 buffer curve and have found good agreement between the two types of cells with $\Delta G°$ (Cr_2O_3) = $-266{,}600 - 59.78T$ (±350)cal for the temperature range 1173°–1523° K.

Similarly, using gas mixing as described by Darken and Gurry (1945), many laboratories have compared the electrolytic cell by introducing known one-atmosphere gas mixtures. Gas impurity, deviations from calculated gas-mixing ratios, as well as deviations from preset temperatures, all systematically affect the agreement between the cell values and calculated values for gas mixtures. Huebner (1975) found agreement between the cell and the JANAF-based thermodynamic calculations of Deines *et al.* (1974) only above 1125°C for the mixtures of CO_2-H_2 and only above 1050°C for mixtures of CO_2–CO. We have mixed preanalyzed CO_2 (typically 99.9% pure with 0.02% O_2) with a similarly pure H_2 in a calibrated capillary manometer system (Nafziger *et al.*, 1971), and the mixtures have been read in both single-cell and double-cell arrangements. A comparison of these electrolytic cell values with the JANAF-based calculated values (Deines *et al.*, 1974) is shown in Figure 1. While agreement at CO_2/H_2 mixing ratios of 10/1

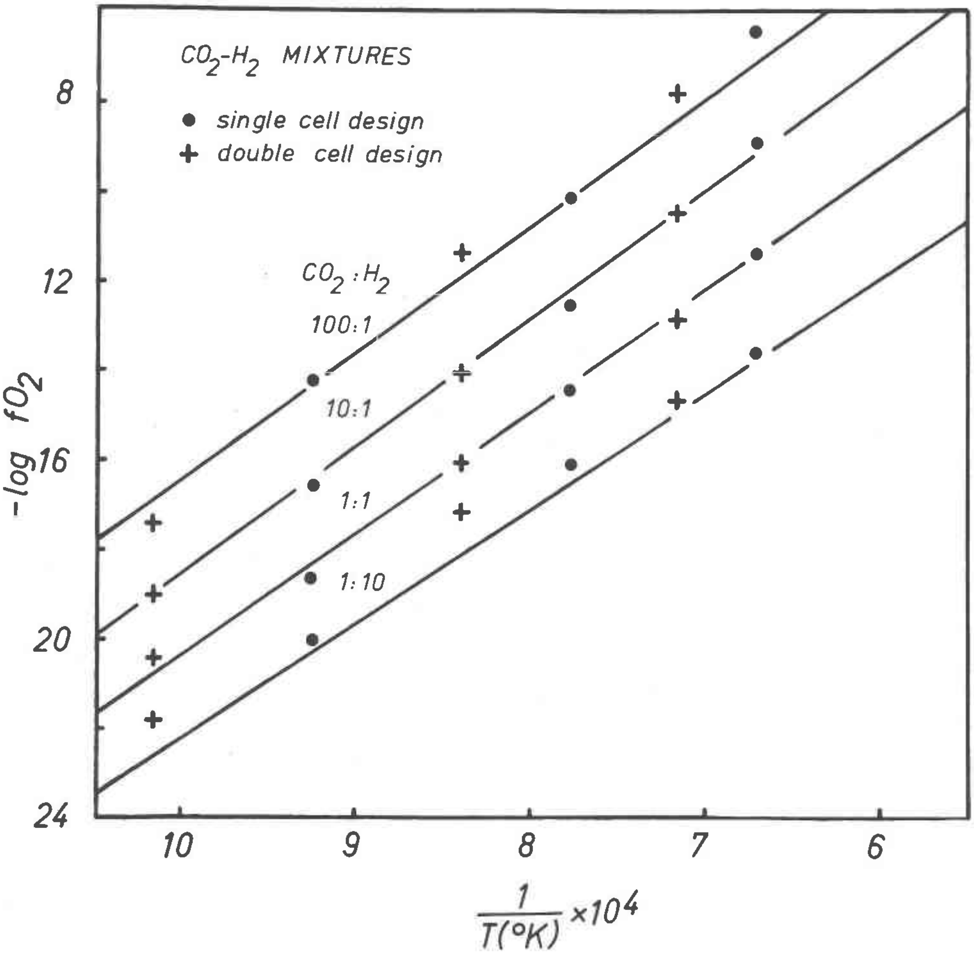

FIG. 1. Comparison between oxygen fugacities determined with a ZrO_2 solid-electrolyte cell and calculated from gas-mixing ratios, using the temperature–oxygen fugacity tables of Deines *et al.* (1974). Data from the single-cell design were obtained in an arrangement similar to that of Huebner and Sato (1970), while the double-cell design was similar to Sato (1971).

and 1/1 is convincingly good from 700° to 1200°C, for mixing ratios as extreme as 100/1 or 1/10, gas purity can produce systematic errors which may be as large as 0.9 log units fO_2. Furthermore, the thermodynamic data base from which one calculates an oxygen fugacity for a given gas mixture can also influence the 'agreement' that appears in Figure 1. For example, if the measured data were compared to calculations based on Wicks and Block (1963) rather than JANAF, the 1 to 10 gas mixture would have a calculated fO_2 at 1200°C that is as much as 0.25 log units more oxidized than is shown in Figure 1. (Deines *et al.*, 1974).

To do petrogenetic fO_2–T work on whole-rock samples as well as on separate minerals, such as feldspar or pyroxene, which have respectively little or no intrinsic buffering capacity, the ZrO_2 double-cell reliability should really be established on synthetic single-phase materials, synthesized under known fO_2–T conditions. For example, magnetite synthesized at 1000°C was prepared under defined fO_2 conditions and quenched for this purpose. Comparison data on these magnetites were obtained in ZrO_2 double-cell equipment in two different laboratories. While the fO_2 values of both laboratories agree within experimental error, the fO_2 values determined were more reduced than the fO_2 employed during synthesis. The magnetic-analysis method of Wasilewski *et al.* (1975) does not rule out the presence of small amounts of wüstite within these magnetites. Thus, we feel that quenching in a fixed-mixing-ratio gas mixture (state-of-the-art) produces at least some reduction of the magnetite pellet. Furthermore, the CO_2/H_2 or CO_2/CO synthesis mixtures may not have

TABLE 1. Data comparisons

Temple University Synthesis			Synthesis Gases	1000°C Cell Data -log $\underline{f}O_2$	
$\underline{T}$	-log $\underline{f}O_2$			Temple University	USGS Reston
(°C)	Gas Mixer	ZrO_2 Cell			
1000	10 $\pm$ 0.1	10 $\pm$ 0.1	CO_2/CO	11.8 $\pm$ 0.1	11.9 $\pm$ 0.1
1000	10 $\pm$ 0.1	not determined	CO_2/H_2	12.4 $\pm$ 0.1	12.3 $\pm$ 0.1

completely equilibrated at the temperature of synthesis (Huebner, personal communication). Nevertheless, the data show excellent agreement obtained for the fO_2–T data for these synthetic magnetites in the double cell at two different laboratories (Table 1).

Comparison experiments between the Temple University Geology Department laboratory and the USGS laboratory at Reston were also done on natural olivine separated from an ultramafic nodule (LBM-11) associated with an African kimberlite. This olivine, kindly supplied by Dr. B. Harte (Cox *et al.*, 1973) gave similar fO_2–T data in both labs; for example, at 1000°C the two values of $-\log fO_2$ were within experimental error of each other at 13.1 ± 0.1 atms.

In yet another study, oxygen fugacity–temperature data were collected for three Cascadian Mt. Hood andesites (Drory and Ulmer, 1974). Using aliquots kindly supplied by Dr. R. Fudali, a comparison could be made of the fO_2–T whole-rock relationships obtained by three different independent methods:

(1) synthetic fO_2 reequilibration at the whole-rock liquidus temperature (Fudali, 1965);

(2) fO_2–T data as deciphered from opaque oxide compositions using the method of Buddington and Lindsley (1964); and

(3) fO_2–T data from the ZrO_2 electrolytic double-cell technique.

When care was taken in method three to use a whole-rock sample that was greater in diameter than the zoned andesine phenocrysts of the andesite, the agreement shown in Table 2 was obtained between the three techniques. While the comparisons of these three totally different oxygen-fugacity methods for rocks with as little as 5 weight percent total iron oxide do show a general convergence of the data, more work is necessary to assess any of the existing methods.

In summarizing the reliability of the ZrO_2 oxygen-fugacity sensor, reproducibility is very convincing, and while accuracy on buffered assemblages is good to excellent, accuracy for single phases has not been independently confirmed because suitable standards are unavailable. The above data do however show that for the ZrO_2 cells, in-house and intra-laboratory comparisons are excellent.

At higher total pressures, preliminary calibration tests of ZrO_2 single cells have only just begun in belt-type pressure equipment. Figure 2 shows the results of a solid-buffer experiment performed in a belt-type apparatus at 34 kbar for Ni–NiO (NNO) versus hematite–magnetite (HM). Calculated emf values for the assemblage NNO *vs.* HM at the given pressure are shown by the lines *a* and *b*, where *a* is the data of Eugster and Wones (1962) and *b* is the data of Huebner (1971). The experimental values were reproducible on subsequent temperature cycles between 700° and 1300° C.

Moreover, since the effect of pressure on the molar volumes of solid phases is small, the pressure effect on fO_2–T equilibria in silicate redox equilibria is also small. For instance, the quartz–fayalite–magnetite buffer assemblage at 1000°C and five kilobars has a value of $\log fO_2$ that is only 0.36 units more oxidized than the same buffer at 1000° C and one atmosphere total pressure, according to the data given by Eugster and Wones (1962). Therefore, working with the double cell at one atmosphere total pressure may still provide meaningful data for oxygen fugacity geothermometry for many shallow intrusive deposits.

Specific geothermometric studies

Many oxygen-fugacity geothermometric investigations have been initiated since 1971, using the double-cell configuration. These geothermometric projects were chosen so that independent or second-method confirmations could be made for the geothermometric results from the ZrO_2 double-cell sensor technique. Reviewed below are geothermometric data for four selected igneous studies:

(1) the *F*-horizon of the northeastern Bushveld Complex, Transvaal
(2) the *G*-zone group of the Stillwater Complex, Montana
(3) the Main Carbonatite Core at Oka, Quebec
(4) the diamondiferous kimberlite at the Premier Mine, Transvaal.

TABLE 2. Comparison of fO_2 measuring techniques

	- Log $\underline{f}O_2$ Results (atms)		
Results at 1200°C	Method 1	Method 2	Method 3
hypersthene augite andesite	8.2 ± 0.1	8.0 ± 0.7	7.8 ± 0.15
hypersthene augite andesite	7.0 ± 0.1	8.0 ± 0.7	7.5 ± 0.15
olivine augite andesite	7.2 ± 0.1	8.0 ± 0.7	8.2 ± 0.15

Northeastern Bushveld Complex

Using drillcore samples supplied by E. Cameron, an investigation was undertaken of cumulate anorthosite (An 78) in the Bushveld Igneous Complex Critical Zone (Flynn *et al.*, 1972). This anorthosite occurs just above a thin (1–2 mm thick) chromitite seam which in turn occurs above a bronzitic pyroxenite horizon. The triple-cumulate unit (the base of the *F*-horizon; Cameron, 1971) has been observed in the field to occur for more than 40 km along the strike of the outcrop of the eastern Bushveld. Because this outcrop represents the first coexistence of cumulate orthopyroxene, chromite, and anorthite in the Bushveld, it became the object of an fO_2–T petrogenetic study. Separate mineral concentrates were hand-picked from crushed drillcore samples, and fO_2–T data were obtained for chromite, pyroxene, and plagioclase (An 78). Each separated fraction was used to obtain fO_2–T data from 800°–1200°C with the ZrO_2 double cell. When these fO_2–T data are plotted within the same graph, three intersections are obtained among the fO_2–T curves for the studied fractions. These intersections involve the following mineral assemblages:

(1) chromite–bronzite
(2) chromite–bronzite–plagioclase (An 78)
(3) chromite–plagioclase (An 78).

The fO_2–T data obtained for these assemblages are plotted for comparison in Figure 3. Philosophically, one can wonder if these intersections do represent any record of an equilibration condition between the natural phases, *i.e.*, is there any petrogenetic information to be obtained? The solidus for an orthopyroxene–plagioclase–magnetite assemblage in the system MgO-FeO-Fe_2O_3-$CaAl_2Si_2O_8$ (Roeder and Osborn, 1966) shows an amazing correspondence of temperature and fO_2 to the determined temperature and fO_2 of the chromite–bronzite–anorthite assemblage in the Bushveld (*cf.* Fig. 3). Furthermore, two independent subsequent checks of the gabbroic solidus for this drill core obtained temperatures of 1110° ± 10°C, and 1115° ± 15°C. Thus, these data would seem to warrant the conclusion that oxygen-fugacity geothermometry has been useful and reliable in establishing the solidus of the natural assemblage, orthopyroxene–spinel–plagioclase, at the Bushveld.[1]

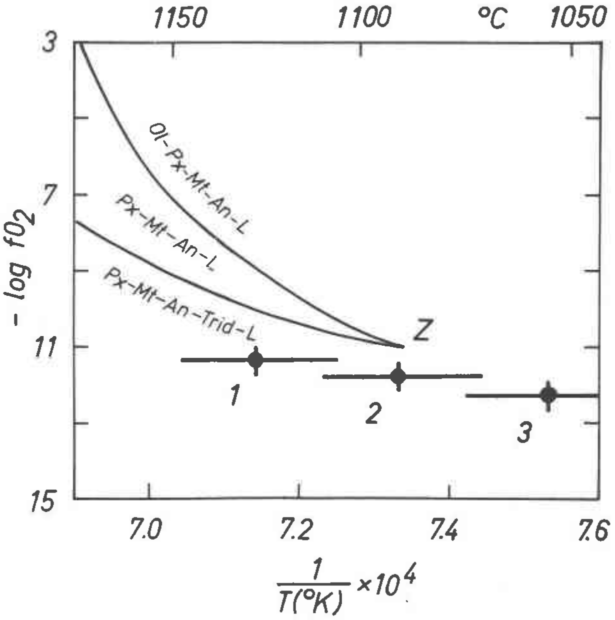

FIG. 3. Point *Z* represents the fO_2–T data for the solidus termination of the assemblage (orthopyroxene–magnetite–plagioclase–liquid) from the equilibria studies of Roeder and Osborn (1966). Also shown are the oxygen-fugacity geothermometry data for the cumulate minerals of the *F*-horizon of the northeastern Bushveld: point (1), probable last equilibration between chromite and plagioclase (An 78), point (2), probable last equilibration between chromite, bronzite, and plagioclase (An 78), and point (3), probable last equilibration between chromite and bronzite. An, L, Mt, Ol, Px, Tr represent respectively, anorthite, liquid, magnetite, olivine, pyroxene and tridymite.

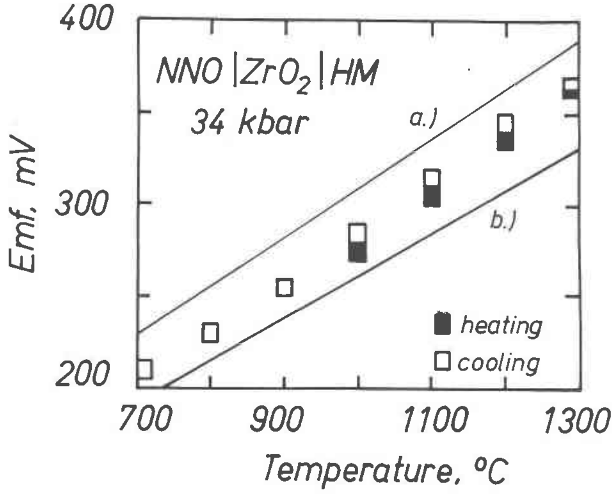

FIG. 2. EMF measurement at 34 kbar with solid-electrolyte cell (flat disk type, Sato, 1971) using Ni-NiO (NNO) *vs.* hematite-magnetite (HM) buffers. Experimental data are compared with two sets of thermodynamic data: (a) Eugster and Wones (1962) (b) Huebner (1971).

Stillwater Complex

Similar work has been done for the Stillwater Complex by Sato (1972). The olivine and chromite

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[1] In a forthcoming paper by Flynn *et al.* (in press) four lines of evidence that suggest the middle critical zone may have magmatically accumulated at fO_2–T conditions near this solidus are reviewed, but these discussions are beyond the scope of this report.

from the Stillwater Complex *G*-horizon shows a temperature of suspected last equilibration of 1000° ± 60°C, whereas distribution coefficients (K_d) for coexisting olivine and chromite calculated from Fe/Mg electron-microprobe data have allowed Jackson (1969) to independently calculate a last temperature for Fe/Mg exchange at 990°C, for at least some layers of the *G*-zone.

Oka Complex

Encouraged by these two results for igneous environments, a second study at Temple was undertaken on a carbonatite located at Oka, near Montreal, Canada (Friel and Ulmer, 1974). Oka is noted for the occurrence of many unusual minerals; one of them is latrappite, a niobium-substituted perovskite. Single crystals of latrappite could be easily and cleanly separated from the calcite matrix. Also obtainable from the carbonatite were euhedral magnetite octahedra and subhedral patches of olivine (Fo 80). These three separates were again subjected to fO_2–T analyses exactly as described previously. The resultant least-squares-fitted data for each mineral were plotted on a single graph. A triple intersection for the three curves was found to occur at an fO_2 of $10^{-17.4}$ (atms) and at a temperature of 710°C, as shown by the Oka data point in Figure 4. Again one can ask the philosophical question: is this the temperature of last equilibration of these phases, and if so, is this an original carbonatite temperature or a later hydrothermal and/or metamorphic reequilibration? Conway and Taylor (1969) have by oxygen isotope studies (O^{18}/O^{16}) come to the conclusion that at Oka the oxygen communication equilibration ceased at 700° C. This constitutes an excellent cross-check by an independent method at a second lab.

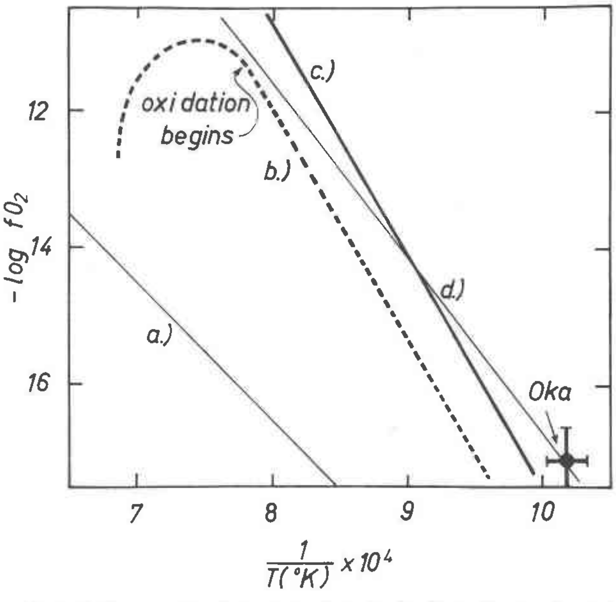

FIG. 4. Summary of carbonatite, kimberlite, diamond, and graphite redox data. The single point labelled Oka represents the last equilibration between latrappite, magnetite, and olivine within the carbonatite in the Oka Carbonatite (Friel and Ulmer, 1974). Curves *a* and *d* are respectively the data for the graphite-CO-CO_2-O_2 buffer (French and Eugster, 1965) and the data for the quartz-fayalite-magnetite (QFM) buffer (Wones and Gilbert, 1969). Curve *c* represents the least-squares-fit for data taken in two labs for a powdered and homogenized sample of diamondiferous black kimberlite from the Premier Mine in South Africa. Finally, curve *b* represents the path of kinetics of oxidation of inclusion-free gem diamond chips in an argon-oxygen mixture. This curve has been determined to be quite similar in two labs, and it is dashed only to emphasize that these are not equilibrium data. Oxidation activation temperature for the diamond is inferred to be 960° ± 15°C as observed by the rapid slope change above 960°C. See further discussion in the text for curve *b*.

As to whether this temperature is that of the original carbonatite formation, consider the solid– liquid–vapor (*s–l–v*) equilibria in synthetic carbonate systems as reviewed by Wyllie (1966). The available data would at least confirm that in pertinent synthetic systems, 680°C is the minimum carbonate-melt solidus and that this solidus temperature is only slightly affected by either CO_2/H_2 ratio or by the total pressure. Thus, for Oka the measured temperature of last equilibration is sufficent to reach the *s–l–v* equilibria in carbonatite systems. Thus, despite the ijolitic banding that has been used to argue that Oka is a metamorphic event, the measured environmental geothermometric parameters allow an igneous genetic interpretation.

Premier Diamond Mine

The final case history that will be discussed involves the redox equilibria surrounding the petrogenesis of diamond. Whole-rock samples of black kimberlite, from the 500m level of the Premier Mine, South Africa, have been subjected to the double-cell fO_2–T technique. This whole-rock kimberlite is known to be diamondiferous, but does contain chlorite and serpentine, both of which are thought to be syngenetic with the kimberlite emplacement (Van Zyl, personal communication).

The fO_2–T data were collected for homogenized powdered samples of this whole-rock kimberlite at both Temple and Reston and show good agreement. The data were least-squares fitted to the following equation: (atms)

$$\log fO_2 = 14.3 - \frac{3.17 \times 10^4}{T(°\mathrm{K})}.$$

These data are portrayed by line *c* in Figure 4. Of the familiar petrologic redox buffers, these kimberlite data approximate the quartz–fayalite–magnetitie buffer (see line *d*, Fig. 4), which is in agreement with the theoretical suggestion of Mitchell (1973) for the oxygen fugacity of kimberlite.

The oxidation of diamond should be a function of temperature, total pressure, and fO_2 of the environment. In Figure 4 the data of French and Eugster (1965) for the one-atmosphere fO_2–T stability of the graphite–CO_2–CO–O_2 buffer is given by line *a*. From the data of Figure 4 it is clear that elemental carbon (diamond should be even more redox-unstable than graphite) should not coexist at one atmosphere at equilibrium with its kimberlite matrix (line *c* Fig. 4). Initial attempts have therefore been made with the ZrO_2 double-cell design to study the oxidation kinetics of inclusion-free gem-diamond chips (type C and D)[2] kindly supplied by Dr. H. K. Mao. Curve *b* in Figure 4 is not from equilibrium data, but is the path of kinetics of the oxidation of diamond in an argon-ambient atmosphere whose fO_2–T values were adjusted to be close (curve *b*) to the fO_2–T values of the kimberlite matrix (curve *c*). Curve *b* shows that in the argon atmosphere the oxidation of the diamond, as determined at both Reston and Temple, did not begin below 960° ± 15°C, but that above this temperature the fO_2 within the argon surrounding the diamond rapidly changed as oxidation of the diamond occurred according to the reaction:

$$C_{diamond} + 1/2\ O_2 = CO_{gas}.$$

The sensitivity of this technique for determining the beginning of oxidation can best be judged by the fact that the amount of oxidation of the diamond chips in this experiment was non-weighable despite the sample size of about 0.250 g. Within the cell containing the diamond it may be true that the number of oxygen atoms in the argon is statistically too small to expect quick reaction; however, at temperatures up to 960°C no detectable oxidation reaction takes place (up to 960°C the slope of curve *b* is constant), even after eight hours, whereas at 970°C oxidation occurs within a matter of minutes. Above 960°C the portion of the curve shown is the locus of the lowest fO_2 measured at each 40°C increment after two hours at each of these studied temperatures. A longer hold at each temperature would have shown further reduction, but in this particular experiment a two-hour data accumulation method was purposely used to evaluate reaction rates. We interpret those data to mean that, at one atmosphere at least, diamond will rapidly oxidize in a cooling kimberlite matrix hotter than 960°C. If kimberlite intrusion took place at lower temperatures than 960°C, it is concluded that diamond would be stable, because even though the kimberlite matrix may have had oxidative capacity for diamond, the activation temperature for oxidation of diamond in kimberlite was not achieved. Moissan (1893) showed that in air the beginning of burning of diamond varied from 760°C–875°C, depending on the quality of the diamond used. More recently Harris and Vance (1974) in diamond oxidation experiments at one kilobar with both degassed and wet (15% H_2O added) kimberlite observed no reaction at 900°C, but did find oxidation-etching at temperatures above 1050°C. While more work in this geothermometric study is desirable, it is already clear that the double-cell ZrO_2 electrolytic oxygen-fugacity technique is capable of giving geothermometric data for the genesis of diamond.

Summary

Oxygen-fugacity geothermometric results have been obtained and interpretations have been made. Geothermometry with the ZrO_2 double-cell has been cross-checked with independent means of evaluation.

The state of knowledge about the utility of fO_2 electrolytic cells for geology is comparable to the era of solution geochemistry after Pourbaix but before Garrels and Christ. For example, using an electrolytic cell called the pH meter, Eh–pH diagrams had been determined but were little used and even less believed until Garrels and his students pioneered the use of these studies in geology.

The petrogenetic possibilities of this oxygen-fugacity geothermometry technique are so tremendous that more use of the technique is warranted. Compared to other proposed geothermometers, this technique *is certainly one of the least uncertain.* For example, if an fO_2–T intersection is suspected to have petrogenetic significance, additional involved phases can be separated and used to test for a multiple fO_2–T intersection. If no geologically reasonable intersection occurs between the two phases, then there never was an equilibrium. Few other geothermometers offer this kind of built-in protection from errors or false assumptions.

Acknowledgments

Urged on by Dr. M. Sato's pioneer work and by his unlimited generosity in providing assistance and available time in his laboratory, several other laboratories have now been able to branch

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[2] Jewelers' nomenclature for gem quality.

heavily into the use of the ZrO_2 double-cell oxygen-fugacity sensor. Certainly the reliability tests described within this report would have been impossible without Dr. Sato's untiring cooperation. Drs. Mao and Harte and the Premier Mine are all acknowledged for their willingness to share samples. Supportative laboratory availability and financial support for various parts of this work have been supplied by (in alphabetical order) Deutsche Forschungsgemeinschaft; Institut für Petrologie, Universität Frankfurt; Research Corporation; Temple University Summer Faculty Fellowship; and the U.S. Geological Survey.

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