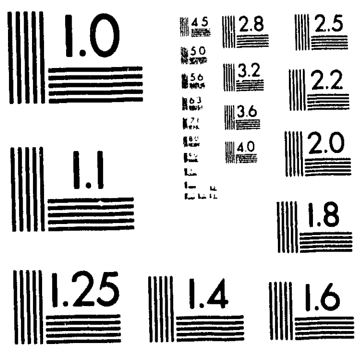
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4.5
2.8
2.5
5.0
3.2
5.6
2.2
6.3
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

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# TRENDS AND ANOMALIES IN GAS EVOLUTION FROM COAL SAMPLES*

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**INTRODUCTION**
The Argonne Premium Coal Samples have been prepared from one-ton lots of coals which were collected from eight different mines (1). The selection of the eight samples was made to cover a range of the available ranks of US coals from lignite through low volatile bituminous. The samples were collected from freshly exposed mine faces and represent channel samples of these seams. The analytical values for the samples are given below.

The eight Argonne Premium Coal Samples:

| # | Name | Rank | State | Dmmf C | Dmmf H | Abbrev. |
|---|---|---|---|---|---|---|
| 5 | Pocahontas #3 | LVB | VA | 91.05 | 4.48 | POC |
| 1 | Upper Freeport | MVB | PA | 88.08 | 4.84 | UF |
| 4 | Pittsburgh | HVB | PA | 83.20 | 5.43 | PITT |
| 7 | Lewiston-Stockton | HVB | WV | 82.58 | 5.44 | WV |
| 6 | Blind Canyon | HVB | UT | 80.69 | 5.81 | UT |
| 3 | Illinois #6 | HVB | IL | 77.67 | 5.20 | IL |
| 2 | Wyodak-Anderson | SUB | WY | 75.01 | 5.42 | WY |
| 8 | Beulah-Zap | LIG | ND | 74.05 | 4.90 | ND |

LVB = Low volatile bituminous, MVB = Medium volatile bituminous, HVB = High volatile bituminous, SUB = subbituminous, LIG = Lignite, State = U. S. A. State of origin, Dmmf = dry mineral matter-free, Abbrev = Abbreviation used later. The number given indicates the order of collection.

The samples were placed into 55 gallon stainless steel drums at the collection site and sealed. As soon as they were at the surface, they were purged with argon gas to reduce the oxygen concentration to below 100 ppm. A truck took the drums to the Argonne National Laboratory (ANL) for processing in a large nitrogen filled glove box. Typically six drums were processed for ampule production, and one was kept for later reference.

The drums were purged in air locks to reduce the oxygen content to below 100 ppm before being admitted to the glove box. The oxygen content of the glove box was maintained below 100 ppm. During sealing of samples it was typically at or below 30 ppm. The coal was crushed to pass between steel bars with 1/2" spacings. The 7 higher rank samples were ground to pass a 20 mesh screen. The ton of sample was collected in a 2000 l mixer-blender capable of holding the entire batch. After thorough mixing the samples were either temporarily sealed in 5 gallon "leverlock" pails for later regrinding or sealed into either 5 gallon glass carboys or 10 gram ampules of coal (60 ml capacity). The "leverlock" pails were passed through airlocks and pulverized a second time to pass through a 100 mesh screen. This coal was accumulated in the mixer-blender, thoroughly mixed and then sealed in 5 gallon glass carboys or 5 gram ampules of coal (30 ml capacity). The samples were then placed in a darkened storage room kept year round at room temperature.

**EXPERIMENTAL**
As part of the stability studies on these samples a number of the samples were given to the Analytical Chemistry Laboratory at ANL for periodic gas analysis. For the first years analyses were carried out with a CEC mass spectrometer. Carbon monoxide could not initially be distinguished from nitrogen and was not reported. A VG Gas Analysis mass spectrometer, model 30-01 equipped with electron multiplier detector, was used starting in 1991 to replace the CEC unit and provide better data. CO could be detected in the nitrogen, and lower limits of detection were established for the oxygen measurements.

**RESULTS AND DISCUSSION**
Table 1 summarizes the data for the $CH_4$ and $CO_2$ evolution. Hydrogen was observed in the gases above the samples, but not in the 55 gallon reference storage drums. It is believed that this hydrogen came from interaction of some fine dust generated during the processing with the palladium catalyst used for oxygen removal. The data obtained are condensed in Table 1 below and extend earlier studies (2).

The data were plotted as concentration of gas versus time since sealing of the ampules. Representative plots are shown in Figures 1-4. They give the concentration of $CH_4$ or $CO_2$ versus time since sealing. Figure 5 gives the gas concentration versus carbon content in the coal.

Table 1. Methane and Carbon Dioxide Concentrations in Argonne Premium Coal Sample Ampules.

| Coal | | -100 mesh | | | | | -20 mesh | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CH_4$ | | | $CO_2$ | | $CH_4$ | | | $CO_2$ | |
| | major gas | trend | max. conc | time | trend | max. conc | trend | max. conc | time | trend | max. conc |
| UF | $CH_4$ | + | .40 | 79 | + | .13 | P | .70 | 79 | + | .15 |
| WY | $CO_2$ | P- | .02 | 63 | P- | .93 | P | .02 | 63 | + | 1.4 |
| IL | $CO_2$ | P- | .23 | 65 | P- | .23 | P- | .46 | 65 | 0 | .66 |
| PITT | $CH_4$ | P- | .8 | 64 | P- | .58 | P- | 14.5 | 64 | 0 | .70 |
| POC | $CH_4$ | P | 1.2 | 62 | + | .78 | P- | 7.6 | 62 | P | 5.1 |
| UT | $CO_2$ | P- | .03 | 61 | + | .10 | 0 | .02 | 61 | P | .37 |
| WV | $CO_2$ | P- | .03 | 59 | + | .13 | P- | .23 | 59 | 0 | .53 |
| ND | $CO_2$ | P- | .02 | 58 | + | 2.68 | 0 | .03 | 58 | P | 3.3 |

major gas = gas at higher concentration in ampule (other than $N_2$), trend = trend of changes in concentration (+ = increasing, 0 = constant, - = decreasing, P = plateau before or after trend), P- = decrease after plateau, max conc = maximum concentration of gas in ampule in %, time = maximum time since sealing in months for data.

**CONCLUSIONS**
1. Higher rank coals evolve methane, and lower rank coals evolve carbon dioxide with some evolution of both gases for the intermediate ranks.
2. The evolution proceeds over times of years for pulverized coals in sealed ampules.
3. Gas concentrations are higher above -20 mesh samples than above -100 mesh material.
4. Carbon monoxide is not evolved.

5. Anomalously high $CH_4$ and $CO_2$ evolution is observed for the Pittsburgh and Pocahontas samples.
6. The gas evolution seems to be associated with release of dissolved species, except for hydrogen which is associated with rection of fine dust with the palladium catalyst in the atmosphere treatment system.

**ACKNOWLEDGMENTS**
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References

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2. Vorres, K.S., Proc., 1991 Intl. Conf. on Coal Science, Vol. I, 147 and Proc., 1989 Intl. Conf. on Coal Science, Vol. II, 1083.

Fig. 1, Six Highest −100 Mesh Methane

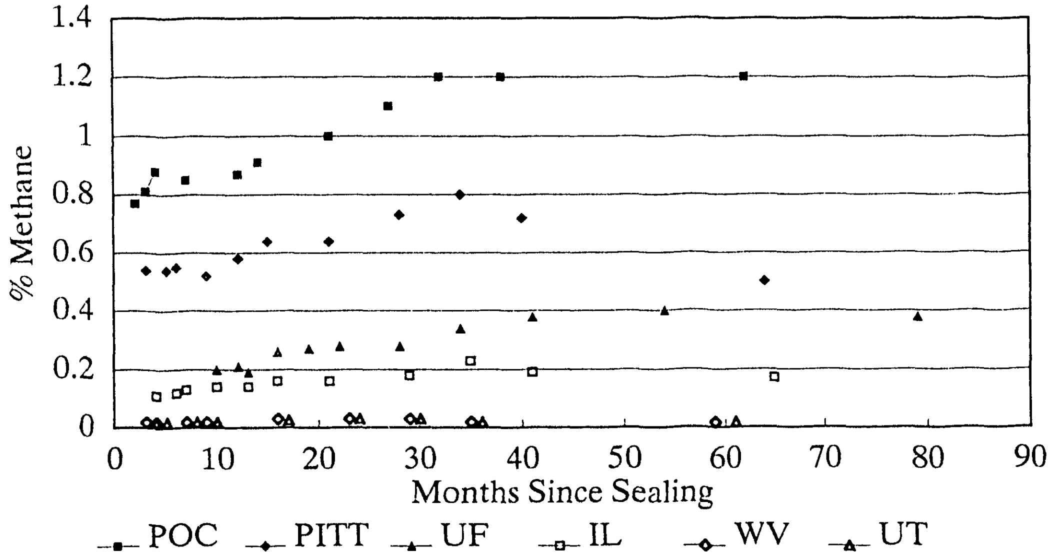



Fig. 2, Six Highest −20 Mesh Methane

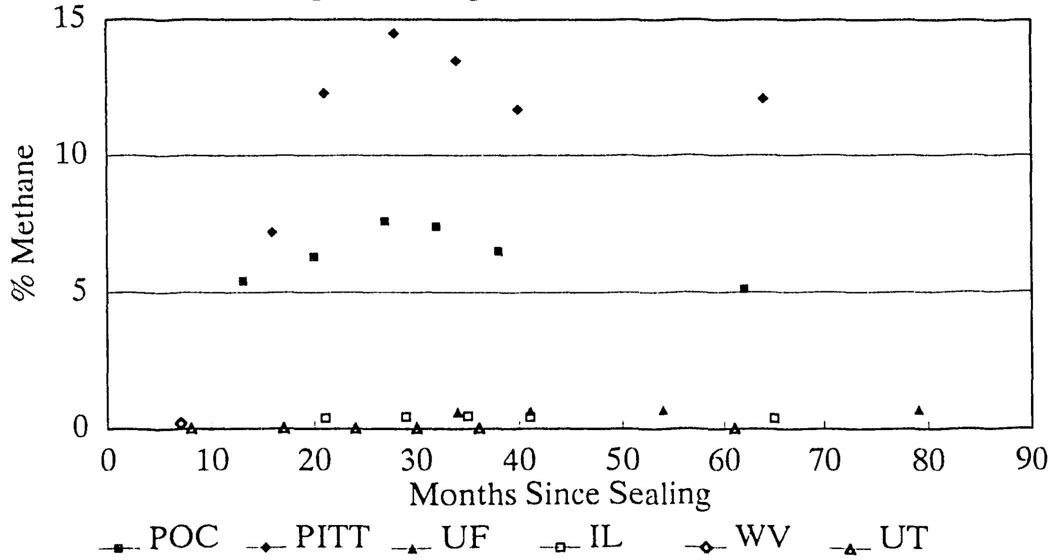


Fig. 3, Six Highest −100 Mesh CO2

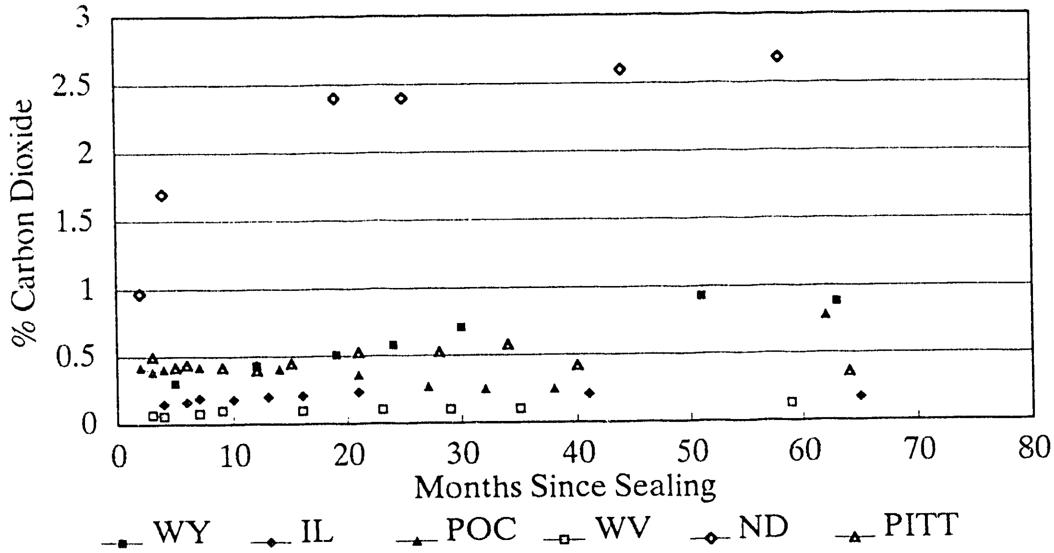



Fig. 4, Six Highest −20 Mesh CO2

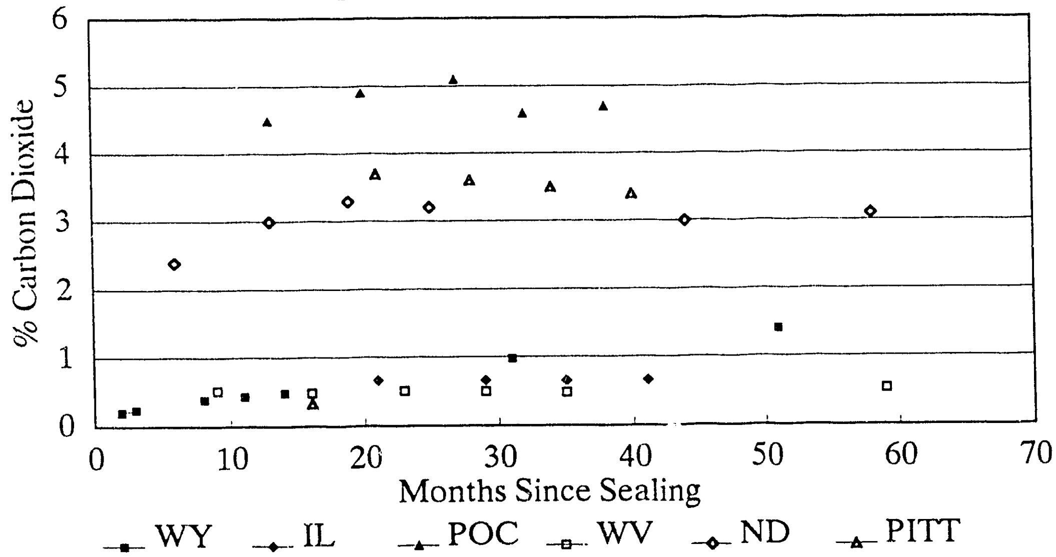
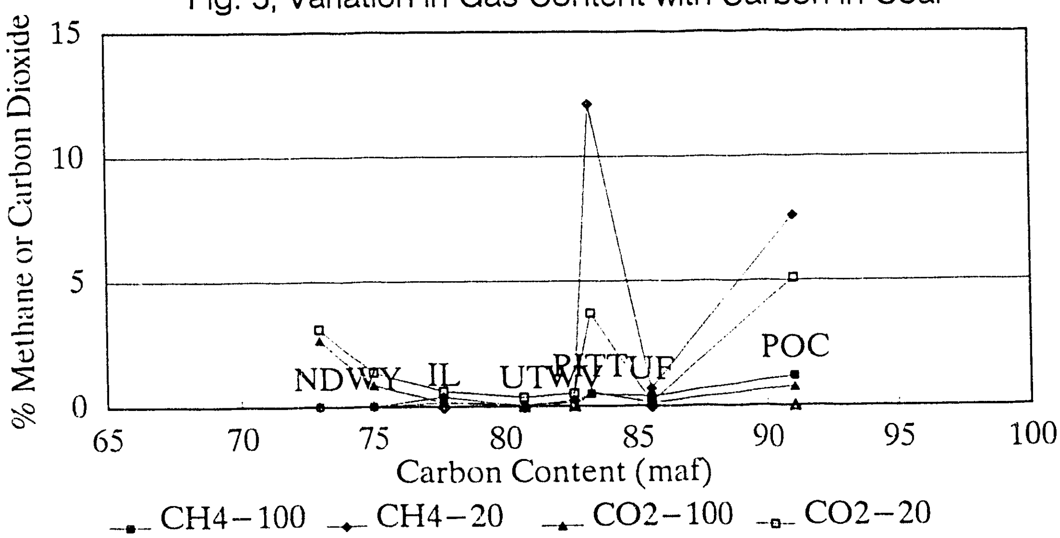



Fig. 5, Variation in Gas Content with Carbon in Coal

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