

# Noble gases and nitrogen in natural gases from Gujarat, India

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## ABSTRACT

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Isotopic and elemental ratios have been measured in three natural gas samples from Gujarat, India. The  $^3\text{He}/^4\text{He}$  ratio is radiogenic for Kalol-166 and Kalol-183, while a mantle component is clearly indicated for Motwan-2. Although Ne is atmospheric in these Kalol gases, for Motwan-2, a clear excess  $^{21}\text{Ne}$  due to  $^{18}\text{O}(\alpha, n)^{21}\text{Ne}$  is present. All three gases have radiogenic  $^{40}\text{Ar}$  and air values for  $^{38}\text{Ar}/^{36}\text{Ar}$ . Krypton is atmospheric in composition for all three gases. Xenon in Kalol-183 is purely atmospheric, but for Kalol-166 a pure fission Xe from  $^{238}\text{U}$  is also present. Xenon from Motwan-2, on the other hand, shows excess  $^{129}\text{Xe}$ ,  $^{131}\text{Xe}$ ,  $^{132}\text{Xe}$ ,  $^{134}\text{Xe}$  and  $^{136}\text{Xe}$  which do not match either  $^{238}\text{U}$  or  $^{244}\text{Pu}$  fission yields. The higher yields of  $^{131}\text{Xe}$  and  $^{132}\text{Xe}$  are most likely a result of preferential migration or leaching of their radioactive precursors from their host rock. But the  $^{129}\text{Xe}$  excess could not be due to such preferential effects, and represents a mantle component. Both  $^3\text{He}$  and  $^{129}\text{Xe}$  excesses can be accounted for by the presence of  $\sim 20\%$  mantle component.

The  $\delta^{15}\text{N}$ -values for the three gases Kalol-166, Kalol-183 and Motwan-2 are (in ‰) +9.27, –12.56 and –11.48, respectively. They indicate a sedimentary source combined with effects due to migration.

## 1. Introduction

Since the discovery of  $^{129}\text{Xe}$  excess due to extinct  $^{129}\text{I}$  in natural gas from Harding County, New Mexico, U.S.A. (Butler et al., 1963; Boulos and Manuel, 1971) and later confirmed by several laboratories (Smith and Reynolds, 1981 and references therein), there has been increasing interest in the noble gases of natural gas wells. Recently Lin and Manuel (1987) and Caffee et al. (1988) have also reported xenon isotope excesses due to the decay of extinct radionuclides in well gases from the U.S.A. and Australia. Some samples of mantle origin like mid-ocean ridge basalts (MORB), ultramafic xenoliths and diamonds have also shown the presence of extinct  $^{129}\text{I}$  decay product (Hennecke and Manuel, 1975a; Staudacher and Allègre, 1982; Honda et al., 1987;

Ozima and Zashu, 1988; Marty, 1989), but the Harding County gas sample has been considered to define the composition of noble gases of mantle origin (Staudacher, 1987) in the models to understand the terrestrial noble gas reservoirs.

While gases from Harding County and Caroline (Australia) entirely consist of  $\text{CO}_2$  (Phinney et al., 1978; Caffee et al., 1988) the gas from Navajo (Arizona, U.S.A.) has only 4.3%  $\text{CO}_2$  (Lin and Manuel, 1987), but all the three gases have fission xenon and  $^{129}\text{Xe}$  excess due to extinct  $^{129}\text{I}$ . On the other hand, Xe in natural gases from other localities of the U.S.A with  $\text{CO}_2$  contents ranging from 0.2% to 28% have Xe with some strange isotopic composition (Bennett and Manuel, 1970). We analysed three well gases from Gujarat, India, having  $\text{CO}_2$  contents <2% in order to determine what kind of noble gas components are

present, since no data exist for noble gases in natural gas from India.

## 2. Experimental

### 2.1. Natural gas collection

The gas has been collected in a thick-walled stainless-steel cylinder with a volume of  $\sim 10$  cm<sup>3</sup>. One end of this cylinder is fitted with a metal valve. The cylinder is directly coupled to the gas pipe and allowed to be flushed with the gas long enough to ensure that air is completely flushed out from the cylinder. The open end of the cylinder is then closed with a threaded cap with Teflon<sup>®</sup> washer to ensure leak-tight sealing. The metal valve at the other end of the cylinder is then closed and the cylinder detached from the gas pipe. The pressure inside the cylinder is  $\sim 30$  atm.

### 2.2. Initial purification of the natural gas

Since natural gas consists mostly of hydrocarbons and CO<sub>2</sub> that can cause background problems in the mass spectrometer, an initial clean-up is carried out in a separate clean-up system to reduce the level of hydrocarbons and CO<sub>2</sub>.

Two aliquots of the gas are processed separately, one for nitrogen and the other for the noble gases. This was necessary to avoid exposure of the gas to active getters (Ti and TiZr) and prevent nitrogen loss during the processing for nitrogen. The clean-up system is so arranged that the nitrogen aliquot only comes in contact with CuO and stainless-steel mesh (SSM) and not with the Ti and TiZr getters or charcoal fingers.

Three sets of break-seal ampoules are attached to the clean-up system, two of the sets without charcoal for collecting a known aliquot of N<sub>2</sub> and He+Ne, respectively, and the third set with some charcoal to completely collect Ar, Kr and Xe by adsorbing at liquid nitrogen temperature.

### 2.3. Clean-up for noble gases

About  $\sim 1$  cm<sup>3</sup> of natural gas is pipetted out from the cylinder. First a quick clean-up is done for He+Ne to reduce blank levels, in the following way. The condensible gases (CO<sub>2</sub>, H<sub>2</sub>O, etc.) are trapped in a cold finger and the rest of the gases (except He, Ne) are trapped on SSM kept at liquid N<sub>2</sub> temperature. The He+Ne fraction is then allowed to react with a Ti sponge at 400°C and TiZr at 500°C in succession, and an ampoule is sealed off with He and Ne. The condensibles are then pumped off. The remaining gas is then treated with CuO at 700°C to convert hydrocarbons to CO<sub>2</sub> and H<sub>2</sub>O which are separated and pumped off. The gas is then reacted with the Ti sponge and TiZr getter in succession to remove all the reactive gases, including N<sub>2</sub>. Ar, Kr and Xe are then collected into a break-seal ampoule by adsorbing on charcoal kept at liquid nitrogen temperature and sealed off.

### 2.4. Clean-up for nitrogen

Another  $\sim 1$  cm<sup>3</sup> of natural gas is pipetted from the cylinder which is allowed to react with CuO at 700°C to convert the hydrocarbons to CO<sub>2</sub> and H<sub>2</sub>O, which are separated and pumped off. The CuO treatment is repeated for a second time and an aliquot of N<sub>2</sub> is sealed off.

A blank is also processed in the same way and the ampoules are sealed off with He+Ne, Ar+Kr+Xe, and N<sub>2</sub>, respectively.

These ampoules from the initial clean-up line are then attached to the main extraction system of the mass spectrometer. After the system is pumped down to an acceptable vacuum, the ampoules are broken, one at a time with the help of a Ni piece in the line which can be manipulated with an external magnet, and the gases are cleaned and analysed.

### 2.5. Mass spectrometry

For He, mass 4 is scanned on a Faraday cup

TABLE I

Isotopic composition of nitrogen and noble gases in natural gases from Gujarat (errors are  $\pm 2\sigma$ )

	Kalol			Motwan			Atr
	183-1	183-2	183-3	166	2-1	2-2	
$^3\text{He}/^4\text{He}$ ( $\times 10^6$ )	-	-	0.40 $\pm$ 0.08	0.33 $\pm$ 0.07	2.1 $\pm$ 0.4	2.0 $\pm$ 0.4	1.4
$^{20}\text{Ne}/^{22}\text{Ne}$	-	9.81 $\pm$ 0.09	10.08 $\pm$ 0.05	9.83 $\pm$ 0.01	10.14 $\pm$ 0.09	10.15 $\pm$ 0.02	9.80
$^{21}\text{Ne}/^{22}\text{Ne}$	-	0.0272 $\pm$ 0.0003	0.0294 $\pm$ 0.0001	0.0286 $\pm$ 0.0002	0.0314 $\pm$ 0.0004	0.0326 $\pm$ 0.0006	0.0290
$^{38}\text{Ar}/^{36}\text{Ar}$	0.1852 $\pm$ 0.0002	0.1858 $\pm$ 0.0002	0.1894 $\pm$ 0.0002	0.1822 $\pm$ 0.0001	0.1875 $\pm$ 0.0007	0.1899 $\pm$ 0.0004	0.1880
$^{40}\text{Ar}/^{36}\text{Ar}$	326 $\pm$ 1	322 $\pm$ 1	355 $\pm$ 1	299 $\pm$ 1	546 $\pm$ 1	536 $\pm$ 1	295.5
$\delta^{15}\text{N}_{\text{air}}$ (‰)	-	-	-12.56 $\pm$ 2.46	9.27 $\pm$ 0.74	-	-11.48 $\pm$ 2.25	0
$^{82}\text{Kr}/^{84}\text{Kr}$ ( $\times 10^2$ )	20.387 $\pm$ 0.110	20.484 $\pm$ 0.100	20.529 $\pm$ 0.128	20.484 $\pm$ 0.029	20.548 $\pm$ 0.152	20.203 $\pm$ 0.042	20.217
$^{83}\text{Kr}/^{84}\text{Kr}$ ( $\times 10^2$ )	20.293 $\pm$ 0.100	20.235 $\pm$ 0.054	20.103 $\pm$ 0.110	20.265 $\pm$ 0.036	19.952 $\pm$ 0.072	19.843 $\pm$ 0.092	20.136
$^{86}\text{Kr}/^{84}\text{Kr}$ ( $\times 10^2$ )	30.350 $\pm$ 0.152	30.133 $\pm$ 0.132	30.442 $\pm$ 0.732	30.311 $\pm$ 0.106	30.442 $\pm$ 0.232	30.603 $\pm$ 0.058	30.524
$^{128}\text{Xe}/^{130}\text{Xe}$ ( $\times 10^2$ )	-	-	49.52 $\pm$ 0.90	47.54 $\pm$ 1.07	46.21 $\pm$ 1.16	47.96 $\pm$ 1.48	47.15
$^{129}\text{Xe}/^{130}\text{Xe}$ ( $\times 10^2$ )	-	-	643.9 $\pm$ 3.2	642.9 $\pm$ 10.1	669.8 $\pm$ 7.4	664.3 $\pm$ 11.5	649.6
$^{131}\text{Xe}/^{130}\text{Xe}$ ( $\times 10^2$ )	-	-	528.3 $\pm$ 6.1	509.2 $\pm$ 12.2	564.2 $\pm$ 6.8	543.6 $\pm$ 7.7	521.3
$^{132}\text{Xe}/^{130}\text{Xe}$ ( $\times 10^2$ )	-	-	669.4 $\pm$ 6.4	656.2 $\pm$ 12.4	714.0 $\pm$ 7.8	702.9 $\pm$ 10.9	660.7
$^{134}\text{Xe}/^{130}\text{Xe}$ ( $\times 10^2$ )	-	-	258.9 $\pm$ 1.8	269.7 $\pm$ 7.3	290.8 $\pm$ 3.3	299.1 $\pm$ 13.2	256.3
$^{136}\text{Xe}/^{130}\text{Xe}$ ( $\times 10^2$ )	-	-	214.2 $\pm$ 2.0	236.7 $\pm$ 4.8	248.3 $\pm$ 3.2	244.1 $\pm$ 8.6	217.6

- = not determined.

while the mass 3 peak is scanned on the multiplier. The contribution to mass 3 from  $\text{HD}^+$  and  $\text{H}_3^+$  is assessed from the peak height of mass 2, since our resolution ( $200\times$ ) is not enough to resolve  ${}^3\text{H}^+$  from the  $\text{HD}^+$  and  $\text{H}_3^+$  peaks. Due to the uncertainties in the gain factor from the Faraday cup to the multiplier and the  $\text{H}_3^+/\text{H}_2^+$  ratio an additional uncertainty is included in the  ${}^3\text{He}/{}^4\text{He}$  ratio as given in Table I.

The Ne ratios have been corrected for contributions from the doubly charged species  ${}^{40}\text{Ar}^{2+}$  and  $\text{H}_2\text{O}_{18}^+$  (for  ${}^{20}\text{Ne}$ ) and  $\text{CO}_2^+$  (for  ${}^{22}\text{Ne}$ ). Nitrogen ratios have been corrected for interferences from CO by using the peak height of mass 30 to assess the CO contribution at masses 28 ( ${}^{12}\text{C}{}^{16}\text{O}$ ) and 29 ( ${}^{12}\text{C}{}^{17}\text{O} + {}^{13}\text{C}{}^{16}\text{O}$ ). The CO contribution has been very small, resulting in a  $< 1\%$  change in the  $\delta^{15}\text{N}$ -values.

The Ar+Kr+Xe mixture has been first separated into individual gases by differential adsorption on charcoal fingers kept at different temperatures ( $-90^\circ\text{C}$  for Xe,  $-120^\circ\text{C}$  for Kr,  $-196^\circ\text{C}$  for Ar) and each gas is separately analysed.

The sensitivities and mass discrimination factors have been obtained by analysing Air Standards for  $\text{N}_2$ , Ne, Ar, Kr and Xe and an artificial  ${}^3\text{He} + {}^4\text{He}$  mixture, which have been cross-checked using the Bruderheim standard from Berkeley.

### 3. Results and discussion

The isotopic data for noble gases and nitrogen are given in Table I. Absolute amounts of the gases cannot be given since the amount of natural gas pipetted is not very precisely known. Instead, the elemental ratios of primordial and radiogenic components are given in Table II.

The errors quoted for all isotopic ratios are  $2\sigma$  and include the errors from blanks as well as mass discrimination. The blank contribution is  $< 2\%$  for all the samples and all the gases analysed, except for Xe. For Xe the blank con-

tribution was up to a maximum of 8% in the case of Motwan-2. The isotopic composition of the blanks are all atmospheric within the experimental uncertainties. The errors in the isotopic ratios of blanks, as well as the errors in the mass discrimination factors have been propagated by quadratic addition. Additionally, the Ne data have been corrected for the doubly charged  ${}^{40}\text{Ar}$  and  $\text{CO}_2$  interferences and the corresponding errors are propagated. The He data have a cumulative error of up to 20% from blanks, mass discrimination and sensitivity fluctuation between the Faraday cup and electron multiplier and interference at mass 3. Due to the low resolution of our mass spectrometer the mass 3 peak could not be resolved into  ${}^3\text{He}^+$ ,  $\text{H}_3^+$  and  $\text{HD}^+$  components. We applied a correction to the peak 3 intensity using the  $\text{H}_2$  peak height and a calibration curve of 2 vs. 3 with pure hydrogen. Generally the hydrogen partial pressure is low and nearly constant during the measurements in the mass spectrometer due to the efficient gettering by SAES® 101.

#### 3.1. He, Ne and Ar

The  ${}^3\text{He}/{}^4\text{He}$  ratios of the natural gas samples are clearly different from the atmospheric value. The Kalol gas is more radiogenic compared to atmospheric while the Motwan-2 gas shows a clear  ${}^3\text{He}$  excess. These ratios have been corrected for atmospheric contamination by assuming that all  ${}^{20}\text{Ne}$  is of atmospheric origin (Torgersen and Jenkins, 1982). If the corrected  ${}^3\text{He}/{}^4\text{He}$  ratios are considered to be a two-component mixture of crustal ( $3/4 \approx 4 \cdot 10^{-8}$ ) and mantle ( $3/4 \sim 1.2 \cdot 10^{-5}$ ) origin, one can calculate the contribution from the mantle component. Mantle components of 2.5%, 3% and 17% are needed to account for the observed  ${}^3\text{He}/{}^4\text{He}$  ratios of Kalol-166, Kalol-183 and Motwan-2, respectively.

The Ne isotopic data are plotted in the three-isotope diagram in Fig. 1. Data taken from the

TABLE II

Elemental ratios of primordial and radiogenic components (errors are  $\pm 25\%$ )

Sample	Primordial component						Radiogenic component				
	$^3\text{He}$	$^{20}\text{Ne}$	$^{36}\text{Ar}$	$^{84}\text{Kr}$	$^{130}\text{Xe}$	$^{28}\text{N}_2$	$^4\text{He}$	$^{21}\text{Ne}$	$^{40}\text{Ar}$	$^{129}\text{Xe}$	$^{136}\text{Xe}$
Kalol-183	$61 \cdot 10^{-4}$	1.83	1	$1.88 \cdot 10^{-2}$	$1.13 \cdot 10^{-6}$	$4.28 \cdot 10^4$	58	0	1	0	0
Motwan-2	$11.1 \cdot 10^{-3}$	1.20	1	$1.08 \cdot 10^{-2}$	$0.87 \cdot 10^{-6}$	$2.49 \cdot 10^4$	23	$1.5 \cdot 10^{-6}$	1	$5.3 \cdot 10^{-10}$	$9.5 \cdot 10^{-10}$
Kalol-166 Air	$11.0 \cdot 10^{-3}$	11	1	$1.64 \cdot 10^{-2}$	$0.26 \cdot 10^{-6}$	$1.32 \cdot 10^4$	$9 \cdot 10^3$	0	1	0	$1.3 \cdot 10^{-8}$
	$2.3 \cdot 10^{-7}$	0.52	1	$2.07 \cdot 10^{-2}$	$1.13 \cdot 10^{-4}$	$2.48 \cdot 10^4$	-	-	-	-	-

- = no data.

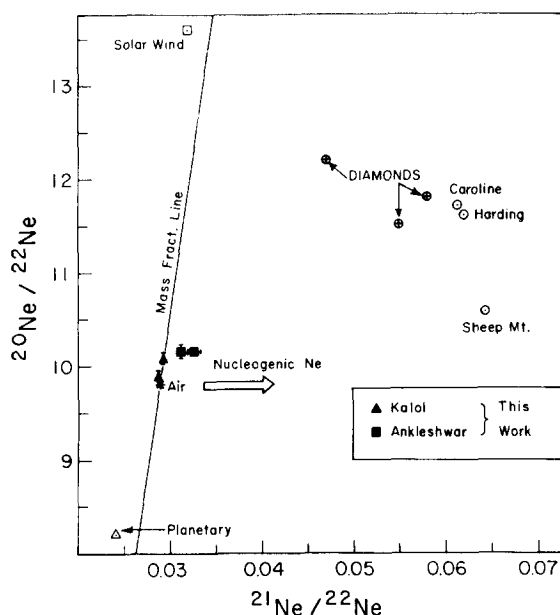


Fig. 1. Three-isotope diagram for neon data of natural gases. Literature data: *DIAMONDS*=Ozima and Zashu (1988); *Harding*=Staudacher (1987); *Caroline* and *Sheep Mt.*=Caffee et al. (1988); *Solar Wind* and *Planetary*=Honda et al. (1987).

literature for some gas wells and diamonds from Zaire are also shown in Fig. 1 (for comparison). The Kalol data plot either close to air value or along the mass fractionation line (MFL). But both the data points of Motwan-2 are shifted to the right of MFL, clearly indicating the presence of nucleogenic  $^{21}\text{Ne}$  from the  $^{18}\text{O}(\alpha, n)^{21}\text{Ne}$  reaction. The  $^{21}\text{Ne}$  excess is calculated by using the mass fractionated  $^{21}\text{Ne}/^{22}\text{Ne}$  ratio that corresponds to the  $^{20}\text{N}/^{22}\text{Ne}$

value, for subtracting atmospheric  $^{21}\text{Ne}$ . For Motwan-2 the  $(^{21}\text{Ne}/^4\text{He})_r$  value comes out to be  $0.66 \cdot 10^{-7}$ , which is within the range of values  $(1-0.28) \cdot 10^{-7}$  for radiogenic production (Kyser and Rison, 1982; Kennedy et al., 1990).

The  $^{40}\text{Ar}/^{36}\text{Ar}$  values for the three gas samples clearly show that there are three different reservoirs, Kalol-166 being the least radiogenic while Motwan-2 is the most radiogenic,  $^{38}\text{Ar}/^{36}\text{Ar}$  ratios for all the three gases are atmospheric within errors.

### 3.2. Kr and Xe

The isotopic data for  $^{124}\text{Xe}$ ,  $^{126}\text{Xe}$  and  $^{78}\text{Kr}$ ,  $^{80}\text{Kr}$  could not be determined precisely due to the small amount of gas and the interference problems due to the hydrocarbon background (for  $^{78}\text{Kr}$ ) and  $^{40}\text{Ar}_2^+$  molecular ion interference (for  $^{80}\text{Kr}$ ), respectively. The Kr isotopic data for  $^{82}\text{Kr}$ ,  $^{83}\text{Kr}$  and  $^{86}\text{Kr}$  for all three gases are similar to the atmospheric values indicating that the mass fractionation effects are very minimal. Xe data on the other hand show interesting trends. Kalol-183 data for xenon are atmospheric within errors. Kalol-166 clearly shows excess  $^{134}\text{Xe}$  and  $^{136}\text{Xe}$ , due to the spontaneous fission of  $^{238}\text{U}$ . Both the Motwan-2 samples show excesses of  $^{129}\text{Xe}$ ,  $^{131}\text{Xe}$ ,  $^{132}\text{Xe}$ ,  $^{134}\text{Xe}$  and  $^{136}\text{Xe}$ . The excess xenon spectrum does not match the fission spectra of either  $^{238}\text{U}_{\text{SF}}$  or  $^{244}\text{Pu}_{\text{SF}}$  or  $^{235}\text{U}_{\text{nf}}$ .

TABLE III

 $\Delta_i/\Delta_{136}$ -values for natural gases

Sample	CO <sub>2</sub> content (%)	$i$					Reference
		129	131	132	134	136	
Motwan-2	0.8	0.66 ± 0.24	1.40 ± 0.22	1.74 ± 0.25	1.12 ± 0.11	1.000	[1]
Kalol-166	2.0	-0.35 ± 0.46	-0.63 ± 0.65	-0.23 ± 0.64	0.70 ± 0.50	1.000	[1]
WG-2	99	2.56 ± 0.11	0.047 ± 0.045	0.532 ± 0.052	0.836 ± 0.033	1.000	[2]
Caroline	99	3.37 ± 0.09	0.017 ± 0.040	0.478 ± 0.041	0.830 ± 0.024	1.000	[3]
Navajo-4	4.3	0.21 ± 0.05	0.134 ± 0.040	0.567 ± 0.046	0.775 ± 0.018	1.000	[4]
C-16	28.5	0.93 ± 0.55	1.14 ± 0.27	1.56 ± 0.44	0.903 ± 0.125	1.000	[5]
<sup>238</sup> U fission	-	-	0.088 ± 0.003	0.568 ± 0.010	0.828 ± 0.012	1.000	[2]
<sup>244</sup> Pu fission	-	-	0.248 ± 0.015	0.893 ± 0.013	0.930 ± 0.005	1.000	[2]

$$\Delta_i = ({}^i\text{Xe}/{}^{130}\text{Xe})_{\text{sample}} - ({}^i\text{Xe}/{}^{130}\text{Xe})_{\text{air}}$$

References: [1] = this work; [2] = Phinney et al. (1978); [3] = Caffee et al. (1988); [4] = Lin and Manuel (1987); [5] = Bennett and Manuel (1970).

In Table III, we listed the  $\Delta_i/\Delta_{136}$ -values for xenon of the natural gases analysed in this study along with some literature data.  $\Delta_i$  is defined as the excess at each xenon isotope with respect to the air value, i.e.:

$$\Delta_i = ({}^i\text{Xe}/{}^{130}\text{Xe})_{\text{sample}} - ({}^i\text{Xe}/{}^{130}\text{Xe})_{\text{air}}$$

The  $\Delta_i/\Delta_{136}$ -values for xenon isotopes 129 to 136 are plotted in Fig. 2. Also plotted in Fig. 2 are some natural gas samples from literature data and the fission yields for <sup>238</sup>U and <sup>244</sup>Pu. The Kalol-166 data are consistent with the presence of pure <sup>238</sup>U fission xenon within errors. Motwan-2 xenon data on the other hand do not match with any known fission xenon spectra. Xenon excesses similar to Motwan-2 have been observed for natural gas samples from the U.S.A. (Clarke and Thode, 1963; Bennett and Manuel, 1970). Bennett and Manuel (1970) have explained the enrichments of <sup>131</sup>Xe and <sup>132</sup>Xe as due to preferential migration of the radioactive precursors of <sup>131</sup>Xe and <sup>132</sup>Xe (i.e. the radioisotopes of Te and I) to the grain surfaces and grain boundaries and consequently relative ease of diffusion from the solid phase. Neutron irradiation experiments on U<sub>3</sub>O<sub>8</sub> have clearly demonstrated the enrichment of <sup>131</sup>Xe and <sup>132</sup>Xe in the low-temperature fraction (~0.6% of total Xe) of the xenon released (Kennett and Thode, 1960). Recent

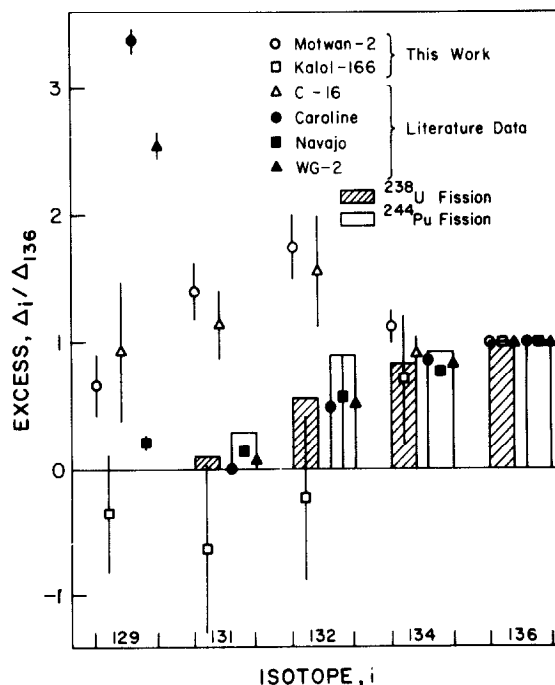
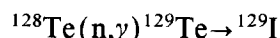


Fig. 2. Excess xenon for heavy isotopes, with respect to atmospheric xenon, is plotted for natural gases. <sup>238</sup>U and <sup>244</sup>Pu fission yields are shown for comparison. Literature data: <sup>238</sup>U, <sup>244</sup>Pu, Fission, WG-2 = Phinney et al. (1978); C-16 = Bennett and Manuel (1970); Caroline = Caffee et al. (1988); Navajo = Lin and Manuel (1987).

studies of fission Xe from diverse samples like the Oklo natural reactor (Gabon), uranium blacks, pitchblende and nuclear explosion sites have all shown the preferential enrichment of <sup>131</sup>Xe and <sup>132</sup>Xe due to migration of radioac-

tive precursors, in the low-temperature fractions or easily leachable phases (Shukolyukov et al., 1987). This preferential migration of the precursors of  $^{131}\text{Xe}$  and  $^{132}\text{Xe}$  and the occurrence of a small fraction of anomalous Xe (with relatively higher yields of  $^{131}\text{Xe}$  and  $^{132}\text{Xe}$  than expected in normal fission xenon) in diverse samples that accumulated the fission Xe in time scales ranging from minutes to millions of years (uranium blacks), clearly show the universality of this phenomenon. If the Xe in the Motwan-2 gas is dominated by such a labile Xe component, it can explain the observed anomalies of  $^{131}\text{Xe}$  and  $^{132}\text{Xe}$ . But even in the most anomalous Xe component from the work of Shukolyukov et al. (1987) the  $^{129}\text{Xe}/^{136}\text{Xe}$  ratio is much smaller than the values found in Motwan-2 and other similar natural gas samples (Bennet and Manuel, 1970) and might have another origin. Two possibilities exist and in both cases the progenitor is the radioisotope  $^{129}\text{I}$ : (1) the  $^{129}\text{I}$  can be of primordial nucleosynthetic origin in which case the  $^{129}\text{Xe}$  anomaly will have a time significance regarding the degassing of the solid Earth; and (2)  $^{129}\text{I}$  can be of in situ origin by specific neutron induced reactions and does not given any time information.

Let us consider the second possibility first. The most probable origin in this case is the neutron capture by:

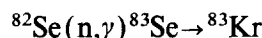


The neutron source being the natural neutrons from  $^{238}\text{U}$  fission and the consequent ( $\alpha, n$ ) reactions. If the source rock has sufficient Te abundance, in principle this process can generate the necessary  $^{129}\text{I}$ . There are two factors that are contradictory to this possibility. Along with  $^{129}\text{Xe}$ , the ( $n, \gamma$ ) reaction on Te also produces  $^{131}\text{Xe}$  via:



and the ratio of  $^{129}\text{Xe}/^{131}\text{Xe}$  produced from Te should be 0.7 (for thermal neutrons) to 4.0 (for epithermal neutrons) (Browne and Ber-

man, 1973). Also the Se that is usually associated with Te should produce a noticeable excess of  $^{83}\text{Kr}$  from:



The calculated  $^{129}\text{Xe}_{\text{excess}}/^{131}\text{Xe}_{\text{excess}}$  of  $< 0.7$  for Motwan-2 and the normal value of  $^{83}\text{Kr}/^{84}\text{Kr}$  are both inconsistent with the origin of excess  $^{129}\text{Xe}$  due to Te.

The alternative left for  $^{129}\text{Xe}$  is the primordial source, a decay product of the extinct  $^{129}\text{I}$ . Excess  $^{129}\text{Xe}$  due to extinct  $^{129}\text{I}$  has been observed in MORB (Staudacher and Allègre, 1982; Marty, 1989) and diamonds (Ozima et al., 1990; Ozima and Zashu, 1991) in addition to some natural gases. Even though the  $^{131}\text{Xe}$ – $^{136}\text{Xe}$  excesses found along with excess  $^{129}\text{Xe}$  in all these samples could not be unequivocally ascertained to either  $^{238}\text{U}$  fission or  $^{244}\text{Pu}$  fission, the arguments of Ozima et al. (1990) tend to support  $^{244}\text{Pu}$  as the source of fission Xe in the mantle component. In Fig. 3, we have plotted the measured ratios  $^{129}\text{Xe}/^{130}\text{Xe}$  vs.  $^{136}\text{Xe}/^{130}\text{Xe}$  for our samples along with some

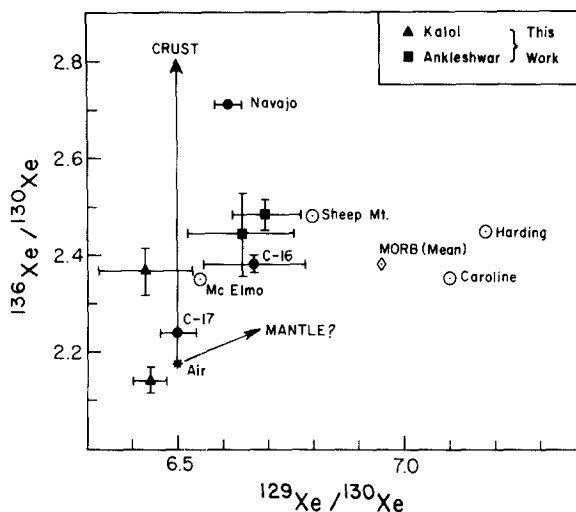


Fig. 3.  $^{136}\text{Xe}/^{130}\text{Xe}$  vs.  $^{129}\text{Xe}/^{130}\text{Xe}$  plot for the natural gas samples. Trends expected by addition of crustal and mantle xenon components to air xenon are indicated by arrows. The same literature data as for Figs. 1 and 2.

literature data. If the Harding County data are considered as pure mantle noble gas components (Staudacher, 1987) then the xenon from natural gas wells as well as from other mantle samples can be explained as a three-component mixture of atmospheric xenon (either from air contamination or through water or sedimentary gases), a pure  $^{238}\text{U}$  fission component from crustal rocks and a mantle xenon component. While Kalol-166 is a simple mixture of atmospheric and  $^{238}\text{U}$  fission components only, MORB and the Caroline gas sample on the other hand seem to be a mixture of air xenon and the mantle component. All the other natural gas well samples including Motwan-2 have all three xenon components in varying proportions.

The isotopic signatures of other noble gases are also consistent with a three-component mixture of air, mantle and radiogenic origin. While  $^{38}\text{Ar}/^{36}\text{Ar}$  and the Kr isotopic ratios are similar in air and other primordial components and thus are non-diagnostic, the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios and neon isotopic composition reveal the presence of radiogenic and mantle components. The higher than air value of  $^{21}\text{Ne}/^{22}\text{Ne}$  for Motwan-2 clearly shows the radiogenic  $^{21}\text{Ne}$  presence due to the ( $\alpha, n$ ) reaction on  $^{18}\text{O}$ , while the higher than air value for  $^{20}\text{Ne}/^{22}\text{Ne}$  could be due to an mixture of mantle Ne component, having a  $^{20}\text{Ne}/^{22}\text{Ne}$  value of  $11.8 \pm 0.4$  (Ozima and Zashu, 1991), though fractionation effects cannot be ruled out.

Another striking difference between the Harding County natural gas as well as the Caroline gas, both of which showed the largest  $^{129}\text{Xe}$  excess, as compared to the other gas well samples, is their  $\text{CO}_2$  content. While the Harding County and Caroline gases contain nearly pure  $\text{CO}_2$  ( $> 99\%$ ), the other gases have  $\text{CO}_2$  values ranging from 0.8% to 28.5% only. If Harding County represents a pure mantle component (Staudacher, 1987), then the lower  $\text{CO}_2$  content of the other gases can be taken as an indication of the dominance of other components in them.

### 3.3. Nitrogen

The nitrogen isotope data are presented in Table I. The  $\delta^{15}\text{N}$ -values of Kalol-183 and Motwan-2 are negative and closely resemble each other while that of Kalol-166 is positive and substantially different. Not much isotopic work on nitrogen of natural gases exists in the literature. Hoering and Moore (1958) made the earliest study of  $\delta^{15}\text{N}$  in natural gases and associated crude oils and found that  $\delta^{15}\text{N}$  in natural gas is negative while that of crude oil is positive. They suggested diffusive fractionation during migration. Bokhaven and Theeuwen (1966) have measured a natural gas from the Netherlands and found  $\delta^{15}\text{N} = +18\%$ , while Stahl (1977) has measured a number of well gases in the north German and Groningen (The Netherlands) Rotliegend reservoirs and found  $\delta^{15}\text{N}$  ranging from  $-8.7$  to  $+18\%$ . This spread has been explained as the result of lateral migration of nitrogen, making the  $\delta^{15}\text{N}$  progressively more positive as the migration distance increases. Hut et al. (1984) have also measured natural gases from Groningen and found  $\delta^{15}\text{N} = 15.98 \pm 0.07\%$ .

The  $\delta^{15}\text{N}$  difference between the two Kalol gases could then be due to a migration process from a reservoir similar to that of Kalol-183 towards that of Kalol-166 or it could be due to different sources of nitrogen.  $\text{N}_2/\text{Ar}_{\text{trapped}}$  values for both Kalol gases are very different from atmospheric values. For Kalol-183 the value (145) is higher than the atmospheric (83.93) and for Kalol-166, the value (44.7) is lower than that of air. Since sedimentary nitrogen has a  $\delta^{15}\text{N}$  range of  $-5$  to  $+12\%$  with a preponderance of heavy values (Sweeney et al., 1978) the Kalol-166 nitrogen could be mostly of sedimentary origin through thermal degradation, but the other two natural gases have  $\delta^{15}\text{N}$ -values lighter than the sedimentary range. A possibility is that for both these gas samples nitrogen is the product of biogenic degradation from sediments, in which case a kinetic isotope effect resulting in  $^{15}\text{N}$  depletion for the  $\text{N}_2$  is to be expected (Heaton, 1986).



### 3.4. Elemental ratios

The radiogenic ( $^4\text{He}$ ,  $^{21}\text{Ne}$ ,  $^{40}\text{Ar}$ ,  $^{129}\text{Xe}$ ) and fission ( $^{136}\text{Xe}$ ) components are calculated, using the following expressions [ $(21/22)^*$  is corrected for mass fractionation, as per the  $(20/22)$  value]:

$$[{}^4\text{He}]_r = [(4/3)_{\text{sample}} - (4/3)_{\text{mantle}}] \times [3]_{\text{sample}}$$

$$[{}^{21}\text{Ne}]_r = [(21/22)^*_{\text{sample}} - (21/22)_{\text{air}}] \times [22]_{\text{sample}}$$

$$[{}^{40}\text{Ar}]_r = [(40/36)_{\text{sample}} - (40/36)_{\text{air}}] \times [36]_{\text{sample}}$$

$$[{}^{129}\text{Xe}]_r = [(129/130)_{\text{sample}} - (129/130)_{\text{air}}] \times [130]_{\text{sample}}$$

$$[{}^{136}\text{Xe}]_r = [(136/130)_{\text{sample}} - (136/130)_{\text{air}}] \times [130]_{\text{sample}}$$

The elemental ratios normalised to  $^{36}\text{Ar}$  (for the primordial component) and  $^{40}\text{Ar}$  for the radiogenic component are shown in Table II and plotted in Fig. 4. Data for some natural gas samples from the literature are also plotted in Fig. 4. The pattern is similar to type-2, which typically represents gases of mantle origin (Ozima and Alexander, 1976). The type-2 trend is reflected by enrichment of  $^{20}\text{Ne}$  and  $^{130}\text{Xe}$  and depletion of  $^{84}\text{Kr}$ , though in our data

a depletion of  $^{130}\text{Xe}$  rather than an enrichment is observed. Only high-temperature dissolution of noble gases in enstatite melt or solar abundances show a depletion in  $^{130}\text{Xe}$  relative to atmospheric abundances (Ozima and Alexander, 1976). This elemental pattern clearly shows that the noble gases of these natural gases are mostly of non-atmospheric origin and are also different from air-saturated water (which is characterised by depletion of Ne relative to Ar).

Elemental ratios of the radiogenic noble gas isotopes also shed light on their origin. All the three gas samples show the presence of radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$ . Kalol-166 and Motwan-2 also have fission xenon while Motwan-2 alone shows the clear presence of  $^{21}\text{Ne}$  excess due to  $(\alpha, n)$  and  $(n, \alpha)$  reactions on  $^{18}\text{O}$  and  $^{24}\text{Mg}$ , respectively. Table II shows the elemental ratios of the radiogenic components. The  $(^4\text{He}/^{40}\text{Ar})_r$ -values of Kalol-183 and Motwan-2 are within the range of values observed for natural gases (Zartman et al., 1961) while that of Kalol-166 is very high. Such a high value can only result from the addition of a pure He component; also the fact that  $^3\text{He}/^4\text{He}$  in Kalol-166 is  $0.3 \times (^3\text{He}/^4\text{He})_{\text{air}}$  suggests that He has preferentially migrated to the Kalol-166 well. Of the three gas samples, only Motwan-2, shows excess  $^{21}\text{Ne}$  of nucleogenic origin. The  $^{21}\text{Ne}/^4\text{He}$  value for Motwan-2 ( $0.66 \cdot 10^{-7}$ ) is very close to the crustal value

TABLE IV

Log  $F_M$ -values for gas samples

Sample	$\log_{10} F_M$					Reference
	$^4\text{He}$	$^{20}\text{Ne}$	$^{36}\text{Ar}$	$^{84}\text{Kr}$	$^{130}\text{Xe}$	
Kalol-183	3.97	0.546	0	-0.238	-2.055	[1]
Kalol-166	4.30	1.324	0	-0.100	-2.646	[1]
Motwan-2	4.52	0.362	0	-0.282	-2.115	[1]
Harding County, WG2	4.68	-0.05	0	0.002	0.434	[2]
Harding County, WG2	3.42	0.835	0	-0.321	-0.102	[3]
C-16	4.08	-0.172	0	0.600	-0.950	[4]

$$F_M = ({}^M\text{X}/{}^{36}\text{Ar})_{\text{sample}} / ({}^M\text{X}/{}^{36}\text{Ar})_{\text{air}}$$

References: [1] = this work; [2] = Phinney et al. (1978); [3] = Hennecke and Manuel (1975b); [4] = Bennett and Manuel (1970).

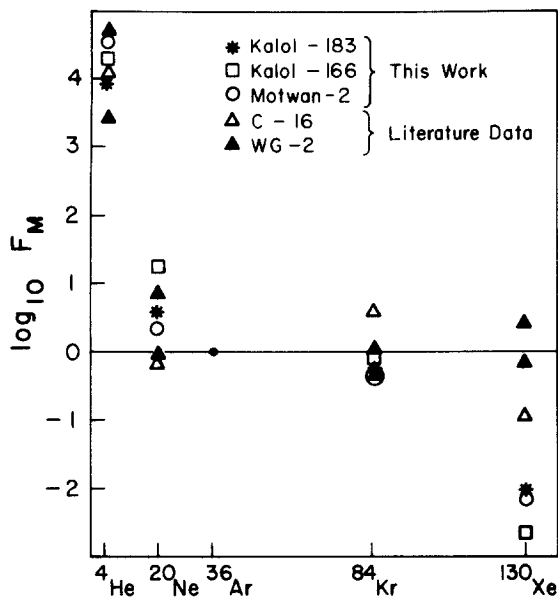


Fig. 4. Elemental ratios of noble gases are plotted in the form of  $\log_{10} F_M$ . The same literature data as for Fig. 3.

$(0.46 \pm 0.08) \cdot 10^{-7}$  (Kennedy et al., 1990). Fission Xe is clearly present in both Motwan-2 and Kalol-166. The  $^{136}\text{Xe}_{\text{SF}}/{}^4\text{He}$  ratio for both samples is lower than the range expected for crustal rocks. The Kalol-166 value is lower by a factor of 1400 and the Motwan-2 value is lower by a factor of 50. This lower value is due to excess  ${}^4\text{He}$  in Kalol-166 and emphasises the fact that the most probable origin of this  ${}^4\text{He}$  is by migration towards the Kalol-166 well as a pure He component.

The lower value of  $^{136}\text{Xe}/{}^4\text{He}$  for Motwan-2, on the other hand, is most probably due to preferential release of  ${}^4\text{He}$  from the crustal rocks into the natural gas reservoir. The anomalously higher values of  $^{131}\text{Xe}/^{136}\text{Xe}$  and  $^{132}\text{Xe}/^{136}\text{Xe}$  of the fission xenon in Motwan-2 can result if only a minor fraction of the fission xenon is released from the rocks, as clearly has been demonstrated by Kennett and Thode (1960) and more recently by Shukolykov et al. (1987).

If  $^{129}\text{Xe}$  in Motwan-2 is a two-component mixture of an upper-mantle component and atmospheric component, then the fraction of

upper-mantle component ( $x$ ) can be calculated from:

$$(^{129}\text{Xe}/^{130}\text{Xe})_{\text{observed}} = x(^{129}\text{Xe}/^{130}\text{Xe})_{\text{UM}} + (1-x)(^{129}\text{Xe}/^{130}\text{Xe})_{\text{air}}$$

Taking  $(^{129}\text{Xe}/^{130}\text{Xe})_{\text{UM}} = 7.18$  (the value for the Harding County well gas; Phinney et al., 1978), we obtain  $x = 29 \pm 11\%$  for Motwan-2, which is consistent with the value of  $x$  obtained using the  ${}^3\text{He}/{}^4\text{He}$  ratio.

### 3.5. Origin of noble gas components in natural gas wells

Both the elemental and isotopic ratios of the noble gases are consistent with the presence of: (1) an atmospheric component; (2) a radiogenic component; and (3) a mantle component for the noble gases. However, the proportion of each component may be different in the three gases analysed here. The atmospheric component is not due to atmospheric contamination as indicated by the  $\text{N}_2/\text{Ar}$  ratios which are non-atmospheric. The isotopic composition of nitrogen is consistent with the sedimentary source, which indicates that the noble gases of atmospheric composition might have originated from sediments. The radiogenic ( ${}^4\text{He}$ ,  ${}^{21}\text{Ne}$ ,  ${}^{40}\text{Ar}$ ) and fissionogenic ( $^{136}\text{Xe}$ ) components must have originated in the crustal rocks and degassed into the natural gas reservoir. In the case of Kalol-166, a pure  ${}^4\text{He}$  component along with some nitrogen has migrated in, as indicated by the radiogenic ratios  ${}^4\text{He}/{}^{40}\text{Ar}$  and  $^{136}\text{Xe}/{}^4\text{He}$ . The positive  $\delta^{15}\text{N}$ -value for Kalol-166 compared to the negative  $\delta^{15}\text{N}$  for Kalol-183, corroborates the presence of a migrated component. Excess  ${}^3\text{He}$  and  $^{129}\text{Xe}$  provide strong evidence for the presence of a mantle component in Motwan-2. This mantle component has been carried into the natural gas source region, most probably by magmas from deeper in the Earth (Butler et al., 1963; Hennecke and Manuel, 1975a; Phinney et al., 1978; Staudacher, 1987).

#### 4. Conclusions

Noble gases and nitrogen of the three natural gas samples from Gujarat have shown that radiogenic  $^4\text{He}$  and  $^{40}\text{Ar}$  are present in all three well gases. Excess  $^3\text{He}$  as well as  $^{129}\text{Xe}$  in Motwan-2 can be accounted by the presence of a  $\sim 20\%$  mantle gas component in it. While Kalol-183 has xenon of atmospheric composition, the other two well gases show the presence of fission xenon. Large excesses of  $^{131}\text{Xe}$  and  $^{132}\text{Xe}$  in Motwan-2 could possibly be due to an artefact resulting from preferential release of volatile radioactive precursors formed in fission. Motwan-2 also had  $^{21}\text{Ne}$  excess of nucleogenic origin. The elemental ratios of noble gases for all three well gases are similar to the type-2 pattern, reflecting their non-atmospheric origin. The ratios of the radiogenic noble gas isotopes  $^4\text{He}/^{40}\text{Ar}$ ,  $^{21}\text{Ne}/^4\text{He}$  and  $^{136}\text{X}/^4\text{He}$  are consistent with the crustal origin for Kalol-183 and Motwan-2, while for Kalol-166 a  $^4\text{He}$  excess is clearly indicated. A preferential migration of  $^4\text{He}$  towards the Kalol-166 well can explain the excess.  $\delta^{15}\text{N}$  signatures of Kalol-183 and Motwan-2 are consistent with a sedimentary source, released by biogenic degradation, while the distinct positive  $\delta^{15}\text{N}$  of Kalol-166 might possibly be due to long-distance migration of nitrogen of sedimentary origin, before being trapped in the Kalol-166 well. The  $^4\text{He}$  excess of Kalol-166 corroborates the migration hypothesis.

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