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Single Isotope Fractionation of ^{16}O -
Implications for Early History of Solar System

Final report on NASA grant NGL-05-009-02

G. Arrhenius, Principal Investigator

Section 1: Results as of 7.30.81

Abstract

Large isotopic anomalies are observed in some abundant elements in the space medium, stellar atmospheres, comets and carbonaceous meteorites. In some cases these are due to chemical fractionation, in others it is difficult to distinguish between chemical and nucleosynthetic effects. Our research aims at experimental and theoretical evaluation of chemical fractionation processes; now with emphasis on selective single isotope fractionation in polyisotopic systems, particularly in oxygen. The related temperature parameters of meteoritic condensates and of their source medium are investigated by a thermometric method that is independent of assumptions regarding temperatures and pressures in the solar nebula.

The crucial non-linear chemical fractionation of ^{16}O has been demonstrated experimentally in the last year's work under this grant. The effect was achieved in condensed CO_2 formed from CO with $^{12}\text{C}^{16}\text{O}$ selectively excited by $\text{H Ly}\alpha$. The effect was verified by mass spectrometric measurements carried out by these isotopic measurements by Prof. R.N. Clayton.

The meteorite paleotemperature estimates which form a related part of our research have been advanced from defining only thermal exposure to evaluating time and temperature independently. Grain temperatures at condensation of refractory inclusion materials are indicated to be less than 900°K in agreement with radiation temperature considerations and observations in circumstellar dust shells.

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1. Scientific objectives

The research reported here represents a continuing effort to clarify by theoretical and experimental investigations what mechanisms are responsible for the large chemical isotope fractionation observed by microwave spectrometry in dark interstellar clouds and by laboratory measurements of primordial meteorite material.

The proposed relationship between the effects seen in the space medium and those observed in meteorites is most applicable to the widely varying isotopic composition of hydrogen, carbon, nitrogen, oxygen and magnesium and possibly some of the effects observed in occluded noble gases, and in odd isotopes of heavy elements such as barium in carbonaceous meteorites. Polyisotopic elements such as oxygen, magnesium and sulfur are of particular interest in this respect since single isotope enhancement as observed in the laboratory (e. g., Liuti et al. 1966; Vikis 1978; Turro and Kraeutler 1978) and predicted to be effective in the space medium (Haberkorn et al. 1976; Arrhenius et al. 1979b) can generally be verified only if at least two other isotopes exist as reference points. Such enhancement of single isotopes or isotope pairs has been shown or predicted to be caused by various mechanisms of selective excitation and/or transition into reaction complexes of predissociating states (see review in Arrhenius et al. 1979b). Selective resonance excitation by spectral line sources has been observed astronomically for several molecular isotopic species in the space medium (Gahm et al. 1977). Chemical effects of this kind, if found to be the likely cause also of nonlinear isotopic anomalies in meteorites, would give useful indications about the physical state of the source medium from which primordial solids formed in our solar system.

An alternative explanation of effects found in meteorites is that not only small anomalies in heavy elements, but also large effects in, e. g., ^2H , ^{16}O , ^{15}N and ^{26}Mg , could be of nucleosynthetic rather than chemical origin. Observational proof one way or another is generally not possible as far as meteorites are concerned, since the effects recorded in them are caused by events in the past, and since confirming nucleosynthetic experiments can in most cases not be carried out. In contrast, observations of currently active processes in the

interstellar cloud medium provide direct evidence of large scale chemical isotope fractionation in carbon, hydrogen and nitrogen, and with more refined techniques the potential exists for discerning the details of selective fractionation of individual isotopes of oxygen and magnesium (Winnewisser 1979). Selective enhancement of ^{16}O relative to $^{17,18}\text{O}$ in CO has been observed in some regions of the interstellar medium and is considered as a puzzling feature if interpreted in terms of nucleosynthetic origin (Penzias 1980).

The chemical isotope effects result from the large thermodynamic disequilibria which are characteristic of the space medium. Since the isotopically "anomalous" meteorite minerals provide a fossil record of the conditions in the space medium in the formative era, reliable estimates of their formation temperatures are desirable as part of the information needed to understand the origin of the isotopic anomalies.

Speculation about the thermal evolution of the refractory oxide and silicate minerals containing the oxygen anomalies, including "condensation temperatures" has been based on observed phase relationships in meteorites coupled with hypotheses about the thermal state of the source cloud from which the solids formed. Since the outcome of such considerations is critically dependent on assumptions concerning temperature and pressure, and since these are a priori unknown, the conclusions remain hypothetical. In those cases where they are based on equilibrium considerations the conclusions also appear unrealistic by an order of magnitude or more when applied to the region of the condensation of the most refractory solids (Arrhenius 1971; De and Arrhenius 1977; Arrhenius and McCrumb 1978). A realistic evaluation of the thermal record should preferably be based on measurements of thermally sensitive parameters that are pressure independent.

Interdiffusion between coexisting solids fulfills this requirement and is particularly sensitive in the temperature region down to about one half of the melting temperature. Simple diffusion couples such as pure platinum spherules overgrown with nickel iron, discovered and measured by El Goresy et al. (1978) were in earlier work under this grant selected for evaluation of thermal exposure during and after formation of the nickel-iron overgrowth on the platinum spheres,

and of the melilite crystals in which the metal couples are encased. The initial choice of pure platinum as an end member avoided the larger uncertainties about the course of diffusion in the more complex platinum metal alloy couples also found in carbonaceous meteorites.

2. Theoretical investigations

Three possible mechanisms

As pointed out above and discussed in detail in the publications resulting from this work, selective isotope effects can arise at molecular excitation (e. g., Liuti et al. 1966), predissociation (Murrell and Taylor 1969; Schaefer and Miller 1971; Arrhenius et al. 1979) or vibrational relaxation (Basov et al. 1974; Arrhenius 1976).

Fractionation by transition into repulsive state at predissociation

Our earlier theoretical work (Arrhenius et al. 1979a, b) specifically examined the isotopic selectivity of Franck-Condon type in predissociation. Numerical approximation indicated that while predissociation in the classically forbidden region is unlikely to lead to large isotope effects, transition into a repulsive state in the classically allowed region could indeed cause such major effects (Fig. 2.1.1). Exact calculation proved to be a demanding computational task. We decided to postpone further efforts in this direction until experiments aiming at isolating this effect from the two others mentioned, have specifically indicated it to be quantitatively significant.

Single isotope selection by resonance excitation

Previous work

Much of this year's theoretical work, accompanied by experiments, has been devoted to evaluation of this mechanism, both in the laboratory and in the space medium (Arrhenius et al. 1980; Corrigan et al. 1980). The fundamental theory for the underlying phenomena is relatively straightforward and the achievement of highly selective isotope fractionation through this mechanism using laser line sources for excitation is well known. The efficiency of UV emission line spectra in resonance excitation of CO was first demonstrated by Harteck and his associates (Liuti et al. 1966; Dunn et al. 1973) and later by Vikis (1977, 1978) as discussed above, who achieved ten and sixfold concentration, respectively, of ^{13}C in product CO and in the central carbon atom of C_3O_2 . A sevenfold concentration of ^{18}O was found in the same photochemical decomposition of CO to CO_2 and C_3O_2 .

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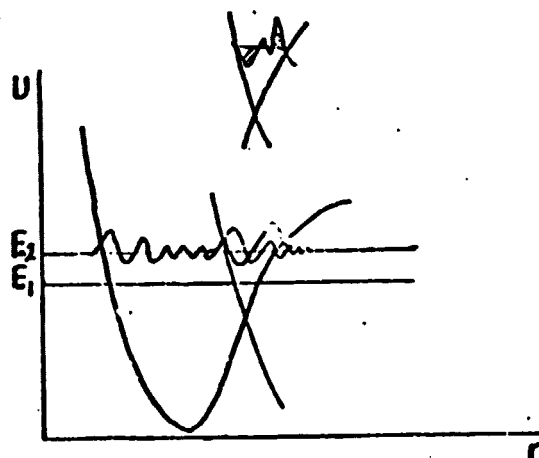
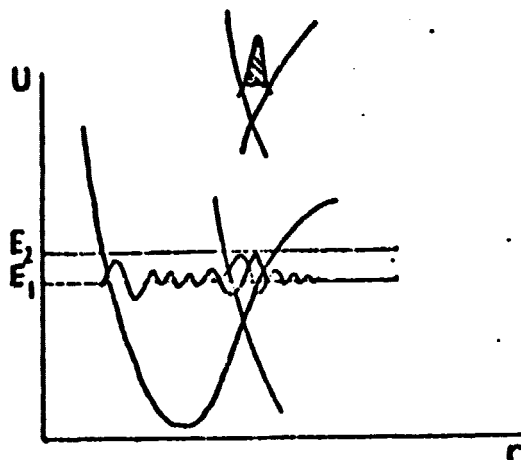


Fig. 2.1.1. Magnitude of overlap integrals (inserts) between the eigenfunctions for the bound (initial) and repulsive (end) states determines the predissociation probability. Two isotopic states, E_1 and E_2 of the same vibration are schematically indicated, one (above) with large and one (below) with small overlap integrals.

Matching of emission and absorption lines in the laboratory
and in the space medium

The close line matching needed for resonance excitation might intuitively seem to make this an exceptional phenomenon achievable only by tunable sources or by combining emitters and absorbers selected among a large number of species, most of them unlikely to be of importance in nature. What makes the phenomenon common in astrophysical settings, however, (Gahm et al. 1977) is the band structure of the spectra of abundantly occurring molecules such as CO or O₂; with each electronic-vibrational level is associated a large number of rotational levels which may be populated under excitation conditions characteristic of the space medium (Fig. 2.1.2; adapted from Tilford and Simmons 1972 and from Purcell and Tousey 1960). This together with the occurrence of several strong emission lines in stellar UV spectra makes appropriate coincidences sufficiently common for isotopic selection to potentially occur in a number of quantitatively important molecular reactions in the space medium. Past year's finding of such a coincidence between a ¹²C¹⁶O absorption band and the hydrogen Lyman α emission line is a case in point (see Fig. 2.1.2). The same effect that we invoke here as an excitation source for isotopically selective reactions is being used as a tool in the detection of specific molecules in the space medium (Gahm 1977). The technique is used for abundant molecules that surround astrophysical objects or regions that have among others strong atomic emission in the Lyman and Balmer lines of hydrogen. The excitation of CO by Lyman α is considered to be undesirable for astrophysical detection purposes because so many rotational lines are excited in CO (Fig. 2.1.2). The more rotational lines excited the more diffuse the fluorescence in terms of spreading the input energy as output over many more lines. This astronomically detrimental circumstance is advantageous to our work because we are interested in efficiency of the molecular reactions which take place before fluorescence can occur.

Of the astrophysical settings that Gahm et al. consider, an interesting one in terms of explaining oxygen effects in meteorites is the circumstellar region around emission line stars of spectral classes O through G, and the

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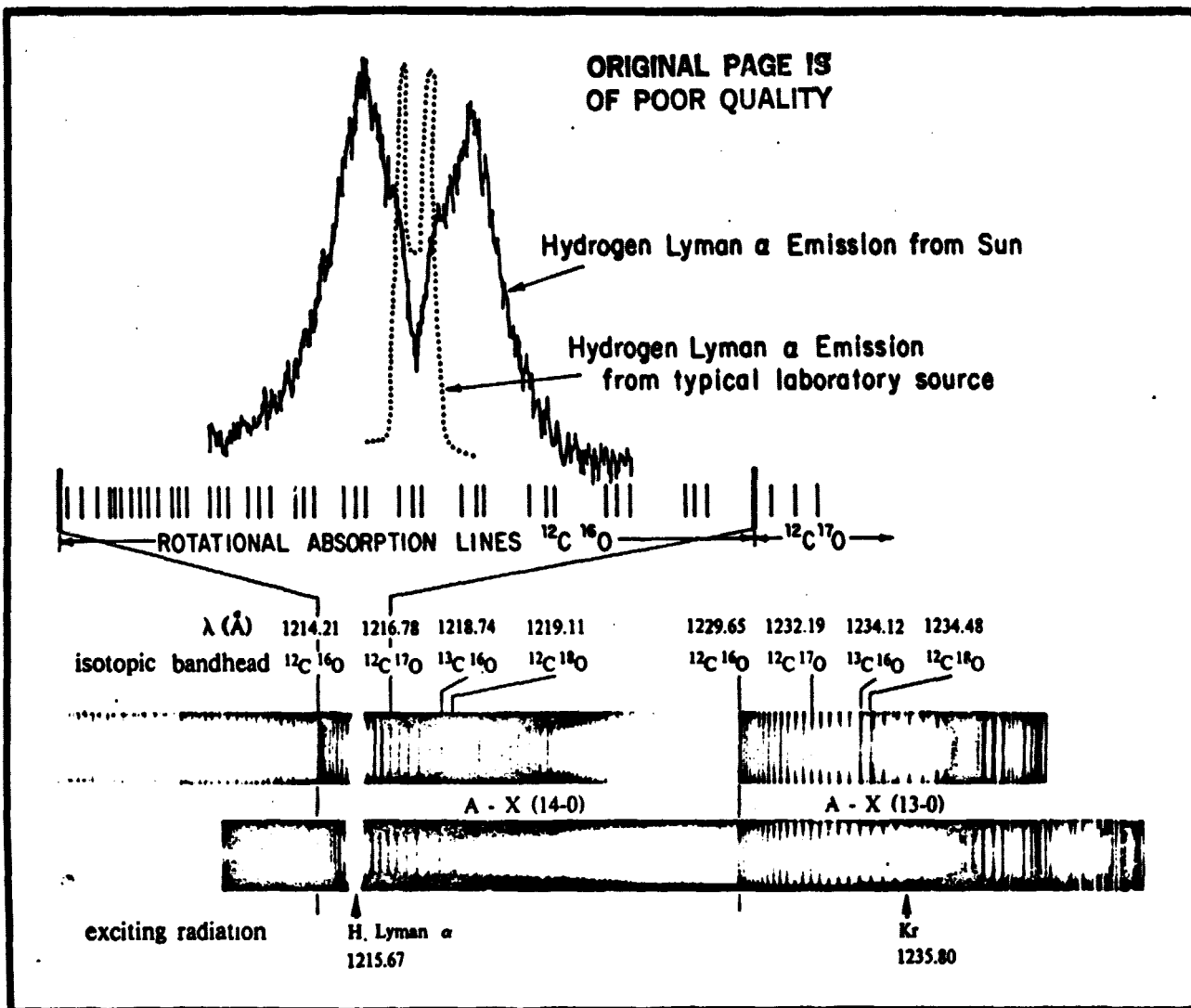


Fig. 2.1.2. (Below) Overlap of laboratory Lyman α emission line with rotational lines of CO in the (14-0) vibrational band of the A-X electronic transition.

The figure illustrates that emission overlaps absorption lines of $^{12}\text{C}^{16}\text{O}$ -isotopic species only, leading to selective excitation of this species.

(Above) Expansion of scale of $^{12}\text{C}^{16}\text{O}$ portion of (14-0) band with schematic rotational absorption lines and with Lyman α emission profiles from laboratory sources and from the Sun. Emission profile width is to scale relative to location of $^{12}\text{C}^{16}\text{O}$ - and $^{12}\text{C}^{17}\text{O}$ -bandheads. Absorption lines of other isotopic CO species are off the figure to the red.

The broadening of the stellar emission profile (with overlap over about 40 rotational $^{12}\text{C}^{16}\text{O}$ lines) leads to an order of magnitude enhancement in astrophysical settings over the effect achieved in the laboratory where the narrow profile lamp source can be made to effectively overlap only two such rotational lines.

T-Tauri stars. The Sun is now a G2v star and in its early evolution it is believed to have passed through a T-Tauri stage. Several other situations where dense protostellar clouds are irradiated by strong line sources have also to be investigated.

Consideration of such selective absorption also forms the basis for our studies of resonance excitation of isotopic lines in the Schumann-Runge bands of O_2 and in the fourth positive band of CO, both important absorbers in space and that of O_2 also in the Earth's atmosphere. This work led to the discovery (McCrumb 1979) of a secondary source of ozone in the Earth's upper atmosphere (Cicerone and McCrumb 1980).

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3. Experimental studies of selective isotope fractionation

Background

Laboratory experiments guided by the theoretical considerations above provide a means for clarifying the mechanisms in space that lead to the large isotope fractionation observed to occur there. Experiments carried out under the present grant have demonstrated large isotope effects in reactions of excited molecules and molecular ions in the systems C-O and N-O. Fractionation up to 42 per cent was observed in ^{15}N (Fig. 2.2.1), 5.6 per cent in ^{13}C and 6.2 per cent in ^{18}O (Fig. 2.2.2), extended to 10 per cent in earlier work, and ~50 per cent in last year's UV experiments (Table 2.2).

The oxygen system is of particular interest in view of the substantial enhancement of ^{16}O found and explored in meteorites by R. N. Clayton and his collaborators. Much of our efforts during the last few years for this reason have been devoted to studying the fractionation of the three oxygen isotopes in reactions of excited molecules. The excited system (C-O)* was used for these model studies because of our earlier findings of large isotope effects, the importance of the system in protostellar cloud chemistry, experimental convenience and the experimental demonstration of large selective fractionation of ^{18}O (sevenfold) in product CO_2 and C_3O_2 by resonance VUV excitation (Liuti et al. 1966; Vikis 1978; further references in Arrhenius et al. 1980). Concurrent fractionation of ^{13}C was also monitored in our investigations.

Selective enhancement of ^{16}O in product CO_2 from H Ly α irradiation of CO

Much experimentation was during the last year devoted to increasing the fractionated product yield from the H Ly α stimulated CO reaction. It was assumed (as later supported by observation) that as a first approximation the selective fractionation of ^{15}O would be proportional to the linear fractionation in the product CO_2 . The latter generally exceeded a few per cent and could be routinely monitored with the SIO Micromass spectrometer. As a result of various technical improvements the yield could be raised sufficiently to permit the production of samples large enough (10-20 μmoles) to be used by

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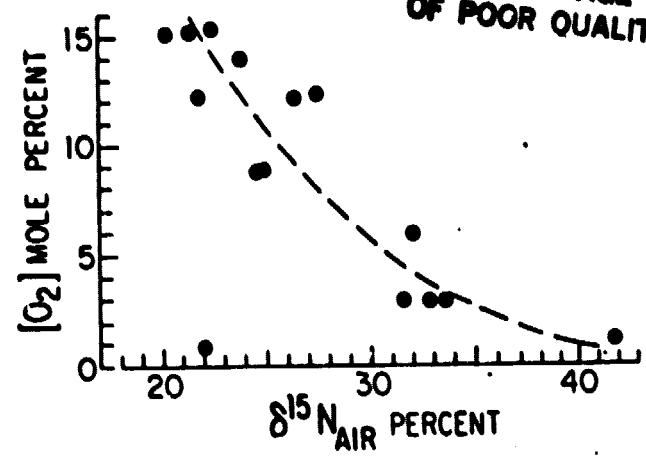


Figure 2. 2. 1. Nitrogen isotope fractionation at formation of nitrogen oxides from a cold plasma (from Arrhenius et al. 1978).

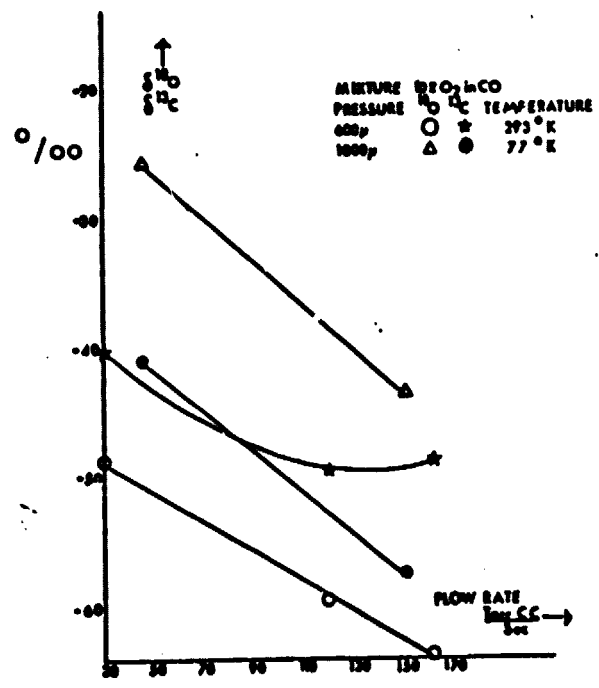


Figure 2. 2. 2. Fractionation of ^{18}O and ^{13}C in excited state reactions at different kinetic temperature, pressure and flow rate (from Arrhenius et al. 1979b).

Table 2.2

Experiment Number	Initial CO Pressure (microns = 10^{-3} torr)	CO ₂ Yield (microns)		H ₂ + H _e - Lamp Pressure (microns)	δ^{18} PDB (°/oo)	δ^{13} PDB (°/oo)	Time Sample Irradiated (hrs)
		H ₂ O	H ₂				
1	1.5×10^3	> 1×10^3	/1.3	190	-22.95	-22.69	7
2	5×10^3	> 1×10^3	/1	176	-59.73	-59.94	7
3	1×10^3	590/N.M.		190	-83.15	-33.29	4.3
4	5×10^3	570/8		175	-45.77	-49.68	4.75
5	500	18/N.M.		176	N.M.	N.M.	5
6	1×10^3	400/4		163	-85.1	-30.18	4.5
7	850	500/2		180	-87.57	-29.96	5
8	750	630/10		175	-86.41	-29.59	5.1
9	1×10^3	590/N.M.		N.M.	-81.64	-48.05	4
10	750	> 1×10^3	/N.M.	173	-83.75	-46.41	12.5
11	500	917/N.M.		185	-89.47	-29.73	5.5
12	500	2.3×10^3	/N.M.	160	-94.17	-52.63	11
13	500	> 1×10^3	/N.M.	150	-97.6	-50.9	12

Notes: N.M. = Not measured or not measurable.

H₂ + H_e - lamp microwave generator power = 40 watts.

Reaction temperature = liquid nitrogen.

Initial CO pressure measured at room temperature (22°C).

Prof. R. N. Clayton for fluorination and isotopic analysis; due to his heavy commitments only two samples have been analyzed at the present time. Both of these show anomalies of the type found in refractory inclusions and of a magnitude that makes Prof. Clayton convinced that they are real. These results must, however, for reasons discussed earlier, be interpreted with caution until the isotopic composition of the source CO has been verified. This is one of the most important undertakings for the completeness of demonstration of ^{16}O single isotope fractionation by resonance excitation. Similar fractionation by isotopic filtering has already been demonstrated by Bally and Langer and has in last year's work under this grant been applied to the Earth's atmosphere. The results indicate that this effect provides a second source of ozone below the present ozone maximum (Cicerone and McCrumb, 1980).

Sample	Size μ mole	CO ₂		O ₂		δ^{17} deviation from "normal"
		δ^{18} O (SMOW)	δ^{13} C (PDB)	δ^{18} O SMOW	δ^{17} O SMOW	
Arrhenius I-2	8	-41.97	-45.74	-30.49	-16.37	-0.40
Arrhenius #54	21	-54.34	-50.77	-50.89	-27.79	-1.00
Antarctic snow	19	-52.62		-49.39	-26.20	-0.21
Antarctic snow				-55.60	-29.02	+0.29

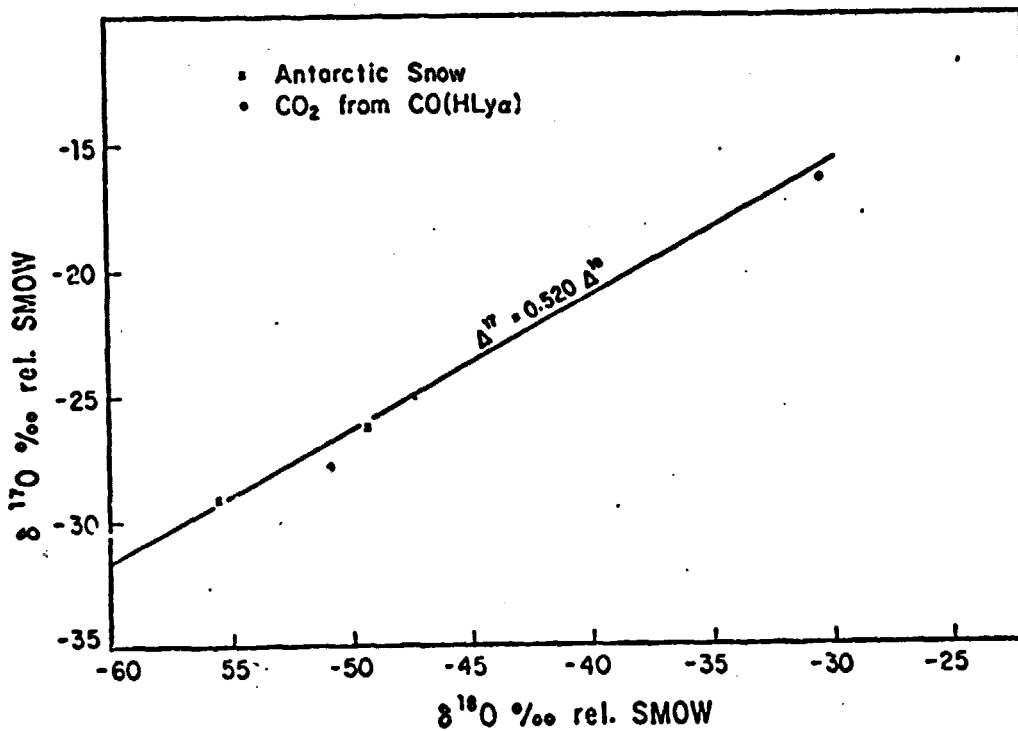


Figure 2. 2. 3. Oxygen isotope fractionation data from R. N. Clayton
(see also, table above).

Reaction system

To minimize the effects of all types of background gases (hydrocarbons, H_2O , CO_2) all seals are metal (couplings and valves) and bakeable to $300^\circ C$. The stainless steel reaction vessel (12 cm dia. \times 35 cm long; Figs. 2.2.4 and 2.2.5) is coupled to the turbo pump by a 3.4 cm diameter vacuum line incorporating a bakeable metal sealed valve. This line is used between experiments to evacuate the reaction vessel to 5×10^{-8} torr during bake out. Bake out times are typically 12 hours.

The reaction vessel lid, incorporating the UV lamp body and a $25 \times 1/2$ mm MgF_2 window, is sealed to the reaction vessel by a 6.25 cm copper gasket.

The lamp body consists of a 9×12 mm quartz tube 12.5 cm long with one end fused to a stainless steel tube of the same diameter. The gas flowing through the lamp is excited by an air-cooled Evenson cavity powered by a 2.5 GHz magnetron. The lamp gas flow system has a gas supply bottle, pressure regulator, needle flow valve, pressure gauge (1000 torr), and LN trapped vacuum waste line (Fig. 2.2.3). The lamp can be operated in a static mode or with continuously flowing source gas. For optimum emission of H Ly α a gas mixture of 2% H_2 in He was used. The 2.5 GHz lamp is typically operated at 40 watts with a gas pressure of 1 torr.

The sample handling system consists of a bakeable stainless steel trap, two digital pressure gauges (0-1 and 0-1000 torr) and gas sample extraction port. This section is connected to the reaction vessel via a four-way cross, an integral part of the 3.4 cm diameter pump line.

The quadrupole mass spectrometer used for on-line mass spectrometry is used to monitor impurity levels in the VUV source and in reactant gases. This spectrometer has also proven most useful in monitoring gas reactions as a function of pressure and temperature, but with limitations that will be eliminated with the readout system requested. For determination of variations smaller than about 20 per cent, the line to background ratio is, however, limiting in the present system; for all such measurements we rely on magnetic sector mass spectrometers.

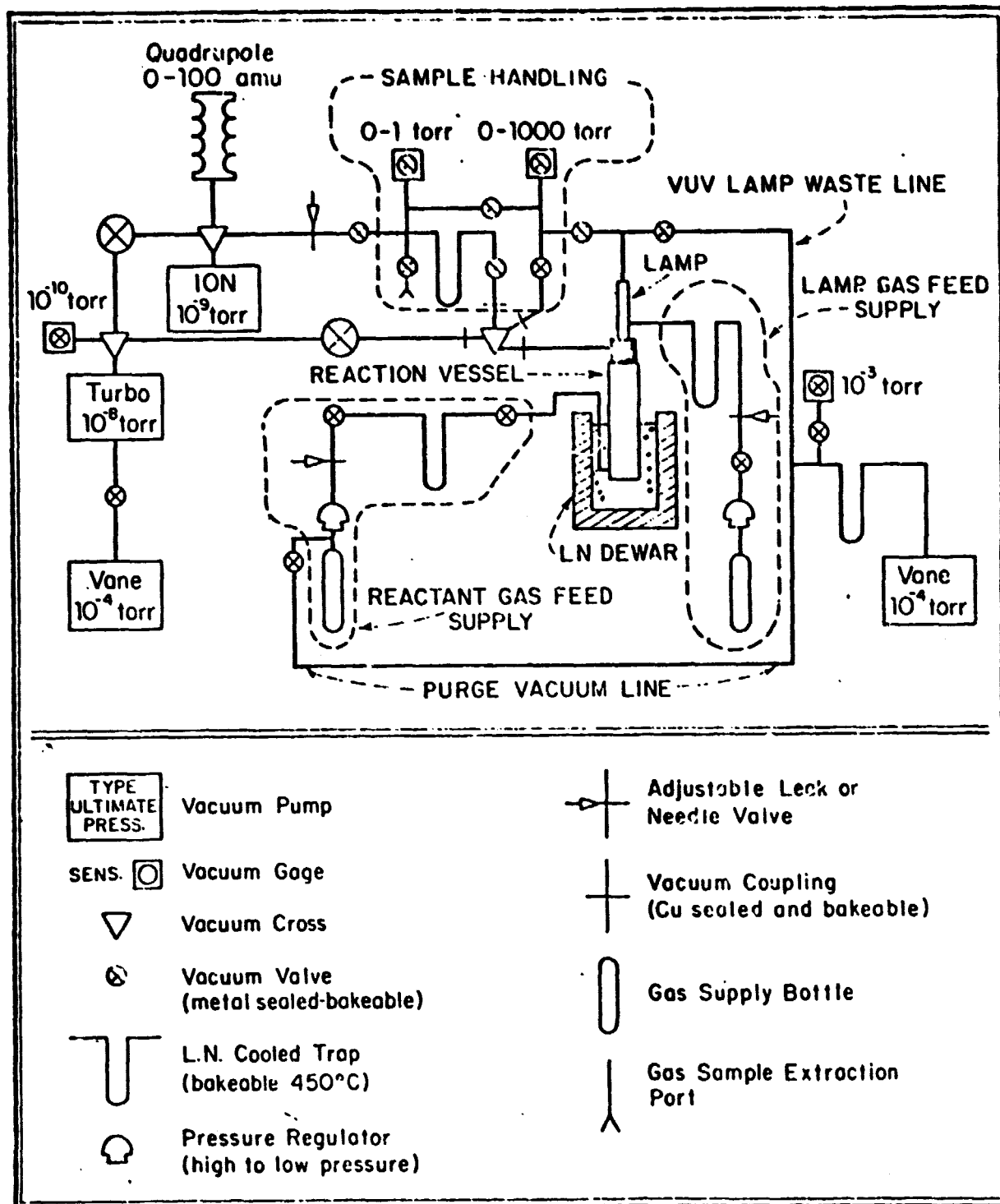
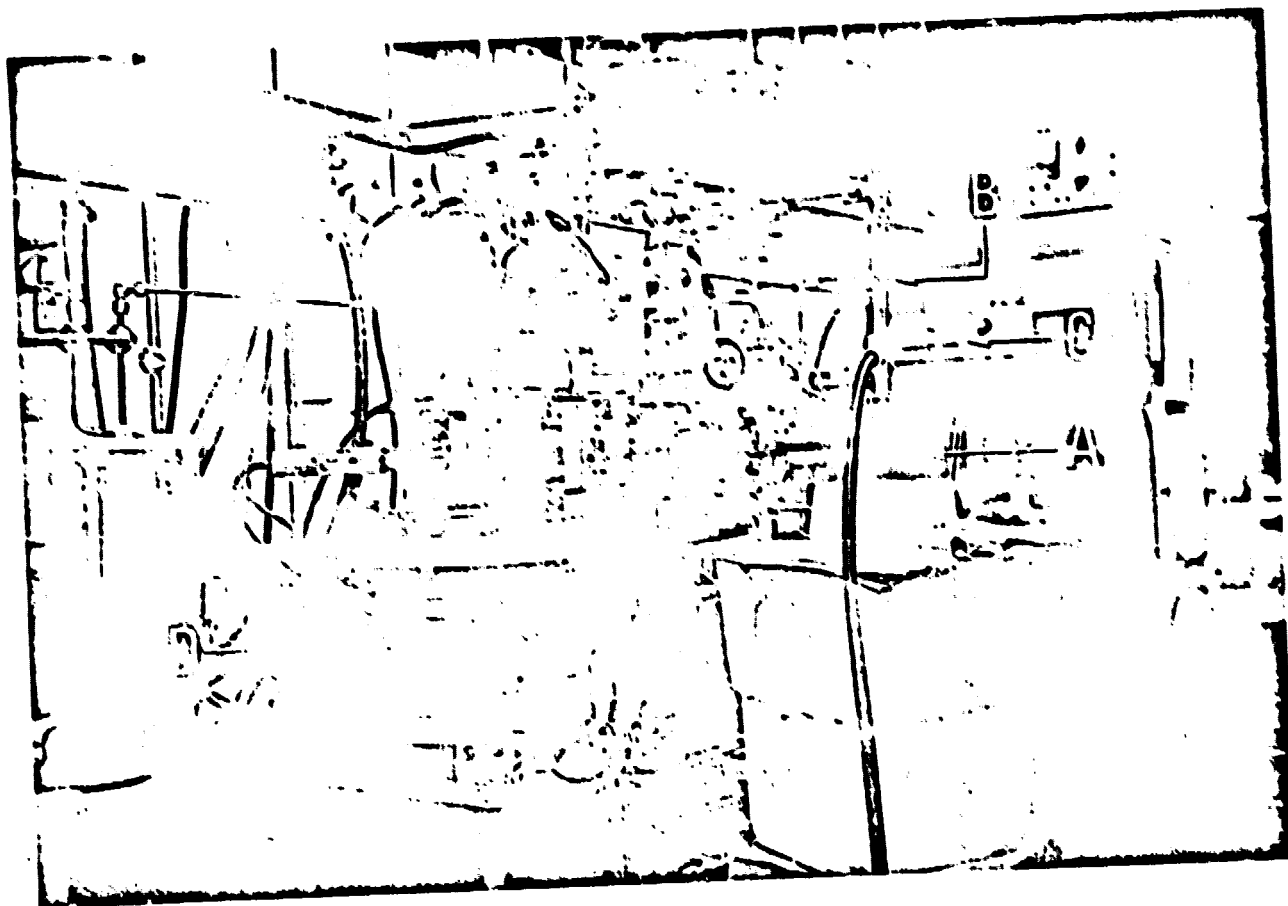


Figure 2.2.4. Stainless steel reaction vessel, feed lines for reactant and VUV lamp gases, gas sample handling, and mass spectrometer systems for VUV resonance excitation experiments. The entire system is stainless steel, bakeable to 300°C with an ultimate vacuum pressure of 1×10^{-8} mm of Hg.

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- A. Reaction vessel
- B. H Lyman α lamp
- C. Air-cooled Evenson cavity
- D. Turbomolecular pump

Figure 2. 2. 5. Apparatus for selective resonance experiments -
schematically shown in Fig. 2. 2. 4.

4. Thermal exposure of grains with enhanced ¹⁶O contentBackground

In the space medium, as observed today, there are typically large differences between rotational, vibrational, translational, neutral, ion and electron temperatures. High internal molecular temperatures coupled with low kinetic temperatures give rise to the large isotope effects maintained in steady state in chemical reaction cycles. Isotopically selective resonance excitation is commonly observed by fluorescence; we have proposed that this excitation results in isotopically enhanced reaction products including refractory oxides in meteorites.

The way in which gas and plasma temperatures couple to solid particles determines the thermal state and growth conditions in condensing grains. We wish to reconstruct these conditions for meteoritic grains using isotopic anomalies as a means for understanding the state of the source medium from which they formed, and as built in solid state thermometers for evaluating the temperature of the grains themselves.

A fundamental requirement for condensation and growth to proceed is that energy is removed from the system, primarily by radiative cooling of the grains since solids are effective IR emitters. Radiative cooling can only take place if the medium surrounding the condensate is optically thin. The rate of condensation in contracting dense regions of protostellar clouds should consequently be inversely proportional to the optical depth of the locale. This has important consequences for the temperature differential between the condensing grains and the source medium; the solid particles characteristically maintain steady state temperatures an order of magnitude below the kinetic temperature of the medium. Accordingly, in the $\sim 7000^\circ$ "cool" plasma in nova shells dust is observed to emit at $\sim 1000^\circ\text{K}$ (Geisel et al. 1970; Clayton and Wickramasinghe 1976); dust particles embedded in $60,000^\circ$ plasma in the Jovian magnetosphere assume temperatures below 200° (cf., Fig. 2.3.1). The radiation balance determining the temperature differential between grains and source medium at condensation has been

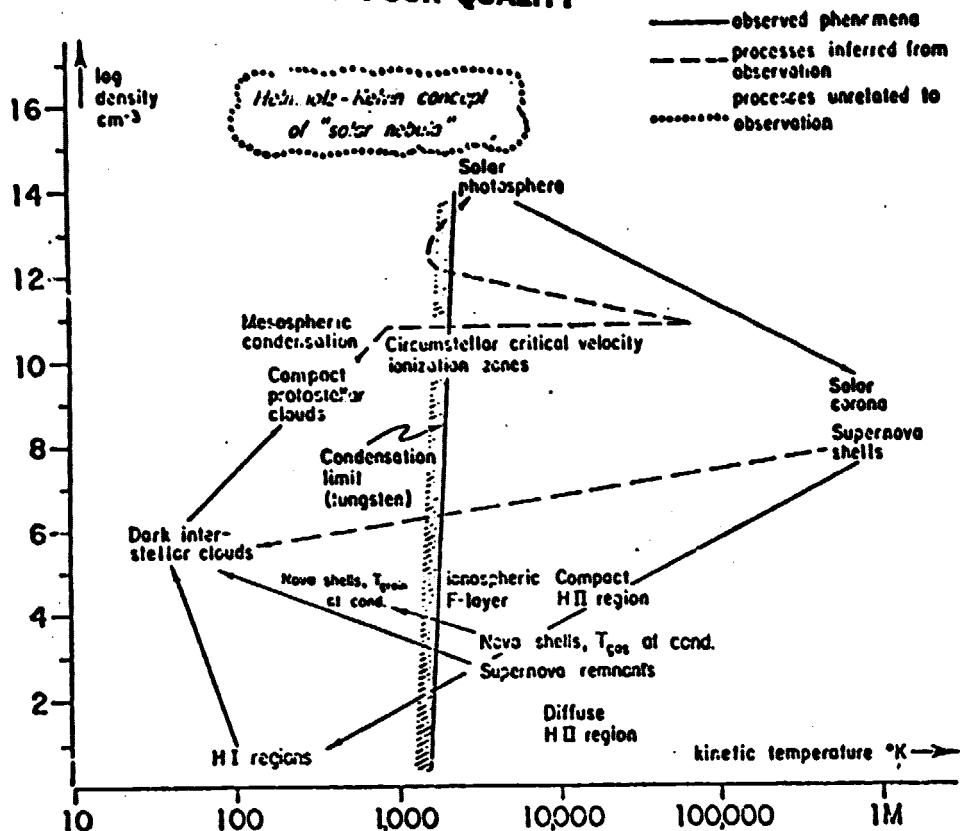


Figure 2.3.1. The astrophysical P-T setting for chemical reactions, isotope fractionation and condensation in interstellar and protostellar clouds with embedded or surrounding UV line radiation sources (from Arrhenius and Raub, 1978).

calculated by Lehnert (1970), Arrhenius (1971) and, as a part of work under this grant, by De and Arrhenius (1979).

Under these circumstances, it is impossible to determine "condensation temperatures" even within an order of magnitude from assumed thermodynamic equilibria, and without distinguishing the relative contributions from isobaric cooling and isothermal compression. The only way to reconstruction of actual grain temperatures would seem to be by measurement of such phenomena in the grains which are sensitive to their thermal exposure, i. e., the length of time which they have spent at specific temperatures.

The intermetallic diffusion studies carried out under the present grant give stringent upper limits for the temperature, and less precisely for the duration of thermal exposure of the refractory minerals which are the carriers of some of the observed isotopic anomalies, notably in oxygen.

The picture that emerges from these studies is an initial condensation of the most refractory oxides and silicates at a grain temperature which could not have exceeded $\sim 1000^\circ\text{K}$ and which could have been much lower (Arrhenius and Raub 1978; Arrhenius, Raub and Schimmel 1980). The excitation temperature (in contrast to the kinetic temperature) of the source medium, would have been sufficiently high to achieve the observed isotope fractionations in nitrogen, carbon and hydrogen (not necessarily in the same region and at the same time), and at least the mass dependent effects in oxygen and magnesium in carbonaceous meteorites.

Earlier measurements

Using diffusion constants and thermal activation energies for Pt-Fe and Pt-Ni in earlier literature, we were able to demonstrate (Arrhenius and Raub 1978) that the melilite and spinel, in which the Pt-(Ni, Fe) metal couples occur abundantly, could only for a small fraction of a second sustain the temperature of 1625 K inferred from chemical equilibration considerations and an arbitrary pressure assumption to be the "condensation temperature" at which the mineral assemblage formed (Grossman 1972). A grain temperature of 900 K could be sustained for a day and 700 K for a year; growth times of this order probably represent the minimum necessary for the formation of the refractory grains investigated.

The phase relationships, including ordering, in the systems Fe-Pt and Ni-Pt are simple and well-known, and the interpolation of phase structure and diffusion kinetics of Pt-(Fe_{0.4}Ni_{0.6}), the composition observed in carbonaceous meteorites, appears reliable at the level of accuracy needed for the discussion above. Larimer (1979) proposed that unknown phases may occur in the ternary system, which would extensively slow down inter-metallic diffusion so as to invalidate the conclusions from the experimental data quoted above. The only phase formation (at low temperature) or precursor phenomenon to be expected in this system is, however, due to ordering at stoichiometric compositions. As is well known and also shown for this system in our work (see below) they result in acceleration of the diffusion rates, not in slowdown.

An experimental study was undertaken during the last grant year of the diffusion of Pt into Fe_{0.4}Ni_{0.6} at a series of temperatures, and the

diffusion coefficient determined as a function of composition in the diffusion path (Arrhenius, Raub and Schimmel 1980). The diffusion coefficients thus measured in this ternary system at 1100 K range from $4.6 \cdot 10^{-6}$ cm²/day at 5% Pt to $7 \cdot 10^{-6}$ at 10% Pt, in concord with earlier published data for the binary systems at the same temperature. For these Kubaschewski and Ebert (1944) found $1.0 \cdot 10^{-5}$ for Pt_{0.85}Ni_{0.15} and Kucere and Million (1975) $4.0 \cdot 10^{-6}$ for Pt_{0.6}Fe_{0.4} and $8.1 \cdot 10^{-7}$ cm³/day for Pt_{0.5}Fe_{0.5}.

The effect of diffusion observed at this rate for one day at 1100 K was to lower the platinum content in the original 5 μm thick pure platinum layer of the diffusion couple to 23 per cent, thus greatly exceeding the diffusion alteration of the platinum spherules in the meteoritic melilite-spinel, which is indistinguishable from 100% Pt.

These measurements thus confirm the conclusion that the melilite-spinel-Pt-FeNi assemblages cannot have formed at grain temperatures exceeding about 1000 K or have been subsequently exposed to temperatures of the solid in this range for more than a few minutes to an hour. Formation of the Pt-(Fe, Ni) couples by exsolution is obviously precluded by the unlimited mutual solid and liquid solubility of these metals.

The physical basis for the relatively low temperature of the condensing refractory solids indicated by these measurements is well understood from the astronomical observations and related theoretical considerations discussed above. Condensation can be brought about by the observed densification of the dilute cold interstellar cloud medium (gravitational or hydromagnetic contraction) or, more hypothetically, by cooling of a hot, dense cloud, or by a combination of these. Each case or combination would result in practically the same condensation sequence; subtle indicative differences are interesting to exploit.

If the temperature of condensing refractory grains were sufficiently low relative to the activation energy for crystallization (100-200 K) a refractory glass would result. The high latent heat of crystallization of the stable, crystalline compounds, released by collision or radiation heating, is capable of momentarily bringing grain temperatures up to the order of 1000 K, resulting in the observed "igneous" texture (Arrhenius 1976).

Oxide diffusion barriers, which have also been invoked as retardants are thermodynamically excluded in this system at temperatures as high as 1600-1700 K and at the reducing gas compositions generally assumed. Measurement of diffusion of metals through iron oxide films demonstrated them to be ineffective as diffusion barriers at the thickness that would have to be involved (less than visible by scanning electron microscopy) (Cabrera 1980). Furthermore, special and unlikely conditions are required for an oxide layer to form on platinum spherules, followed by growth of metallic nickel-iron.

Information from diffusion experiments during the last grant year

The investigations summarized above confirm that diffusion measurements in platinum-nickel iron couples overgrown with refractory silicates in carbonaceous meteorites provide observational evidence for the upper limits of temperatures for which these refractory minerals have been exposed during their lifetime, including their formation and metamorphism. Considering the still more detailed information potentially retrievable from these and different types of diffusion couples in meteorites, a series of new experiments were undertaken. They aim at measuring the difference in diffusion rate between iron and nickel in platinum and utilizing this difference as an independent temperature indicator. With measurements of both total and differential diffusion it should be possible to separate the time and temperature parameters in the fossil diffusion record.

Theoretical considerations

Diffusion theory is based on two assumptions. First that the rate of transfer of matter, the flux, across a plane perpendicular to a chemical gradient is proportional to that gradient. This is known as Fick's first law and is written $F = M \cdot \nabla u$. Second, it is assumed that matter is conserved over time, t , for a closed system, i. e. $\nabla F + \nabla C = 0$.

For the case of diffusion in a binary alloy along a unidirectional composition gradient the flux,

$$J = -D \cdot dC/dx \quad (1)$$

where J is in units of $g/cm^2/sec$, and D , the diffusion coefficient, is in units of cm^2/sec . If we choose a fixed reference plane, thus fixing the diffusion of

both components to one coordinate axis, then \tilde{D} , the interdiffusion coefficient, measures both the rate of movement of the individual atoms and the bulk flow of the lattice (Kirkendall effect), caused by differences in the rates of diffusion of the components.

Assuming a closed system we derive a relationship which can be dealt with experimentally, namely

$$dC/dt = -d/dx \cdot (-D \cdot dC/dx) \quad (2)$$

For most systems the interdiffusion coefficient is a function of concentration. Matano (19) developed a solution assuming that certain conditions are maintained during the experiment: (1) for $t=0$, $C=0$ at $x < 0$, and $C=1$ at $x > 0$, (2) for all t , $dC/dx \Big|_{\pm\infty} = 0$, and (3) $x/\sqrt{t} = C$, where C is constant for a given concentration, x the distance migrated from the "Matano interface" and t the time period of migration. By substituting $\lambda = x/\sqrt{t}$ into equation (2), rearranging and then integrating, it is found that

$$\int_0^C x dC = -(2t)(dC/dx) \tilde{D}_c$$

Given a $c-x$ curve for some time temperature combination, we can calculate \tilde{D}_c , where c denotes a specific composition.

It is found that the temperature dependence of \tilde{D}_c is typical for chemical reaction rates in that it follows the expression

$$D_c = (D_o)_c \exp(Q_c/RT)$$

The pre-exponential factor $(D_o)_c$ and the activation energy Q_c , which is related to the bond enthalpy, can be determined by graphing $\ln \tilde{D}_c$ vs $1/T$.

Diffusion in an n -component system is described by an extension of Fick's first and second laws (Kirkaldy 1958). The flux of a component i , relative to a fixed reference plane is given by

$$J_i = - \sum_{j=1}^{n-1} \tilde{D}_{ij}^n dC_j/dx, \quad i=1, 2, \dots, n-1$$

where \tilde{D}_{ij}^n is an interdiffusion coefficient with n as the dependent variable, and dC_j/dx is the gradient of the component j , there being $n-1$ independent concentrations. By Fick's second law

$$dC_i/dt = d/dx \cdot \sum_{j=1}^{n-1} \tilde{D}_{ij}^n dC_j/dx$$

The Matano evaluation can be extended to the multi-component system (Kirkaldy, 1958) and the solution for \tilde{D}_{ij}^n is found to be

$$\frac{C_i}{C_{i_0}} x dC_i = -2t \sum_{j=1}^{n-1} \tilde{D}_{ij}^n dC_j/dx$$

For the ternary system of Pt-Ni-Fe this reduces to

$$\int_{C_{Ni_0}}^{C_{Ni}} x dC = -2t \left[\tilde{D}_{NiNi}^{Pt} dC_{Ni}/dx + \tilde{D}_{NiFe}^{Pt} dC_{Fe}/dx \right]$$

$$\int_{C_{Fe_0}}^{C_{Fe}} x dC = -2t \left[\tilde{D}_{FeNi}^{Pt} dC_{Ni}/dx + \tilde{D}_{FeFe}^{Pt} dC_{Fe}/dx \right]$$

(Note that any element can be taken as the dependent variable.) Since each of these equations contains two unknowns, it is necessary to design the experiment so that, for a given temperature, two separate diffusion paths will intercept simultaneously for all three components. In most studies the initial diffusion couples cover a wide range of compositions.

Assuming that these ternary diffusion coefficients also exhibit normal reaction rate behavior, then for a given diffusion path evaluation for a specific concentration requires the simultaneous solution of four equations. Since in virtually every system the species are diffusing at different rates it is expected that the solution would yield a unique temperature, a result of primary importance here.

Experimental and analytical procedure

The initial semi-infinite experimental media used last year simulated typical natural assemblages of pure platinum spherules in Ni_2Fe (Arrhenius and Raub 1978); the diffusion couple consisted of a 5 μm thick layer of pure Pt sputtered onto a sheet of Ni_2Fe , 1 mm thick.

This year's experiments employed an infinite source for both the Pt and the Ni_2Fe which yields more extensive information about diffusion processes in this system. The Pt was prepared from Pt foil (with impurities of less than 1%), which was arc melted under argon atmosphere into a bead. This was pressed into a disc, then the surfaces were ground flat and polished with 1 μm diamond grit. The discs were annealed at 1100° for 5 days to develop the crystals and to remove imperfections in the lattice. Then the surface of each disc was lightly repolished with 1 μm diamond grit to remove any contamination.

The Ni_2Fe from the previous experiments was utilized, the plates were polished in the same manner as the Pt discs and annealed at 900° for 5 days. Again, the surfaces were polished with 1 μm grit. The diffusion couples were fixed in a small vise of stainless steel and were sealed in quartz tubing under argon atmosphere. The couples were welded for 1 hour at 900°, quenched and then sectioned. The diffusion experiments were then carried out at temperatures ranging from 900°C to 1300°C, with an error of $\pm 5^\circ$. They were then mounted in epoxy and prepared for quantitative analysis.

The concentration measurements were done on a Cameca electron microprobe, and were carried out in two stages. Each couple was scanned along numerous traverses while recording the analog, and in the quantitative measurements the digital output for each of the elements. All results were found to be reproducible within $\pm 1\%$.

Results

Eleven samples were annealed at 1173°K (68.5 and 183 hours), 1223°K (74.5 and 121 hours), 1273° (39.5 hours), 1373°, 1473° and 1573°K (3.99 and 5.53 hours). Three concentration profiles are presented in Figs. 2, 3, 2a - c.

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Caption for Figure 2.3.2 -- Next page.

Diffusion profiles for Fe and Ni in Pt, and Pt in Ni₂Fe at three different temperatures (three graphs) and after different lengths of diffusion time (indicated in graphs; 16.2 hours at 1373°K).

Two interesting features can be seen. One is the beginning of ordering at 1223°K, manifested by acceleration of the diffusion in the composition region around Pt_{0.5}Fe_{0.25}Ni_{0.25} (Pt[FeNi]).

The other is the rapid increase in the diffusion rate of iron relative to that of nickel, beginning between 1223 and 1373°K. This phenomenon provides a temperature indicator independent of diffusion time. The degree of interdiffusion of nickel in platinum in graph c), for example, can be achieved during 16.2 hours at 1373°K as shown, but also at an infinite number of other combinations of longer times with lower temperatures and vice versa; at higher temperature the times rapidly become unrealistically short. A distinguishing feature is, however, that Fe is seen to have raced ahead of Ni into the Pt, pinpointing the temperature as being above ~ 1280°K. On the basis of this and the total diffusion, the time is fixed at around 1 day or less.

In the meteorite spherules investigated no perceptible diffusion of either iron or nickel has taken place.

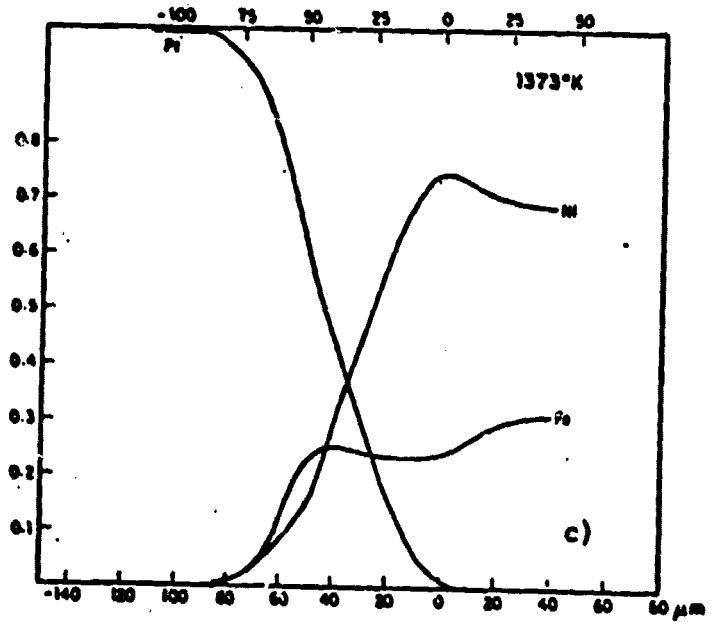
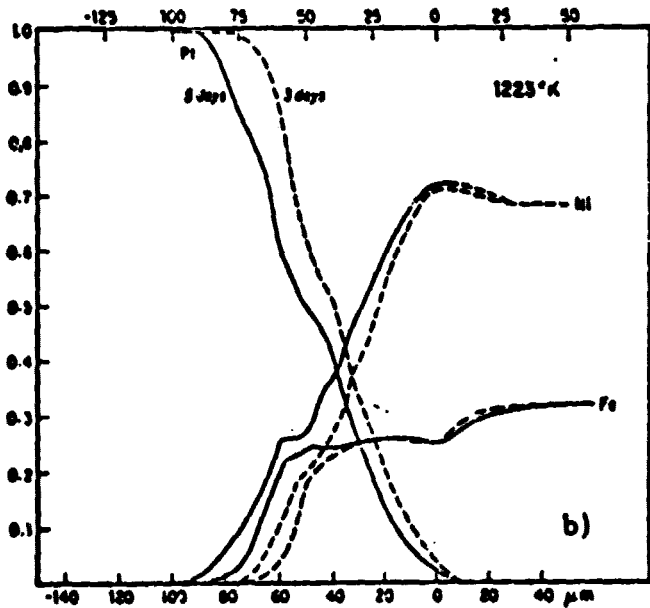
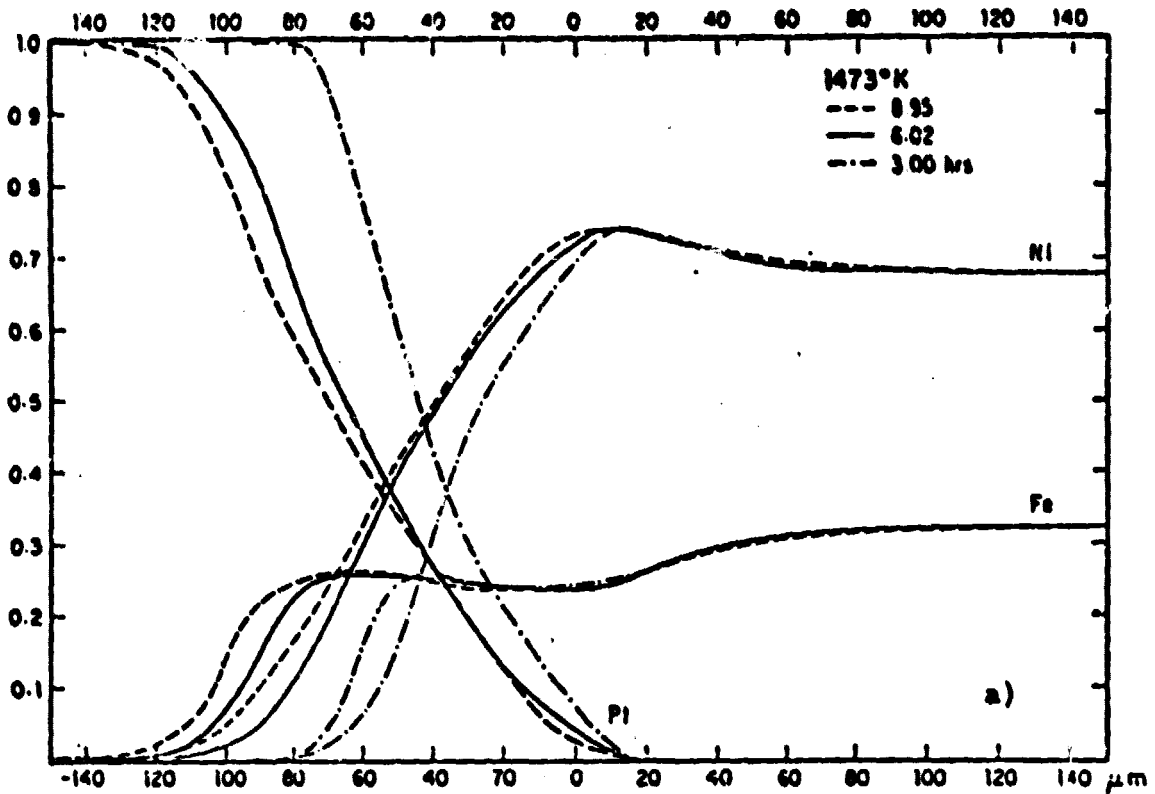


Figure 2.3.2

The position of the initial boundary between the members of the diffusion couple was in each sample indicated by a plane which contained voids developed from the separation of minute argon pockets during annealing. All analyses were made in regions without voids.

Any ambiguity about the position of the initial phase boundary in the diffusion couples does not affect calculation of the diffusion coefficients, because movement is taken relative to a hypothetical plane, the "Matano interface," where the diffusion is equivalent in both directions. Table 2.3.1 contains the interdiffusion coefficients for the pseudo-binary system Pt-M, where M = Fe, Ni. The assumption that Fe and Ni behave like species is reasonable on the basis of similar phases in the Ni-Pt and Fe-Pt phase diagrams. Also, Fe and Ni form a continuous solid solution and there is only one ordered phase, Ni_3Fe , which has a low thermal stability. Our continued work aims at making the additional still more elaborate measurements that will be needed to evaluate the ternary diffusion coefficients. In the present work we are interested in observing the system over a broad range of temperatures.

Discussion

It is apparent from the concentration profile that, as expected, ordered phases occur in this system; corresponding irregularities in the curves are particularly distinct for 1173°, 1223° and 1273°. When translated into diffusion rates (Fig. 2.3.3), this ordering is represented by maxima and minima around the stoichiometric compositions MPt_3 and MPt . MPt is the most stable and is the only phase to affect rates (by accelerating them) at 1000°. These observations correlate well with the known ordered phases in the Ni-Pt and Fe-Pt systems. They all show the strongest ordered phase at 50% Pt. In the binary systems ordering is observed at 25% Pt while in the ternary system ordering is more pronounced at 75% Pt, where also the phase FePt_3 has been reported.

Indications that ordering can affect diffusion at temperatures well above the order-disorder transition has been presented before. Kučera and Million (1975) used the phenomenon of short range ordering to explain anomalies in the

Table 2. 3. 1

Interdiffusion coefficients for the pseudo-binary system Pt-(Ni, Fe)

	10	20	30	40	50	60	70	80	90
$\bar{D}_i(1173) \cdot 10^{12}$ $t=16.2$	1.61	2.44	3.50	5.21	5.29	6.09	5.07	1.49	1.81*
$\bar{D}_i(1225) \cdot 10^{12}$ $t=21$	5.81	6.59	6.42	6.68	13.65	7.51	3.71	6.70	3.57
$\bar{D}_i(1273) \cdot 10^{12}$ $t=37.5$	7.74	7.57	7.67	13.45	27.59	21.28	7.37	5.58	5.00
$\bar{D}_i(1373) \cdot 10^{10}$ $t=16.2$	3.04	3.54	4.51	5.07	4.73	3.67	3.36	3.28	3.25
$\bar{D}_i(1473) \cdot 10^{10}$ $t=6.02$	2.85	3.00	3.35	3.12	3.72	2.38	1.87	1.63	1.57
$\bar{D}_i(1473) \cdot 10^{10}$ $t=8.75$	1.37	2.14	2.73	2.88	2.64	2.32	1.42	1.18	1.15
$\bar{D}_i(1573) \cdot 10^{10}$ $t=8.53$	7.88	10.0	11.4	11.1	9.3	8.4	6.6	4.9	3.9
$\bar{D}_i(1573) \cdot 10^{10}$ $t=3.99$	7.35	12.60	13.7	14.4	14.4	12.4	8.65	5.76	3.70

* \bar{D}_i (cm^2/sec) t (hours)

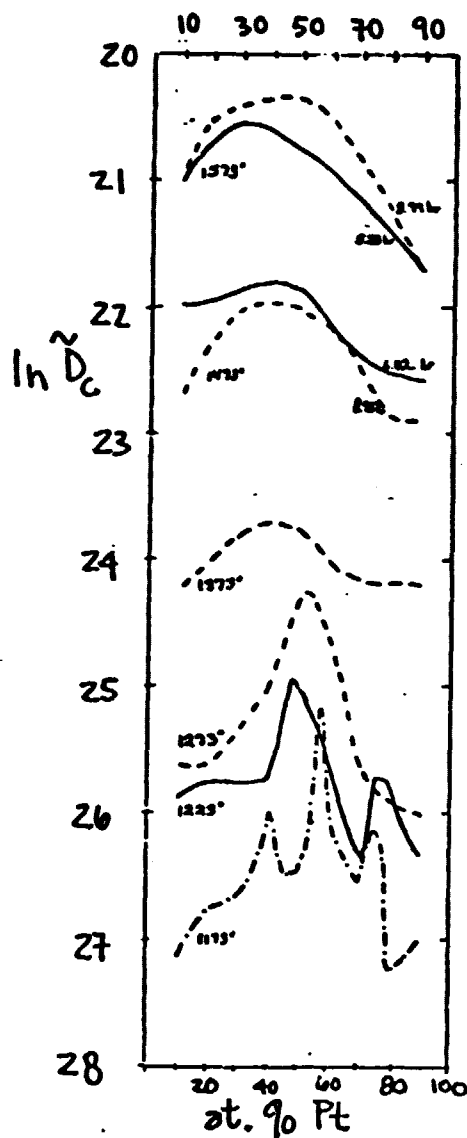


Figure 2. 3. 3. Diffusion constant as function of composition at various temperatures, showing the increased rate of diffusion around integral stoichiometries (25, 50, 75 at. % Pt) and at low temperatures where ordered compounds begin to form.

In contrast to what has been implied by Larimer (1979), the formation of ordering compounds in this system thus does not impede but accelerates diffusion and makes the present technique even more sensitive in these composition-temperature regions.

diffusion of Ni into NiFe. The rate of diffusion peaked at the composition Ni_3Fe for diffusion temperatures of 814°C, 924°C and 1076°C. The actual phase transition occurs only below 503°C. They also interpreted data for diffusion of Co into NiCo in a similar way. The rate peaked at NiCo_3 and Ni_3Co for temperatures below 1300°C. The ordering transition for Ni_3Co is reported to occur at and below 1033°C.

In all the concentration profiles in this study (e. g. those shown in Fig. 2. 3. 2), it can be seen that Ni_3Fe is a particularly stable composition. This is most apparent for 1173° (68. 5 hours)(Fig. 2. 3. 3). Yet the actual formation of this phase occurs only at and below 773°K. An important point is that the ordering phenomena result in acceleration of the diffusion rates, making our conclusions about thermal exposure conservative (Arrhenius and Raub 1978; Arrhenius, Schimmel and Raub 1980).

Also evident from the concentration profiles is the interesting and useful fact that the relative rates of diffusion of Ni and Fe change with temperature. For 1273° and below Ni penetrates more deeply than Fe; for 1373° and above the reverse is true. It is interesting to note that tracer diffusion data by Kučera (1975) for Pt into Pt-Fe shows a large jump in the rate of diffusion for temperatures above 1273°.

Figure 2. 3. 4 contains graphs of $\ln D_c$ against $1/T$. If a single rate were involved, these points should lie on a straight line with slope Q_c/R . Obviously, this is not the case and we choose to interpret the data as representing a break in diffusion rates between 1273° and 1373°K. Irregularities below 1273° are due to the short range ordering preceding the formation of ordered phases. Above 1273°, the rapidly increasing disorder leads to a change in bond energy which affects the diffusion rate of iron more strongly than that of Ni.

A major conclusion from these results is that in multicomponent diffusion systems of the kind occurring in meteorites, the temperature dependence of the diffusion rates of individual components such as Fe and Ni permits us, in principle, to determine the fossil temperature of diffusion as a parameter separate from the total extent of diffusion, which measures total thermal exposure (time \times exp. temperature).

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Caption for Figure 2.3.4 -- Next page.

Plot of the (negative) logarithm of the diffusion coefficient against inverse temperature for increasing platinum concentrations in the system Pt-Fe, Ni (top row 10, 20 and 30% Pt; second row 40, 50, 60; third 70, 80, 90% Pt). The diagrams show over this entire concentration range an increase in the diffusion rate with onset around 1323°K (1050°C). The increasing dependence of the diffusion constant on stoichiometry as temperatures drop into the ordering range is also seen, with anomalously high diffusion constants for the incipiently ordered compounds (cf. also Fig. 2.3.2).

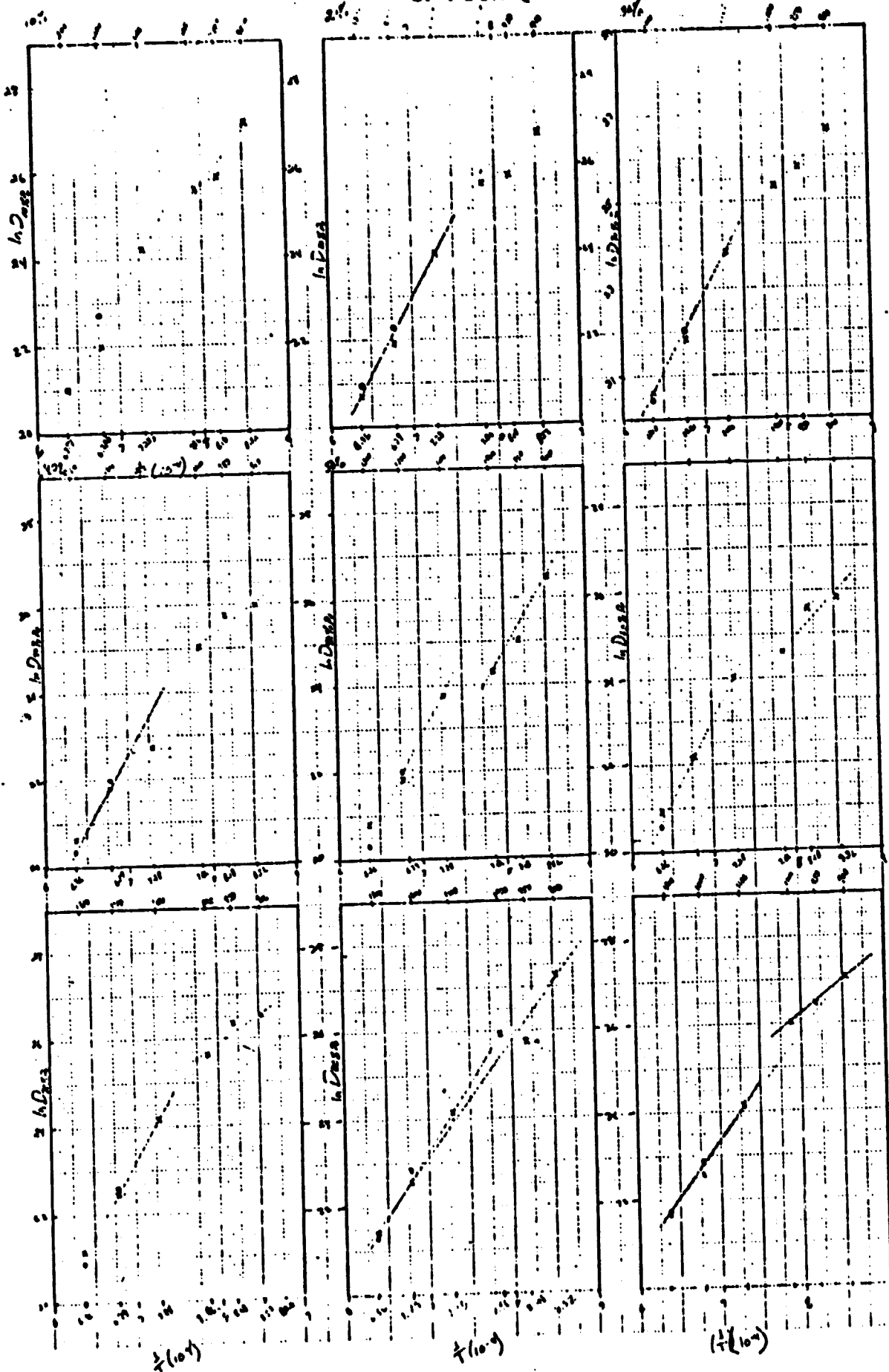


Figure 2 3 4

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