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NOBLE GAS SOLUBILITY IN SUPER-CRITICAL WATER: IMPLICATIONS FOR INERT GAS STUDIES AND GEOCHRONOLOGY

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RESUMEN

Los gases inertes exhiben idealmente solubilidad infinita en agua supercrítica. Las implicaciones de este fenómeno son discutidas en el contexto del reestablecimiento del sistema K-Ar durante metamorfismo regional y emplazamiento de granitos. Las abundancias de los gases inertes en rocas y lutitas del suelo marino, posiblemente puedan ser interpretadas como consecuencia (al menos en parte) de partición entre agua y fases silicatos en las que los gases inertes ligeros son tomados preferentemente en agua. El desempeño del agua supercrítica como un medio de transporte para gases inertes, ofrece una importante alternativa a los procesos poco probables de difusión volumétrica a bajas temperaturas.

ABSTRACT

Inert gases will ideally exhibit infinite miscibility with super-critical water. The implications of this phenomenon are discussed in the context of the resetting of the K-Ar system during regional metamorphism, and emplacement of granites. Inert gas abundances in oceanfloor rocks and shales may also be interpreted as a consequence (at least in part) of partioning between water and silicate phases in which the light inert gases are preferentially taken up in water. The function of super-critical water as a transport medium for inert gases offers an important alternative to the unlikely process of volume diffusion at low temperatures.

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INTRODUCTION

At all crustal depths greater than 12 km, water behaves as a super-critical fluid. Above its critical temperature (374°C), water and any noble gas would be perfectly miscible if both phases behaved in an ideal way (Pray *et al.*, 1952). While recognizing the non-ideal behaviour, particularly of water, under geological conditions, we nevertheless believe that the very high miscibility of inert gases in this fluid has major implications for inert gas systematics and chronologies. Even at shallower depths in the crust and on the ocean floor, locally elevated temperatures attained in hydrothermal systems and in contact metamorphism demand that water be treated as a super-critical fluid.

WATER-ROCK INTERACTION

As was pointed out by Fyfe *et al.* (1978), "Water is the dominant low-density fluid, the dominant solvent, the dominant chemical transport agent . . . in the crust". The purpose of this note is to qualitatively recognize some of the profound implications of this statement in the behaviour of inert gases in continental and oceanic lithosphere.

The critical pressure and temperature for water are 221 bar and 374°C respectively (Clark, 1966). With an average geothermal gradient in the continents of 30°C per km, the maximum depth threshold at which water in the lithosphere will become a super-critical fluid is around 12 km, i.e. at approximately half the average crustal depth of 35 km. The role of pressure is less important since at a depth of less than 1 km in the crust, the pressure will have exceeded the critical pressure of water. Ocean water depths in excess of 2 km will similarly lead to the establishment of super-critical conditions when the water temperature exceeds 374°C. It is apparent, therefore, that all of the following processes take place under temperature and pressure conditions corresponding to the super-critical field of water:

The development of all metamorphic facies during regional metamorphism, since the critical point lies almost on the boundary for the "lower limit of metamorphism" (Fig. 1).

ii The solidification of the majority of plutonic rocks.

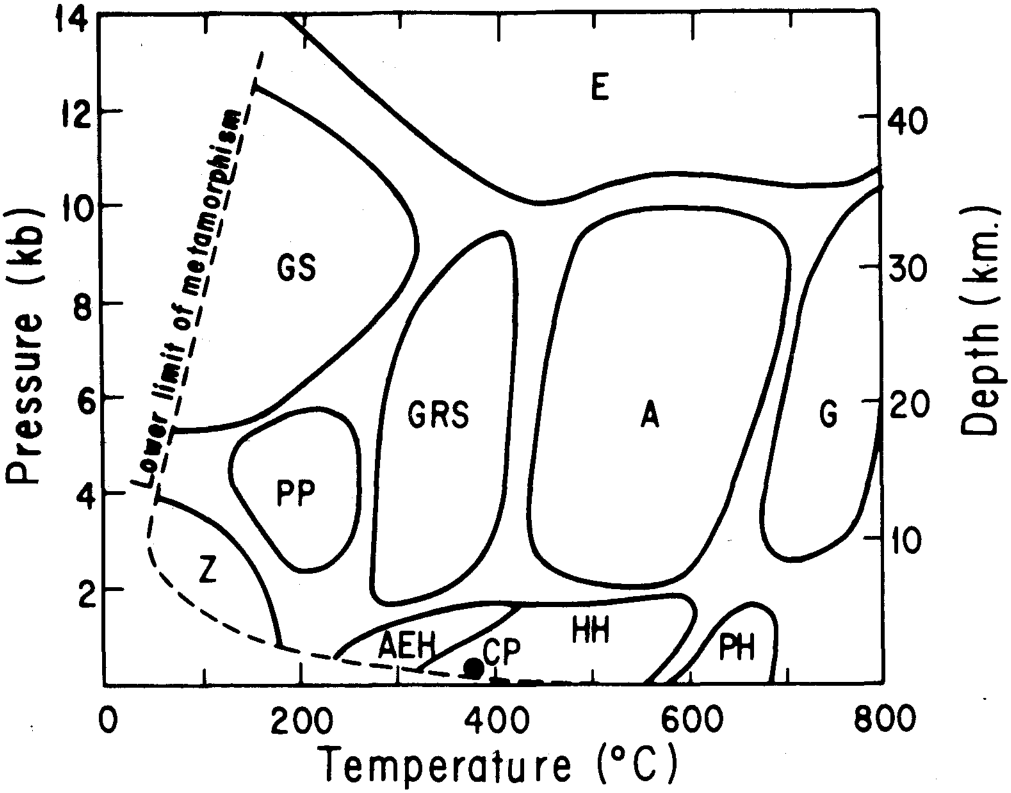

Fig. 1. Pressure-depth-temperature fields of metamorphic facies (Turner, 1968) Z = Zeolite; PP = Prehnite-Pumpellyite; GS = Glaucophane Schist; E = Eclogite; GRS = Greenschist; A = Amphibolite; G = Granulite; AEH = Albite-Epidote Hornfels; HH = Hornblende Hornfels; PH = Pyroxene Hornfels; CP = Critical Point of Pure Water.

iii Hydrothermal alterations of mid-ocean ridge basalts (MORB) in the immediate vicinity of their parent ridge.

iv Contact metamorphism and hydrothermal circulation at depths greater than 1 km.

NOBLE GAS TRANSPORT AND K-Ar DATING

One of the assumptions implicit in determining the K-Ar "age" of a geological specimen is that no "excess" or "initial" argon is incorporated into a mineral at the time of its formation. It is a remarkable fact that the great majority of continental metamorphic, plutonic and extrusive rocks are amenable to K-Ar dating and yield geologically acceptable ages. The question of *how,* for example, the accumulated radiogenic argon from a pre-Cambrian sediment is removed during metamorphism in the Caledonian earth movements in the N. W. Highlands, has never been satisfactorily explored. With no local concentration gradients down which to diffuse, there is apparently no physically acceptable process operating to cause "resetting" of the K-Ar system due to *complete* argon loss during regional metamorphism. Nor has the question of how a granite pluton (which passed the blocking temperature for argon diffusion while still under perhaps the blocking burden) lost all "initial" argon to manifest itself as an ideal candidate for K-Ar studies. Again diffusion mechanisms seem unacceptable.

The key to these and other unanswered questions in inert-gas behaviour in rocks may lie in the role of the super-critical water as a vehicle for inert gas transport. Above its critical point (374°C) water (were it ideal) would be infinitely miscible with the inert (or any other) gases Pray *et al.*, 1952).

Since the majority of reactions in prograde metamorphism are dehydration reactions with abundant super-critical water being made available from interstitial and combined water during metamorphism of sediments and sedimentary rocks (though not necessarily from igneous rocks where breakdown of relatively scarce hydrous minerals would be the only source of water), we believe that it is unnecessary to invoke mechanisms of bulk inert gas diffusion to explain the resetting of the K-Ar system, mechanisms which have been shown to be irrelevant in most geological settings (Mussett, 1969). Circulating water-rich pore fluids provide an ideally infinite reservoir to physically transport dissolved gases away from the focus of metamorphism. A similar argument we believe applies to the case of plutonic rocks, particularly granites. Water occurs dissolved in magmas, and may also occur as a separate supercritical fluid if saturation occurs, say, in response to falling pressure as the magma ascends to the surface. The super-critical fluid which separates will tend to rise as bubbles to the top of the magma chamber, effectively 'degassing' the magma by virtue of the very high miscibility of gases (including argon) in the fluid.

Studies of inert gases in oceanic rocks, which formed in an environment where water was super-critical, may also be elucidated by these observations. We have shown previously (Terrell and Mitchell, 1982) that samples of MORB from DSDP Site 504B have K-Ar ages which are broadly consistent with their stratigraphic age, provided they are sampled more than 60 m below the basalt/sediment interface. These samples which came from both pillow-basalts and more massive basaltic units did not show obvious high temperature alteration. One in particular coming from a thick flow was considered to be representative of "fresh" basalt and because it came from near the surface it cooled faster thus retaining some of its magmatic noble gases. The calculated K-Ar ages of these uppermost samples is completely anomallous, contrary to those of samples obtained from basalts deeper than the 60 m mentioned before. Apparently, these deeper MORB samples, by virtue of their greater depth and overburden, have experienced a longer period of alteration above 374°C than their shallower counterparts. This has allowed them to be degassed (by loss to super-critical water) of any magmatic argon which would otherwise have produced anomalously old ages (Dalrymple and Moore, 1968) (such as were determined in the shallower samples from the same hole). One remarkable implication is that *highly* altered (by short term-high temperature alteration) MORB samples may be more likely to yield geologically acceptable ages than their 'fresh' counterparts. The short duration of this alteration is essential in this hypothesis as it is known that high-temperature alteration decreases the K concentration in MORB (Edmond *et al.*, 1979). On the other hand low temperature alteration (like halmyrolysis) prevents us from dating by the K-Ar method (Seideman, 1978) as there is ample evidence that K increases during low temperature alteration (Hart, 1970; Terrell *et al.*, 1979; Verma, 1981) and it prevails until the sample is recovered.

Below the critical point of water (where noble gas solubility is appreciable), we believe that elemental fractionation of the inert gases may occur as a consequence of differing partition coefficients for the separate gases between water and rock, though regrettably quantitative data for such partitioning is non-existent. Dymond and Hogan (1973) have, for example, examined the behaviour of inert gases in pillow lavas, and concluded that in the slowly cooled interior of pillows (where alteration has occurred to the greatest degree), the "water pattern" of gases has been established through "equilibrium" with water (Fig. 2). The phenomenon is one of almost total He loss, extensive Ne loss with *gain* of Ar, Kr, and Xe, relative to the glassy rim of the pillow. It is evident that when inert gases are liberated during the breakdown of miner-

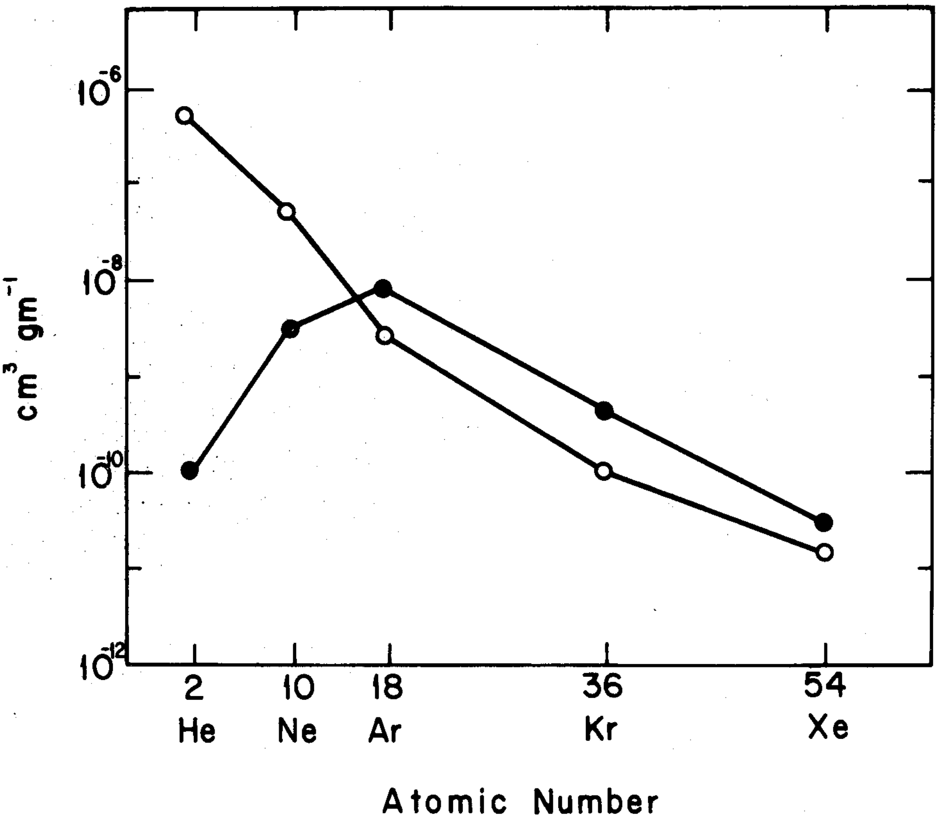

Fig. 2. Rare gas abundance patterns for rim and core of MORB pillow (Dymond and Hogan, 1973): ○ Glassy margin, ● Holocrystalline interior.

al structures during alteration, the light inert gases (He, Ne) display a partition coefficient which favours take-up in water rather than in the secondary mineral phase. The heavy gases (Ar, Kr, Xe) appear to partition into the silicate phases. An experiment performed by Fyfe *et al.*, (1969) supports this hypothesis, as they melted samples of a Precambrian granite in sealed capsules they found that ^{40}Ar is incorporated back into the quenched melt, an important source of error in K-Ar dating. The progressive enrichment in shales of the heavier noble gases in comparison with the proportions in air, recognized by Podosek *et al.* (1980) could be another manifestation of element fractionation resulting from water circulation during low-grade metamorphism at temperatures around 100°C (Hower *et al.*, 1976) leading to selective loss of light inert gases (Aronson and Hower, 1976) and addition of heavy inert gases, as water-rich fluid participates in the metamorphic reactions occurring during diagenesis. The role of such fluids in sweeping diagenetically formed hydrocarbons out of shale into reservoir rocks has already been recognized by Powers (1967).

We believe that insufficient regard has been paid to the thermal and chemical aspects of water interaction in determining the inert gas inventory of rocks. Observed inert gas abundances are normally regarded as resulting from physical "mixing", "equilibration" or "partitioning". Element fractionation (without isotopic fractionation) is an implicit aspect of the processes we have described and recognition of the high miscibility of inert gases in super-critical water may be an additional factor in understanding the increasing volume of data obtained through inert-gas studies.

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