polar stainless steel electrodes placed in the stratum radiatum. Stimuli were delivered at 0.1 Hz unless otherwise stated, and stimulus strength remained constant throughout the experiment. We measured EPSC amplitudes by averaging a 10-ms window around the peak and subtracting the average value obtained during a 10-ms window immediately before the stimulus. We measured the amplitudes of the second EPSCs evoked by paired stimulation in the same way after subtracting an averaged scaled trace, obtained from the pathway that was given single stimuli, from the trace obtained with paired stimulation. The data are expressed as means  $\pm$  standard errors of the mean. Student's *t* test was used to determine whether there was a significant difference in the mean between two sets of data.

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# Retention of Helium in Subducted Interplanetary Dust Particles

I welcome the report by H. Hiyagon (1) of diffusive loss of He and Ne from interplanetary dust particles (IDPs) as a significant contribution to the evaluation of Anderson's hypothesis (2) that the high <sup>3</sup>He/<sup>4</sup>He ratios in ocean island basalt (OIB) hotspots reflect He introduced into the mantle by subduction of IDP-containing sediments. Hiyagon's measurements of the high diffusivities of He and Ne in IDPs at the temperatures of subducting slabs should lay this proposal (2) to rest.

Here I wish to comment on the results of the diffusion experiments with particular reference to the deviations of the measured diffusivities from a linear Arrhenius plot at the low-temperature end of the data (500 and 600°C). The samples used in these experiments were magnetite separates from Pacific Ocean sediments. Hiyagon's measurements show that the diffusivities of both He and Ne are significantly greater at 500 and 600°C than are the values predicted by the close fit to a linear Arrhenius plot of data measured at higher temperatures. I believe this is a result of conversion of some of the magnetite to metallic  $\alpha$ -iron at the lower temperatures. In the high-temperature experiments magnetite would be converted by deoxidation to wüstite (FeO<sub>.95</sub>) and magnetite, which should have only a minor effect on diffusive loss of gases.

Figure 1 shows the Fe-O phase diagram (3) at the temperatures of interest, 400 to 1200°C, the highest temperature at which diffusive loss was measured. At  $T < 560^{\circ}$ C, pure magnetite lies on the boundary between the two-phase regions (magnetite + hematite) and (magnetite +  $\alpha$ -iron). At  $\sim 500^{\circ}$ C, pure magnetite is stable over the range of equilibrium gas compositions given by  $p(O_2) = 10^{-18}$  to  $10^{-29}$  bars,  $p(H_2)/p(H_2O) = 10^{-5}$  to 3.2, and  $p(CO)/(CO_2) = 2 \times 10^{-6}$  to 1, these being the limiting values between the two-phase stability fields (magnetite + hematite) and (magnetite +  $\alpha$ -iron), respectively (4). Thus, un-

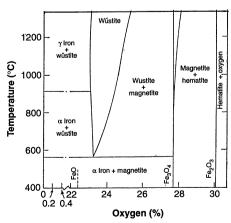
der the high-vacuum conditions of the experiments (1), low  $O_2$  fugacities and high  $CO/CO_2$  and  $H_2/H_2$  ratios will shift pure magnetite into the stability field of magnetite +  $\alpha$ -iron. The relevant equilibria are:

 $Fe_3O_4 = 3Fe(\alpha) + 2O_2$ 

### $Fe_3O_4 + 4CO = 3Fe(\alpha) + 4CO_2$

The effect of these reactions on diffusive gas loss is due to the large density change in the conversion of magnetite ( $\rho = 5.2$ ) to metallic Fe ( $\rho = 7.9$ ), resulting in a large volume decrease that strongly enhances diffusive loss of gases. Observations (5) show that in the conversion of magnetite to metallic iron the magnetite grains become deeply fissured with a large increase of surface area per unit volume, which significantly increases the rate of diffusive gas loss. In the experiments above 600°C, however, the stable phases on deoxidation become magnetite and wüstite ( $\rho = 5.75$ ), and conversion to wüstite is accompanied by a negligible volume change with no fissuring (5), and thus no enhanced diffusive loss of gases.

In sediments undergoing subduction the



**Fig. 1.** Fe-O phase diagram at 400 to 1200°C (3). Oxygen values are in weight percent.

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environment is highly anoxic and magnetite will undergo at least partial direct reduction to Fe at lower temperatures, followed at higher temperatures by a two-stage reduction to wüstite and then to metallic Fe (Fig. 1). The mechanisms involved have been described in detail (5) and show that diffusive loss will also be enhanced by fissuring at the higher temperatures when deoxidation reaches the stage of conversion of wüstite to metallic iron. Therefore the measured diffusive losses (1), under conditions probably not reached in the higher-temperature experiments but certainly achieved in subducted sediments, should be regarded as lower limits for the actual diffusive loss rates in subducted IDPs. A final, and ultimately conclusive experiment on diffusion losses could be carried out by mixing an IDP concentrate back into a small volume of the original sediment (reduced to fit the experimental apparatus) and measuring diffusive losses and temperature directly, and in a sealed container in which CO, CO<sub>2</sub>, and O<sub>2</sub> fugacities are controlled within limits appropriate to sediments in subducting slabs. Examination of the magnetite residues from the various heating cycles would document the phase changes resulting from deoxidation with the diffusion losses of He and Ne in each experiment.

Nevertheless, it appears certain from the present experimental results (1) that He and Ne in IDPs cannot survive the subduction process to become significant components in the upper mantle. Observations on mantle-derived basalts in subduction arc regimes reinforce this conclusion: the <sup>3</sup>He/ He ratios observed in all the major circum-Pacific arc volcanic gases and basalts (6) are always at least equal to, and generally lower than, the ratios in the worldwide reservoir tapped by mid-ocean ridge basalt (MORB) lavas. In some arcs, such as Indonesia, the ratios are much lower, indicating the incorporation of radiogenic helium from continental sources (7). If He with the high <sup>3</sup>He/<sup>4</sup>He ratios characteristic of IDPs were to survive the subduction process, one would expect to observe ratios greater than those of MORBs, if anywhere, in the lavas and volcanic gases derived from the mantle wedge above the subducting slabs, where He accumulates by volatile transport from the downgoing slab. However, <sup>3</sup>He/<sup>4</sup>He ra-

#### **TECHNICAL COMMENTS**

tios greater than MORB have never been observed in arc terrains.

Anderson (8) now argues that a "correlation between <sup>3</sup>He and C suggests a recycling mechanism (IDP-rich sediments)," despite the facts that (i) He and  $CO_2$  are both degassed from MORB and OIB lavas prior to and during eruption, so that concentrations of these gases in the original magmas are not known, and that (ii) no data exist for comparison of C and He concentrations in OIB magmas. He further argues (8) that there is no mechanism for material transport by mantle plumes. Be that as it may, Hiyagon's experiments (1) and the considerations detailed here show that there exists no mechanism for significant transport of extraterrestrial He and Ne into the source regions of hotspot magmas by subduction of IDPs in downgoing slabs. Harmon Craig

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Response: I appreciate Harmon Craig's comment on my diffusion experiment (1) of solar He and Ne in IDPs in deep sea sediment as it gives me a chance to further examine the reliability of the experimental results.

The samples used in my diffusion experiment were not pure magnetite, but contained silicate minerals, clay minerals, and so on, which might also have contributed to control of oxygen fugacity. Furthermore, it is not certain whether the phase change could be accomplished within the relatively short heating duration of the experiment.

To answer this question, I conducted again the heating experiment under the same conditions as in the diffusion experiment and examined the run products as well as an the unheated sample with x-ray diffraction. I prepared three samples of a magnetic separate from Pacific Ocean sediment. The samples were wrapped with platinum foil, placed in a vacuum line, and heated in a molybdenum crucible at 500°C, 800°C, and 950°C for 2 hours. Partial decomposition of magnetite into a metallic phase is presumed to take place at 500°C according to Craig's suggestion, and at 800°C and 950°C the obtained diffusion data show linear correlations in the Arrhenius diagram. After cooling the furnace to room temperature, the samples were taken out from the crucible for analysis.

In the x-ray diffraction analysis, magnetite peaks were observed as major peaks together with many other peaks of silicate minerals. However, noticeable changes in the peaks were not observed among the samples; the intensities of the magnetite peaks were almost the same for all the heated samples and an unheated sample; no peaks of FeO, Fe<sub>2</sub>O<sub>3</sub>, or Fe were observed. The results suggest that magnetite remained as a major constituent of the magnetic fraction during the heating experiment, and that the effect of the phase change, if it occurred, may have been minimal under the present experimental conditions. The magnetite sample could have been self-buffered inside the platinum foil during the heating experiment, which could have prevented the magnetite from partial decomposition into iron within a few hours.

From these observations, I conclude that the release of solar gases from IDPs in my previous experiment was mostly a result of diffusion, and that phase changes of magnetite, if present, must have only a minor contribution to the gas release. An x-ray diffraction analysis, however, gives only qualitative information, and hence the possibility of a small amount of phase changes, pointed out by Craig, may not be ruled out completely. In any case, the results of the x-ray analysis further support the reliability of the diffusion data and support my conclusion that solar He and Ne would be lost from IDPs at shallow depths in the subduction system.

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# **Function of Maspin**

We have examined the primary structure of the tumor-suppressing serpin, maspin, recently discovered by Z. Zou *et al.* (1). Unlike most serpins, maspin is most likely not an inhibitor, but may be a ligand-binding serpin, possibly of thymosin  $\beta_{4}$ .

Serpins are a highly diverse group of proteins most of which are inhibitors of serine proteases. Some have evolved new functions, such as cortisol-binding globulin; others have no recognized function, such as ovalbumin. Although the amino acid sequences of serpins are diverse, certain regions are virtually invariant. The reactive center loop, situated near the COOH-terminus, is one of the highly variable regions and is the domain which binds to the active site of the serine protease. The sequences flanking the enzyme-binding site are highly conserved, such as the hinge region on the NH<sub>2</sub>-terminal side of the reactive center. This motif is important for the function of serpins as inhibitors, mutations within it interfere with inhibitory function (2), frequently resulting in the proteolysis of the serpin reactive center loop by proteases that would otherwise be inhibited.

A survey of serpin hinge regions (Table 1) shows that the non-inhibitors have diverged in sequence from the consensus at positions P14, and P12 to P8 [P-numbering according to Schechter and Berger (3)]. The equivalent region of maspin has also diverged from the consensus. In particular, the P8 to P12 residues share no homology with any known inhibitory serpin, thus maspin is probably one of the serpins that have evolved new functions.

What then might be the role of maspin? Both maspin (1) and thymosin  $\beta_4$  (4) have been shown to suppress cell motility and tumor metastasis, but not to have any effect

**Table 1.** A comparison of the hinge region sequence of maspin with that of other serpins, inhibitory and non-inhibitory. The hinge regions of 21 serpins that have been demonstrated to be inhibitors and 5 serpins that, although well known, have not been shown to have any inhibitory activity were aligned by hand. The sequences were taken from C. J. Marshall (6). Abbreviations for the amino acid residues are as follows: A, Ala; C, Cys; D, Asp; E, Giu; F, Phe; G, Giy; H, His; I, Ile; K, Lys; L, Leu; M, Met; N, Asn; P, Pro; Q, Gin; R, Arg; S, Ser; T, Thr; V, Val; W, Trp; and Y, Tyr.

Residue position	P17	P16	P15	P14	P13	P12	P11	P10	P9	P8
Consensus sequence	E	E/K	G	Т	E	А	А	А	Α	Т
Absolute conservation in inhibitors (%)	100	55	100	77	61	94	72	55	55	77
Absolute conservation in noninhibitors (%)	60	60	80	20	80	20	40	20	0	20
Maspin sequence	Е	D	G	G	D	S	I	Е	V	Ρ

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