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Diamond formation due to a pH drop during fluid-rock interactions

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Diamond formation has typically been attributed to redox reactions during precipitation from fluids or magmas. Either the oxidation of methane or the reduction of carbon dioxide has been suggested, based on simplistic models of deep fluids consisting of mixtures of dissolved neutral gas molecules without consideration of aqueous ions. The role of pH changes associated with water-silicate rock interactions during diamond formation is unknown. Here we show that diamonds could form due to a drop in pH during water-rock interactions. We use a recent theoretical model of deep fluids that includes ions, to show that fluid can react irreversibly with eclogite at 900 °C and 5.0 GPa, generating diamond and secondary minerals due to a decrease in pH at almost constant oxygen fugacity. Overall, our results constitute a new quantitative theory of diamond formation as a consequence of the reaction of deep fluids with the rock types that they encounter during migration. Diamond can form in the deep Earth during water-rock interactions without changes in oxidation state.

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Diamonds record fluid migration events over billions of years in the deep carbon cycle in the Earth's interior^{1–3}. Major advances in our understanding of the origin of diamonds in the deep Earth have come from studies of these fluids^{4–12}. Aqueous fluids, melts and/or supercritical mixtures of the two are suspected to have been involved in the origin of diamonds in both the cratonic lithospheric mantle^{1,9,11–15} and the ultra-high pressure metamorphic environments^{4,5}. However, previous quantitative models of the fluids involved in diamond formation have been so simplistic as to severely restrict the scope of theories about the origin of diamonds.

Traditional models of the fluids involved in diamond formation have long treated the fluids as mixtures of neutral gas molecules such as CO₂, CH₄, H₂ and H₂O (that is, COH fluids) without consideration of aqueous ions or species derived from silicate rock components^{4,16}. Consequently, the only link in the models between the fluids and their silicate host environments is the fugacity of oxygen (f_{O_2}). For this reason, the cause of diamond precipitation has typically been attributed to redox changes^{1–4,13,17}. Addressing alternate possibilities, such as the possible role of evolving fluid chemistry during fluid–rock interaction as a cause of diamond precipitation, has not been possible. Modelling diamond formation during silicate alteration

reactions involving aqueous ions and aqueous species derived from silicate rocks could not be attempted, because COH models at high pressures do not contain any ions or silicate rock components.

Recent advances in theoretical and experimental aqueous geochemistry resulting in the Deep Earth Water (DEW) model enable calculation of equilibrium constants involving minerals and aqueous ions, metal complexes and organics to 6.0 GPa and 1,200 °C (refs 18–21). In the present study, we use these advances to address the potential role of evolving aqueous fluid chemistry in the origin of diamonds. We first calibrate our model at 5.0 GPa and 900 °C using experimental data (see Calculation Methods and Supplementary Table 1 and Fig. 1), then we model diamond formation during the irreversible chemical mass transfer associated with aqueous fluid–rock interactions^{22,23}, to investigate the role of pH changes in driving diamond precipitation. The model uses a conceptual scenario in which fluids from the oceanic mantle lithosphere in a subducting plate react with eclogitic mineral assemblages at 900 °C and 5.0 GPa, as a generic scenario of subcratonic lithospheric diamond formation (Calculation Methods). The aim of the present study is not to model the formation of specific diamonds and their fluid and solid inclusions. Instead, we demonstrate how it is now possible

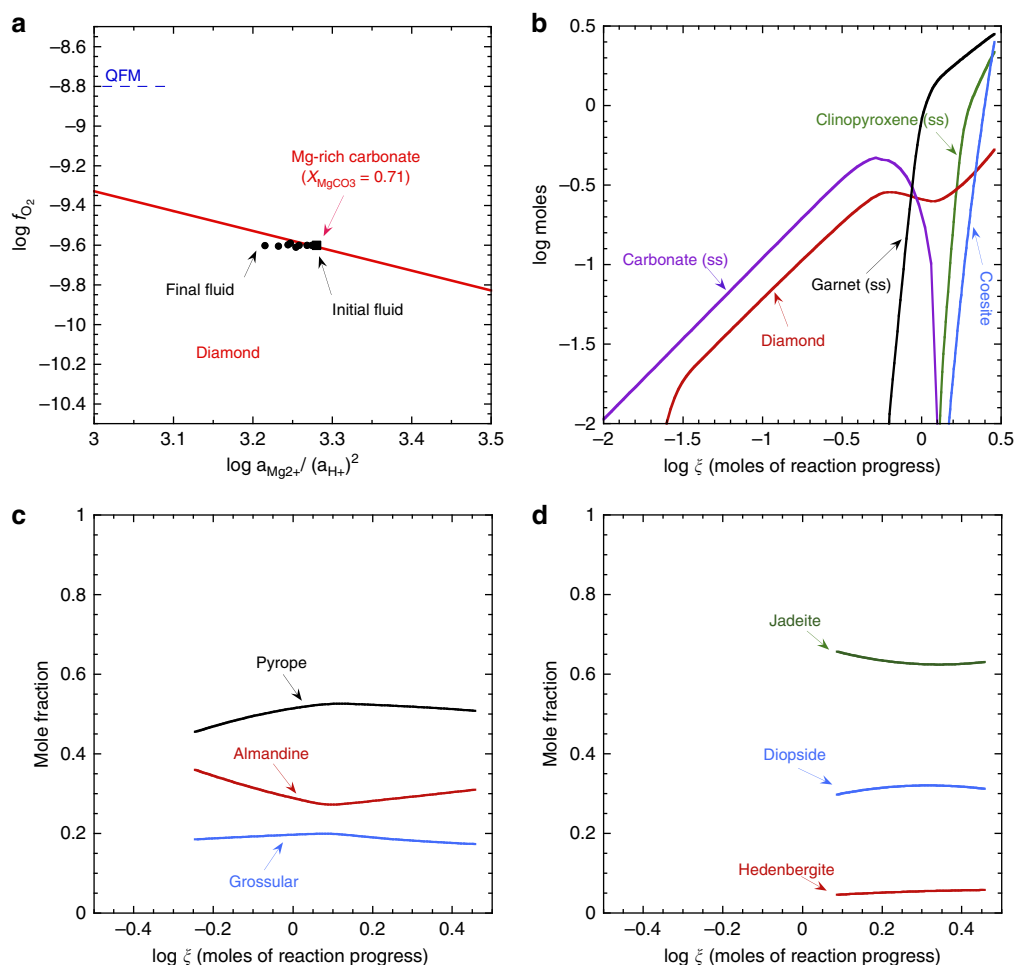


Figure 1 | Predicted reaction path and mineral products of the fluid-rock interactions forming diamond. (a) Reaction path of the fluid (black dots) relative to the equilibrium boundary between a specific magnesite component composition in a carbonate solid solution, diamond, aqueous species and $O_{2,g}$. (b) Minerals produced during the reaction of the fluid with eclogite (Supplementary Table 2). (c) Composition of the garnet solid solution produced during the reaction of the fluid with eclogite (Supplementary Table 2). (d) Composition of the clinopyroxene solid solution produced during the reaction of the fluid with eclogite (Supplementary Table 2). All calculations refer to 900 °C and 5.0 GPa. In b,c,d, the x axis represents the logarithm of the reaction progress variable ξ , which is equal to the number of moles of each reactant mineral destroyed during the reaction progress.

to monitor evolving fluid chemistry during diamond formation and the potential importance of pH drop as a new mechanism for diamond formation.

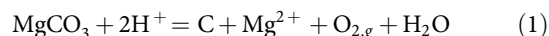
Results

Mineral products during fluid–rock interaction. An initial fluid chemistry (Supplementary Table 2) was set by reaction of water with a carbonated mafic rock²⁴ resulting in a fluid very close to equilibrium with a Mg-rich carbonate solid solution and diamond (Fig. 1a). The fluid was then permitted to react with a model metasedimentary eclogite^{25,26} consisting of clinopyroxene (mole fractions of jadeite 0.7, diopside 0.2 and hedenbergite 0.1), garnet (mole fractions of pyrope 0.6, almandine 0.3 and grossular 0.1) and coesite. The final fluid chemistry is given in Table 1 (see also Supplementary Note 1 for the full reaction path). The reactions produced abundant diamond, while reactant silicate minerals were destroyed (Fig. 1b). As the initial fluid was in equilibrium with Mg-rich carbonate solid solution (magnesite 0.71, siderite 0.12 and calcite 0.17), secondary Mg-rich carbonate was predicted to precipitate and replace eclogite at small extents of reaction progress ($\log \xi$ values of -2.0 to about -0.30 ; Fig. 1b). However, at large extents of reaction progress ($\log \xi$ values greater than about -0.30 , Fig. 1b), carbonate and eclogite are replaced by diamond, secondary garnet, clinopyroxene and coesite. The predicted secondary garnet and clinopyroxene compositions (Fig. 1c,d) could serve as models of the solid inclusions typically preserved in natural diamonds¹³. Future studies could include more detailed comparisons of predicted evolving solid solutions in garnet and pyroxene during diamond formation with specific inclusion compositions in natural diamonds.

It is interesting to note that the first part of the reaction path shown in Fig. 1b ($\log \xi < -0.30$), corresponding to the smallest extents of fluid–rock interaction, could correspond to the formation of diamond in a Mg-rich carbonate-metasomatized eclogite. It might be expected that the carbonate phase could disaggregate during transport in a kimberlite magma¹, which would result in xenocryst diamonds hosted by kimberlite rock.

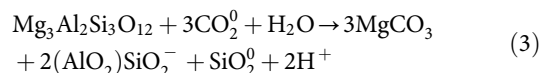
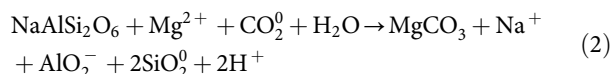
In contrast, the second part of the reaction path in Fig. 1b ($\log \xi > -0.30$), corresponding to much larger extents of fluid–rock interaction, could correspond to the formation of diamond, clinopyroxene and garnet-metasomatized eclogite. Under these circumstances, diamonds may well be preserved in their eclogitic host–rock during the kimberlitic eruption process. If such large extents of fluid–rock interaction are uncommon, the overall model in Fig. 1b may help to explain the comparative rarity of diamonds set in a matrix of eclogite²⁷ rock.

Changes in the aqueous phase during fluid–rock interaction. It can be seen in Fig. 1a that the $\log f_{\text{O}_2}$ is almost unchanged (< 0.01 log units) during the entire reaction path. However, in Fig. 2a, it can be seen that the pH decreases during most of the reaction path. It should be noted here that neutral pH under these conditions is about 2.7 because of the drastic increase in the dissociation constant of water at this temperature and pressure. The reason for the pH decrease of the reacting fluids can be seen in the irreversible reaction path traced on the diagram in Fig. 1a. In contrast to traditional COH models, the equilibrium between a given activity of the magnesite component of a carbonate mineral and diamond represented by the solid line in Fig. 1a is univariant at constant temperature and pressure according to the reaction



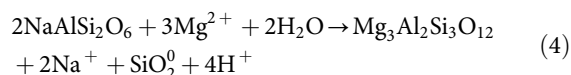
The univariance of the equilibrium in equation (1) arises, because HCl is a chemical component that provides ions²⁸.

It can be seen in Fig. 1b that reaction of the fluid with eclogitic minerals in the earliest stages of reaction progress ($-2.0 < \log \xi < -0.30$) causes the precipitation of diamond and a secondary Mg-rich carbonate mineral according to the reactions



These reactions remove the Mg^{2+} ion and add the $(\text{AlO}_2)\text{SiO}_2^-$ complex and H^+ ions to the fluid, causing the ratio of $a_{\text{Mg}^{2+}}/(a_{\text{H}^+})^2$ and the pH to decrease, which results in the fluid chemistry moving into the diamond stability field in Fig. 1a.

In the later stages of reaction progress ($-0.30 < \log \xi < +0.1$), the fluid is directly altering primary eclogitic clinopyroxene to secondary garnet with an increasing pyrope component (Fig. 1c) according to the reaction



These reactions remove the Mg^{2+} ion and add H^+ ions to the fluid, again causing the ratio of $a_{\text{Mg}^{2+}}/(a_{\text{H}^+})^2$ and the pH to decrease, which results in the fluid chemistry moving further into the diamond stability field in Fig. 1a.

Aqueous organic carbon species during diamond formation.

The overall decrease in the pH of the fluid seen in Fig. 2a also causes changes in the most abundant carbon species in the fluid (Fig. 2b): the concentration of the aqueous species $\text{CO}_{2,\text{aq}}$ increases by 623 mmolal, which is mainly balanced by decreases in the concentrations of the $\text{Ca}(\text{HCO}_3)^+$ complex, HCO_3^- and CO_3^{2-} (-300 , -75 and -62 mmolal, respectively) plus a decrease of about -160 mmolal of C from organic carbon species (Supplementary Table S1). However, it can be seen in Fig. 2c that the trend of the number of moles of carbon precipitated as

Table 1 | Comparison of the predicted final fluid composition after reaction with eclogite at 900 °C and 5.0 GPa with the measured composition of a highly siliceous fluid inclusion*.

Final model fluid	Parameter value†	Siliceous fluid inclusion*	Parameter value†
Na	0.94	Na	0.84
K	1.69	K	1.69
Mg	0.24	Mg	0.78
Ca	3.07	Ca	1.62
Fe	0.14	Fe	0.87
Al	0.68	Al	1.0
Si	5.18	Si	5.2
Cl	0.10	Cl	0.7
S	0.18		
C	33.7		
pH	4.74		
$\log f_{\text{O}_2}$	-9.60		
Mole ratio of C/(C + H ₂ O)	0.4	Mole ratio of C/(C + H ₂ O)	0.1‡
wt.% H ₂ O in fluid	32	wt.% H ₂ O in fluid	Up to 40‡
wt.% CO ₂ in fluid	47	wt.% CO ₂ in fluid	Up to 11§

*Ref. 55, inclusion number Sp.BR-1(inner) normalized to the K content of the model eclogitic fluid given above (1.69 m).

†Concentrations given in molality (m) unless otherwise noted.

‡Ref. 6.

§Calculated from the given mole ratio of C/(C + H₂O) equal to 0.1 and the given upper limit of the wt.% H₂O in fluid equal to 40%.

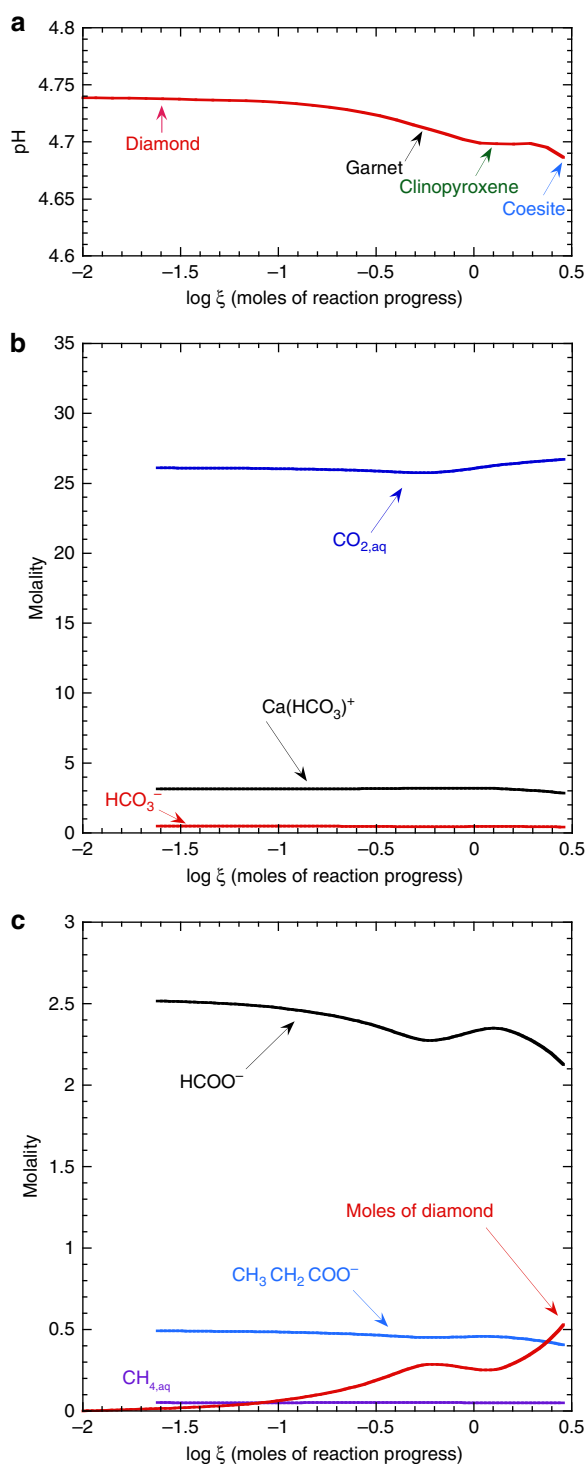
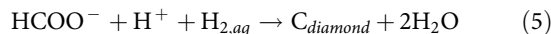


Figure 2 | Predicted aqueous phase evolution during fluid-rock interactions forming diamond. (a) Evolution of the pH of the fluid during reaction with eclogite. (b) Evolution of the concentrations of the major inorganic oxidized carbon species. (c) Number of moles of diamond precipitated per kg of water compared with the evolution of the concentrations of the major aqueous organic carbon species. In **a,b,c**, the x axis represents the logarithm of the reaction progress variable ξ , which is equal to the number of moles of each reactant mineral destroyed during the reaction progress. All calculations refer to 900 °C and 5.0 GPa.

diamond is closely mirrored by the changes in the organic carbon species formate. In fact, a total of 529 mmol of carbon is precipitated as diamond, which comes from the destruction of

405 mmol formate and 264 mmol carbon from propionate, according to the reactions:



(as noted above, the small excess of organic carbon destroyed compared with diamond precipitated was converted to CO_2 and $\text{Ca}(\text{HCO}_3)^+$). Although each of the reactions in equations (5) and (6) are redox reactions, the sum of these reactions is independent of the dissolved $\text{H}_{2,\text{aq}}$ concentration and therefore of the f_{O_2} . Consequently, the overall reaction precipitating diamond is independent of f_{O_2} , and the f_{O_2} barely changes during the calculated reaction path in Fig. 1a.

Discussion

Diamond precipitation in Fig. 1a,b is driven by pH drop and not by changes in redox conditions. The formation of diamond is a direct consequence of changes in aqueous fluid chemistry associated with metasomatic reactions involving silicate minerals under upper mantle conditions. Furthermore, in the same reacting chemical system, diamond dissolution can be driven by changes in fluid chemistry at almost constant redox states. For example, it can be seen in Figs 1b and 2c that diamond is predicted to partially dissolve during the interval of $(-0.25 < \log \xi < +0.1)$ because of small fluctuations in solution chemistry associated with the disappearance of the Mg-rich carbonate solid solution. This predicted behaviour may mirror the often noted precipitation and dissolution features in natural diamonds¹.

It is also interesting that the precipitation reactions for diamond in Figs 1 and 2 involved aqueous organic carbon species, not just the CO_2 or CH_4 previously pictured as the only possible sources of carbon for diamond formation. The involvement of aqueous organic species in our model arises, because it is predicted that at pressures above ~ 3.0 GPa it is possible to have a complete equilibrium between all oxidation states of aqueous carbon species²⁹. The proposed involvement of these organic carbon species in the formation of diamond has implications for the carbon isotopic composition of diamond^{29–35}. For example, it can be expected that the carbon isotopic compositions of diamonds in equilibrium with an aqueous fluid will be a function of both pH and redox state. A change in either pH or redox state could, in principle, cause changes in the carbon isotopic composition of diamond, depending on the magnitude of the equilibrium fractionation factor between diamond and aqueous C-species. This inference is exactly analogous to that predicted for graphite under crustal hydrothermal conditions³⁶. To date, most studies of the carbon isotopic compositions of diamonds invoke redox fluctuations³. However, in at least one instance, changes in the carbon isotopic composition of diamond have been suggested to be independent of redox changes³⁷. The potential for a dependence on pH changes offers an alternate hypothesis that might be testable with experiments. Similar considerations involving a potential dependence on either redox state or pH variations during metasomatic reactions may apply to the large variability exhibited in the nitrogen isotopic compositions of individual diamonds³⁸.

The predicted model evolution of the fluid chemistry during the precipitation of diamond is shown in Fig. 3 for comparison with worldwide trends in the chemistry of fluid inclusions in diamonds. The initial fluid chemistry is Ca-rich and Si-poor but progressively changes towards a silica-rich composition. After equilibration with the reactant eclogitic minerals, the final fluid chemistry (Supplementary Table 2) is extremely enriched in Al and Si, and depleted in Ca relative to the initial fluid. It can be

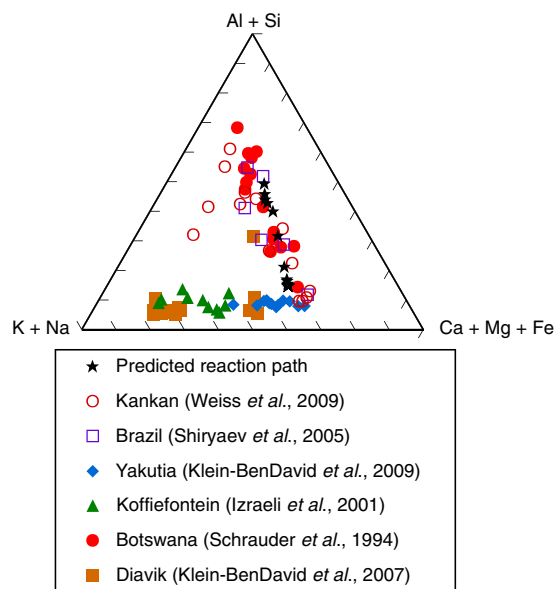


Figure 3 | Predicted versus measured fluid chemistry during diamond formation. Theoretical evolution of the fluid chemistry from the model in Figs 1 and 2 (black stars). Measured compositions of fluid inclusions from worldwide diamonds^{6,39,55–58} (coloured symbols). The predicted fluid composition evolves from a carbonatitic end-member fluid towards the silicic end member of fluid composition from natural diamonds.

seen in Fig. 3 that these changes are qualitatively consistent with one of the major trends in the chemistry of fluid inclusions in diamonds that extends from a carbonatitic fluid to a silicic fluid⁶. This trend has previously been suggested to be the result of equilibration with eclogites³⁹. As a first step, given our current limited information about element solubility and speciation in high-pressure fluids, this approximation shows a reasonable agreement between predicted and actual fluid compositions.

Significant differences, however, are apparent when a more detailed comparison of individual elemental concentrations is made. For example, in Table 1 a more detailed comparison of the final eclogitic fluid composition from the model (Fig. 2) is made with the composition of a silicic fluid inclusion from a diamond from Brazil. To facilitate the comparison of elemental values, the fluid inclusion analysis was normalized to the molality of K in the predicted eclogitic model fluid. Excellent agreement can be seen between the concentrations of Si, Al and Na. However, the predicted model concentrations of Mg, Ca and Fe are either too high or too low by factors of 3.3, 1.9 and 6, respectively. This could be due to inaccurate speciation of these elements in the fluid model, for which we need more experimental data. The most significant difference that can be seen in Table 1 is that the wt.% CO₂ is much higher in the model fluid (47%) than has been derived for the natural fluid inclusions (11%). A possible cause of this discrepancy might be the simplistic assumption of a unit activity coefficient for the aqueous CO₂ species in the model. Finally, it should be emphasized that the calculations plotted in Fig. 3 refer only to 900 °C and 5.0 GPa, whereas the fluid inclusion compositions of the natural diamonds plotted in Fig. 3 probably refer to a very wide range of temperatures, pressures and geologic environments¹³. Nevertheless, the overall comparison is encouraging. The model fluid speciation presented here is only a first step in modelling the chemistry of the evolution of fluids during diamond formation. Much more experimental and theoretical work needs to be done, to characterize the most important fluid species under such extreme conditions.

Our theoretical calculations provide a model clearly demonstrating that diamond can form by pH decreases during water–rock interaction under constant redox conditions in subcratonic lithospheric mantle environments. The theory implies that diamonds and their solid and fluid inclusions could be the natural, and perhaps even the common result of changes in water chemistry rather than redox changes alone. We wish to emphasize that our proposed pH-change mechanism for diamond formation represents a mechanism in addition to potential changes in redox, temperature and pressure². Indeed, combined pH decreases and f_{O_2} increases could result in multiple cycles of diamond precipitation and dissolution, which might explain some observed diamond resorption features¹ as well as the evidence for evolving fluid chemistry during individual diamond formation⁴⁰.

The theoretical model developed here could also be used to investigate subcratonic lithospheric diamond formation in peridotites. Furthermore, the model could be expanded to include more sophisticated models of solid solution in the minerals, the partitioning of trace elements between the minerals and fluids, a much wider range of aqueous organic species, and liquid and crystalline hydrocarbons. It would then be possible to integrate quantitative theoretical models of evolving fluid chemistry with detailed studies of natural diamonds including their solid and fluid inclusions, their trends with time during diamond growth and their relationships to host eclogites and peridotites^{7–9,27,41,42}. Ultimately, such integrated studies hold the potential for helping to unravel specific reaction histories of fluids in the deep Earth and in deep time. The theoretical model could also be used to predict the cooling behaviour of individual fluid inclusions to room temperature, including the formation of daughter crystals, enabling independent comparisons to be made with the extensive studies of fluid inclusion and their daughter crystals^{5,10}.

Methods

Conceptual model of diamond formation. Diamond formation occurs particularly in the roots of continents known as mantle keels that extend from about 40 to 250 km depth. In this subcratonic mantle lithosphere environment, diamonds have formed at temperatures in the range of 900–1,400 °C and pressures of about 4.0–8.0 GPa (ref. 13). Diamonds are also described from ultra-high pressure metamorphic rocks referring to temperatures as low as 600 °C and pressures of >3 GPa (ref. 13). In the present study a model was constructed for subcratonic lithospheric mantle diamond formation in eclogite at 900 °C and 5.0 GPa. Although this temperature is at the low end of the range of recorded temperatures for subcratonic mantle diamond formation, the reactions described here should also apply to higher temperatures. It should be emphasized that the model is a generic one for the purpose of illustrating the role of pH in diamond-forming systems in which the fluid chemistry is coupled to the silicate rock mineralogy of eclogites.

The initial fluid was derived by reaction of fluids assumed to be low in chloride with a carbonated peridotitic mineral assemblage envisioned as passing through the carbonated mafic part of a subducting slab²⁴. As a first approximation, the fluid was assumed to have moved through the slab at constant temperature and pressure, to infiltrate and react with a model metasedimentary eclogite consisting of clinopyroxene, garnet and coesite also based on previous model calculations²⁶. Ideal site mixing was used for the silicate solid solution model.

Calculation methods. The calculations referred to in Figs 1–3 were carried out with versions of the Fortran computer codes EQ3NR and EQ6 (refs 22,23) modified for use at elevated pressures and temperatures. The code EQ3NR is used to set up a speciated initial fluid chemistry in equilibrium with a specified set of minerals that represents a model of a rock as described above. This fluid is then used in the code EQ6, to react with eclogitic minerals as described above. The irreversible mass transfer calculations were carried out assuming relative reaction rates of unity with excess amounts of each reactant mineral. In this mode of calculation, if the fluid reaches equilibrium with a given reactant mineral, it is subsequently assumed that the mineral remains in equilibrium with the fluid, although some of it may dissolve or precipitate during further reaction progress.

The two codes use a database of equilibrium constants calculated in advance using the DEW model¹⁸. The DEW model is based on an extension of the Helgeson–Kirkham–Flowers aqueous species equation of state, traditionally limited to an upper pressure of 0.5 GPa because of lack of knowledge of the dielectric

constant of water at high pressures^{43,44}. We have taken advantage of recent experimental and theoretical advances^{19,20} that enable this limitation to be overcome and we have further shown that the Helgeson–Kirkham–Flowers formalism can be applied to experimental solubility and aqueous speciation data for quartz, forsterite + enstatite, corundum, calcite and aragonite at pressures up to 6.0 GPa, enabling theoretical predictions of equilibrium constants involving aqueous inorganic and organic ions, neutral species and metal complexes up to pressures and temperatures of the upper mantle. Overall uncertainties in the DEW model may be of the order of ± 0.3 to 0.5 units in equilibrium constants for aqueous species at high temperatures and pressures. It should be emphasized that all the aqueous species used in the calculations rest on experimental calibrations for as wide a range of temperatures or pressures as is available (see also below). Activity coefficients for neutral aqueous species were set to unity, whereas those for ions were approximated by the Debye–Hückel equation in which the long-range interaction parameters were calculated using dielectric constants and densities of water from the DEW model. Owing to a lack of sufficient data on mineral solubilities at elevated pressures as a function of ionic strength, the short-range interaction parameter in the Debye–Hückel equation was set to zero²¹.

Comparison of model calculations and experimental data. Remarkably, little experimental data exist for mineral and silicate-rock solubilities in aqueous fluids at elevated temperatures and at pressures > 3.0 GPa, in particular as the melting point of the rocks is approached^{45–51}. Considerable uncertainties surround the nature of the fluid phase in equilibrium with silicate rocks under these conditions. In the present study, we calibrated our high temperature–pressure aqueous model using experimental measurements of a synthetic K-free eclogite at 900 °C and 5.0 GPa (ref. 50). The high solubilities of the elements Si, Mg, Fe and Al in these experiments almost certainly reflect complexes between metals and silicate as the temperatures approach the melting point of the eclogite^{51,52}. Although the exact nature of these complexes remains uncertain and is the topic of intense interest^{49,53,54}, as a first approximation we assumed they were 1:1 metal–bisilicate complexes, for example, $\text{Mg}(\text{HSiO}_3)^+$, because of the predicted abundance of the bisilicate anion HSiO_3^- at high pressures²⁹. Based on equilibrium constants calculated using the DEW model, the experimental eclogite solubility data were used to retrieve new equilibrium constants for the dissociation of the aqueous silica monomer to the bisilicate anion, and the bisilicate complexes of Mg, Fe, Ca and Al (Supplementary Table 1). Comparison between the experimental and calculated fluid composition is shown in Supplementary Fig. 1. Given the overall uncertainties in the experiments and the calculations, the agreement in Supplementary Fig. 1 was deemed to be sufficiently good for the application of the present study to diamond formation. Sensitivity calculations with and without metal–silicate complexes emphasized that the overall conclusion of the present study regarding the importance of a pH drop causing diamond formation did not depend on either the precise values of the equilibrium constants or even the existence of the metal–silicate complexes in the model. This is a consequence of the fundamental importance of reactions such as the one given in Eqn. (4) in controlling the pH of the fluids.

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Author contributions

D.A.S. initiated the project, carried out the calculations for Fig. 1 and wrote the manuscript; F.H. prepared Fig. 2a, contributed to the characterization of the thermodynamic data underlying the modelling and participated in discussion of the modelling.

Additional information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

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