

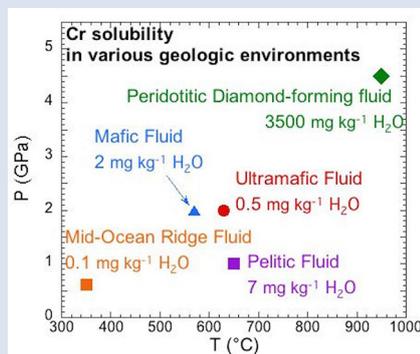
# Mobility of chromium in high temperature crustal and upper mantle fluids

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## Abstract



Chromium is mobile in ultramafic magmas but its mobility in high temperature fluids has long been unclear. Studies of some chromium-rich ophiolites have suggested chromium mobility in upper mantle fluids. However, the mechanism is poorly understood because Cr(III) is so insoluble in water. We used previous estimates of aqueous Cr species and published experimental and *ab initio* studies of the solubility of Cr<sub>2</sub>O<sub>3</sub> in HCl and KCl fluids at 500–1200 °C and 0.1–6.0 GPa together with the Deep Earth Water Model to calibrate a thermodynamic equation of state for the Cr(II) complex CrCl(OH)<sup>0</sup>. Our model predicted low Cr solubilities (0.1 mg kg<sup>-1</sup> H<sub>2</sub>O) in a mid-ocean ridge fluid and very high solubilities (3500 mg kg<sup>-1</sup> H<sub>2</sub>O) in saline, peridotitic diamond-forming fluid consistent with expectations for these environments. In pelitic, mafic eclogitic, and serpentinite fluids, predicted Cr solubilities varied widely depending on the oxygen fugacity and Cl concentration. The predicted predominance of Cr(II) in deep fluids and Cr(III) in minerals suggests that precipitation of Cr mineral components is a redox reaction.

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## Introduction

Chromium is a mobile element in ultramafic or mafic magmas but its mobility in high temperature fluids has long been unclear. Recent studies of chromium-rich geological settings have suggested that chromium could be mobile in deep crustal and upper mantle fluids. For example, fluid inclusions in chromite from New Caledonia (Johan *et al.*, 2017) and in diopsidites and anorthosites associated with chromite and uvarovite from Oman (Akizawa *et al.*, 2016) suggest the mobility of Cr in hydrothermal fluids at temperatures of about 500 to 800 °C. In addition, garnet inclusions in peridotitic diamonds are characteristically Cr-rich (Stachel and Harris, 2008), suggesting that Cr could be involved in the metasomatic processes of diamond formation under sub-solidus conditions. However, aqueous Cr<sup>3+</sup> is highly insoluble in water at near neutral pH (Rai *et al.*, 1987; Saleh *et al.*, 1989; Ziemniak *et al.*, 1998; Sander and Koschinsky, 2000), so a mechanism for Cr mobility has remained mysterious.

One potential mechanism for Cr solubility at high temperatures is the likelihood of an aqueous Cr(II) oxidation state (Fig. 1a,b). Many metals exhibit the tendency for a lower oxidation state in aqueous solution at elevated temperatures, *e.g.*, aqueous Cu<sup>+</sup> *vs.* Cu<sup>2+</sup> (Mei *et al.*, 2013), Fe<sup>2+</sup> *vs.* Fe<sup>3+</sup> (Testemale *et al.*, 2009), and Eu<sup>2+</sup> *vs.* Eu<sup>3+</sup> (Sverjensky, 1984).

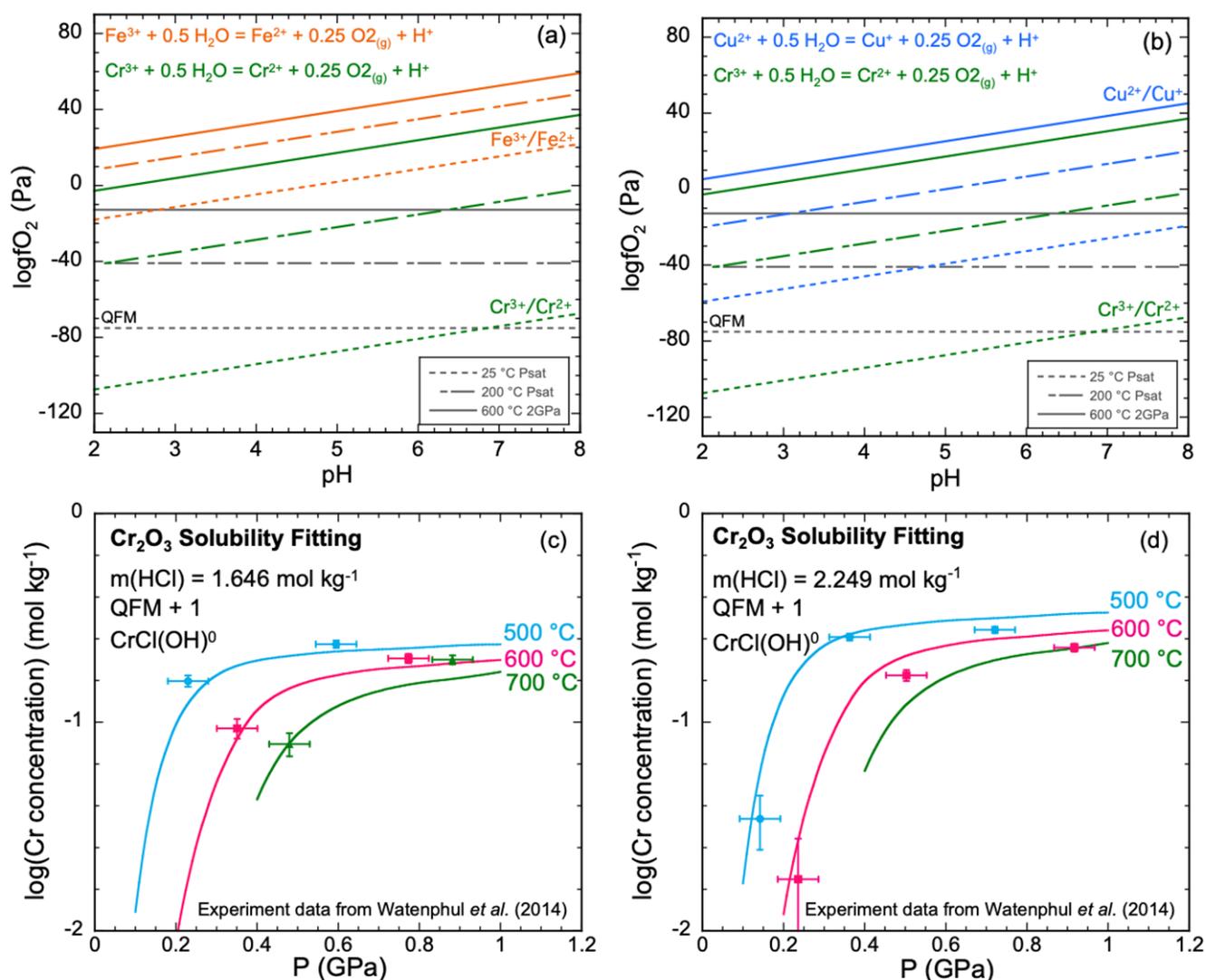
To investigate the potential mobility of Cr(II) and Cr(III) in deep fluids, we predicted the solubility of Cr oxide minerals by updating previous estimates of aqueous Cr species (Shock *et al.*, 1997; Hao, 2016) in the Deep Earth Water (DEW) model (Sverjensky *et al.*, 2014). We then regressed experimental solubility data for Cr<sub>2</sub>O<sub>3</sub> to characterise a proposed new Cr(II) complex CrCl(OH)<sup>0</sup> and obtain a predictive model for Cr solubility. Our model was applied to a wide range of geological settings: mid-ocean ridges (MOR), subduction zones and the subcontinental lithospheric mantle environment of diamond formation. Models and calculation methods are given in the Supplementary Information (SI).

## Results

**Analysis of solubilities in solutions.** We used published solubilities of Cr<sub>2</sub>O<sub>3</sub> in HCl-rich fluids containing 1.646 mol kg<sup>-1</sup> and 2.249 mol kg<sup>-1</sup> HCl from 500–700 °C and 0.1–1.0 GPa (Watenphul *et al.*, 2014) to test the predicted properties of aqueous Cr species. The thermodynamic properties of eskolaite (Cr<sub>2</sub>O<sub>3</sub>) and picrochromite (MgCr<sub>2</sub>O<sub>4</sub>) were obtained from published experimental data (SI). The data points in Figure 1c,d represent the logarithms of measured Cr concentration *vs.* pressure. Cr concentrations at 400 °C were not considered in our analysis because the reactions may not have reached

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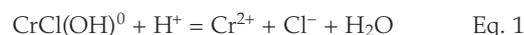
**Figure 1** (a, b) Effect of temperature and pressure on the valence state of ions at 25 °C and Psat (dashed lines), 200 °C and Psat (dotted dashed lines) and 600 °C and 2.0 GPa (solid lines). Horizontal lines represent the QFM buffer (black): (a)  $\text{Fe}^{3+}/\text{Fe}^{2+}$  (orange) and  $\text{Cr}^{3+}/\text{Cr}^{2+}$  (green) (b)  $\text{Cu}^{2+}/\text{Cu}^+$  (blue) and  $\text{Cr}^{3+}/\text{Cr}^{2+}$  (green). (c, d) Experimental  $\text{Cr}_2\text{O}_3$  solubilities in HCl-rich fluids at 500–700 °C and 0.1–1.0 GPa. (c)  $\text{HCl} = 1.646 \text{ mol kg}^{-1}$ . (d)  $\text{HCl} = 2.249 \text{ mol kg}^{-1}$ . Solid curves are fitted to the experimental data at QFM + 1.

equilibrium (Watenphul *et al.*, 2014). The horizontal error bar is the random error of pressure ( $\pm 0.05 \text{ GPa}$ ). The vertical error bar is the standard error of the Cr concentration ( $0.01 \text{ mol kg}^{-1}$ ) calculated from the minimum detection limit of Cr (Watenphul *et al.*, 2014).

Our preliminary solubility model considered the previously estimated properties of aqueous Cr(II), (III), and (VI) species (Table S-3; Shock *et al.*, 1997; Hao, 2016). This model resulted in predicted solubilities much lower than measured. For example, at 600 °C, 1.0 GPa and  $2.249 \text{ mol kg}^{-1}$  solution, the predicted Cr concentration was  $87.5 \text{ mmol kg}^{-1}$ , about 2.6 times lower than the measured result at a similar pressure ( $228 \text{ mmol kg}^{-1}$  at 0.917 GPa) (Table S-2b). Even larger discrepancies would be obtained in the KCl solutions at high pressures to be discussed below. The predominant oxidation state of the aqueous Cr was overwhelmingly +II at an oxidation state of QFM + 1 as expected by comparison with other metals. Despite the uncertainties in our overall approach, these results suggest that an additional Cr complex, probably of Cr(II), is needed to explain the high measured Cr solubilities.

The apparent importance of aqueous Cr(II) species raises the concern that there was no measurement of the oxygen fugacities for the experiments shown in Figure 1c,d.

However, Watenphul *et al.* (2014) suggested that the experiments reflected oxidation states about 1.0 log unit above the QFM buffer. Under these conditions, we found that Cr(II) was the predominant valence. A second concern is the lack of experimental data for Cr speciation. However, based on *ab initio* simulations, Watenphul *et al.* (2014) suggested mixed Cr complexes with Cl, OH<sup>-</sup>, and/or H<sub>2</sub>O. After repeated trials of complexes such as  $\text{CrCl}^+$ ,  $\text{Cr}(\text{OH})^+$  and  $\text{CrCl}(\text{OH})_2^0$ , we found a satisfactory fit to the experimental data using the mixed complex  $\text{CrCl}(\text{OH})^0$ . This complex may also have H<sub>2</sub>O coordinated to the Cr, but we cannot determine how many with the available experimental data. Therefore, we have omitted writing them. The curves in Figure 1c,d show our best fit to the experimental data at both low and high HCl concentrations. These calculations enabled us to retrieve the log K of the dissociation reaction of  $\text{CrCl}(\text{OH})^0$  according to



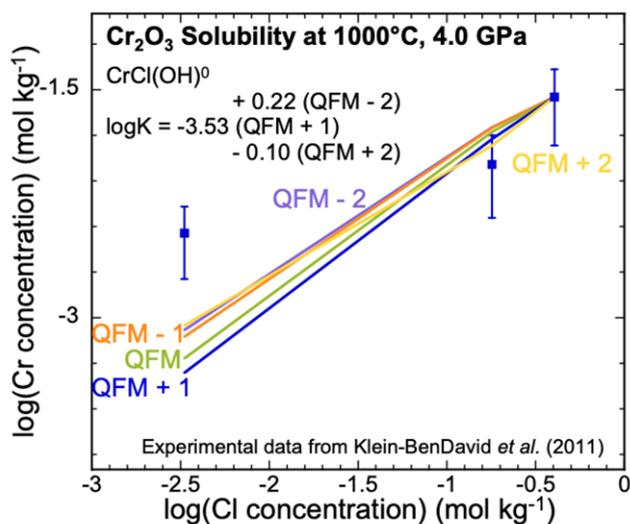
The retrieved log K values have an uncertainty of  $\pm 0.3$  units (Table S-2a). It should be noted that retrieval of the equilibrium constant for Equation 1 was carried out with simultaneous consideration of the other aqueous Cr species mentioned above as well as species such as HCl and OH<sup>-</sup> (SI). Because  $\text{CrCl}(\text{OH})^0$

was by far the predominant Cr species in the solubility model, the overall solubility reaction studied experimentally can be approximated by the reaction



which is a redox reaction that depends on the  $\log f\text{O}_2$  used in the calculations.

**Analysis of  $\text{Cr}_2\text{O}_3$  solubilities in KCl solutions.** The only experimental data for Cr solubility at upper mantle conditions (Klein-BenDavid *et al.*, 2011) refer to the solubility of  $\text{Cr}_2\text{O}_3$  at three KCl concentrations using the diamond trap method at 1000, 1200 °C and 4.0, 6.0 GPa. The solubilities varied with KCl concentration but did not vary significantly with temperature and pressure. Therefore, at each KCl concentration, we averaged the measurements at the different temperatures and pressures. We found that the complex  $\text{CrCl}(\text{OH})^0$  could be fitted to the data at the two highest concentrations. The data points in Figure 2 represent the experimental Cr concentrations with a standard deviation as a vertical error bar. The scatter in the experimental data precludes fitting all three data points with a single complex. However, we do not have sufficient data to justify using more than one complex. We therefore calibrated our  $\text{CrCl}(\text{OH})^0$  complex at the highest Cl concentration (Fig. 2). As a result, our predicted curve lies between the mid-KCl and low-KCl data points. The oxygen fugacity was again not controlled or measured in the experiments but was suggested to lie near to the QFM buffer. To test the sensitivity of our model calculations to the oxygen fugacity, we carried out calculations over a range of  $\log f\text{O}_2$  from QFM - 2 to QFM + 2 (Fig. 2). We subsequently used the equilibrium constant for the complex  $\text{CrCl}(\text{OH})^0$  referring to QFM + 1 for comparison with the equilibrium constants retrieved from the solubility data in Figure 1c,d. The corresponding log K values have an uncertainty of  $\pm 0.3$  units (SI).

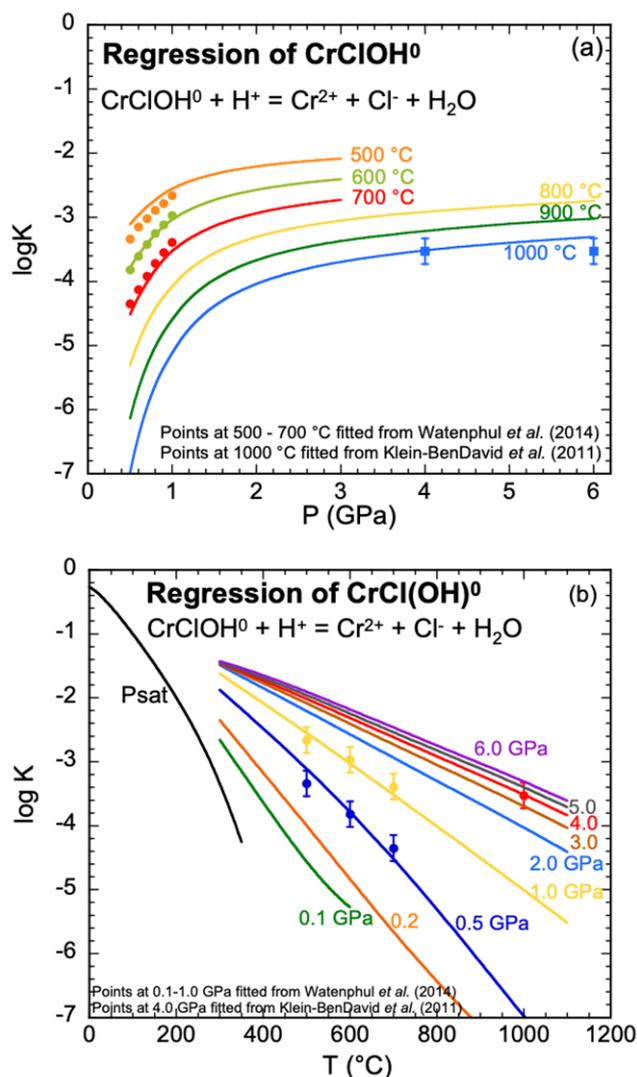


**Figure 2** Experimental  $\text{Cr}_2\text{O}_3$  solubilities in KCl fluids at 1000 °C and 4.0 GPa. Curves were fit to the highest two KCl points from QFM - 2 to QFM + 2.

**Equation of state for  $\text{CrCl}(\text{OH})^0$ .** Assuming  $\text{CrCl}(\text{OH})^0$  was the main Cr species in both the HCl and KCl experimental fluids, we combined the values of log K retrieved from the solubility of  $\text{Cr}_2\text{O}_3$  in HCl and KCl fluids. For the HCl experiments, each log K value shown in Figure 3 represented a fit to the trend of experimental solubilities with pressure in Figure 1 (Table S-2a). The curves in Figure 3 represent regression using the DEW model. Estimated uncertainties are on the order of  $\pm 0.3$  log units. It can be seen in Figure 3a that, as expected,

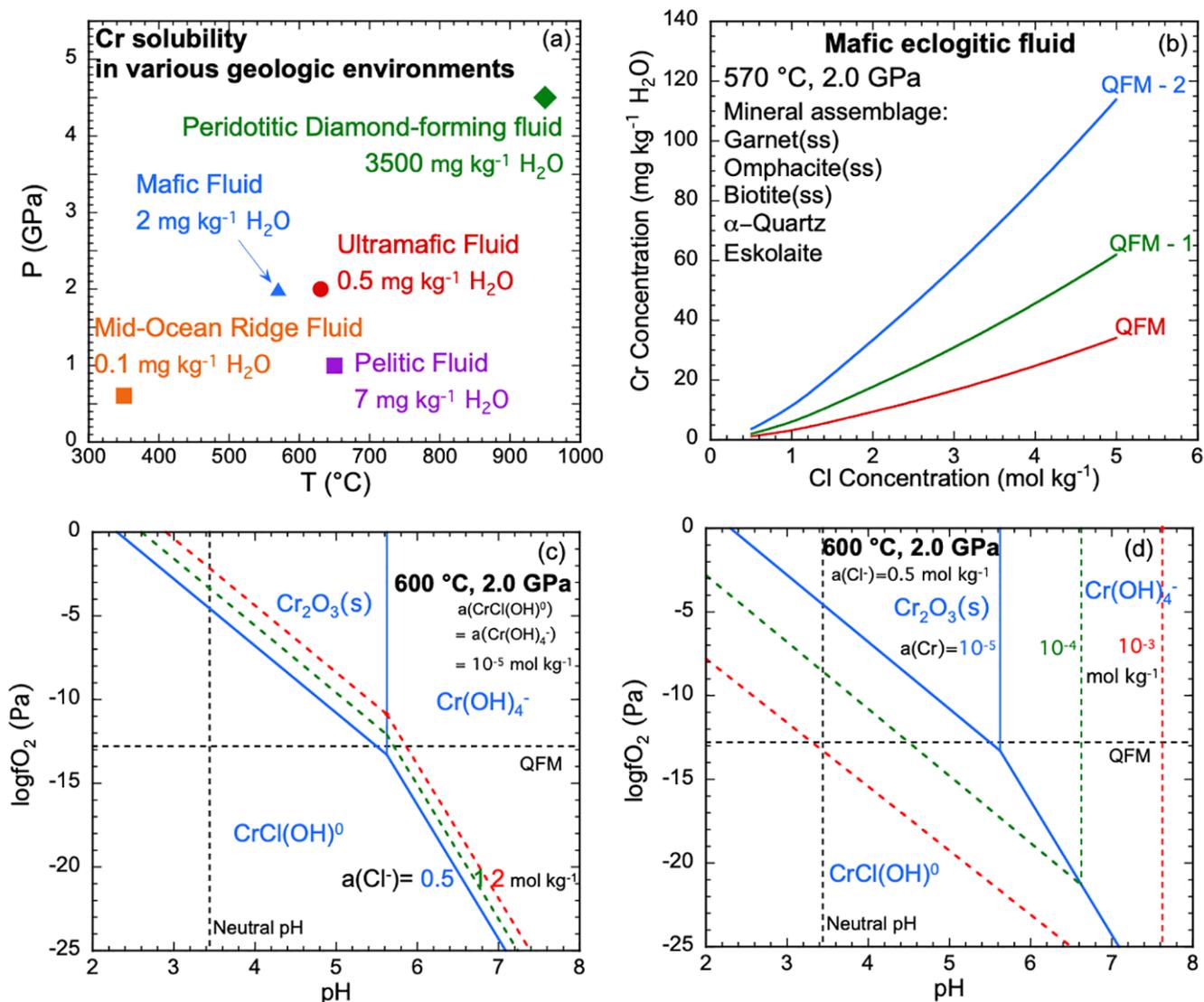
the  $\text{CrCl}(\text{OH})^0$  complex becomes stronger with increasing temperature and decreasing pressure, but the influence of pressure diminishes above about 2.0 GPa.

Although the curves agree within the estimated uncertainties with the experimentally calibrated log K values, it should be emphasised that the present characterisation is just a first approximation because no experimentally calibrated log K values are known below 500 °C. Nevertheless, the results serve as a valuable bridge between experiments involving  $\text{Cr}_2\text{O}_3$  in chemically simple but different systems, *i.e.* HCl and KCl solutions, and enable extrapolation over a wide range of temperatures and pressures as shown in Figure 3b and Table S-4. We tested our model by applying it to the geochemically more complex systems of interest discussed below, some of which occur at temperatures and pressures well outside the range of calibration of the model.



**Figure 3** Regression of log K for  $\text{CrCl}(\text{OH})^0$  for dissociation reaction versus (a) pressure and (b) temperature up to 6.0 GPa and 1100 °C.

**Predictions of Cr solubility in crustal hydrothermal and upper mantle fluids.** In order to test the model, we used a range of different mineral assemblages (Table S-5) to constrain aqueous speciation and solubility model predictions of the fluid chemistry. The results (Table S-6) are not sensitive to the amounts of minerals but are sensitive to temperature, pressure and Cl concentration as discussed below. Figure 4a displays the predicted Cr solubility in five model fluids over a range of



**Figure 4** Prediction of Cr solubility in model fluids. (a) MOR, subduction zone, and diamond-forming fluids. (b) mafic eclogitic fluid at 570 °C and 2.0 GPa, Cr concentration versus Cl at QFM (red), QFM - 1 (green) and QFM - 2 (blue). Effects of Cl concentration and activity of Cr species on the solubility of Cr<sub>2</sub>O<sub>3</sub>(s) and Cr speciation at 600 °C and 2.0 GPa: (c) a(Cl<sup>-</sup>) = 0.5 (solid blue), 1 (dashed green) and 2 (dashed red) mol kg<sup>-1</sup>, assuming a(CrCl(OH)<sup>0</sup>) = a(Cr(OH)<sub>4</sub><sup>-</sup>) = 10<sup>-5</sup> mol kg<sup>-1</sup>. (d) a(CrCl(OH)<sup>0</sup>) = a(Cr(OH)<sub>4</sub><sup>-</sup>) = 10<sup>-5</sup> (solid blue), 10<sup>-4</sup> (dashed green), 10<sup>-3</sup> (dashed red) mol kg<sup>-1</sup>, when a(Cl<sup>-</sup>) = 0.5 mol kg<sup>-1</sup>.

conditions: a crustal MOR fluid, pelitic, mafic, and ultramafic subduction zone fluids, and a peridotitic, diamond-forming fluid (Tomlinson *et al.*, 2006; Huang, 2017). The Cl concentrations are 0.5 mol kg<sup>-1</sup>, except in the peridotitic fluid where it is 8.0 mol kg<sup>-1</sup> (Huang, 2017). The ultramafic subduction zone fluid and the peridotitic fluid are in equilibrium with picrochromite, while the others are in equilibrium with eskolaite. Because these are pure minerals, the predicted solubilities are maxima. The predicted range of Cr solubilities is enormous: from 0.15 mg kg<sup>-1</sup> H<sub>2</sub>O in the MOR fluid to 3500 mg kg<sup>-1</sup> H<sub>2</sub>O in the peridotitic fluid. In all the models, CrCl(OH)<sup>0</sup> is the major Cr species.

## Discussion

**Crustal mid-ocean ridge (MOR) hydrothermal fluid.** Prediction of the Cr content of MOR fluids is an important test of our model because the temperatures are much lower than in the experiments used to calibrate the model (Fig. 4a). At 350 °C and P<sub>sat</sub> (0.017 GPa), the MOR fluid in Figure 4a is predicted to contain only 0.1 mg kg<sup>-1</sup> H<sub>2</sub>O of Cr. The low predicted value is

consistent with observations by Sander and Koschinsky (2000) who suggested that Cr was about 1200 nM (0.062 mg kg<sup>-1</sup>) in their hydrothermal fluids. One difference from our prediction is that Sander and Koschinsky (2000) further suggested that hydrothermal Cr was predominantly Cr(III). However, the Cr(III) concentration was not measured directly. Instead, it was obtained from the difference between the total Cr and the Cr(VI) concentrations at ambient temperatures and pressures where Cr(III) is expected to predominate.

**Subduction zone fluids.** In the subduction zone fluids, the predicted Cr concentrations are 0.5, 2, and 7 mg kg<sup>-1</sup> H<sub>2</sub>O in ultramafic, mafic, and pelitic fluids, respectively. Although much higher than in the MOR fluid, Cr is still a trace element at these higher temperatures (570–650 °C) and pressures (1.0–2.0 GPa). The model ultramafic fluid has the lowest Cr because the fluid is at QFM + 2, buffered by magnetite, antigorite and chlorite (Debret and Sverjensky, 2017). The pelitic schist fluid has a higher Cr than the mafic eclogitic fluid, because the major Cr species CrCl(OH)<sup>0</sup> favours high temperature and low pressure. The strongest influences on Cr solubility are oxygen fugacity and Cl concentration.

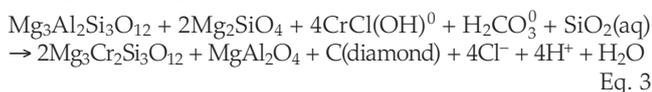


### Upper mantle peridotitic diamond-forming fluids.

Cr in the peridotitic diamond-forming fluid is three orders of magnitude higher than in the other fluids. There are two reasons for this. First, the diamond-forming fluid contained 8.0 mol kg<sup>-1</sup> Cl, much higher than in the other fluids. Second, the oxygen fugacity was low (QFM - 4). Although Cr was not detected in fluid inclusion studies of the Panda diamonds (Tomlinson *et al.*, 2006), our prediction of 3500 mg kg<sup>-1</sup> H<sub>2</sub>O of Cr is reasonable because it is below the detection limit of about 4000 mg kg<sup>-1</sup> (Tomlinson, pers. comm.).

A comparison can also be made with an experimental study of the solubility of a mafic eclogite in Cl-free fluids (Elazar *et al.*, 2019). Chromium concentrations measured at 4.0–5.0 GPa and 900–1200 °C were 17–96 mg kg<sup>-1</sup> H<sub>2</sub>O. Our predicted Cr concentration is about 20 mg kg<sup>-1</sup> H<sub>2</sub>O with only Cr-OH complexes at 950 °C and 4.5 GPa, which is consistent with the experiments.

As already noted, Equation 2 shows that equilibrium between a Cr(III) mineral component and aqueous Cr(II) in a high temperature fluid is a redox reaction. Consequently, precipitation of a Cr(III) mineral component will also be a redox reaction. In the peridotitic, diamond-forming environment, garnet inclusions contain 3–20 wt. % Cr<sub>2</sub>O<sub>3</sub> (Stachel and Harris, 2008). A possible redox reaction that could account for such garnets might be



where H<sub>2</sub>CO<sub>3</sub><sup>0</sup> is reduced to C (diamond) while Cr(II) is oxidised to Cr(III).

**Can Cr be more soluble in subduction zone fluids?** To investigate further the factors influencing Cr solubility, Figure 4b presents the predicted Cr concentrations at 570 °C and 2.0 GPa in the mafic fluid as a function of Cl concentration and oxygen fugacity. At QFM and with Cl increasing from 0.5 mol kg<sup>-1</sup> to 5.0 mol kg<sup>-1</sup>, the Cr solubility increases up to 34 mg kg<sup>-1</sup> H<sub>2</sub>O, about a 30-fold increase. The increase at QFM - 2 with Cl is even more dramatic. These results suggest that mafic fluids could transport large concentrations of Cr at Cl-rich or reducing conditions. Such concentrations of Cr are consistent with a metasomatic origin for the occurrence of Cr-rich pyroxene in eclogitic veins in a metagabbro complex (Spandler *et al.*, 2011).

In the mafic eclogitic fluid, we tested the Cr solubility with no Cl and found a Cr solubility of 0.06 mg kg<sup>-1</sup> H<sub>2</sub>O, much lower than the original prediction when Cl was 0.5 mol kg<sup>-1</sup>. The major Cr species is Cr(OH)<sub>4</sub><sup>-</sup>. Therefore, we explored the effect of Cl concentration and activity of CrCl(OH)<sup>0</sup> and Cr(OH)<sub>4</sub><sup>-</sup> on Cr<sub>2</sub>O<sub>3</sub> dissolution, presented in Figure 4c,d as diagrams of log*f*O<sub>2</sub> versus pH. It can be seen that the stability field of CrCl(OH)<sup>0</sup> expands with increasing Cl concentration and total Cr in the fluids. As mentioned above, elements tend to occur with lower valence state with increasing temperature. Figure 1a,b show that ions of Fe, Cu and Cr obey this trend. Although the stability field of Cr<sup>2+</sup> is very small at 25 °C and *P*<sub>sat</sub>, at 600 °C and 2.0 GPa, Cr<sup>2+</sup> is stable above QFM at most pH values.

## Conclusions

The model presented here provides a framework for assessing the mobility of Cr in deep crustal and upper mantle fluids. Predicted chromium solubilities range widely. In MOR fluids Cr is almost insoluble. However, Cr can be highly soluble in reducing, Cl-bearing, subduction zone fluids. High predicted Cr concentrations in a peridotitic, diamond-forming fluid

imply that Cr could be involved in the formation of diamond and Cr(III) garnet *via* a redox reaction. Chromium in the fluid could be oxidised and incorporated into garnet while C is reduced and precipitated as diamond. Such a redox reaction would explain the strong geologic linkage between diamonds and Cr-rich garnets.

## Acknowledgements

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## Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1926>.



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