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## DIAMOND SURVIVAL IN KIMBERLITE MAGMA: THE IMPORTANCE OF FLUID

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### INTRODUCTION

Economic significance of a kimberlite pipe determined by the content and quality of diamonds inherited from the mantle region also depends on the degree of diamond dissolution in the ascending kimberlite magma. The importance of the later process is the topic of our investigation. The most important factors contributing to diamond preservation in kimberlite magma are: crystallization temperature (T) and oxygen fugacity ( $fO_2$ ) of the magma, composition of the melt and the fluid phase, behavior of volatiles, presence of free fluid phase during the emplacement, and the ascent rate of kimberlite magma. We evaluate the importance of each of these factors by systematical examination of: 1) the experimentally derived relationship between each factor and diamond dissolution rate; 2) the range of variation of each parameter in natural kimberlites compared to its effect on diamond resorption; 3) correlation between the value of each parameter and diamond grade in natural kimberlite samples. Our earlier study (Fedortchouk et al., 2010) showed that the presence and composition of fluid plays an important role in diamond dissolution reaction. We use three independent methods to investigate magmatic fluid in several kimberlite pipes from Ekati Mine property, Northwest Territories, Canada. The work uses experiments and examination of natural samples to integrate study of surface dissolution features on diamond and other mantle minerals (chromite) as a sensitive measure of the presence of fluid with examination of hydrogen zoning and its variable attenuation in olivine macrocrysts during the kimberlite ascent. We suggest that presence of aqueous fluid in kimberlite magma may increase the ascent rate of the magma, as a result, help to better preserve the diamonds.

### FACTORS OF DIAMOND PRESERVATION

#### The effect of the intensive variables

Diamond resorption at the conditions in kimberlite magma is an oxidation reaction with the rate dependent on the temperature (T), pressure (P), and oxygen fugacity ( $fO_2$ ). Experiments show that T exponentially increases the rate of

diamond dissolution. At 1 GPa and  $fO_2$  corresponding to wustite-magnetite buffer T change from 1150 to 1250°C increases diamond dissolution rate by an order of magnitude, whereas T increase from 1250° to 1350°C increase the rate by more than three orders of magnitude (Fedortchouk et al., 2007). The kinetics of diamond dissolution below 1000°C is too slow to produce any notable difference in diamond grade even over a large range of  $fO_2$  values (Fedortchouk and Canil, 2009). High P notably suppresses the reaction of diamond dissolution (Arima and Kozai, 2008), but very limited experimental data and the absence of a geobarometers applicable to kimberlitic mineral assemblages preclude evaluation of the P effect. Estimates of crystallization T of natural kimberlites are limited to thermometry of chromite and ilmenite inclusions in the rims of olivine phenocrysts (Fedortchouk et al., 2005). Using this method, crystallization T of eight kimberlites from the Lac de Gras kimberlite field, Canada, which diamond grade varies from 0.2 to > 4 ct/tonne and the proportion of octahedron to rounded tetrahexahedron diamond forms varies from 0.5 to 6.5, ranges only between 967°C to 1140°C. Moreover, Misery kimberlite with the highest diamond grade has the highest crystallization T. Experimentally derived relationship between diamond dissolution rate, T, and  $fO_2$  (Fedortchouk and Canil, 2009) shows that the recorded T range cannot produce any notable difference in diamond grade unless  $fO_2$  differs by several orders of magnitude. According to  $fO_2$  values obtained for phenocrystal assemblage using olivine-spinel oxygen barometer, low diamond grade in kimberlite correlates with the more oxidized conditions and higher grade – with more reduced conditions for the studied pipes, and yet the maximum  $fO_2$  variation is only within one log unit of  $fO_2$  (Fedortchouk et al., 2005). At the estimated crystallization T this variation in  $fO_2$  may not be sufficient enough to make a notable effect on diamond preservation.  $fO_2$  estimates for the groundmass assemblage based on the composition of perovskite produced ten log units variation in  $fO_2$  (Canil and Bellis, 2007). However, calculations show that if the T of groundmass crystallization are <1000°C, this will not make a significant affect on the grade either. It is worth notice, that some kimberlites have similar  $fO_2$  during crystallization



of phenocrystal assemblage and groundmass, whereas others experienced serious oxidation during the groundmass crystallization (Canil and Bellis, 2007) that perhaps may be an indication of different fluid history in these magmas.

### **The effect of composition of kimberlite melt and fluid**

Certain chemical constituents on the melt, such as elements with variable valence state and alkalis, can notably affect the rate of diamond dissolution at atmospheric pressures (Rudenko et al., 1979, Kulakova et al., 1989). At elevated pressure > 1 GPa diamond dissolution rate is remarkably similar in natural Wesselton kimberlite (Arima and Kozai, 2008), in simple synthetic Ca-Mg-Si-O-H system, and in H<sub>2</sub>O-rich fluid (Fedortchouk et al., 2007). Furthermore, dissolution in fluids with variable ratio H<sub>2</sub>O: CO<sub>2</sub> while produces different secondary morphologies does not notably affect the rate of the reaction at elevated pressures. Examination of bulk rock composition of natural kimberlites did not find any strong evidence of the effect of magma composition on diamond preservation or geology of kimberlite (Berg and Carlson, 1998). The effect of melt composition on diamond dissolution rate was not systematically studied at P and T of kimberlite crystallization and therefore is not well understood. It is possible that elevated concentrations of certain elements can influence the reaction rate of diamond dissolution, but if these critical concentrations are within the limits of natural magmas still has to be determined.

### **The effect of fluid phase and emplacement rate**

Experiments show the importance of magmatic fluid in kimberlites for diamond dissolution reaction (Fedortchouk et al., 2007, Chepurov et al., 1985, Khokhryakov and Palyanov, 2010). The H<sub>2</sub>O-CO<sub>2</sub> ratio of the fluid determines resorption style and secondary morphology of diamond. Rounding into tetrahedron (THH) form happens at much lower diamond weight loss in the presence of H<sub>2</sub>O-rich fluid than CO<sub>2</sub>-rich fluid, suggesting that proportion of THH stones in a diamond population may not necessarily be an indication of degree of resorption. For example, Misery kimberlite has the highest proportion of THH and yet the highest diamond grade. The presence of free fluid phase determines if diamond oxidation develops natural-type resorption features or irregular cavities accompanied by surface graphitization. The two processes have different activation energy and different reaction rate. These experimental findings applied to natural kimberlites from Ekati showed that regardless of the geology of a pipe all kimberlites carry diamonds with resorption features indicative of aqueous fluid. However, retention of this fluid and the depth of its formation vary between different kimberlites and correlate with their geology and features of

diamond population. Kimberlites with good preservation and quality of diamonds show indications of ascent in the presence of abundant fluid phase, whereas those with poor diamond population show evidence of fluid loss (Fedortchouk et al., 2010). Since diamond loses its weight in the presence of fluid faster than through more slow irregular etching accompanied by surface graphitization, the way the fluid preserve the diamonds is through faster ascent of fluid-rich magmas. In order to predict diamond preservation based on the behavior of kimberlitic fluid, the methods for fluid examination independent from the features of diamond population are needed. Here we present the results of two approaches – dissolution features on other kimberlite-hosted mantle minerals and zoning of hydrogen defects in kimberlitic olivines.

Experimental study of chromite dissolution was done in piston-cylinder apparatus. Grounded natural mineral grains were placed in synthetic mixture of Ca-Mg-Si-C-H-O composition with 0, 5, 13 and 15 wt% H<sub>2</sub>O and 0-100 wt% CO<sub>2</sub> and heated to 1350 – 1400°C at 1 GPa. The results showed that angular step-like dissolution surfaces, which are common for natural kimberlitic chromites, develop only in the presence of H<sub>2</sub>O-rich fluid phase. Chromite reaction with H<sub>2</sub>O dissolved in the melt and with dry melt cause smoothing of chromite surfaces. Chromite dissolution in CO<sub>2</sub>-rich melts produced rounded polyhedral relief features. Both types of features are not typical for natural kimberlite-hosted chromite grains. Comparison with natural chromite grains recovered from Misery, Beartooth, and Grizzly kimberlites, Ekati Mine, show that Misery and Beartooth grains have very similar features resembling the run products of H<sub>2</sub>O-rich experiments. This confirms the abundance of aqueous fluid in these magmas constrained from diamond studies. Surface features on Grizzly chromites are very different and do not resemble any of our run products.

Grouping of the Ekati kimberlites based on the similarity of diamond resorption style corresponds to their grouping based on the spectra of Fourier transform infrared spectroscopy (FTIR) of olivine macrocrysts that also reflect the activity of aqueous fluid in the magma (Fedortchouk et al., 2010). For example, group 2 OH bands of the spectra are present only in kimberlites, which diamond population suggests presence of aqueous fluid. We further investigated this phenomena and found that loss of OH defects from the marginal zones of olivine xenocrysts is more profound in kimberlites with low diamond content and much less in kimberlites with good diamond population. Attenuation of different bands in FTIR spectra varies and may have different kinetics in the rising kimberlite magma. Therefore, profound OH zonation in olivine macrocrysts indicates either slow emplacement of the magma or conditions close to anhydrous.



## SUMMARY

We propose that while intensive variables of kimberlite magma (T, P, fO<sub>2</sub>) can produce notable effect on diamond dissolution rate, the range of their values in natural kimberlites limits the effect of each of these parameters. Furthermore, the comparison between the values of these parameters in natural kimberlites and the content and quality of diamonds is inconsistent. At the same time, the results of three independent methods applied to constrain presence and composition of fluid phase in kimberlite magmas agree with each other and with the geological features of the Ekati kimberlites used in this study. Experiments confirm that in the presence of aqueous fluid, resorption develops morphologies of good quality diamonds. More importantly, presence of free fluid is important for fast emplacement of kimberlite magma and, as a result, short time of diamond dissolution reaction. This helps to preserve diamond grade of kimberlite. Finally, the empirically detected correlations between fO<sub>2</sub> values, composition, and diamond content, may be a result of different volatile history in these magmas.

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