ABSTRACT

The crystal-chemical variations of spinels grown as a function of cooling rate \(\Delta T/\Delta t\) were analyzed via X-ray electron-microprobe (EPMA) maps. Maps were collected serially by using a fixed distance. Spinels solidified from a tholeiitic MOR basaltic liquid (B\(_{100}\)) cooled at cooling rate \(\Delta T/\Delta t\) of 1, 7, 60 and 180 °C/h, between 1300 and 800 °C and at ambient \(P\) and \(fO_2\). As \(\Delta T/\Delta t\) increases, the amount of spinel is invariably < 5 area% and its size decreases. Compared to the previous dataset
collected by common single and selected EPMA analytical points (112), the kinetic effects induced by
\( \Delta T/\Delta t \) are here quantitatively captured by a large number of analyses (2052).

The TiO\(_2\), Al\(_2\)O\(_3\), MgO and FeO\(^{tot}\) show large compositional variations at low cooling rates (from
1 to 60 °C/h) and only the average TiO\(_2\) concentration shows a well-defined trend as a function of \( \Delta T/\Delta t \).
However, calculated average cation amounts (apfu) unveil quantitative kinetic effects. When \( \Delta T/\Delta t \)
increases (from 1 to 180 °C/h) only Ti\(^{4+}\) shows a linear decreasing trend, whereas the other major Al\(^{3+}\),
Fe\(^{3+}\), Fe\(^{2+}\) and Mg\(^{2+}\) cations alone are scattered. Conversely, the sums of trivalent (Al\(^{3+}\) + Fe\(^{3+}\)) and
divalent (Mg\(^{2+}\) + Fe\(^{2+}\)) cations quantitatively capture the effect of the \( \Delta T/\Delta t \). These new outcomes could
be the base of novel geospeedometers with significant implications in volcanology, geophysics and
material sciences in regard to silicate melt rheology on Earth. They should be extended to high pressure,
hydrated and low oxygen fugacity conditions. Further, the analytical approach used here to capture
kinetic effects on spinel growth and compositions can be also applied to other crystalline phases grown
from silicate liquids.

**Keywords**: spinel, crystal-chemistry, kinetic, cooling rate (\( \Delta T/\Delta t \)), EPMA maps

**INTRODUCTION**

Magnetite, ulvospinel, chromite and spinel sensu stricto are the most common minerals of the
spinel supergroup in magmatic rocks. They are almost ubiquitous in igneous rocks but occur in a
proportion of only few units of area% or vol% (e.g., Toplis and Carroll 1995; Jang et al. 2001; Freda et
al. 2008; Mollo et al., 2013, 2015; Xu et al., 2022; Keller et al., 2023). However, they can be found as
major mineral phases in several magmatic-hydrothermal ore deposits (e.g., Dare et al., 2014, 2015;
Nadoll et al., 2014; Chen et al., 2019). Minerals along the magnetite (Mt, \(^{t}\)Fe\(^{3+}\)Mg\(^{2+}\)Fe\(^{3+}\)O\(_4\)) and
ulvospinel (Usp, $^{T \text{Fe}^{2+}}$M$^{2+}$Fe$^{2+}$M$^{4+}$Ti$^{4+}$O$_4$) join, followed by the spinel sensu stricto (Sp s.s., $^{T \text{Mg}^{2+}}$M$^{2+}$Al$^{3+}$O$_4$) are the most common non-aluminosilicate phases in igneous rocks (Deer et al., 1992; Bosi et al., 2019).

Many studies demonstrate that the crystal-chemistry of spinel-structured oxides (hereafter referred as spinels) is able to reconstruct crystallization conditions, such as equilibrium (or dis-equilibrium) growth, $T$, $P$ and $f$O$_2$ of solidification (Ghiorso and Sack 1991; Toplis and Carroll 1995; Scaillet and Evans 1999; Mollo et al., 2013; Coulthard et al., 2021; Keller et al., 2023). Experiments have also highlighted that the crystal-chemistry of magmatic spinel depends on the chemical solidifying system and crystallization of other silicate phases (Hammer, 2006; 2008; Iezzi et al., 2008, 2011; Mollo et al., 2013; Mollo and Hammer, 2017; Giuliani et al., 2022). These studies highlight how solidification kinetics can have a significant effect on the crystal-chemistry of spinels; the variation in kinetics has been largely investigated as a function of variable cooling rate, i.e., $\Delta T/\Delta t$ (Hammer, 2008; Mollo et al., 2013; Mollo and Hammer, 2017; Giuliani et al., 2022). Since the cooling conditions of a solidifying silicate liquid can change by many orders of magnitude (Hammer, 2008; Giuliani et al., 2022), it is thus important to better quantify its effect and, on the basis of the argument depicted above, to focus also on the crystal-chemistry of spinels (Mollo et al., 2013; Giuliani et al., 2022), as already done for pyroxenes and plagioclases (Muncill and Lasaga 1987; Lofgren et al. 2006; Hammer 2008; Iezzi et al. 2008, Mollo et al. 2010, 2011, 2012; Giuliani et al., 2022).

Until now, it is known that when $\Delta T/\Delta t$ increases the spinel sensu stricto molecule enriches and the ulvospinel component decreases (Mollo et al., 2013; Giuliani et al., 2022). If not considered, these effects may partially or totally invalidate the estimations of intensive parameters occurring during solidification of magmas based on the crystal-chemistry of spinels (Ghiorso & Sack, 1991; Ishibashi, 2013; Mollo et al., 2013; Arato & Audetat, 2015; Mollo et al., 2015; Pontesilli et al., 2019; Xu et al., 2022). Kinetic effects on the crystal-chemistry of spinels are also extremely important because they impart the magnetic properties of their host igneous rocks (O’Reilly, 1984; Banerjee, 1991; Pick and Tauxe 1994; Harrison
and Putnis, 1998; Zhou et al. 2000; Lattard et al., 2006; Bowles et al., 2011; Jackson & Bowles, 2014; Alva-Valdivia et al., 2021; Dudzisz et al., 2022). Further, the crystal-chemical variations induced by kinetics are potentially relevant for spinel-bearing ore deposits (Dare et al., 2012, 2014, 2015; Nadoll et al., 2014; Canil et al., 2016; Zhao et al., 2018); similar to other crystalline phases, sluggish and rapid solidification can enrich or deplete spinels with certain cations.

To refine and quantify the actual relationship between crystal-chemistry of spinels and cooling rate, we re-investigated in this study some previous solidification experiments performed on a tholeiitic mid-ocean ridge (MOR) basaltic system (labelled B\textsubscript{100}). This initially superliquidus basalt was cooled at 1, 7, 60 and 180 °C/h down to 800 °C (Vetere et al., 2015; Giuliani et al., 2020). The compositions of spinels in the four run-products were based on 112 single EPMA-WDS point analysis (Giuliani et al., 2022), following the classical subjective selection of crystals. This classical routine approach has several limitations that can mask the real relationship between crystal-chemistry and ΔT/Δt, because: i) only some crystals or parts of them are considered, ii) the number of analyzed crystals is limited and iii) the selected crystals for analysis are poorly representative (Iezzi et al., 2014; Xu et al., 2022). These limitations are here partially overcome by using X-ray electron-microprobe (EPMA) maps (Iezzi et al., 2014; Higgins et al., 2021), allowing to collect thousands (2052) micro-chemical point analyses in a serial way. The selected micro-chemical data unveil new and better-quantified relations between spinel compositions and the kinetics of solidification. This analytical procedure and related outcomes are uniquely able to capture the actual crystal-chemical variations recorded by crystals during their crystallization.

MATERIALS AND METHODS

The syntheses of the four run-products considered here are described in detail by Vetere et al. (2013, 2015). Briefly, the starting B\textsubscript{100} glass material was prepared through cycles (quenching, grinding,
heating) of melting at 1600 °C for several hours from a mid-ocean ridge tholeiitic basalt at known P and 
fO₂. The bulk composition of the sample is (wt%) SiO₂: 47.3(0.5), TiO₂: 1.0(0.0), Al₂O₃: 15.4(0.1), 
FeOtot: 10.2(0.0), MnO: 0.2(0.1), MgO: 9.4(0.2), CaO: 12.8(0.2), Na₂O: 1.9(0.1), K₂O: 0.1(0.0), while 
H₂O is 53 ppm and the Fe²⁺/Fetot ratio is 0.386 (Vetere et al., 2015; Giuliani et al., 2022). The four run-
products were then solidified by loading about 50 mg of the B₁₀₀ glass into Pt tubes. Subsequently, the 
sample charges were heated up to 1300 °C, kept at this temperature for 2 hours and then cooled down to 
800 °C along four ΔT/Δt paths of 1 (~ 21 days), 7 (~ 3 days), 60 (~ 8 hours) and 180 (~ 3 hours) °C/h, at 
air P and fO₂. The chosen cooling rates were already discussed in former papers (Vetere et al., 2013; 
2015), where the global crystallization behaviour of all crystalline phases was discussed. The quenched 
charges were recovered, embedded in epoxy, ground flat, polished and carbon-coated for acquiring 
micro-chemical maps at the HP-HT Laboratory of Experimental Volcanology and Geophysics of the 
Istituto Nazionale di Geofisica e Vulcanologia in Roma (Italy).

The X-ray chemical EPMA-WDS maps were acquired by an electron probe micro-analyser JEOL-JXA8200 combining EDS-WDS (equipped with five wavelength dispersive spectrometers with 12 
crystals), following the same approach as reported by Iezzi et al. (2014). The selected representative 
areas were designated on basis of previous textural characterizations (Giuliani et al., 2020). Each single 
analytical point in the EPMA maps was acquired under vacuum using a focused electron beams with a 
diameter of < 2 μm, an accelerating voltage of 15 kV and an electric current of 10 nA. The dwell time 
per pixel was of 120 msec, for total acquisition times between 18 h 40 min and 22 h 33 min. X-ray 
EPMA-WDS chemical maps were performed by stage rastering, keeping the electron beam stationary 
while the stage moved. The collected EPMA point analyses were acquired with constant distances in 
each run-product with resolution between 1 and 2 μm, on run-product portions with areas estimated 
around 1 and 2 μm² (Table 1).
A linear off-peak correction was adopted, with each pixel scanned per element corresponding to a full quantitative analysis, attained by correcting the intensity of each analytical point for background, k factors and matrix effects. The used JEOL software permitted to export point analyses for each map on basis of x-y coordinates. The reliability of chemical compositions obtained with EPMA maps was checked by analyzing the same portion of 10 single spinels for each run-product using longer counting times of 20 s on peak and 10 s on background, respectively, following the approach already reported in Iezzi et al., (2014). Differences between these two analytical methods are less than 1 wt% for all oxides. Thus, each point analysis or pixel of an EPMA map is a quantitative determination of the major oxide components (Figure 1).

All EPMA-WDS single data points were first tabulated; then, only the point analyses with totals comprising between 90 and 102 wt% were considered. The second screening was on the maximum amounts of totally incompatible SiO$_2$, CaO, Na$_2$O and K$_2$O imposed to be < 2, < 1, < 2 and < 1 wt%, respectively, whereas TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ and MgO contents were always accepted (Deer et al., 1992; Mollo et al., 2013; Giuliani et al., 2022). The third step was the calculation of the cations (atom per formula unit, apfu), ferric and ferrous speciation and molecules of spinels considering electric charge neutrality, four oxygens, three cations and typical crystallographic site occupancy (Stormer, 1983).

RESULTS

The salient textural features of the four run-products are extensively discussed in Giuliani et al. (2020) and are here shortly summarized. They are characterized by the solidification of plagioclase (plg), clinopyroxene (cpx), spinel (sp) and glass (Table 1). As the cooling rate increases from 1 to 180 °C/h, the run-products become progressively richer in cpx and poorer in plg, whereas the abundance of sp accounts for < 5 area%; glass is present in significant abundance only at 180 °C/h. In parallel, the sizes of crystals decrease, their number per area increases and their shapes switch from faceted to dendritic as...
$\Delta T/\Delta t$ increases (Figure 1). These general features are here mirrored by the X-ray EPMA-WDS maps displayed in Figure 1 for each oxide.

The number of selected analytical points of spinels decreases when the cooling rate increases due to the reduction in size and number of crystals (Figure 1). At 180 °C/h only one spinel crystal with a suitable size (~ 20 µm) was available (Figure 1). The average oxide compositions and related variations are displayed in Table 2, while the abundance of their major oxides (wt%) are shown in Figure 2, where the TiO$_2$, Al$_2$O$_3$, MgO and MnO contents are plotted against FeO$^{tot}$. The final and reliable analytical points of each spinel crystal per run-product are reported in Tables S1a-d. At low $\Delta T/\Delta t$, the significant variations around average contents (Table 2) reflect the high compositional zonation of single spinel crystals (Figure 2). The highest oxide content in these synthetic spinels is invariably FeO$^{tot}$, ranging between 62-90 wt%; the FeO$^{tot}$ range shifts towards 62 wt% when $\Delta T/\Delta t$ increases from 1 to 180 °C/h (Figure 2). The ranges of MgO, Al$_2$O$_3$ and TiO$_2$ oxides tend to decrease when the cooling rates increases. They are extremely variable at 1 and 7 °C/h, with ranges up to 17, 15 and 17 wt% respectively (Figure 2). By contrast, these oxides show only limited variations at 180 °C/h (Figure 2). The MnO ranges are relatively limited due to its absolute low content in the B$_{100}$ system (Figure 2). Overall, MgO and Al$_2$O$_3$ augment and TiO$_2$ decreases as $\Delta T/\Delta t$ changes from 1 to 180 °C/h (Figure 2), while at 1 and 7 °C/h MgO, Al$_2$O$_3$ and TiO$_2$ display clustered compositions (Figure 2). The contents of TiO$_2$ and Al$_2$O$_3$ shift towards the bulk chemical B$_{100}$ composition (see above) as $\Delta T/\Delta t$ increases from 1 to 180 °C/h (Figure 2).

The trends depicted by oxides are mirrored by calculated cations (Figure 3). The content of Mn$^{2+}$ is invariably < 0.1 apfu, while Mg$^{2+}$, Al$^{3+}$ and Ti$^{4+}$ are < 1, < 0.7 and < 0.5 apfu, respectively; the ranges of Fe$^{2+}$ and Fe$^{3+}$ are between 0.2-1.4 and 1-2 apfu, respectively (Figure 3). Again, at 1 and 7 °C/h Mg, Fe$^{2+}$, Fe$^{3+}$ and to a lesser extent Al$^{3+}$ display clustering and large apfu variations, whereas Ti$^{4+}$ follows an almost linear decreasing trend when Fe$^{3+}$ increases (Figure 3). Overall, the increasing of Fe$^{3+}$ is linked to the depletion depletion in Fe$^{2+}$ and enrichments of Mg$^{2+}$ and Al$^{3+}$ (Figure 3). Hence, an increase of...
Fe$^{3+}$ favors a depletion of the Usp and an enrichment of the spinel sensu stricto components (Figure 3, Table 2).

The presence of clustering of cation abundances requires an analysis of their frequencies. The variations of Mg$^{2+}$ and Ti$^{4+}$ cations were divided in ten classes, while those of Fe$^{2+}$, Fe$^{3+}$ and Al$^{3+}$ in twenty classes, each encompassing 0.1 apfu (Figure 4). An increase of the cooling rate results in a progressive depletion of Ti$^{4+}$ from 0.4-0.1 down to 0.1 apfu, the most abundant Al$^{3+}$ content changes from 0.1 to 0.4 apfu and the Fe$^{3+}$ maximum moves from about 1.8 down to 1.5-1.6 apfu (Figure 4). The two divalent Mg$^{2+}$ and Fe$^{2+}$ cations display a bimodal distribution at 1°C/h, becoming unimodal for the other three run-products. The maximum content of Fe$^{2+}$ first decreases, then increases and again decreases when $\Delta T/\Delta t$ changes from 7 through 60 to 180 °C/h, whereas Mg$^{2+}$ displays an opposite behavior (Figure 4).

The synthetic spinel crystals grown in the four experimental charges can be rigorously classified following the recent scheme reported in Bosi et al. (2019). All these spinels have $\Sigma R^{3+} (= \text{Cr}^{3+}+\text{Fe}^{3+}+\text{Al}^{3+}) > 1.0$ apfu and the $\Sigma R^{3+}/R^{2+}$ ratio is between 2/3 and 2, so they belong to the 2-3 spinel subgroup ($A^{2+}B^{3+}O_4$). The by far dominant B-cation is Fe$^{3+}$, whereas dominant A-cations are Fe$^{2+}$ and Mg$^{2+}$ as a function of run-products and crystals (Tables 2 and S1, Figures 3 and 4). Therefore, these spinels are either magnetite or magnesioferrite. However, in petrological studies, such discrimination of the dominant A-cation is rarely considered and the Fe$^{3+}$-rich spinels are referred to as magnetite (Stormer, 1983; Mollo et al., 2013). Following the common classification of spinels in magmatic rocks, they are classified according to the magnetite [Mt, $^{T}\text{Fe}^{3+}\text{M}(\text{Fe}^{2+}\text{Fe}^{3+})\text{O}_4$], spinel sensu stricto [Sp s.s., $^{T}\text{Mg}^{2+}\text{Al}^{3+}_2\text{O}_4$] and ulvospinel [Usp, $^{T}\text{Fe}^{2+}\text{M}(\text{Fe}^{2+}\text{Ti}^{4+})\text{O}_4$] molecular end-members (Table 2). Their average compositions are plotted in Figure 5.

**DISCUSSION**
The average oxide, cation and molecular compositions of the same spinel crystals analyzed by a classical set of single EPMA analytical points (Giuliani et al., 2022) and those attained here by serial points from EPMA maps are different (Figure 5). Such differences can be related only to the subjective selection of analyzed crystals, as well as to the relative low number of single EPMA analytical points when compared to maps, i.e., 112 vs. 2052 (Iezzi et al., 2014). However, the companion study conducted with the classical selection of single EPMA analytical points already highlighted that average Al\(_2\)O\(_3\) qualitatively increases, FeO\(_{\text{tot}}\) and TiO\(_2\) both decreased, whilst spinel sensu stricto increases as the cooling rates increased (Giuliani et al., 2022). In summary, the average oxide, cation and/or molecular compositions of solidified spinels were apparently only in part able to capture the kinetic of solidification induced by \(\Delta T/\Delta t\) experimental rates (Figures 2, 3, 4 and Table 2).

The X-ray EPMA-WDS maps provide the micro-chemical characterizations of a large and systematic number of spinel crystals and related portions. These spinels, cooled from the same bulk anhydrous silicate liquid at room \(P\) and redox state, follow quantitative trends, never reported before. The variations of mean values of single cations vs. \(\Delta T/\Delta t\) indicates that only Ti\(^{4+}\) follows a very well defined trend \((R^2 = 0.94)\) in agreement with the previous finding reported in Giuliani et al. (2022), whereas Al\(^{3+}\) is relatively poorly defined \((R^2 = 0.67,\) Figure 6) (only a qualitative evolution trend was observed in Giuliani et al., 2002). By contrast, Fe\(^{3+}\), Fe\(^{2+}\) and Mg\(^{2+}\) display scattered evolution trends as a function of \(\Delta T/\Delta t\), with different average values from those previously determined. Further, their average values differ from those previously determined by single EPMA analytical points (Figure 6).

These apparently absent relationships between each trivalent and divalent cations with respect to cooling conditions is overcome when considering their sums, i.e. Al\(^{3+}\) + Fe\(^{3+}\) and Mg\(^{2+}\) + Fe\(^{2+}\). In fact, their average apfu highly and linearly correlate \((R^2 = 0.96\) and 0.92\) with \(\Delta T/\Delta t\) (Figure 6). From a molecular view, the magnetite pole is clearly the most abundant in all run products. However, when \(\Delta T/\Delta t\) increases, the ideal magnetite pole, on average, slightly decreases, the spinel sensu stricto, strongly increases and
the ulvospinel end-member decreases in response to the significant depletion of Ti\textsuperscript{4+} (Table 2 and Figure 7). These trends quantitatively complement and modify the results reported in previous experimental investigations (Mollo et al., 2013; Pontesilli et al., 2019; Giuliani et al., 2022).

The linear relationships between crystal-chemical formulas and cooling rate represent a geospeedometer based on spinel-structured oxides at ambient $P$ and $fO_2$. The corollary of these outcomes is that the crystal-chemical variations of spinel in basaltic liquids can be entirely captured only if the sum of tetra-, tri- and di-valent cations are considered, as shown in Figure 7. It is also worth noting that only TiO\textsubscript{2} or Ti\textsuperscript{4+} is able to track the effect of $\Delta T/\Delta t$ since the other cations recognize the effect of kinetics only if considering trivalent and divalent cations together (Figure 6). In line, the observed large variations (standard deviations) of crystal-chemical features of spinels especially at low cooling rates (Table 2) reflect their evolution, i.e. zonation of crystals and multiple crystallization events, in response to progressive crystallization. All these considerations can be extended to other mineral species and can be captured only by using serial EPMA point analytical procedures, as shown for plagioclase by Iezzi et al. (2014) and Higgins et al. (2021). Other reinvestigations following this procedure may be able to decipher the actual absence of significant trends between crystal-chemistry of phases and kinetics.

Based on textures of solidified crystals and thermodynamic estimations performed on clinopyroxenes and plagioclases, spinel was interpreted to be one of the first phases to precipitate, followed by chain-silicates and finally feldspars (Vetere et al., 2013, 2015; Giuliani et al., 2020, 2022). This interpretation is further corroborated here by the very high linear variations of Ti\textsuperscript{4+}, Al\textsuperscript{3+} + Fe\textsuperscript{3+} and Mg\textsuperscript{2+} + Fe\textsuperscript{2+} induced through changes in $\Delta T/\Delta t$ (Figures 6 and 7). Indeed, such variations can be achieved only if the silicate liquid composition (B\textsubscript{100}) from which spinel precipitates is constant. Starting from this point, it is possible to explain the depicted behavior displayed by cations as a function of kinetics in the light of nucleation and crystal growth. Below the liquidus temperature and among thermodynamic stable
phases, dynamic solidification favors the nucleation of phases with the lowest energetic barriers of formation (Kirkpatrick, 1983, Lasaga, 1998, Iezzi et al., 2008, Zhang, 2008).

This qualitative principle is now relatively well established for silicate crystalline phases grown from natural and chemically complex silicate liquids (Iezzi et al., 2009, 2011). First, it explains that Fe-rich phases like spinel are more rapidly nucleated than silicates like clinopyroxenes and plagioclases. Second, it also furnishes an explanation for the evolution of crystal-chemical formulas of spinels (Figures 6 and 7). The formation of stable nuclei is attained by random compositional fluctuations of molecular units in the melt below the liquidus temperature (Lasaga, 1998, Zhang, 2008). The probabilistic compositional fluctuations involve the continuous breaking and formation of chemical bonds; however, strong chemical bonds have a more limited compositional space to explore, i.e., a limited compositional difference between the initial liquid and the final structural arrangement (Roskosz et al., 2005, 2006; Iezzi et al., 2014). Hence, the energetic barrier of nucleation scales with the number and strength of chemical bonds of cations with oxygens.

Spinels solidified in this system incorporate Ti$^{4+}$, Al$^{3+}$, Fe$^{3+}$, Mg$^{2+}$ and Fe$^{2+}$ (Figures 6 and 7). Indeed, the strongest bonds are those between Ti$^{4+}$ and O$^{2-}$, followed by those of Al$^{3+}$ and Fe$^{3+}$ and finally of Mg$^{2+}$ and Fe$^{2+}$ with oxygens (Pauling, 1960; Kirkpatrick, 1983; Dingwell, 2006). In light of these considerations, the increase in cooling rate progressively disadvantages the incorporation of Ti$^{4+}$ (Figures 4, 6 and 7). At low rates, TiO$_2$ incorporation spans very broad chemical composition variations, but at 180 °C/h its amount is very close to that of the starting silicate liquid (Figure 2). The incorporation of progressively lower amounts of Ti$^{4+}$ and the electric charge neutrality then drive up the amounts of trivalent and divalent cations. Since the incorporation of Ti$^{4+}$ is reduced, divalent cations follow the same trend and the trivalent cations are introduced to compensate their decrease (Figures 6 and 7). This further explains the poor preference between the two trivalent and divalent cations in the crystallized spinels.
Although SpinMelt-2.0 (Nikolaev et al., 2018a, 2018b) is the most recently developed suite for calculating the theoretical crystal-chemical formula of spinel at equilibrium with its liquid, it is not suitable for the B_{100} experimental material synthesized in this his study, since the bulk composition of B_{100} is practically Cr-free and solidification occurred at too high f_{O_2}. In turn, the calculated equilibrium composition was obtained via alphamelts 1.9 (Asimow and Ghiorso, 1998; Ghiorso et al., 2002; Smith and Asimow, 2005; Giuliani et al., 2022) at ambient P and at redox conditions as high as possible (i.e., QFM + 2.5). This theoretical composition is Ti_{0.52}Fe^{3+}_{0.78}Al_{0.17}Fe^{2+}_{1.23}Mg_{0.29}O_4 and differs even from the average spinel Ti_{0.12}Fe^{3+}_{1.62}Al_{0.12}Fe^{2+}_{0.71}Mg_{0.40}O_4 grown at 1°C/h (Table 2). When compared with the ideal equilibrium spinel, the experimental one is strongly depleted in Ti^{4+} and Fe^{2+} and highly enriched in Fe^{3+} (Figure 3). The increased rate of cooling exacerbates these differences since at 180 °C/h the average spinel is Ti_{0.01}Fe^{3+}_{1.57}Al_{0.37}Fe^{2+}_{0.33}Mg_{0.66}O_4 (Table 2 and Figure 3). It is also important to consider that the average ratio of ferrous vs. ferric follows a scattered trend with respect to ΔT/Δt (Table 2). All these differences between theoretical thermodynamic and observed kinetic compositions, if not considered, can alter the reconstruction of crystallization conditions. Similarly, low amounts of Ti^{4+} could be misinterpreted to derive from entrainment of foreign spinel crystals (xenocrystals) into the host magmas.

**IMPLICATIONS AND CONCLUSIONS**

In this study, we report the chemical compositions of spinels, experimentally synthesized from basaltic liquid at different cooling rate, as obtained from EPMA maps. The increase of cooling rate (from 1 to 180 °C/h) strongly influences the cations distribution between the melt and the crystallized phases. Spinel enriches continually in Al^{3+} and depletes in Ti^{4+}, therefore spinel sensu stricto is favored at higher cooling rate with respect to ulvospinel and magnetite components. The linear relationships between the crystal-chemical formulas (especially for Ti^{4+}, Mg^{2+} + Fe^{2+} and Al^{3+} + Fe^{3+} sums) and cooling rate are at
the base of a novel geospeedometer for spinels at ambient $P$ and $fO_2$. Actually, the experimental conditions considered in this study are directly relevant for natural basaltic liquids (aphyric or residual melts, McCarthy et al., 2023) after their eruptions and emplacements under subaerial and submarine conditions. The $fO_2$ calculated for our experimental spinels using the oxybarometer of Arato and Audédat (2017) computes high redox conditions such as $\Delta QFM$ of +2 for $\Delta T/\Delta t$ of 1 and 7 °C/h, and +4 and +8 respectively for spinels produced at 60 and 180 °C/h; these estimations are in line with those already estimated in Giuliani et al. (2022) and more importantly several MORBs are now considered to be emplaced at $fO_2$ close to QFM (Cottrell et al., 2021).

The range in cooling conditions of 1, 7, 60 and 180 °C/h occurs in natural MORB lavas and magmas in response to thermal contrasts between silicate liquid and the surrounding environment, such as wall-rocks, water, air as well as based on the volume and thickness of the solidifying melt or magma (Vetere et al., 2015; Lanzafame et al., 2017; Giuliani et al., 2022). Previous numerical simulations indicate that cooling rates of 1 and 7 °C/h can develop in the innermost portions of $B_{100}$-like lavas with a thickness of a few meters, whereas 60 and 180 °C/h are typical for outermost portions of meter-thick lavas or in central parts of dm-thick lavas and bombs (Vetere et al., 2015; Giuliani et al., 2022; McCarthy et al., 2023). Spinels crystallize early and have a high density with respect to silicate melts (about 5000 vs. 2600 kg/m$^3$, respectively). According to Giordano et al (2008) viscosity model and utilizing the Stokes low as for the falling sphere viscometry (Vetere et al., 2006) as temperature goes from 1350 to 1200 °C, $B_{100}$ (MORB) viscosity ranges between 2 and 16 Pa*s. Under these conditions, a crystal with a size of 0.1 mm can fall with a velocity ranging from $2.77 \times 10^{-5}$ m/s (high $T$) and covering a sinking distance of 2.4 m in 1 day or $2.77 \times 10^{-6}$ but in this case the falling distance is only 24 cm.

Finally, it must be noted that the very low amount of spinels (< 5 area% Giuliani et al., 2022) at the beginning of the crystallization path do not significantly impact on the rheology of the entire
suspension (Vetere et al., 2022). At the same time, this low amount is only able to changes the Fe content in the residual melt. Our system is almost anhydrous and, as SEM proved, tiny bubbles are absent.

In turn, spinels crystallized at different cooling conditions (with different crystal-chemistries) at variable thicknesses into a silicate liquid (lavas, dykes, etc.) can accumulate at similar levels and mimic disequilibrium crystal assemblages. By contrast, if crystallized spinels remain at the positions where different cooling rates develop, the crystal-chemical variations will be indicative of cooling regimes they experienced. Such a scenario has been observed for pillow basalts, dykes and lavas (Zhou et al., 2000; Kissell et al., 2010; Mollo et al., 2011; McCarthy et al., 2023). In pillow basalts the very thin carapace hosts tiny, Fe-rich and Ti-poor spinels, whereas moving towards the innermost parts the spinel increases its size and the amount of Ti (Zhou et al., 2000) in line with the textural (Giuliani et al., 2020) and chemical trends unveiled here (Figures 6 and 7).

The changes of cations in spinels induced by cooling affect their magnetic properties (Harrison and Putnis, 1996, 1998; Lattard et al., 2006; Chadima et al., 2009) and agree with magnetic variations observed in basaltic dikes with progressive reduction of cooling conditions from external to internal parts (Smith and Prévot, 1977). Again, these results can be captured only by the use of X-ray EPMA maps and understood using the linear cation variations reported here (Figures 6 and 7).

The preference of element incorporations in spinel as a function of $\Delta T/\Delta t$ is also useful to concentrate in them toxic or critical elements from waste (Zhao et al., 2017). Cations with affinities with Ti$^{4+}$, Al$^{3+}$, Fe$^{3+}$, Fe$^{2+}$ and Mg$^{2+}$ can be preferentially enriched (or depleted) in spinels during crystallization as a function of cooling dynamics only, i.e., by modulating the thickness of the melt or the temperature of its environment. Since the incorporation of tetravalent (Ti$^{4+}$) and divalent is reduced upon the increase of the cooling rate, trivalent cations are introduced, enriching spinel in minor and trace trivalent elements as Cr and REE.
Acknowledgements

This study was funded by the PRIN (2009PZ47NA_003) project “Time Scales of Solidification in Magmas: Application to Volcanic Eruptions, Silicate Melts, Glasses, Glass-Ceramics” awarded to G. Iezzi. Most of this study was conducted during the post-doc of E. Gennaro.

We would like to thank the editors and the reviewers for their thorough and constructive comments, which helped to improve this manuscript.

REFERENCES


and spinel solidified at variable cooling rates from a mid-ocean ridge basaltic liquid. Earth-Science Reviews 204, 103165.


Nikolaev, G.S., Ariskin, A.A. and Barmina, G.S. (2018b) SPINMELT-2.0: Simulation of spinel-melt equilibrium in basaltic systems under pressures up to 15 Kbar: II. Description of the program package, the topology of the Cr-spinel–melt model system, and petrological implications. Geochemistry International 56, 125–135.


cultural investigation of phases forming in highly supercooled aluminosilicate liquids. Journal of Non-
Crystalline Solids 351, 1266–1282.


equilibria and pre-eruption P-T-/O2-/H2O conditions of the dacite magma. Journal of Petrology 40:381–
411.


Smith, P.M., and Asimow, P.D. (2005) Adiabat_1ph: a new public front-end to the MELTS,
pMELTS, and pHMELTS models. Geochemistry, Geophysics, Geosystems 6, Q02004.


on Fe–Ti oxide stability, phase relations, and mineral-melt equilibria in ferro-basaltic systems. Journal
of Petrology 36, 1137–1170.

experimental data and a revised calculation model. Chemical Geology 228, 233-245.

Vetere, F., Iezzi, G., Perugini, D. and Holtz, F. (2022) Rheological Changes in Melt and Magma
https://doi.org/10.5802/crgeos.125


List of figure captions

**Figure 1.** X-ray EPMA-WDS maps of the distribution of SiO$_2$, TiO$_2$, Al$_2$O$_3$, FeO$^{\text{tot}}$ (two ranges), MgO CaO and Na$_2$O, plus the textural features by back-scattered SEM micro-photographs (top). The changes from blue to red colors indicate an increasing for each oxide wt% range. The horizontal white (black) bars correspond to 100 µm.

**Figure 2.** Major oxides (wt%) in spinel as function of FeO$^{\text{tot}}$ and number of selected EPMA-WDS analyses. The TiO$_2$, Al$_2$O$_3$, FeO$^{\text{tot}}$ (Fe$_2$O$_3$ in Giuliani et al., 2022) ranges obtained by single-selected EPMA points are all comprised in the corresponding ranges measured here, whereas only some of the MgO data analysis presented in Giuliani et al., (2022) are higher than the maximum value measured here (up to ~ 20 wt.%).

**Figure 3.** Abundances of cations (apfu) in spinel as function of Fe$^{3+}$ content and number of selected EPMA-WDS analyses. Red star symbols represent the theoretical composition of spinel as computed by alphamelts 1.9 (Asimow and Ghiorso, 1998; Ghiorso et al., 2002; Smith and Asimow, 2005; Giuliani et al., 2022).

**Figure 4.** Distribution of cations (apfu) in spinel (Sp) calculated from the data in Figure 3, as a function of cooling rate.

**Figure 5.** Ternary plot showing the average Usp (ulvospinel), Mt (magnetite), Sp s.s. (spinel sensu stricto) molecular components in spinel as determined in this study with X-ray EPMA maps and in the previous one (Giuliani et al., 2022) that used the classical set of single EPMA analytical points.

**Figure 6.** Average of cations (apfu) in spinel as function of the cooling rate (°C/h). Mg$^{2+}$+Fe$^{2+}$ and Al$^{3+}$+Fe$^{3+}$ sum are also shown. Only linear regression with $R^2 > 0.6$ are plotted. Red symbols in some plots represent the average cations of spinel from Giuliani et al. (2022).
**Figure 7.** Ternary plot showing the distribution of average amounts of Ti$^{4+}$, Al$^{3+}$ + Fe$^{3+}$ and Mg$^{2+}$ + Fe$^{2+}$ cations in spinel.

**Table 1.** Experimental conditions of solidification experiments, phase assemblages and analytical EPMA-WDS features.

<table>
<thead>
<tr>
<th>sample label</th>
<th>cooling rate (°C/h)</th>
<th>crystal content</th>
<th>map area (mm$^2$)</th>
<th>distance between adjacent analytical points (µm)</th>
<th>number of reliable single analytical points</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>1</td>
<td>Plg+Px+Sp</td>
<td>0.68</td>
<td>1.65</td>
<td>902</td>
</tr>
<tr>
<td>E7</td>
<td>7</td>
<td>Plg+Px+Sp</td>
<td>1.00</td>
<td>2.0</td>
<td>993</td>
</tr>
<tr>
<td>E60</td>
<td>60</td>
<td>Plg+Px+Sp</td>
<td>0.25</td>
<td>1.0</td>
<td>133</td>
</tr>
<tr>
<td>E180</td>
<td>180</td>
<td>Px+Sp+glass</td>
<td>0.25</td>
<td>1.0</td>
<td>24</td>
</tr>
</tbody>
</table>

footnote: Plg=plagioclase, Px=pyroxene, Sp= spinel
Table 2. Average contents of oxides, cations and molecules in spinel.

<table>
<thead>
<tr>
<th># selected analyses</th>
<th>E1 (n=902)</th>
<th>E7 (n=994)</th>
<th>E60 (n=133)</th>
<th>E180 (n=24)</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxide (wt%)</td>
<td>av.</td>
<td>σ</td>
<td>av.</td>
<td>σ</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.37</td>
<td>0.37</td>
<td>0.33</td>
<td>0.37</td>
</tr>
<tr>
<td>TiO₂</td>
<td>4.34</td>
<td>4.01</td>
<td>4.06</td>
<td>3.03</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.86</td>
<td>1.90</td>
<td>3.41</td>
<td>1.64</td>
</tr>
<tr>
<td>FeO₉⁰ˌ</td>
<td>78.31</td>
<td>4.58</td>
<td>73.50</td>
<td>3.05</td>
</tr>
<tr>
<td>MgO</td>
<td>7.73</td>
<td>4.48</td>
<td>11.11</td>
<td>2.78</td>
</tr>
<tr>
<td>CaO</td>
<td>0.13</td>
<td>0.26</td>
<td>0.13</td>
<td>0.26</td>
</tr>
<tr>
<td>MnO</td>
<td>0.61</td>
<td>0.48</td>
<td>0.93</td>
<td>0.53</td>
</tr>
<tr>
<td>tot.</td>
<td>94.36</td>
<td>2.94</td>
<td>93.46</td>
<td>2.45</td>
</tr>
<tr>
<td>cations (apfu)</td>
<td>av.</td>
<td>σ</td>
<td>av.</td>
<td>σ</td>
</tr>
<tr>
<td>Si⁴⁺</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Ti⁴⁺</td>
<td>0.12</td>
<td>0.11</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.12</td>
<td>0.08</td>
<td>0.14</td>
<td>0.06</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>1.62</td>
<td>0.19</td>
<td>1.62</td>
<td>0.16</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0.71</td>
<td>0.34</td>
<td>0.51</td>
<td>0.22</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.40</td>
<td>0.22</td>
<td>0.57</td>
<td>0.14</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0.02</td>
<td>0.01</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe²⁺/Fe³⁺</td>
<td>0.44</td>
<td>0.31</td>
<td>0.43</td>
<td>0.22</td>
</tr>
<tr>
<td>components (mol%)</td>
<td>av.</td>
<td>σ</td>
<td>av.</td>
<td>σ</td>
</tr>
<tr>
<td>Sp s.s.</td>
<td>17.48</td>
<td>9.39</td>
<td>24.05</td>
<td>5.78</td>
</tr>
<tr>
<td>Mt</td>
<td>62.55</td>
<td>3.45</td>
<td>60.63</td>
<td>3.31</td>
</tr>
<tr>
<td>Usp</td>
<td>19.96</td>
<td>11.20</td>
<td>15.32</td>
<td>7.70</td>
</tr>
</tbody>
</table>

footnote: Sp= spinel sensu stricto, Mt=magnetite, Usp=Ulvospinel
Figure 1

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>1 °C/h, 7 °C/h, 60 °C/h, 180 °C/h</td>
</tr>
<tr>
<td>TiO₂</td>
<td>[40-70 wt%]</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>[0-30 wt%]</td>
</tr>
<tr>
<td>FeO&lt;sub&gt;tot&lt;/sub&gt;</td>
<td>[0-18 wt%]</td>
</tr>
<tr>
<td>FeO&lt;sub&gt;tot&lt;/sub&gt;</td>
<td>[50-80 wt%]</td>
</tr>
<tr>
<td>MgO</td>
<td>[0-25 wt%]</td>
</tr>
<tr>
<td>CaO</td>
<td>[0-30 wt%]</td>
</tr>
<tr>
<td>Na₂O</td>
<td>[0-7 wt%]</td>
</tr>
</tbody>
</table>

Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7