INTRODUCTORY NOTE. Oxidative Color Modification of Ruby: A Defect Kinetics Model for Reducing the Purplish Tinge

AUTHOR: Ted Themelis
AFFILIATION: Independent Researcher, Gemlab, Bangkok, Thailand
ORCID: 0000-0002-4493-6623
Email: ted@themelis.com

Abstract
This study establishes a defect kinetics model demonstrating that controlled heating below 1200°C in dry air reduces the purplish tinge in ruby by oxidizing ferrous iron (Fe'_{Al}) and expelling hydroxyl defects [OH^{*}_{o}], The oxidation process increases the ferric iron population ([Fe^{x}_{A}l]), reducing the blue component while maintaining chromium luminescence ([Cr^{x}_{Al}]). Successful execution of the heating process results in reducing the purplish tinge in the ruby and increasing its commercial value.

Keywords: *Corundum; Ruby; Redox Kinetics; Kröger-Vink Notation; Iron Oxidation; Hydroxyl Expulsion.*

1. Experimental Setup & Verification

Atmospheric Control. The heat treatment process was conducted using a V50-1300 bottom-loaded tube furnace, fabricated by the author for precision atmospheric control. To isolate the kinetics of hydroxyl (OH^{-}) expulsion from the external variables, a four-stage filtration assembly integrated into the primary gas line, ensuring the delivery of high-purity, zero-moisture dry air to the reaction chamber.

System Dynamics. The system maintained constant positive low pressure via a low-flow dry air purge. The exhaust was routed through a PTFE bubbler jar, functioning as a one-way valve to prevent atmospheric backflow. This stabilized pressure environment ensured a consistent oxygen partial pressure (pO_2) throughout the low temperature (<1200°C) soaking period, allowing for the precise mapping of the Fe^{2+} → Fe^{3+} transition and the resulting reduction in the purplish tinge.

2. Role of Defects

Ferric Iron (Fe^{3+}, Fe^{x}_{Al} — Ferric Iron Population, Rising Curve)

- **Event:** As oxygen is incorporated, Fe^{2+} is oxidized to Fe^{3+}.
- **Implication:** Rising Fe^{3+} concentrations introduce yellow/brown components that neutralize blue/purple tinges, shifting the ruby toward a "purer" red saturation.

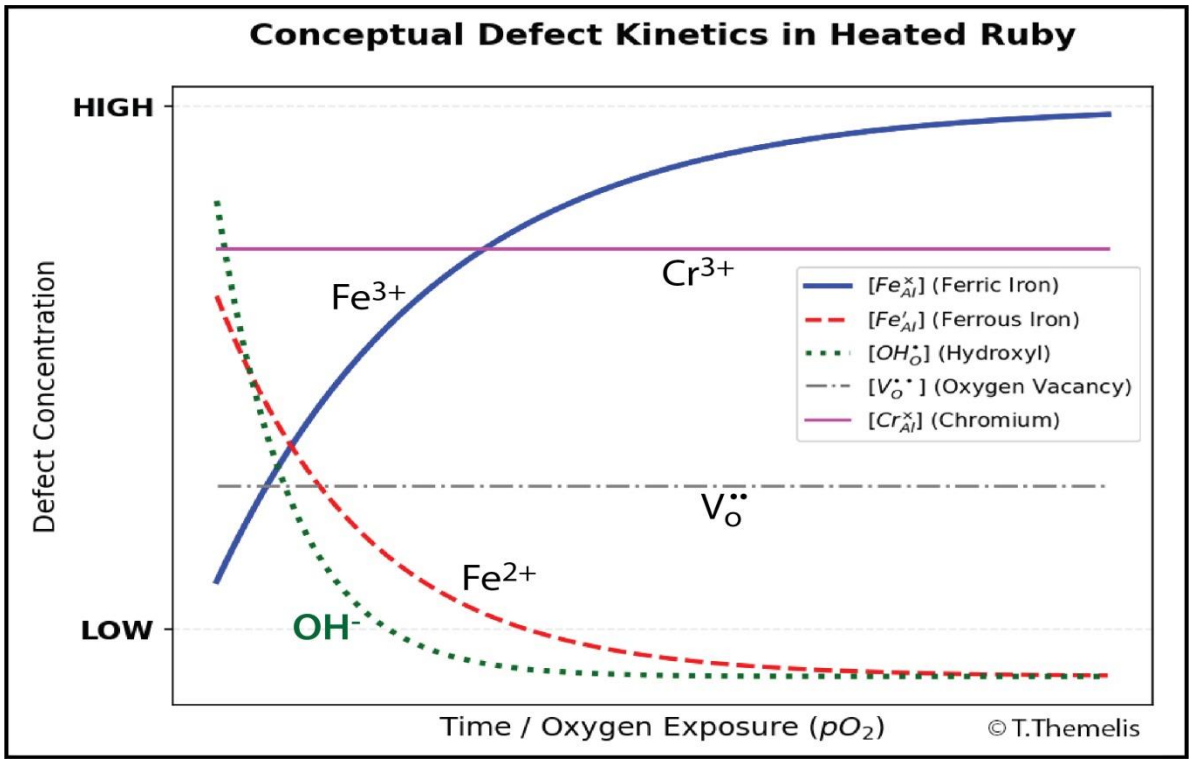

Fig.1. This diagram illustrates the relative concentration shifts of point defects during oxidative heating. The y-axis tracks population density from Low to High. The x-axis (Time / Oxygen Exposure (pO_2) represents the soaking period—the duration where the purple-tinged ruby is exposed to a dry air environment, forcing the reduction of the purplish tinge and clearing hydrated haziness. Oxidation-driven depletion of Fe^{2+} and $(OH)^{-}$, accompanied by Fe^{3+} growth, effectively neutralizes the blue contribution responsible for the purplish tinge.

Ferrous Iron (Fe^{2+}, Fe'_{Al} — Reduced State, Sharp Declining Curve)

- **Event:** Fe^{2+} concentration drops sharply as oxidation proceeds.
- **Implication:** Removal of Fe^{2+} eliminates the "darkening" agents associated with over-saturated, "inky" stones, improving brightness and transparency.

Hydroxyl (OH^- , OH^*_O — Hydroxyl/Moisture (Steep Declining Curve)

- **Event:** Rapid expulsion under low temperature (1200^oC<) thermal stress in zero-moisture air environment, hydrogen is rapidly expelled.
- **Implication:** Removal of hydrated defects reduces haziness, increases diaphaneity, and "oxidized glow."

Oxygen Vacancy ($V_{\cdot\cdot o}$) — Oxygen Vacancy (Stable Reference)

- **Event:** Concentration remains approximately constant at equilibrium.
- **Implication:** Vacancies act as essential charge compensators during oxidation ($Fe^{2+} + ½\ O_2 + V^{\cdot\cdot}_o \rightarrow Fe^{3+} + O^x_o$), maintaining lattice stability.

Chromium (Cr^{3+}, Cr^x_{Al} — Ruby Luminiscence)

- **Event:** Chromium remains in a trivalent state throughout .
- **Implication:** Cr^{3+} does not participate in iron-driven redox at these temperatures; the red "base" remains unchanged.

3.Technical Observations

- Atmospheric Sensitivity: Accidental reducing conditions during heating would increase purple tinge relative to Fe + Ti concentration.
- Selective Modification: Chromium, vanadium, and titanium do not significantly influence the color modification in these specific conditions
- Recovery: The purple tinge is only partially reducible. Yields for this dry-air process average <15%.
- Furnace Type: This process requires electric muffle-type furnaces; combustion-based furnaces are unsuitable
- Material Suitability: Effective for previously heated Thai-Cambodian basaltic rubies (with intense purple overtones) and unheated metamorphic rubies (Myanmar (Mogok), Tanzania, etc.).
- Comparative Methodologies: Other commercial methodologies used to reduce the purplish tinge include the Beryllium process and various flux-heated processes.

4.Conclusion

Controlled dry-air oxidation at <1200°C effectively neutralizes the purplish tinge in ruby by stabilizing the Fe^{3+} population and expelling hydroxyl defects while preserving the gemstone's natural inclusion integrity. While oxidizing heat treatment is standard practice in the trade to reduce the blue component in rubies, the specific dry air process—utilizing precision-filtered, zero-moisture air—remains a niche, scientific methodology largely isolated to author's documented research and high-precision furnace configurations.

References

Kröger, F. A., & Vink, H. J. (1956). *Solid State Physics*, 3, 307-435.
Lagerlöf, K. P. D., & Grimes, R. W. (1998). *Acta Crystallographica Section B*, 54(4), 446-459.
Beran, A., & Rossman, G. R. (2006). OH in naturally occurring corundum. *European Journal of Mineralogy*, 18(4), 441–447
Themelis, T. (2010-2026). *The Heat Treatment of Ruby & Sapphire*. Monograph Series.