

Carmeltazite, $ZrAl_2Ti_4O_{11}$:

A new mineral from the volcanic rocks of Mt. Carmel, northern Israel

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The new mineral species carmeltazite [1] has been discovered in pockets of trapped melt interstitial to, or included in, corundum xenocrysts from the Cretaceous Mt Carmel volcanics of northern Israel, associated with tistarite, spinel, osbornite and an unnamed REE phase, in a Ca-Mg-Al-Si-O glass. The ideal chemical formula is $ZrAl_2Ti_4O_{11}$, with Ti present as Ti^{3+} , and the crystal structure is similar to a defective spinel structure. The name derives from Mt Carmel ("CARMEL") and from the dominant metals present in the mineral, i.e. Titanium, Aluminum and Zirconium ("TAZ"). The mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (2018-103).

Paragenesis In the Mt Carmel area of northern Israel, a series of small volcanoes produced mafic to ultramafic pyroclastic rocks (vent breccias, tuffs) in upper Cretaceous time [2,3]. These rocks contain a wide variety of xenocrysts, including megacrysts of clinopyroxene, ilmenite, zircon and corundum. Among them, aggregates of skeletal corundum crystals (Carmel Sapphire™) are common in pyroclastic ejecta and in associated alluvial deposits.

These aggregates have trapped large pockets of their parental melts, which have crystallized a wide variety of phenocrysts; >120 phases have been identified, most previously undescribed, or known only from meteorites. The earliest paragenesis consists of tistarite (Ti_2O_3) ± carmeltazite ± Mg-Al spinel in a matrix of Ca-Mg-Al-Si-O glass. Tistarite is typically rounded and resorbed, and then overgrown by euhedral crystals of carmeltazite.

Table 1. Chemical data of carmeltazite.

Oxide	wt (%) (n = 8)	Range	Standard Deviation
SiO ₂	1.50	1.24–1.70	0.24
ZrO ₂	24.9	23.7–27.9	1.45
HfO ₂	0.53	0.48–0.67	0.07
Al ₂ O ₃	18.8	18.0–20.1	0.78
Ti ₂ O ₃	50.6	48.8–52.2	1.30
Sc ₂ O ₃	0.76	0.59–1.24	0.27
Y ₂ O ₃	0.39	0.30–0.51	0.08
MgO	1.89	1.50–2.93	0.50
CaO	0.51	0.29–1.45	0.43
Total	100.12	98.87–100.5	0.28

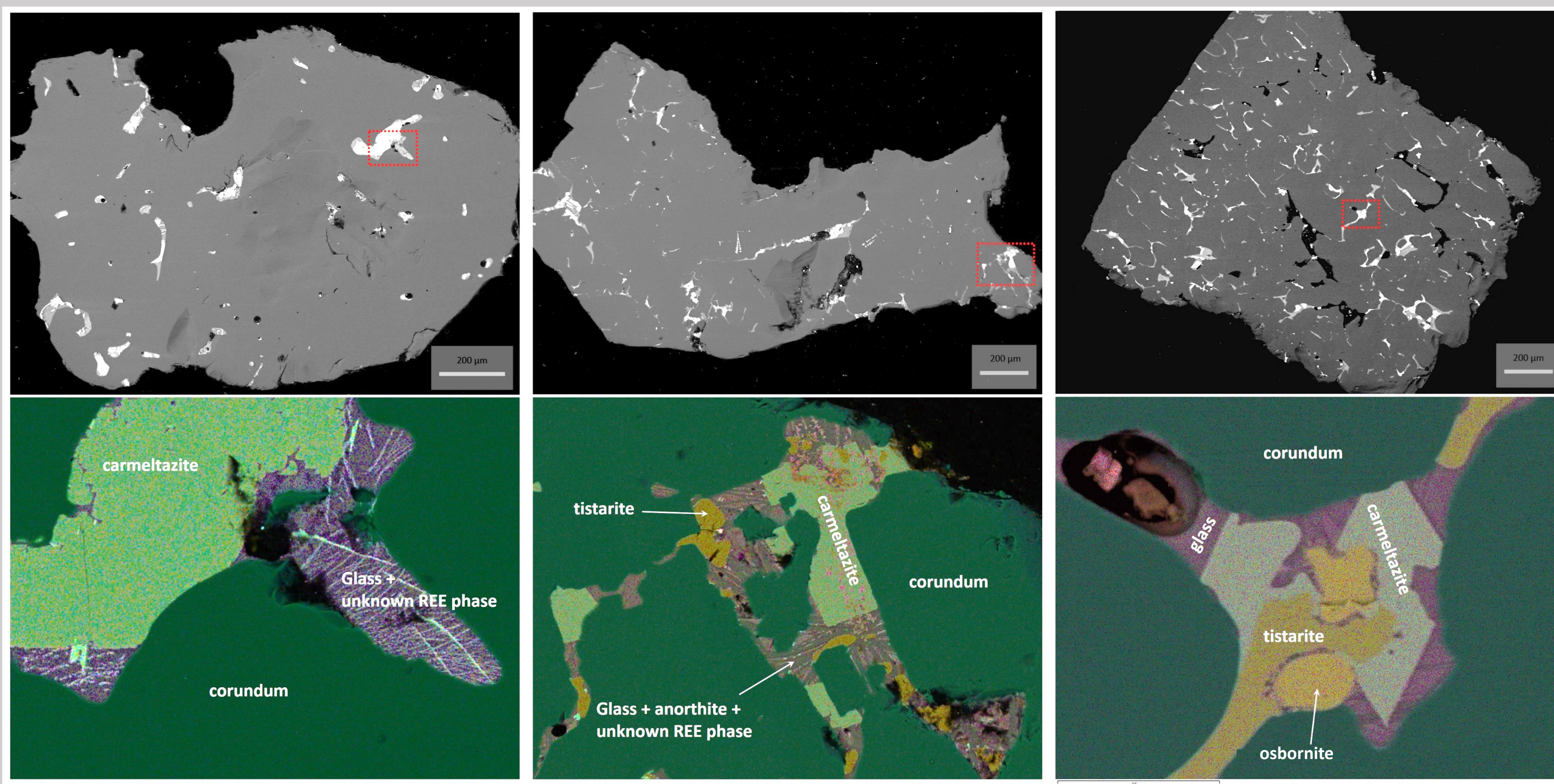


Figure 1. (Top images) Scanning Electron Microscope – Backscattered Electron (SEM-BSE) image of carmeltazite (in corundum); and (Bottom images) phase map of the region highlighted in the top image with a red dashed rectangle.



Chemical data

Quantitative chemical analyses were carried out using a CAMECA-100X electron-microprobe (CAMECA Instruments), operating in WDS mode. Carmeltazite is chemically homogeneous within the analytical uncertainties of our measurements. Table 1 gives analytical data (average of 8 spot analyses).

The empirical formula (based on 11 oxygen atoms *pfu*, and assuming all Ti and Sc as trivalent) is $(Ti^{3+}_{3.60}Al_{1.89}Zr_{1.04}Mg_{0.24}Si_{0.13}Sc_{0.06}Ca_{0.05}Y_{0.02}Hf_{0.01})O_{11}$. The simplified formula is $ZrAl_2Ti_4O_{11}$, which requires ZrO₂ 24.03 wt%, Al₂O₃ 19.88 wt%, Ti₂O₃ 56.09 wt%.

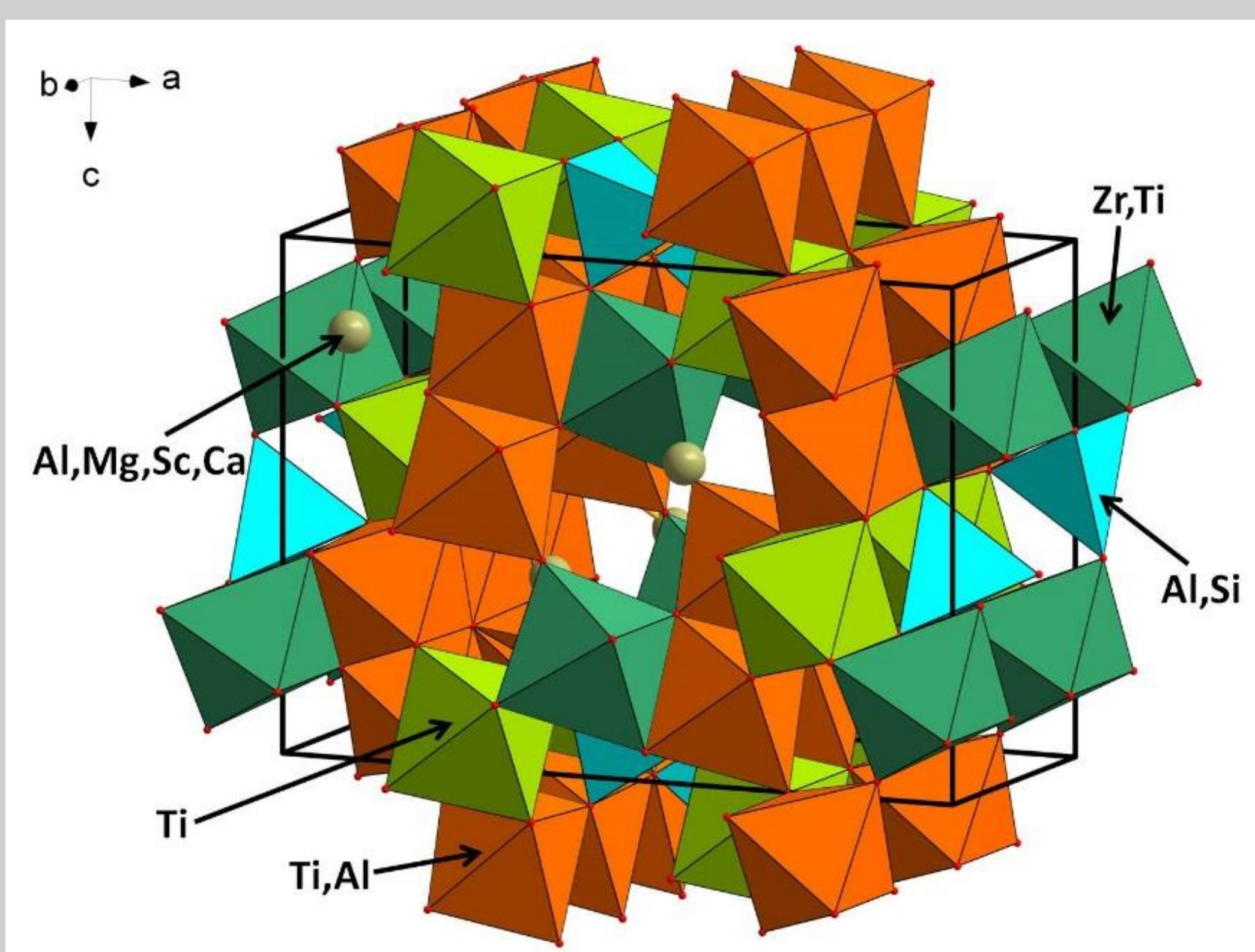


Figure 3. The crystal structure of carmeltazite. The unit-cell and the orientation of the figure are outlined.

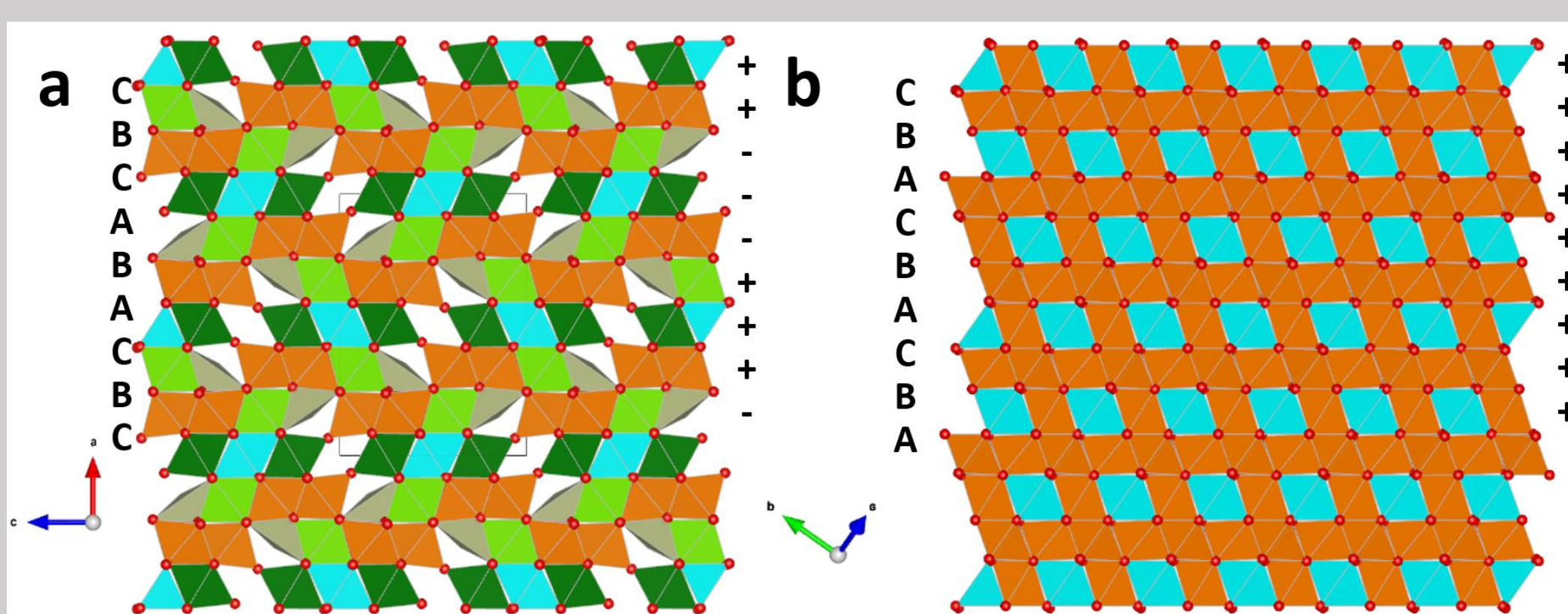


Figure 4. Comparison of the crystal structure of carmeltazite (a) and spinel (b). Observe the alternation of the layers, promoting the presence of vacant sites and pyramidal coordination for the M1 site in carmeltazite.

Crystal structure A small carmeltazite fragment was extracted from the polished section shown in Figure 1 and mounted on a 5 μm diameter carbon fiber, which was in turn attached to a glass rod. X-ray single-crystal intensity data (1546 unique reflections) were collected using an Oxford Diffraction Xcalibur 3 diffractometer. The statistical tests ($|E_2 - 1| = 0.980$) and the reflection conditions indicated the space group *Pnma*. The refined unit-cell parameters are $a = 14.0951$ (9), $b = 5.8123$ (4), $c = 10.0848$ (7) Å, $V = 826.2$ (1) Å³.

The crystal structure of carmeltazite (Figure 3) is close to a defective spinel structure. The M_9O_{12} stoichiometry of a spinel becomes M_7O_{11} as one oxygen and two cations are lost. Nevertheless, the stacking of oxygen layers is not a cubic-close-packing yielding a standard ABCABC sequence along the cubic direction [111]. In carmeltazite the sequence is hexagonal, i.e. ABACBC along [100]. Therefore, the two central layers are shifted and that changes the coordination of some atoms.

Origin of carmeltazite The corundum aggregates in which the carmeltazite occurs appear to have formed near the crust-mantle boundary (*ca* 30 km depth; [3, 4]), and temperatures of 1250–1450°C, in the presence of excess volatiles. The silicate melts parental to this assemblage had previously been progressively depleted in Fe, and then desilicated, by the exsolution of immiscible Fe and Fe-Ti oxide melts and Fe-Ti-Zr-silicide melts (found also as inclusions in carmeltazite), and the crystallization of moissanite and khamrabaevite (TiC), at $fO_2 = \Delta IW - 6$ or less. This process continued to progressively lower fO_2 , witnessed especially by the appearance of Ti^{2+} -bearing phases (osbornite, khamrabaevite, unnamed TiB_2 , unnamed TiO) and native vanadium [5].

The abundance of carbon in the system (SiC, TiC and amorphous C as common phases) and the low fO_2 required by the observed assemblages ($\Delta IW - 6$ to -10 ; [1]) suggests that the volatiles were dominated by mantle-derived $CH_4 + H_2$, which reduced a volume of mafic to ultramafic melt. The unusual conditions have resulted in a large number of previously unknown phases, which are the subject of ongoing investigations.

References

- [1] Griffin, W.L.; Gain, S.E.M.; Bindi, L.; Toledo, V.; Cámara, F.; Saunders, M.; O'Reilly, S.Y. Carmeltazite, $ZrAl_2Ti_4O_{11}$, a New Mineral Trapped in Corundum from Volcanic Rocks of Mt Carmel, Northern Israel *Minerals*. **2019**.
- [2] Griffin, W.L.; Gain, S.E.M.; Adams, D.T.; Huang, J.-X.; Saunders, M.; Toledo, V.; Pearson, N.J.; O'Reilly, S.Y. First terrestrial occurrence of tistarite (Ti_2O_3): Ultra-low oxygen fugacity in the upper mantle beneath Mount Carmel, Israel. *Geology* **2016**.
- [3] Xiong, Q.; Griffin, W.L.; Huang, J.-X.; Gain, S.E.M.; Toledo, V.; Pearson, N.J.; O'Reilly, S.Y. Super-reduced mineral assemblages in "ophiolitic" chromitites and peridotites: the view from Mount Carmel. *Eur. J. Mineral.* **2017**.
- [4] Griffin, W.L.; Huang, J.-X.; Thomassot, E.; Gain, S.E.M.; Toledo, V.; O'Reilly, S.Y. Super-reducing conditions in ancient and modern volcanic systems: Sources and behaviour of carbon-rich fluids in the lithospheric mantle. *Min. & Petr.* **2018**.
- [5] Bindi, L.; Cámara, F.; Griffin, W.L.; Huang, J.-X.; Gain, S.E.M.; Toledo, V.; O'Reilly, S. Solar nebula conditions on Earth produced the first natural hydride. *Am. Mineral.* **2019**, in press.