

Methods

Sampling

The Shefa Yamim exploration project was aimed at the discovery of economically viable placer deposits of gemstones (mainly sapphire, ruby, hibonite, moissanite) and other commodities within the drainage basin of the Kishon River. Over >10 years, the project has sampled the Cretaceous pyroclastic centers on Mt Carmel (Fig. SD1: Rakefet, Har Alon, Bat Shelomo, Muhraka and Beit Oren complexes) and adjacent areas (Ein Ha-Shofet), and minor and major drainages in the Yaz'rael Valley. Samples range in size from several kg to >1000 tonnes. All samples were run through a static grizzly screen to remove pieces larger than 100mm in diameter. Rock samples from the vents were coarsely crushed and then treated in the same way as alluvial samples. The <100mm fraction was washed in a scrubber that breaks up any clods. The <0.5mm component is suspended in the wash water and pumped to settling ponds; fractions larger than 25 mm are used to backfill exploration pits. Samples in the +8mm-16mm and +16mm-24mm size fractions are sorted by hand on a picking belt. The +0.5 -8mm component of the sample is washed and classified into 5 fractions: 0.5-0.7mm, 0.7-1mm, 1-2mm, 2-4mm, 4-6mm, 6-8mm. These fractions are transferred to a pulsating jig plant for gravity separation. Samples in the 2mm-8mm size fractions are visually inspected after the jigging process and sorted in the recovery laboratory. The three smallest size fractions are jigged separately. The heavy concentrate in the center of the jig pan is collected and dried; material on the outer part of the jig pan is discarded. The sorters in the laboratory have demonstrated their efficiency in identifying and recovering a wide range of mineral species, including garnet (pyrope), ilmenite, spinel, chrome-diopside, diamond, moissanite, sapphire, ruby, Carmel Sapphire™, hibonite, rutile and zircon. The material described here is dominated by samples from the Rakefet Magmatic Complex, and the alluvial deposits of the Kishon River mid-reach, because these localities have been most thoroughly bulk-sampled, providing abundant material.

The unprocessed heavy mineral concentrates of several samples were hand-picked under a binocular microscope in the CCFS laboratories. Several rock samples also have been processed by SelfFrag (electrostatic disaggregation) techniques at CCFS, sieved and hand-picked after magnetic and heavy-liquid separation.

Analytical Techniques

SEM, EMP

Samples were mounted in epoxy blocks, polished and coated with carbon. A Zeiss EVO MA15 scanning electron microscope (SEM) at the Geochemical Analysis Unit (GAU), Macquarie University, Sydney, Australia was used to capture Backscattered Electron (BSE) images and Energy Dispersive X-ray spectrometry (EDS) was used to map the elemental composition of the samples, and to analyze phases of interest. An accelerating voltage of 15 keV and a beam current of 1 nA was used.

Major and minor elements were determined by electron microprobe (EMP) using a CAMECA SX100 equipped with five wavelength-dispersive spectrometers at the Macquarie University GeoAnalytical (MQGA; formerly GAU), Macquarie University, Sydney, Australia. Analyses were performed using a focused beam (1-2 μm) with an accelerating voltage of 15 keV and a beam current of 20 nA. Standards were a suite of natural and synthetic minerals. Peak counting varied between 10 – 20 s, and background was counted for 5 – 10 s on either side of the peak. Oxygen and carbon were measured directly; matrix corrections were carried out by the ZAF software.

Major and minor elements also were determined by electron microprobe (EMP) using a JEOL 8530F electron microprobe equipped with five wavelength dispersive spectrometers at the Centre for Microscopy Characterisation and Analysis (CMCA), The University of Western Australia, Perth, Australia. Analyses were performed using a fully focussed beam with an accelerating voltage of 15 keV, a beam current of 15 nA. Standards were a suite of natural and synthetic minerals. On-peak counting times were 30 seconds for all elements. X-ray intensity data was corrected for Time Dependent Intensity (TDI) loss (or gain) using a self-calibrated correction for Si $\text{K}\alpha$, Ti $\text{K}\alpha$, Mn $\text{K}\alpha$, Na $\text{K}\alpha$, K $\text{K}\alpha$ and mean atomic number (MAN) background corrections were used throughout (Donovan & Tingle, 1996; Donovan et al., 2016). Unknown and standard intensities were corrected for deadtime. Oxygen was measured, matrix corrections and ZAF correction were applied throughout.

Transmission Electron Microscopy

FIB foils from the region of interest were prepared for TEM using a dual-beam FIB system (FEI Nova NanoLab 200). High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) imaging and element mapping were carried out using an FEI Titan G2 80-200 TEM/STEM with ChemiSTEM Technology operating at 200 kV at the

Centre for Microscopy Characterisation and Analysis (CMCA), The University of Western Australia, Perth, Australia. The element maps were obtained by energy dispersive X-ray spectroscopy using the Super-X detector on the Titan with a probe size ~ 1 nm and a probe current of ~ 0.25 nA. Total acquisition times of 20-30 minutes were used to obtain good signal-to-noise ratios. Electron diffraction was carried out using a field limiting aperture that selected an area approximately 400nm in diameter.

3D- μ CT

For X-ray micro-computed tomography (μ CT) at the CMCA, the grain was mounted on a finger of rigid PVC plastic with double-sided tape and a separate tomogram was collected for each grain using a μ CT system (Versa 520 XRM, Zeiss) running Scout and Scan software (v11.1.5707.17179, Zeiss). Samples were scanned at 50 kV and 77 μ A with the source detector positions set to -17.7 and 117 mm, respectively. An LE1 source filter was applied to screen out low energy X-rays. A 0.4X objective lens was used together with 2x camera binning to achieve an isotropic voxel resolution of 9 μ m. Each scan comprised 2501 projections through 360° with an exposure of 3s for each projection. Raw data were reconstructed using XMReconstructor software (v11.1.5707.17179, Zeiss) following a standard centre shift and beam hardening correction. The standard 0.7 kernel size recon filter setting was also used. The visualization and analysis of data generated from μ CT scans were performed using Avizo (v8.1.1, FEI) software.

Raman Spectroscopy

Raman spectra were collected with a Horiba LabRAM HR Evolution microscope with a Sincerity OE detector, using 532-nm laser at the Department of Earth Sciences, University of Milan. Reflected and transmitted light optics were used to select analysis locations. Hibonite from Sierra de Comechingones was studied from a polished thin section. Hibonite from Mt. Carmel was studied using a raw fragment. The analysis was performed using a 100x objective and 600 (500 nm) grating. Laser power was attenuated to 50% of the power. To maximize the signal-to-noise ratio, two spectra were collected using an exposure time of 30 s, and then merged together at the end of the acquisition. Spectra were taken at two polarizations at right angles to check for changes in intensity of the Raman shifts. The system was calibrated using the 520 cm^{-1} Raman line of metallic silicon. Spectra were processed using LabSpec v.6 (Horiba®). Peak positions were obtained by fitting Gaussian peaks.