

APPENDIX

Sampling

The Shefa Yamim exploration project is 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 Selfrag (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 $K\alpha$, Ti $K\alpha$, Mn $K\alpha$, Na $K\alpha$, K $K\alpha$ and mean atomic number (MAN) background corrections were used throughout (Donovan and 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.

Trace element analysis

Trace elements were obtained using a Photon Machines Excite 193 nm ArF EXCIMER laser system coupled to an Agilent 7700x ICP-MS at the GAU, Macquarie University, Sydney,

Australia. Detailed method descriptions have been given by Jackson et al. (2004). The ablation conditions included beam size (50 μm), pulse rate (5Hz) and energy density (7.59 J/cm²). Ablation was performed in an HelEx II cell and helium was used as the carrier gas at a total flow rate of 0.825L/min. Average analytical runs comprised of 20 analyses, 2 analyses of reference materials and 10 analyses of unknowns, bracketed by two analyses of NIST610 standard glass at the beginning and end of each run. Analyses consisted of 60 second of background and 120 seconds of ablation. Trace element concentrations were calculated from the raw signal data using the on-line software package GLITTER (Griffin et al. 2008a; www.mq.edu.au/GEMOC). GLITTER calculates the element concentrations and relevant isotopic ratios for each mass sweep and displays them as time-resolved data. This allows homogeneous segments of the signal to be selected for integration. GLITTER then corrects the integrated ratios for ablation-related fractionation and instrumental mass bias by calibration of each selected time segment against the identical time-segments of the standard glass (NIST610 using the GeoReM values). An appropriate major element was used as an internal standard to quantify trace element concentrations and the synthetic BCR2 and NIST612 glasses were used as reference materials (GeoReM).

Transmission Electron Microscopy

FIB foils from the region of interest were prepared for TEM using a dual-beam FIB system (FEI Helios G3CX). 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.

Raman Spectroscopy

Raman spectra were collected with and Horiba LabRAM HR Evolution microscope with a Sincerity OE detector, using 532-nm laser the Department of Earth Sciences, University of

Milan. Reflected and transmitted light optics were used to select analysis locations. The analysis was performed using a 100x objective and 600 (500 nm) grating. Laser power was attenuated to 50% of the power (64.5mW). To maximize the signal-to-noise ratio, two spectra were collected using an exposure time of 20 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 520.70 cm^{-1} Raman line of metallic silicon. Spectra were processed using LabSpec v.6 (Horiba[®]). Peak positions were obtained by fitting Gaussian peaks. Raw Raman spectra have been deposited as supplementary material.

X-ray diffraction

A small fragment of kahlenbergite was extracted from the grain 1210B1 in the polished section under a reflected light microscope using a needle and mounted on a glass rod. Another fragment of Na- β -alumina (diaoyudaoite) was extracted from grain 1210B4 in the same way and mounted on a glass rod. Both fragments were tested by single-crystal X-ray diffraction. Single-crystal X-ray studies were carried out at Dipartimento di Scienze della Terra, Università di Milano using a four circles κ -geometry Rigaku XtaLAB Synergy diffractometer, PhotonJet (Mo) X-ray Source operating at 50 kV and 1 mA, with a monochromatized MoK α radiation ($\lambda = 0.71073\text{ \AA}$), and equipped with a Hybrid Pixel Array detector at 62 mm from the sample position, and with 1 s exposure time per frame for kahlenbergite and s exposure time per frame for diaoyudaoite.

The structure of kahlenbergite and diaoyudaoite were solved by direct methods in the space group $P6_3/mmc$ and then refined using the program Shelxl-2012 (Sheldrick 2015). The site occupancy factor (s.o.f.) at the cations sites was allowed to vary (Al³⁺ versus Cr³⁺, and K⁺ versus structural vacancy in kahlenbergite and Na⁺ versus structural vacancy in diaoyudaoite) using scattering curves for ionized atoms taken from the International Tables for Crystallography (Wilson 1992). At the last refinement stage, with anisotropic atomic displacement parameters, the residual value settled at $R1(F) = 0.0288$ for 687 unique reflections $F_o > 4\sigma(F_o)$ and 0.0364 for all 827 data, and 46 parameters for kahlenbergite and $R1(F) = 0.0312$ for 715 unique reflections $F_o > 4\sigma(F_o)$ and 0.0370 for all 827 data, and 45 parameters for diaoyudaoite. The refinement are in good agreement with chemical analyses: observed site scattering at the cation sites is 163.97 electrons per formula unit,

epfu, vs. 164.65 epfu from chemical analyses for kahlenbergite; and observed site scattering at the cation sites is 158.43 epfu, vs. 157.66 epfu from chemical analyses for diaoyudaoite. Crystallographic data are available as supplementary material¹.

¹ For a copy of CIF, document item visit the American Mineralogist website.