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Cathodoluminescence as a tool to discriminate impact melt, shocked and unshocked volcanics: A case study of samples from the El'gygytgyn impact structure

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Abstract–El'gygytgyn (Chukotka, Arctic Russia) is a well-preserved impact structure, mostly excavated in siliceous volcanic rocks. For this reason, the El'gygytgyn structure has been investigated in recent years and drilled in 2009 in the framework of an ICDP (International Continental Scientific Drilling Program) project. The target rocks mostly consist of rhyodacitic ignimbrites and tuffs, which make it difficult to distinguish impact melt clasts from fragments of unshocked target rock within the impact breccia. Several chemical and petrologic attempts, other than dating individual clasts, have been considered to distinguish impact melt from unshocked volcanic rock of the targets, but none has proven reliable. Here, we propose to use cathodoluminescence (imaging and spectrometry), whose intensity is inversely correlated with the degree of shock metamorphism experienced by the investigated lithology, to aid in such a distinction. Specifically, impact melt rocks display low cathodoluminescence intensity, whereas unshocked volcanic rocks from the area typically show high luminescence. This high luminescence decreases with the degree of shock experienced by the individual clasts in the impact breccia, down to almost undetectable when the groundmass is completely molten. This might apply only to El'gygytgyn, because the luminescence in volcanic rocks might be due to devitrification and recrystallization processes of the relatively old (Cretaceous) target rock with respect to the young impactites (3.58 Ma). The alteration that affects most samples from the drill core does not have a significant effect on the cathodoluminescence response. In conclusion, cathodoluminescence imaging and spectra, supported by Raman spectroscopy, potentially provide a useful tool for in situ characterization of siliceous impactites formed in volcanic target.

INTRODUCTION

Impact craters on Earth can be considered analogs of those on the Moon, Mars, and other planetary bodies with solid surfaces, except for the general target composition. Craters excavated in volcanic rocks are rare on Earth: Lonar in India (Kieffer et al. 1976), Logancha in Russia (Masaitis 1999), as well as Vista Alegre and Vargeão in Brazil (Crósta et al. 2010, 2012) were all formed in basaltic target rocks, and the El'gygytgyn impact structure in Russia (Dietz and McHone 1976) that was formed in siliceous volcanic rocks. The Monturaqui impact crater was formed in target rocks that include some ignimbrites, but the impact event mostly affected the underlying granites (e.g., Ugalde et al. 2007). Impact craters excavated in volcanic rocks provide information on shock metamorphism in volcanic terrains, and, for instance, those formed in basalts are comparable to the craters on the crust of the Moon. In particular, El'gygytgyn represents the only known impact structure excavated in a Cretaceous volcanic suite of mostly rhyodacitic

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composition (Gurov et al. 1979; Gurov and Koeberl 2004). Scientific deep drilling of the structure, supported by the International Continental Scientific Drilling Program (ICDP), took place in 2009 for investigating the paleoclimatic evolution in the Arctic region during the last 3.6 Ma and for studying the shock metamorphism in this peculiar volcanic target rock (Brigham-Grette et al. 2007; Melles et al. 2011; Koeberl et al. 2013).

The most challenging task in investigating rocks from the El'gygytgyn drill core was the distinction of possible impact melt clasts from the petrographically similar, siliceous volcanic target rock fragments in the suevite. The only reliable technique so far would be dating individual particles, as the target rock (83.1–88.5 Ma; Stone et al. 2009) is significantly older than the impact event (3.58 ± 0.04 Ma; Layer 2000). Several approaches have been tried, from the chemical and petrographic comparison with confirmed impact melts and glasses, using optical and electron microscopes, electron microprobe, X-ray fluorescence and instrumental neutron activation (Pittarello and Koeberl 2013a; Pittarello et al. 2013; Raschke et al. 2013a), to quantitative petrography, and by image analysis for clast size distribution and shape characterization (Pittarello and Koeberl 2013b), but none of them has provided a reliable criterion. A similar issue was studied by Neal et al. (2015), in an attempt to distinguish pristine lunar mare basalts from impact melts. These authors succeeded by using a quantitative petrographic method, similar to that described in Pittarello and Koeberl (2013b), but the applicability of this technique seems controlled by the nature of the material and the type of impact event and was not completely successful for El'gygytgyn rocks.

Cathodoluminescence (CL) is based on emission of photons in the range of visible (400–700 nm), ultraviolet (UV; <400 nm), and infrared (IR; >700 nm) light through sample excitation by high-energy electron flow (Marshall 1988; Hayward 1998). The emission results from the transition of ions from an excited to a lower energy electronic state. This excitation is a reversible process and, therefore, does not permanently affect the investigated material (Götze 2012). However, as there is no consensus on the physical explanation for the different CL effects, this technique is mostly used for revealing the internal texture of minerals (e.g., Nasdala et al. 2004).

Cathodoluminescence detectors can be attached to an optical (Optical CL), or a scanning electron microscope (SEM-CL), or an electron microprobe (EPMA-CL). Optical CL is based on two systems, known as cold and hot cathode instruments. In the hot cathode CL, electrons are generated by a heated filament and are accelerated at low voltage (generally ca. 14 keV) toward the anode; using a cold cathode the chamber is filled with ionized gas. The instrument is mounted on a standard polarization microscope (Götze 2002). In SEM-CL, the source of excitation is the electron beam and the detectors can be set on the whole spectral range (~200–800 nm, namely panchromatic spectrum), providing grayscale images, or can be wavelength-filtered for red, green, and blue (monochromatic), providing three separate gray-shade images that can be combined to yield a "true color" image. Monochromatic images are obtained by selecting a certain wavelength, while panchromatic images result from the integration of the luminescence over all emissions. Panchromatic images are dominated by the strongest emissions, whereas monochromatic images can show specific luminescence effects (Nasdala et al. 2004). A spectrum, i.e., a scan of wavelength versus intensity, can be collected with a spectrophotometer.

Quantitative CL can be obtained by converting the wavelength datum into energy units and deconvolving the obtained corrected spectrum into the Gaussian components with dedicated software, revealing each emission center (Kayama et al. 2013). In some instances, the correlation between intrinsic features of the material, including ion substitution or lattice defects, and the position of the respective peaks is known (Götte 2009; Götze 2012). Carbonates can produce a strong phosphorescence phenomenon in SEM-CL, resulting in streaking on the image. Some technical adjustments can reduce this effect. Among the rock-forming minerals, quartz and feldspars show generally moderate to bright luminescence, whereas most mafic minerals, such as pyroxene, amphibole, and biotite, show low luminescence due to their relatively high content in Fe that inhibits luminescence emission. Many accessory, late-stage minerals, such as apatite and zircon, have strong luminescence, due to the preferred incorporation of rare earth elements and Hf into their crystal lattice. Phyllosilicates are not particularly luminescent, but there are a few exceptions, such as the kaolinite-group minerals and pyrophyllite (e.g., Richter et al. 2003; Götte 2009).

Cathodoluminescence is commonly applied for the evaluation of trace element microdistribution, quantitative analysis of phase distribution, age determination in young sediments, and characterization of the crystal structure (Götze 2002; Nasdala et al. 2004), but has been also applied for investigating impact glasses and tektites (e.g., Gucsik et al. 2004), and in particular shock-induced deformation in quartz (Owen and Anders 1988; Boggs et al. 2001; Götze et al. 2001; Okumura et al. 2009) and shocked target rocks (e.g.,

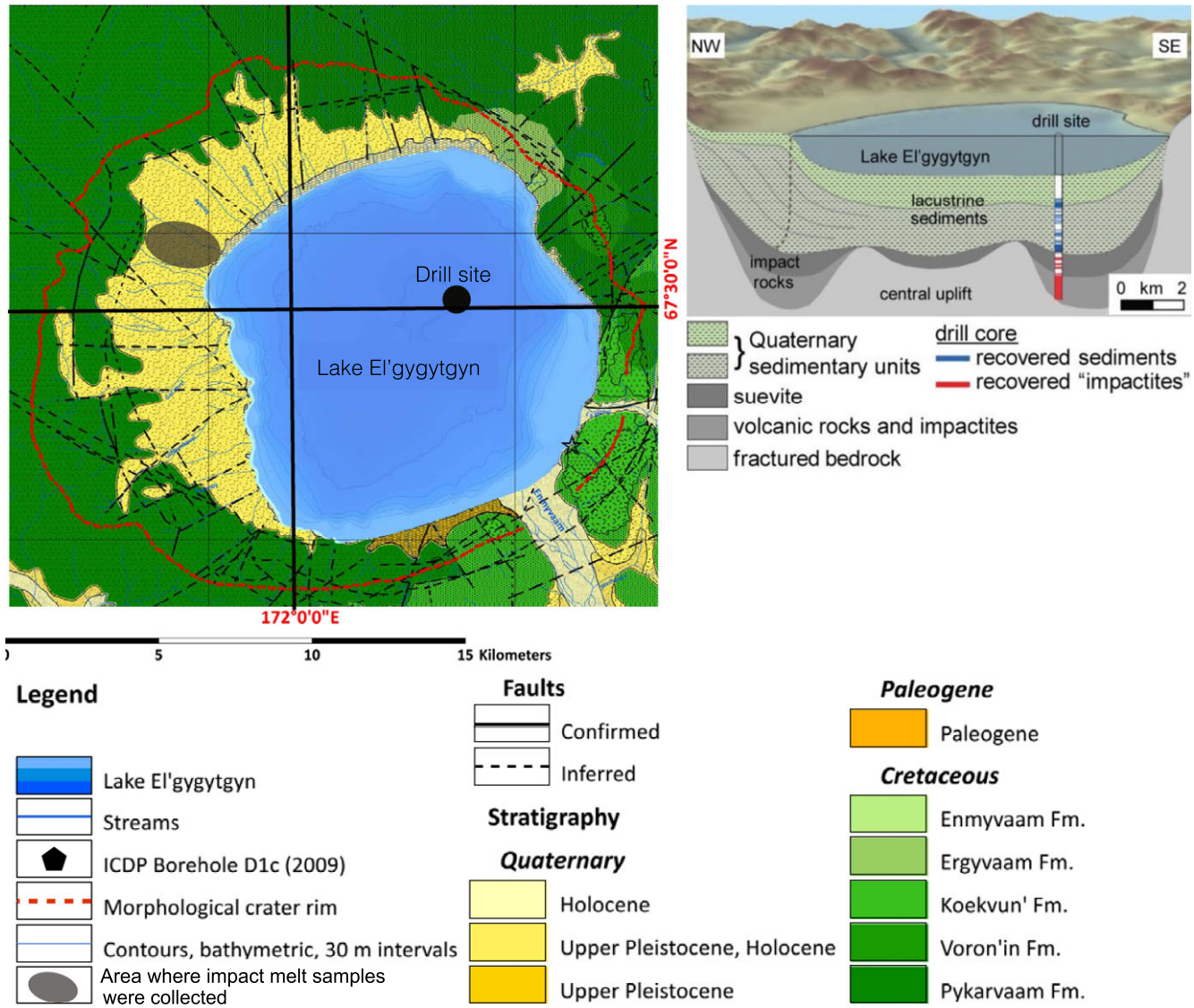

Fig. 1. Geological map and cross section of the El'gygytgyn impact structure, showing the drill site and the area where impact melt samples were collected. Modified after Raschke et al. (2014).

Ramseyer et al. 1992). An attempt to calibrate a shock barometer based on the quantitative evaluation of CL spectra of shocked feldspar was proposed by Kaus and Bischoff (2000) and Kayama et al. (2012). However, the only characterization of impact melts was provided by Götte (2009), who investigated the change of luminescence in shocked minerals, the luminescence of suevite impact breccia and impact glass, and the effect of postimpact hydrothermal alteration. Among the possible applications, there is also the opportunity to investigate other planetary bodies with probes equipped with this facility, as discussed in Bost et al. (2011), e.g., for classifying the thermal metamorphism of chondrules in meteorites (e.g., Sears et al. 2013).

Here, we discuss combined optical and SEM cathodoluminescence, as a tool for the characterization of El'gygytgyn impact rocks. Other than information on the shock history of the sample, this technique provides also a potential criterion for identifying impact melts that were preserved from recrystallization, devitrification, and alteration.

GEOLOGICAL SETTING

The El'gygytgyn structure, Chukotka, Arctic Russia, consists of a circular depression centered at 67°30′ N and 172°00′ E and with a diameter of about 18 km (Fig. 1). The depression is largely filled by a

lake, of about 12 km diameter and 170 m maximum depth, which is surrounded by a complex system of lacustrine terraces (Gurov et al. 2005, 2007). The (not exposed) central uplift has been revealed by geophysical investigations and is centered on the crater rim rather than on the lake (Gebhardt et al. 2006). The impact event was dated at 3.58 ± 0.04 Ma using the ^{40}Ar-^{39}Ar method (Layer 2000).

The depression is excavated in rocks of the Late Cretaceous Okhotsk-Chukotsky Volcanic Belt, mainly involving the Pykarvaam series (88.5 ± 1.7 Ma; Layer 2000; Stone et al. 2009; Raschke et al. 2014). The volcanic sequence includes lava, tuffs, and ignimbrites of rhyolitic to dacitic composition, but locally also andesites and andesitic tuffs occur, as well as local basalt (Gurov and Koeberl 2004; Raschke et al. 2014). Ignimbrites and tuffs of rhyolitic-dacitic composition are the most abundant rock types of the crater basement, at 89% (Gurov et al. 2005). Therefore, the rhyolitic ignimbrite is considered representative of the target rock. It consists of quartz; orthoclase ($Or_{60–80}$); plagioclase ($An_{20–30}$); biotite; and, rarely, amphibole, embedded in a fine-grained clastic matrix that contains glass, quartz, and feldspar fragments. The rhyolitic-dacitic ignimbrites and tuff have textures ranging from fluidal-glassy to fine-grained granular and spherulitic (Gurov et al. 2005). Andesites and andesite tuffs, which occur locally, are characterized by the occurrence of andesine (An_{45} to An_{40}), and a minor amount of clinopyroxene and amphibole (Gurov and Koeberl 2004). A detailed description of the target lithology can be found in Pittarello et al. (2013) and Raschke et al. (2014).

Impact melt rocks in the El'gygytgyn crater are mainly redeposited in lacustrine terraces and probably originate from the strongly eroded ejecta blanket or from slumping off the crater rim. Such impact melt rocks include aerodynamically shaped glass bombs and impact melt breccia (Pittarello and Koeberl 2013a). The impactites collected at the crater are generally relatively fresh, and most of them display neither significant postimpact hydrothermal alteration nor weathering (Gurov et al. 2005).

Drilling in 2009, within the framework of an ICDP project, focused on the lacustrine sediment record in the Arctic region and on the impact features in acidic volcanic rocks (Melles et al. 2011; Koeberl et al. 2013). Part of the drill core DC1 investigated for shock metamorphism covers the interval from 316 m to 517 m depth below lake bottom (blb) and includes the impactites (suevite) underlying the lake sediments and fractured target rocks (mostly rhyodacitic ignimbrite). Detailed descriptions of the core stratigraphy were provided by Koeberl et al. (2013), Pittarello et al. (2013), Raschke et al. (2013a, 2013b), and Wittmann et al. (2013).

SAMPLES AND METHODS

Samples of impact melt rocks and impact glasses collected at the crater rim and of suevite from the drill were selected for this study (Fig. 2). The selected impact melt rocks and glasses, described in Pittarello and Koeberl (2013a), comprise samples 1D, 1E, and 1G. Three samples of suevite from the drill core, including 98Q6_W7-11 from 318.0 m below lake bottom (mblb), 101Q6_W11-13, 326.7 mblb, and 124Q2-W18-20, 387.22 mblb (see Pittarello et al. [2013] for a general description), were selected for this study. All samples were analyzed in the form of polished thin sections and were previously investigated with optical and scanning electron microscopy (SEM) and by electron microprobe analysis (EMPA) at the Department of Lithospheric Research, University of Vienna, and at the Natural History Museum, Vienna, Austria (details about the instrumentation are provided in Pittarello et al. [2013] and Pittarello and Koeberl [2013a]). Additional Raman spectroscopy analysis was performed at the Materials and Chemistry Department, Research Group Electrochemical and Surface Engineering (SURF) of the Vrije Universiteit Brussel, Brussels, Belgium, using a confocal LabRAM HR Evolution (HORIBA Scientific) Raman microscope. The instrument is equipped with a multichannel air-cooled CCD detector that has a spectral resolution <1 cm^{-1}, lateral resolution of 0.5 μm, and axial resolution of 2 μm, has a solid-state laser corresponding to green light (532 nm), and at 1.25 mW excitation with 10% filter for preventing any sample damage. The obtained Raman spectra were compared with those from reference minerals in the online Rruff database (Downs 2006).

Sample Description

Sample 1D: Droplet-shaped impact glass, blackish in hand sample, transparent in thin section under plane-polarized light. Fluidal structure is marked by the occurrence of abundant microlites of pyroxene, with star-shaped arrangement and curved terminations. Vesicles are rare in the sample and generally elongated in the flow direction. In the central part, some unidentified unmelted material is preserved.

Samples 1E and 1G: Impact melt rock consisting of alternating glass layers with *schlieren* and domains with unmelted material and variously shocked to unshocked volcanic clasts in a fine-grained (μm-sized) matrix. Along the glassy domains, dense aggregates of

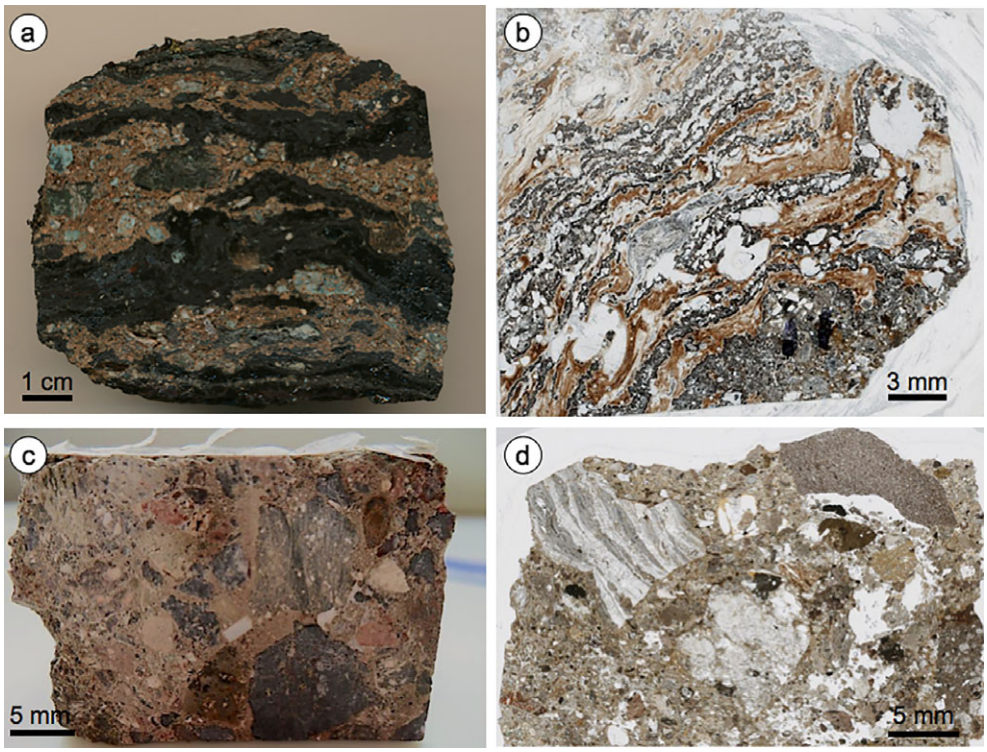

Fig. 2. Selected samples from El'gygytgyn. a) Impact melt rock (sample Glass_2D), collected within the crater, consisting of alternating layers of impact glass (blackish) and impact melt breccia that includes target rock clasts. b) Thin section scan of sample Glass_1E, which shows similar features to those described in (a): brownish impact glass alternating with domains of impact melt breccia. c) Fragment of suevite from the drill core (sample 98Q5_W11-15, 317.9 m). Target rock clasts and impact melt fragments are suspended in a fine-grained matrix. d) Thin section scan of sample 98Q6_W7-11, 318.1 m, consisting of suevite with abundant volcanic clasts from the target and impact melt clasts, almost indistinguishable from optical observations.

plagioclase microlites have crystallized. Vesicles are abundant across the samples and generally have amoeboid shapes and irregular margins.

Drill core samples 98Q6_W7-11 and 101Q6_W11-13: Suevite including up to several mm size clasts of volcanic rocks and impact melt and variously shocked volcanic clasts and mineral grains, in a fine-grained (<1 μm) matrix that includes glass shards. The samples overall are quite altered and the pores are locally filled with zeolites.

Drill core sample 124Q2-W18-20: Impact breccia, dominated by a large (cm) clast of shocked volcanic rock, likely ignimbrite. The shocked clast contains variously shocked feldspar phenocrysts in a glassy matrix. The breccia consists of mm-sized unshocked to shocked volcanic clasts and individual mineral grains in a fine-grained clastic matrix. Very likely impact melt occurs in this sample, allowing the classification as suevite (Stöffler and Grieve 2007).

Glass and impact melt breccia samples (1D, 1E, and 1G) are quite fresh and not affected by weathering. Drill core samples appear slightly altered, with vesicles filled by secondary zeolites, but alteration mostly affected the matrix and not the individual clasts. Luckily, both impact melt and volcanic rock clasts are present in the drill core samples. This allows the direct comparison of the two lithologies under the same weathering conditions.

Optical CL microscopy on carbon-coated polished thin sections was performed with a LUMIC HC5-LM, operated with a beam energy of 14 keV and a beam current of ~0.20 mA. Image acquisition was performed with a KAPPA DX 40 C camera system, at the Department of Lithospheric Research, University of Vienna, Austria.

Selected thin sections were carbon-coated and examined with Gatan MiniCL and MonoCL (MonoCL4 ®) systems attached to a JEOL JSM 6610-LV scanning electron microscope (SEM), at the Natural History Museum Vienna, Austria. For selection of relevant areas, MiniCL analysis was first performed using an accelerating voltage of 15 kV, a beam current of 0.2 nA, and operating at a working distance of 10 mm.

The operating conditions for obtaining all SEM-Mono CL images were 15 kV accelerating voltage and 1.2 nA beam current. CL images were recorded at a

working distance of ~10 mm and at room temperature in the wavelength range of 200–800 nm, with 1 nm spatial resolution from scanned areas of 60 × 40 μm. Representative composite RGB (false-color) images were obtained by obtaining wavelength-filtered spectra of selected areas. Cathodoluminescence spectra were acquired with the Gatan MonoCL4 system, operated at 15 kV accelerating voltage and 1.2 nA beam current. All spectra were recorded in the range of 200–800 nm with a step size of 2 nm using a dwell time of 0.5 s, exposure time of 0.4 s, and a grating of 150 lines/mm. The scanned areas of selected clasts were about 100 and 400 μm^2, respectively. The selected areas were also analyzed by SEM-EDS for major and minor element compositions and to check for possible interference from adjacent mineral phases.

RESULTS

Optical Cathodoluminescence (Glasses and Suevite)

Optical CL on impact glass was performed for providing a reference for clasts in the suevite. Sample 1D consists almost exclusively of glass with a few pyroxene microlites. The glass gives no luminescence signal and pyroxene microlites are not visible due to the presence of Fe, which inhibits luminescence (Figs. 3a and 3b). Some luminescence is present in the domains where unmelted material is partially preserved (Figs. 3c and 3d), although very low, if compared with the response of the epoxy in the hole. On the other hand, in areas where unshocked or slightly shocked volcanic clasts are present, the luminescence is quite high (Figs. 3e and 3f). The color seems to confirm the identification of the phenocrysts as determined by SEM-EDS and EMPA: blue for K-feldspar and greenish for plagioclase. The blue luminescence of K-feldspar is related to the substitution of Si^{4+} with Al^{3+}, whereas the greenish luminescence in plagioclase is generally referred to the substitution of Mn^{2+} in Ca^{2+} sites (Götze 2009). Although clearly detected in transmitted light, schlieren do not show obvious differences in luminescence. The local aggregates of plagioclase microlites show a weak luminescence. With a longer exposition time and following image processing, the resulting color, although it is a weak signal, confirms the feldspathic nature of microlites, as determined by EDS-SEM.

Optical CL in impact rocks from the drill core is obliterated by the occurrence of secondary carbonates, calcite in particular, which has a strong orange luminescence that dominates the images, flattening the different response of other phases (Fig. 4). Nevertheless, clasts in the suevite exhibit a huge variety of CL responses, even when clasts are optically similar to each other. Although strongly altered, volcanic clasts locally preserve the typical CL features, such as the CL color emission of the phenocrysts (Figs. 4a and 4b) or internal features in the crystals due to magmatic growth. Areas identified as impact melt by petrographic observations (Pittarello et al. 2013) show absent to very low luminescence, consistent with results reported by Götte (2009). Individual quartz and feldspar crystals are quite common in the suevite. These crystals are shocked to various degrees and the response to CL varies accordingly (Figs. 4c–f). Unshocked grains exhibit magmatic features due to crystal growth. Shocked grains, according to their degree of shock metamorphism, exhibit a reduced luminescence, locally down to none in the case of complete transformation into diaplectic glass. This is consistent with shock effects observed for CL spectra in variably shocked plagioclase grains (Kaus and Bischoff 2000) and quartz (e.g., Boggs et al. 2001). Raman spectroscopy on selected grains allows the evaluation of the true state of the material (Figs. 4g–h), revealing the presence of preserved crystalline domains or the complete transformation into diaplectic glass (for comparison, see Stähle et al. 2008).

SEM-CL

SEM-CL provided different types of data: panchromatic CL images at higher resolution than with the optical CL, represented in gray-shades, and CL spectra from selected areas for a semiquantitative evaluation of the observed features. High-resolution CL images in impact glasses have revealed the occurrence of feldspathic microlites, as suggested by the bright luminescence in panchromatic CL image (Fig. 5a) and the bluish and greenish color appearance in RGB combination of composite CL images (Fig. 5b). The occurrence of microlites with feldspathic composition was confirmed by SEM-EDS measurements (Pittarello and Koeberl 2013a). With longer exposure time (up to 20 s), magmatic features (e.g., growth zoning) of relict crystals are visible (Fig. 5c). In volcanic clasts, the different colors of the unshocked groundmass, as revealed in composite RGB images in SEM-CL, correspond to the different contributions of crystalline material, as confirmed by Raman spectroscopy on the area (Fig. 5d). In the impact breccia, the shock stage of clasts can be roughly evaluated by the response in luminescence (Figs. 5e and 5f). Individual grains exhibit different luminescence depending on the shock stage, from very bright, in case of unshocked crystals, to completely dark for diaplectic glass (Figs. 5e and 5f), whereas the matrix of volcanic clasts in the suevite is generally bright, suggesting a microcrystalline groundmass.

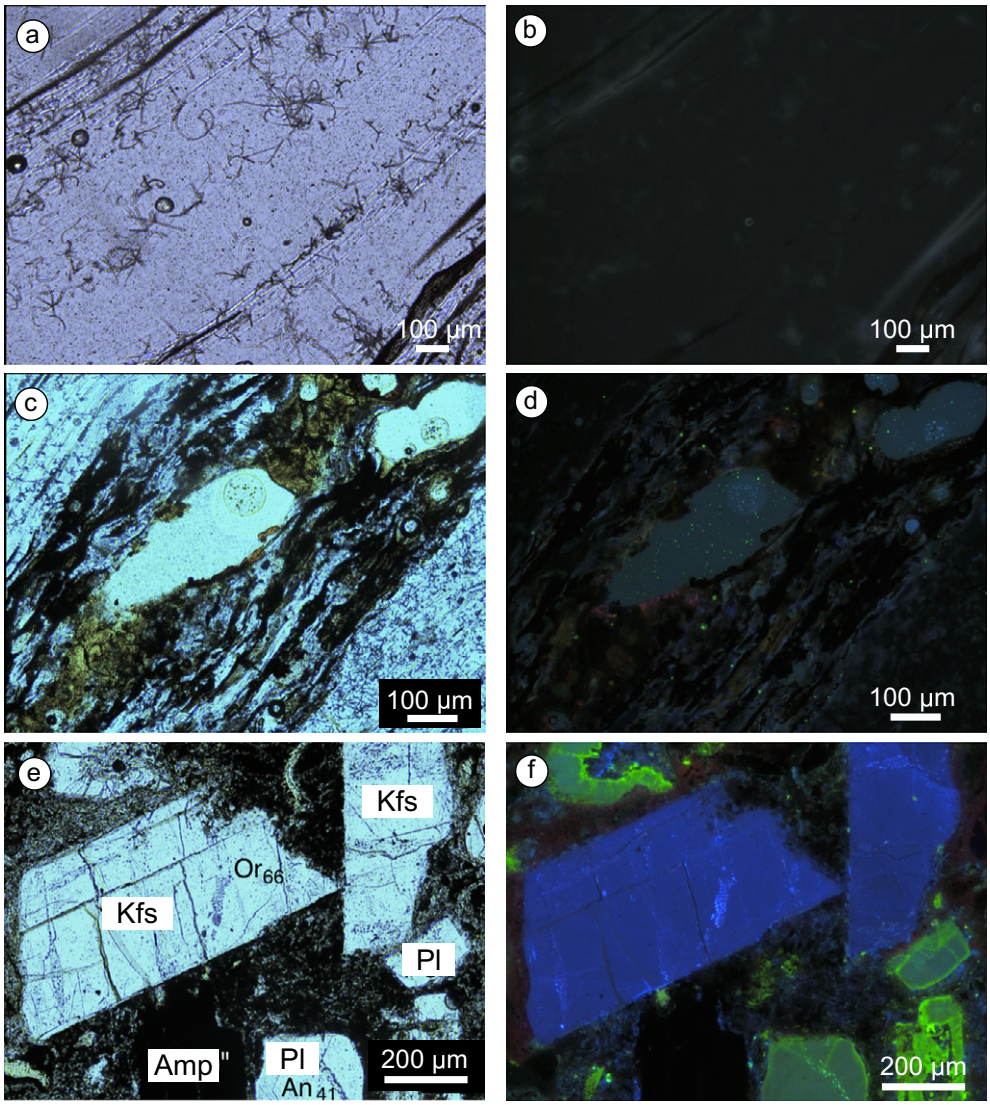

Fig. 3. Optical CL in impact melt rocks and glasses from the crater area. The series on the left (a, c, and e) comprises plane-polarized light images of the locations investigated by optical CL in the right column (b, d, and f). a, b) Impact glass with pyroxene microlites with curved terminations. Sample Glass_1D. c, d) Partially unmelted domains and vesicles in impact melt. Sample 1D. e, f) Unshocked clast of volcanic target rock in impact melt. In CL, unshocked phenocrysts are identifiable by color: bluish for K-feldspar (Kfs) and greenish for plagioclase (Pl). Altered amphibole (Amp) has no luminescence because of the inhibiting effect of Fe. Sample Glass_1E.

Unshocked plagioclase, as individual grains or phenocrysts in volcanic rock clasts, has a distinctive spectrum, with bands at 450, 560, and 690 nm that are generally related to substitution of Al^{3+} in Si^{4+} sites, Mn^{2+} in Ca^{2+}, and Fe^{3+} in Al^{3+}, respectively (Götze 2009). These bands correspond to a greenish color in optical CL or in composite RGB images in SEM-CL. A similar response has been observed in K-feldspar, with bands at 450 and 700 nm, related to replacement of Al^{3+} in the Si^{4+} site and Fe^{3+} in Al^{3+}, respectively (Götze 2009), and corresponding to bluish color in optical CL or in composite RGB SEM-CL images. In the case of impact glass with crystallization of microlites, as the investigated area can be reduced to the beam size in SEM-CL, the nature of microlites can be also measured. The spectrum of quartz generally shows characteristic bands at 420 and 650 nm, but the band position may vary depending on shock stage (e.g., Boggs et al. 2001).

Impact glasses, consisting entirely of melted and quenched material, exhibit CL spectra with similar shape but different intensities (Fig. 6a). If incipient crystallization of the glass occurs, microlites can be identified by both their color in SEM-CL images (e.g., Fig. 5b) and the corresponding CL spectrum (Fig. 6a),

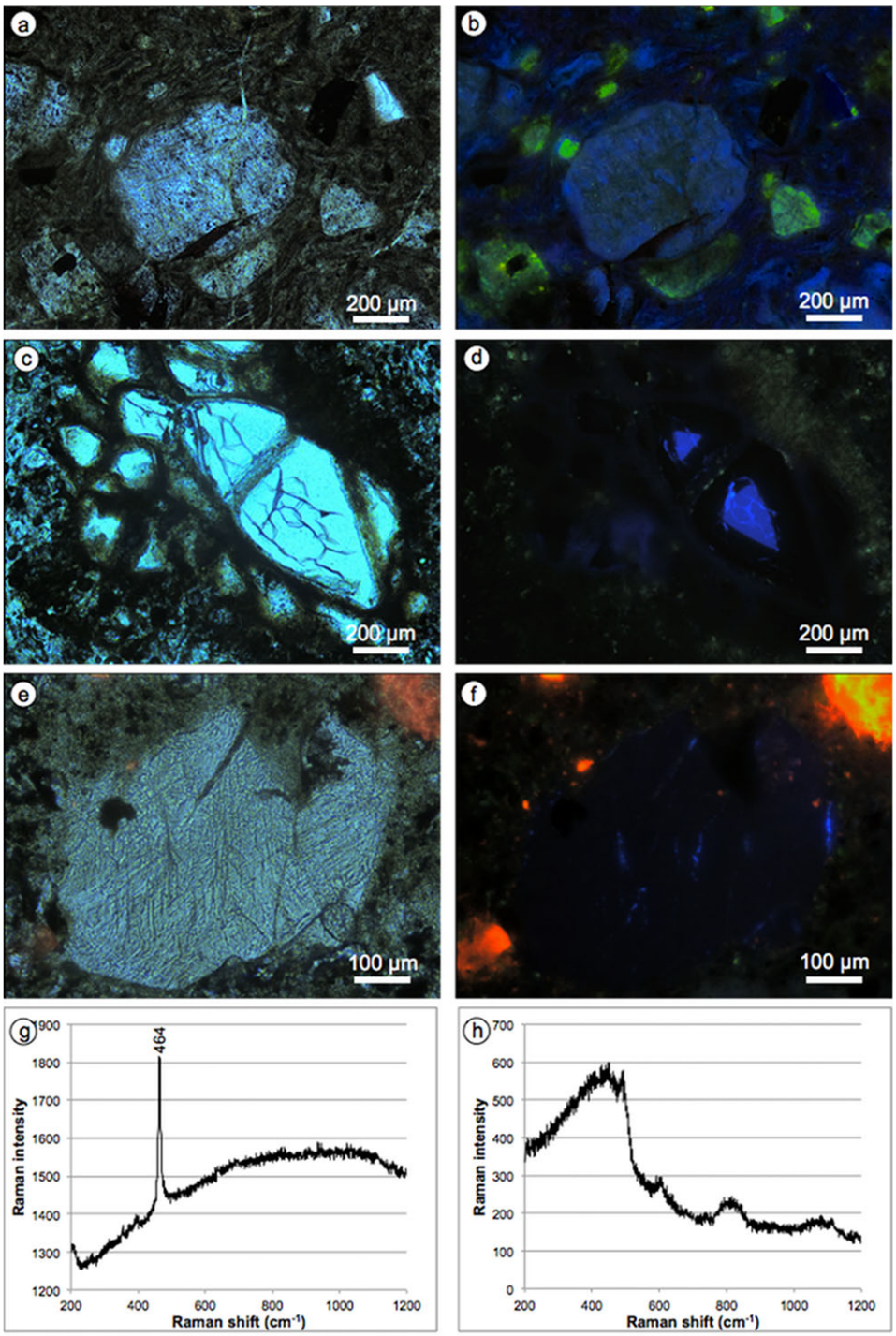

Fig. 4. Optical CL and Raman spectra of representative samples of the suevite from the drill core. As in Fig. 3, the left series (a, c, and e) represents plane-polarized light images of the area investigated with optical CL in the right series (b, d, and f). a, b) Clast of volcanic rock in the suevite. Despite strong alteration, the luminescence is still visible and plagioclase phenocrysts are recognizable, similar to Figs. 3e–f. Sample 98Q6_W7-11, 318.1 m. c, d) Partly shocked grains. Note that only at the core of the largest grain the original luminescence is preserved. Sample 101Q6_W11-13, 326.7 m. e, f) Shocked quartz grain. The crystal exhibits planar features, likely produced by shock, and no remnant luminescence. The orange areas mark the occurrence of secondary carbonate. Sample 101Q6_W11-13, 326.7 m. g) Raman spectrum of the quartz grain in (e), in a preserved portion of which the characteristic peak at 464 cm^{-1} is still visible; but the large background suggests the presence of diaplectic glass. h) Raman spectrum of the grain in (c), likely showing diaplectic material, also observed in the luminescent domain. For comparison, similar spectra are shown in Stähle et al. (2008).

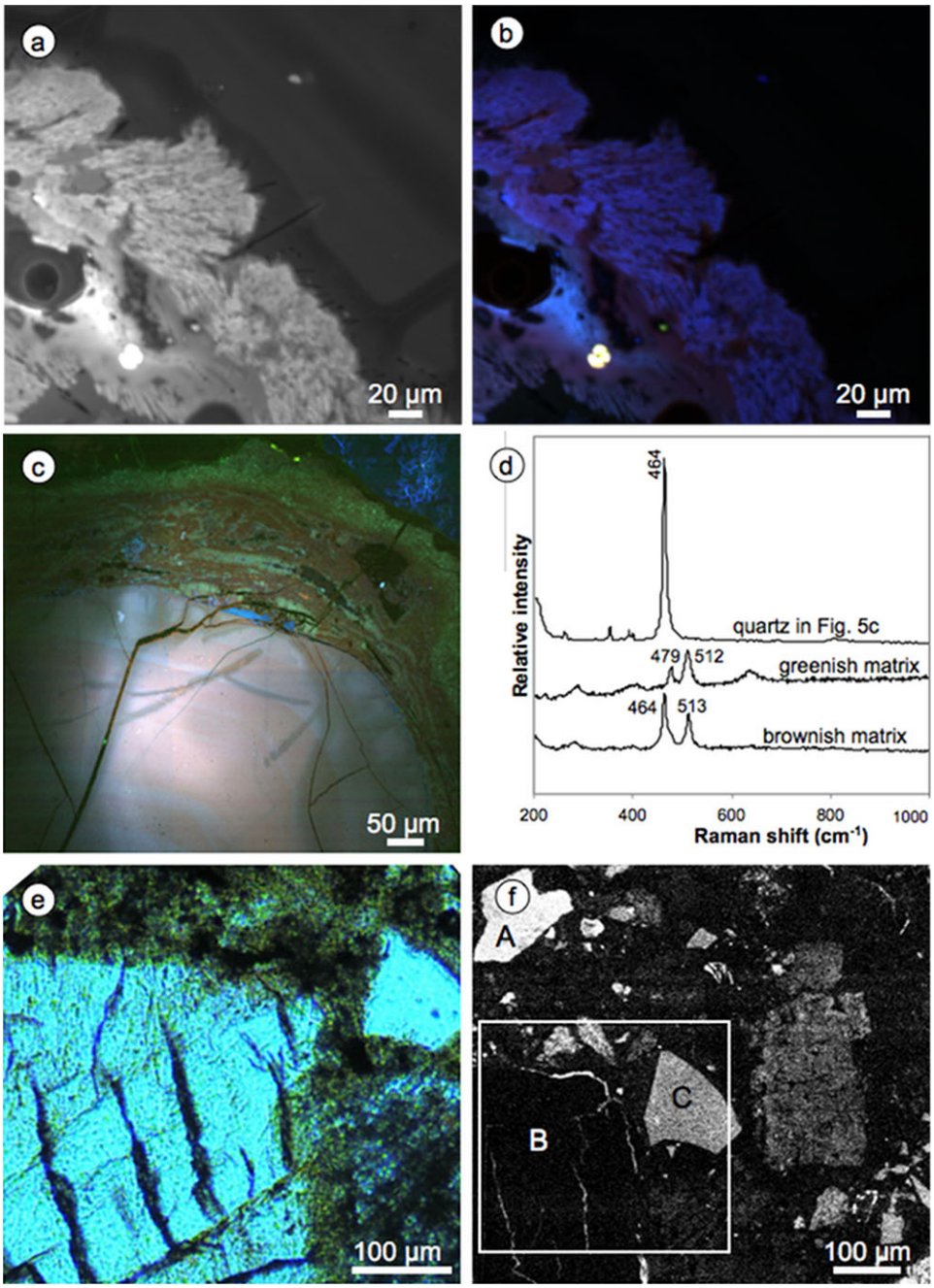

Fig. 5. SEM-CL in impact rocks from El'gygytgyn. a) Panchromatic CL image of impact glass with devitrification features and crystallization of microlites. Sample Glass_1E. b) Composite RGB CL image of the area in (a), showing bluish-reddish luminescence in the microlite-bearing domains and no luminescence in the silicic glass. Sample Glass_1E. c) False-color, wavelength-filtered (RGB) image, obtained with SEM-CL, of a quartz phenocryst in an unshocked volcanic clast in suevite. Concentric features related to magmatic growth are obvious. The crypto-crystalline groundmass surrounding the phenocryst exhibits different colors, reflecting the feldspathic-silicic composition, previously determined by electron microscopy (see Pittarello and Koeberl 2013a). Sample 98Q6_W7-11, 318.1 m. d) Raman spectra from the different domains in (c), including the magmatic quartz, with the characteristic peak at 464 cm^{-1}, and the greenish and brownish domains, where Raman peaks suggest the presence of microcrystalline feldspar, and quartz and feldspar grains, respectively. e) Domain of the suevite including differently shocked lithic clasts and individual mineral fragments. Plane-polarized light image. Sample 98Q6_W7-11, 318.1 m. f) Panchromatic SEM-CL image of the area in (e), marked with a white box, revealing the different shock stage experienced by the clasts. Note the large crystal of K-feldspar on the lower right, which has no luminescence and is highly shocked and likely transformed to diaplectic glass, whereas the small adjacent crystal, in contrast, appears quite bright and is unshocked. Sample 98Q6_W7-11, 318.1 m.

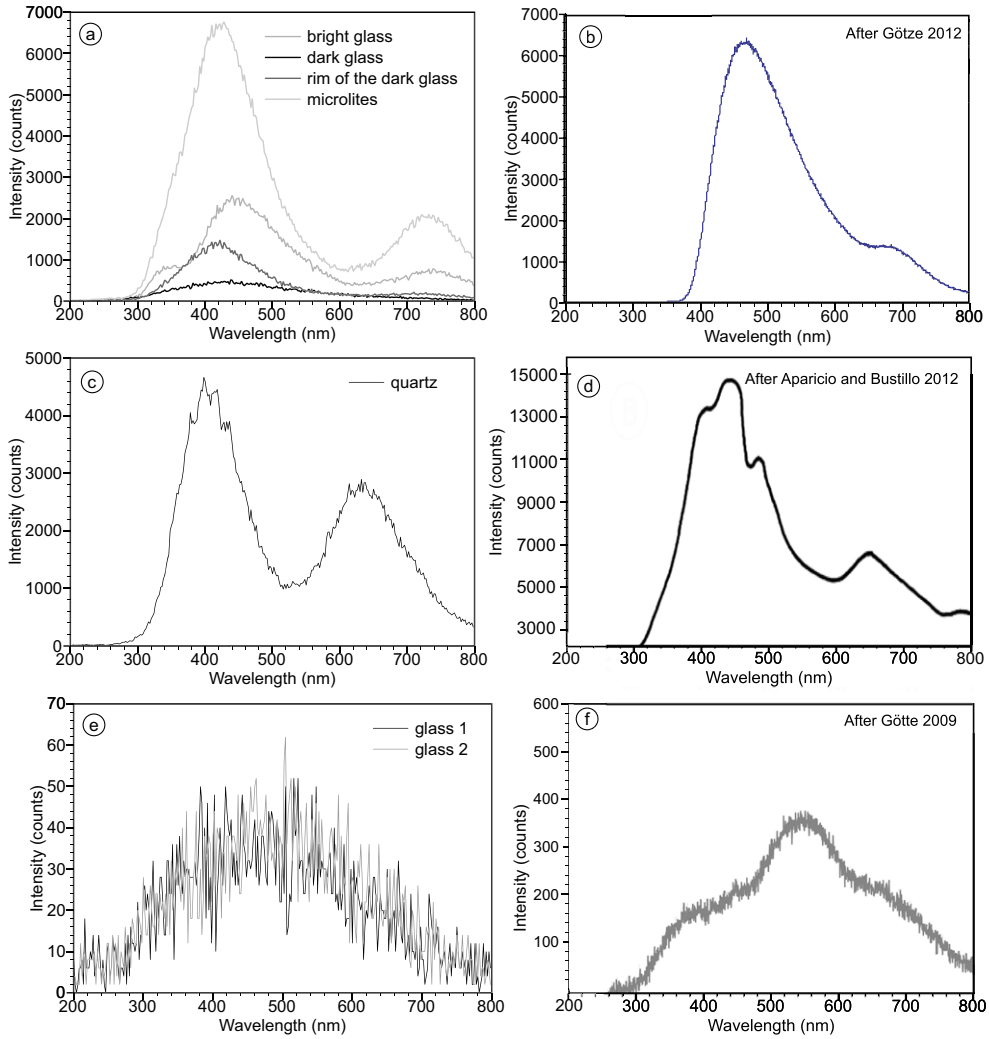

Fig. 6. SEM-CL spectra of selected features in the investigated impact rocks and from the literature for comparison. a) Spectra obtained from preserved and devitrified impact glass. Note the high intensity of the spectrum of microlites, with bands consistent with those of K-feldspar. Sample Glass_1E. b) Spectrum of unaltered K-feldspar, with emission bands at 450 nm (Götze 2012). c) Spectrum of preserved (unshocked) quartz grain. Sample 98Q6_W7-11, 318.1 m. d) Spectrum of primary magmatic quartz from Aparicio and Bustillo (2012). e) Spectra of two impact glasses in the suevite. 98Q6_W7-11, 318.1 m. f) Spectrum of impact melt from Wabar (Saudi Arabia, after Götte 2009).

with the latter showing broad bands at ca. 450 and 700 nm suggesting a feldspathic composition. Individual relict, unshocked quartz grains in the melt exhibit the characteristic spectrum of unshocked quartz, with high-intensity bands for the expected wavelength (Fig. 6c). Glasses without incipient crystallization have a low-intensity spectrum, with a broad band centered at intermediate wavelength (Fig. 6e), similar to that observed by Götte (2009) in impact glasses from Wabar (Fig. 6f).

In the suevite (Fig. 7), an area with different clasts was selected for SEM-CL investigation. In BSE-SEM images, the different clasts are almost undistinguishable. The SEM-CL image provides a qualitative characterization of the shock stage experienced by the clasts. The comparison of CL spectra from each clast, taken over a defined area and under the same analytical conditions, allows the characterization of the shock stages for individual clasts. For instance, clast D likely represents an impact melt clast that exhibits a spectrum that is similar to that observed in Figs. 6e and 6f. Clast A is strongly shocked and likely represents a fragment of impact melt breccia rather than a shocked volcanic clast. Clast B has partially molten matrix, but there are still unshocked phenocrysts that contribute to high intensity of CL response. Finally, clast C is an unshocked volcanic clast, with bands at ca. 450 and 700 nm wavelength, suggesting the presence of

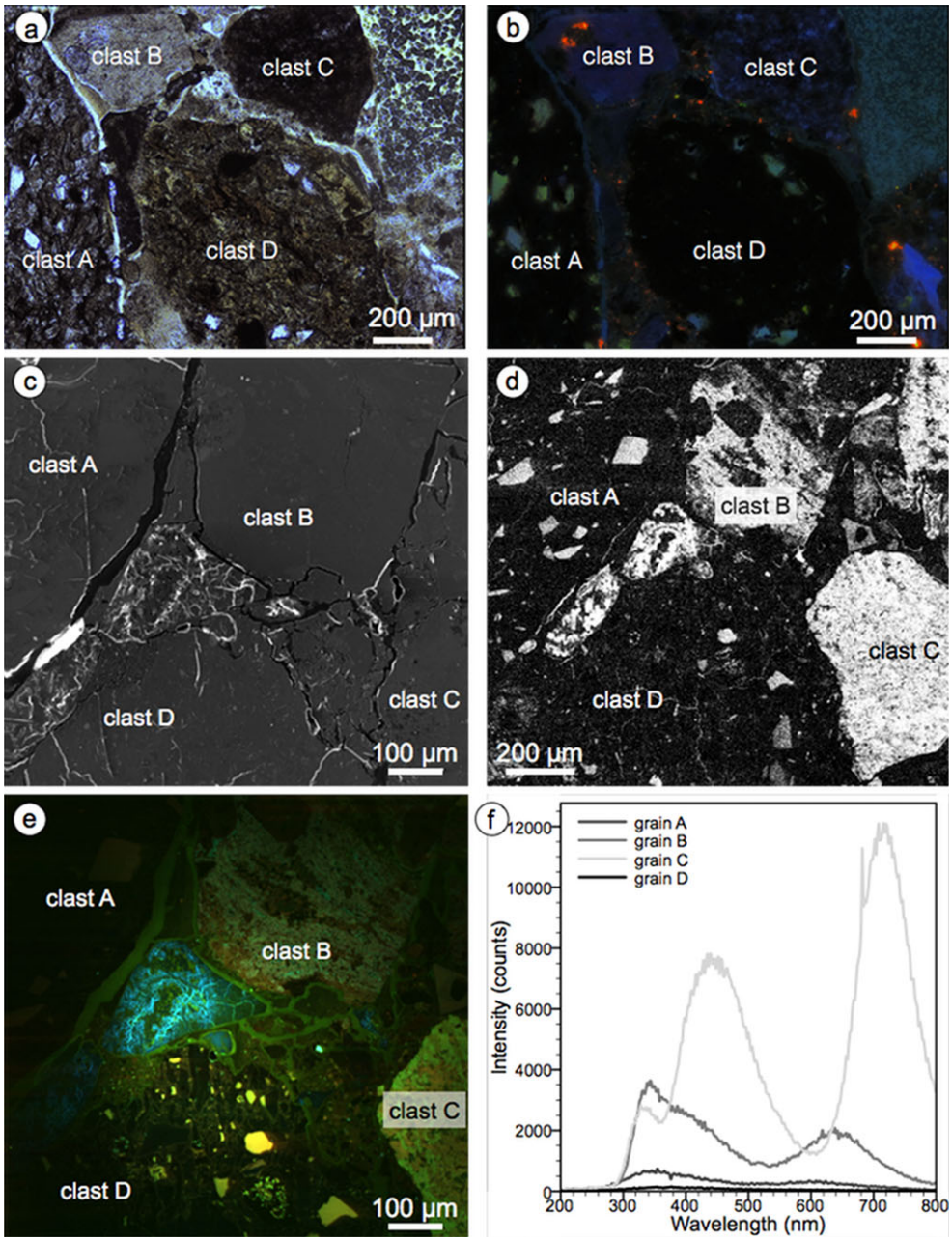

Fig. 7. A selected area from the suevite in the drill core sample 98Q6_W7-11, 318.1 m. a) Plane-polarized light image, showing four clasts. The yellowish domain in the upper-right corner consists of epoxy. b) Optical CL of the same area shown in (a), with a generally low luminescence of the clasts. The red spots likely correspond to secondary calcite. c) Detail SE-SEM image of the selected clasts. d) Panchromatic SEM-CL image of the same area, revealing different brightness among clasts. e) Composite RGB image of the same clasts, showing further details of the nature and the shock stage of the clasts (see text for further explanations). Note the bright bluish area in the center, which likely consists of secondary zeolites. f) SEM-CL spectra obtained for the selected clasts. Note the order of magnitude difference of signal intensity between clasts.

K-feldspar crystals. Note the order of magnitude in intensity is four times higher than in the impact melt, although optically the clasts are not significantly different. This interpretation is supported by Raman spectroscopy on the same grains, considering both the groundmass and individual phenocrysts (Fig. 8).

DISCUSSION

Quartz

Cathodoluminescence allows the identification of quartz crystals, discriminating their origin: blue to violet

luminescence corresponds to plutonic quartz as well as quartz phenocrysts in volcanic rocks and high-grade metamorphic quartz, reddish luminescence to quartz in the groundmass of volcanic rocks and locally occurring as phenocrysts, brownish luminescence to quartz formed by regional metamorphism, none or weak luminescence corresponds to authigenic quartz, and short-lived (meaning that the signal is exposure-time sensitive) blue-green luminescence to hydrothermal and pegmatitic quartz (Götze 1996). The different colors in the CL signal of quartz are related to variable Al^{3+} content in the crystal lattice and to other lattice defects (Ramseyer et al. 1988; Götze et al. 2001). As a consequence, CL easily reveals volcanic growth features (e.g., Ruffini et al. 2002). The most common emission bands in quartz are at 450 nm and 650 nm. The relative intensity of these bands and of other possible bands provides information on the origin of quartz (Ramseyer et al. 1988; Götze 2012). The correlation between emission bands in quartz CL and specific point defects has been established: the 390 nm emission is generally observed in hydrothermal quartz and is related to the Al content, the 450 nm emission is due to an electron hole pair on an oxygen vacancy and a O-O bond, the 500 nm emission is caused by substitution of impurity ions (e.g., Al, Ge), the rare emission at 580 nm is also related to oxygen vacancies, the common emission at about 620–650 nm is due to the recombination of electrons in nonbridging oxygen gaps, and the 705 nm emission is likely related to the incorporation of Fe into quartz (Nasdala et al. 2004). Although Götte (2009) did not observe large differences between shocked and unshocked quartz, according to Gucsik et al. (2003), shocked quartz shows characteristic spectra with slight shift of band position and with different intensity, with respect to the unshocked quartz. Planar deformation features in quartz, likely filled by diaplectic silica, generally show weak or no luminescence (Boggs et al. 2001; Kayama et al. 2010), but red luminescence has been reported, similar to amorphous silica (Ramseyer et al. 1992; Hamers and Drury 2011).

In El'gygytgyn rocks, unshocked individual grains of quartz in both the impact melt rocks collected in the crater area and in the suevite from the drill core exhibit pinkish-bluish emissions, revealing structural internal layering clearly related to magmatic growth (Figs. 5c and 5d), similar to those shown in Ruffini et al. (2002). Some grains have no or very weak luminescence in both optical and SEM-CL, suggesting high shock and transformation into diaplectic glass, as confirmed by optical microscopy. In addition, planar deformation features (PDFs) occur locally in quartz grains. In this work, PDFs were not analyzed in detail, but SEM-CL overview did not reveal any luminescence from PDFs. In the investigated samples, quartz does not show any alteration and its CL response is consistent with that of unaltered quartz. The CL spectrum of quartz allows the identification of the original source material for detrital quartz, which survived weathering and transportation (Götze 2012), and the identification of newly formed, hydrothermal quartz (Aparicio and Bustillo 2012). This is not the case for El'gygytgyn samples, which contain unaltered magmatic quartz.

Feldspar

Shocked feldspar generally shows a shift of the characteristic bands in CL spectra, band broadening, and overall a decrease in emission intensity (Ramseyer et al. 1992; Kaus and Bischoff 2000; Gucsik 2009). Alkali feldspars seem to have an opposite behavior with respect to plagioclase (Kayama et al. 2009), with strong emissions in the bluish to ultraviolet field in shocked samples transformed into diaplectic glass (Kayama et al. 2010, 2012). However, even shocked plagioclase seems to record the appearance of a bluish emission for maskelynite (Kayama et al. 2009) and a characteristic spectrum (Rubio-Ordóñez et al. 2012). The CL colors and spectra observed in El'gygytgyn samples suggest the occurrence of unshocked grains in the majority of samples, but low to extensive shock is recorded locally (e.g., Figs. 4f and 5f). Feldspars seem strongly altered in the suevite, with locally strong orange luminescence that suggests incipient carbonatization (e.g., Leichmann et al. 2003). Nevertheless, CL spectra from preserved areas have the same shape as that from fresh feldspar. However, heavy weathering of primary feldspar might result in brownish emission replacing the expected blue emission in optical CL (e.g., Wendler et al. 2012). This might be the case for the feldspar in the clast in Fig. 4b, although SEM-CL on the same area suggests that both the reduced luminescence and the resulting yellowish color in optical-CL are likely due to shock rather than alteration (Fig. 7).

Impact glasses of siliceous composition that were collected in the crater area exhibit no to low luminescence and spectra with a broad band at intermediate wavelengths (Figs. 6e and f). Similar observations, with spectra with a broad band in the range 300–400 nm and zoned luminescence depending on composition, where Fe-bearing layers have inhibited luminescence, have been previously reported in impact glasses by Gucsik et al. (2004).

Combining our observations in impact glasses and those in individual mineral grains, the CL response of clasts in the suevite can be predicted: unshocked

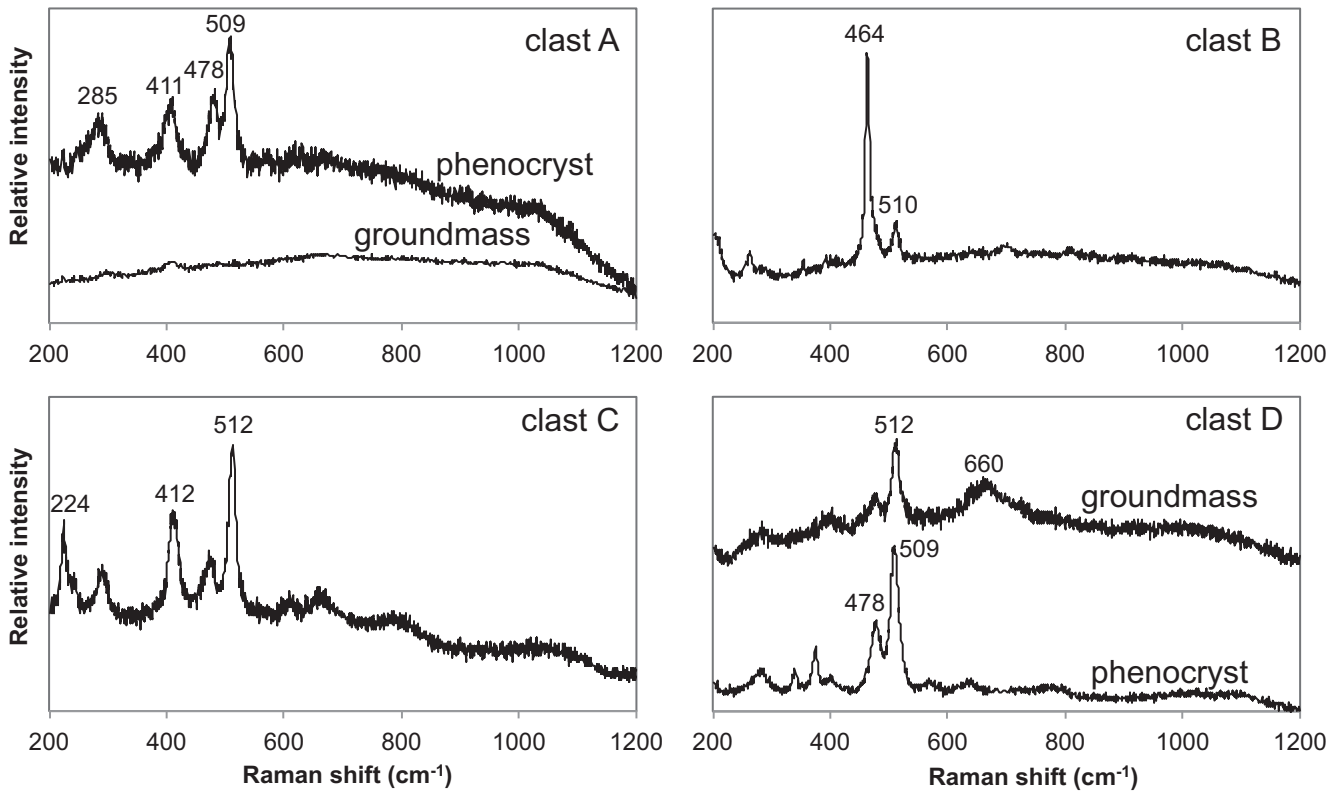

Fig. 8. Raman spectra of the clasts illustrated in Fig. 7. In clast A, the groundmass appears amorphous, whereas the phenocrysts consist of plagioclase. In clast B, the typical quartz spectrum is recognizable, suggesting the presence of microcrystalline quartz in the groundmass. In clast C, the spectrum of K-feldspar is visible, also suggesting the presence of crystalline silicates in the matrix. In clast D, the groundmass has a weak signal, most likely derived from relict feldspar crystals. The grains that appear yellowish in CL (Fig. 7e) clearly consist of plagioclase.

volcanic rocks, with a completely crystallized or devitrified groundmass, will have strong luminescence and impact melts, with homogeneous composition, will have no or very low luminescence. This is verified in El'gygytgyn samples, showing that the shock stage of target rock clasts can be also deduced from CL response, due to a reverse correlation between the intensity of the CL signal and the progressive destruction of the crystal lattice. An alternative explanation for the low CL intensity observed in impact melt might be related to the high temperature experienced during shock and possible diffusion and homogenization of luminescence centers and inhibitors in the resulting melt. Quenching was so fast that crystallization could not take place, except at the rim of some preserved crystals, where tiny microlites formed (e.g., Figs. 5a and 5b). However, in the case of the El'gygytgyn structure, the different CL response between impact and volcanic melts might be related to differences in age of the impact event (3.58 ± 0.04 Ma; Layer 2000) with respect to the age of the Cretaceous volcanic target (83–89 Ma; Stone et al. 2009). Thus, the volcanic target has been exposed to weathering and alteration, which favored devitrification and recrystallization of the glassy groundmass. On the other hand, the impact is a quite recent event and only little alteration followed the crater formation, providing the chance for a better preservation of the quenched glass.

Hydrothermal activity might have occurred in the crater area, as suggested by the alteration observed in the suevite (Pittarello et al. 2013; Raschke et al. 2013b). However, newly crystallized quartz or feldspar due to hydrothermal alteration, easily recognizable by spectral CL (Aparicio and Bustillo 2012), was not found in El'gygytgyn samples. The minor alteration observed in feldspar (Pittarello et al. 2013) does not affect the CL spectra of the investigated grains. Given the unique conditions verified at the El'gygytgyn structure, which are in summary (1) similar bulk composition between the dominant target lithology and the impact melt, and (2), large difference in age between the target rock and the impact event, CL allows the identification of impact melt clasts among volcanic lithic clasts. No other impact structures excavated in siliceous volcanic rocks are known on Earth, so far, and this technique cannot be applied for impact rocks formed in basaltic target

due to the inhibiting effect of Fe. Therefore, at the moment, further tests on structures that are older than El'gygytgyn and where impact glasses are likely completely devitrified cannot be planned. Nevertheless, CL might be applied for investigation of planetary materials, in the case of intermediate to silicic composition of the target rock or in the study of shocked plagioclase in basaltic target, together with Raman and similar spectroscopic techniques.

CONCLUSIONS

The El'gygytgyn impact structure is unique on Earth because it formed almost exclusively in siliceous volcanic rocks, which makes it challenging to identify impact melts among volcanic materials. To evaluate the application of CL imaging and spectroscopy for the discrimination of impact melts from volcanic target rocks, a total of six impact breccia samples, all of them including clasts of the target rock, were selected for CL investigation from the samples collected in the crater area and from a drill core. Results of SEM-CL demonstrate that impact melts generally display very low luminescence with respect to the unshocked volcanic rocks from the target. The shock degree seems qualitatively correlated with the intensity of luminescence, which significantly decreases for increasing shock degree, as supported by CL spectral analysis. This inverse correlation is likely related to the progressive destruction of the crystal lattice of the rock-forming minerals due to impact shock, but also due to the low devitrification and recrystallization of impact melt with respect to the groundmass of the significantly older volcanic target materials. The weathering observed in some samples is seemingly irrelevant for CL observations. Under conditions similar to those observed in the El'gygytgyn impact structure (i.e., recent impact event in old volcanic target rocks of roughly similar bulk composition), a combined optical and SEM-CL approach might provide a useful tool for detecting impact melt fragments in the suevite. Therefore, combined CL imaging and spectroscopic analyses are applicable for the identification of impact rock material in a matrix of mineralogically similar target material and potentially applicable in planetary exploration.

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