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Alteration fabrics and mineralogy as provenance indicators; the Stonehenge bluestone dolerites and their enigmatic “spots”

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Abstract

Stonehenge is dominated by the large, locally derived sarsen stones which comprise the Outer Sarsen Circle and the Inner Sarsen Trilithon Circle. Lithologically they are a hard form of sandstone called silcrete. Less obvious are the smaller ‘bluestones’ which form the Outer Bluestone Circle and Inner Bluestone Horseshoe. The bluestone assemblage is composed of a variety of lithologies, including dolerite (almost all carrying small, cm scale, white to pink ‘spots’), rhyolites, volcanic tuffs and two different types of sandstone. The majority of the bluestones have been provenanced to the Mynydd Preseli area in west Wales some 200 km

west of Stonehenge, and the distinctive spots in the dolerites were crucial evidence in making that link. However, despite the importance of the spots in that provenancing model, which provides evidence for one of the most remarkable feats of Neolithic time in north-west Europe, they have been little studied and are not fully characterized. One reason for this is the fact that they are difficult to study using standard optical microscopy because of the fine grain size of the component minerals. In order to gain a greater understanding of the mineralogy and origin of the spots we have used a range of alternative optical and analytical techniques, including high resolution photomicrography, 'standard' electron microscopy (SEM-EDS), automated scanning electron microscopy with linked energy dispersive analysis (automated SEM-EDS) and X-ray diffraction. These investigations, based primarily on samples from Carn Goedog and Carn Meini in the Mynydd Preseli, lead us to conclude that the spots result from a two-stage alteration history involving firstly saussuritization of primary igneous calcium-rich plagioclase phenocrysts/glomerocrysts. The saussuritization was probably a late-stage magmatic event, possibly occurring at ca. 400°C, and led to the development of the secondary minerals clinozoisite, zoisite, albite and muscovite. Subsequently, the dolerites were affected by regional low-grade metamorphism at ca. 250-300°C, at the transition from the prehnite-pumpellyite to the greenschist facies. During this metamorphism the background (non-spot) areas of the samples were altered with the development of the secondary minerals chlorite, actinolite, epidote, quartz, titanite and further albite. Interpretation of these data shows that the Carn Goedog sample has a higher percentage of secondary minerals compared to the Carn Meini sample, suggesting that the former shows a higher degree of alteration. Further analyses of dolerite samples from the Mynydd Preseli should provide insight into the potential of the extent of rock alteration in the further refinement of understanding the source or sources of the Stonehenge bluestone dolerites.

1. Introduction

Stonehenge is one of the World's most iconic and recognisable ancient historic monuments, forming an imposing feature on the Salisbury Plain landscape some 13 km to the north of Salisbury, in Wiltshire, England. It is dominated by large, upright sarsen stones which

form the monument's Outer Sarsen Circle and Inner Sarsen Trilithon Horseshoe. Composed of a type of very hard sandstone called silcrete, these stones are thought to have been derived locally, possibly from some 25-30 km to the north of Stonehenge (see Parker Pearson 2016; Nash et al., 2020). A less imposing set of smaller stones form the monument's Outer Bluestone Circle and Inner Bluestone Horseshoe and, although collectively called "bluestones", they are composed of a range of lithologies including dolerites, rhyolites, volcanic tuffs and two types of sandstone. All of these lithologies are exotic to the local geology of the Salisbury Plain and consensus is that the majority are derived from the Mynydd Preseli area in west Wales (Figure 1) some 200 km away. Indeed, the transport of the bluestones to Stonehenge is considered to be one of the most remarkable feats of Neolithic time in north-west Europe (Parker Pearson et al., 2015).

Why the bluestones were selected for the construction at Stonehenge is a matter of speculation; it has been argued that the stones possess magical healing properties (see Darvill, 2006), whilst others have proposed that the dolerites of the Mynydd Preseli have special acoustic properties (Deveraux and Wozencroft, 2013). More recently, Parker Pearson et al. (in press) have argued that the stones were originally used in a stone circle in the Preseli area before it was dismantled and the stones transported to Stonehenge, a notion suggested originally by Thomas (1923).

The Mynydd Preseli potential source was first proposed as early as 1858 by A.C. Ramsay and colleagues in their account of the geology of parts of Wiltshire and Gloucestershire (Ramsay et al., 1858). However, the first detailed account of the provenance of the bluestones was not until the investigation by H.H. Thomas, who examined lithic fragments from Stonehenge at the request of the Society of Antiquaries of London (Thomas, 1923). A key character in provenancing the bluestones is the enigmatic, distinctive, white to pink spots which typify the dolerites. These spots are commonly referred to as 'feldspar crystals' (e.g. Thomas, 1923) but have also been described as metamorphic porphyroblasts (Thorpe et al., 1991). Despite their critical significance, they have been comparatively little studied, and their genesis is presently uncertain. However, understanding their formation is significant in recognizing their potential distribution in the source lithologies. A problem lies in the fact that the spots are

composed largely of very fine-grained, randomly orientated crystal aggregates and cross-cutting veinlets which are difficult to resolve using standard optical microscopy. In view of their role in establishing a match between doleritic bluestones (so-called 'preselites') at Stonehenge and potential sources in west Wales it is important to have a clear understanding of their character, mineralogy and origin as well as their distribution both within and between outcrops.

In this paper we first review previous descriptions of the dolerites and their spots and then present the results of a detailed mineralogical investigation of the spots and their host dolerite utilising standard optical microscopy including high resolution photomicrograph imagery, 'standard' scanning electron microscopy (SEM-EDS), automated scanning electron microscopy with linked energy dispersive analysis (automated SEM-EDS), and X-ray diffraction (XRD). Data obtained are used to interpret the genesis of the spots as well as to gain a greater understanding of the low-grade metamorphic mineralogy in two Preseli spotted dolerites, one from Carn Meini, considered by Thomas (1923) and Darvill and Wainwright (2016) to be one of the main sources of the Stonehenge spotted dolerites, and one from Carn Goedog, more recently proposed on geochemical grounds by Bevins et al. (2014) to be the source of the majority of the Stonehenge dolerites (comprising their geochemical Group 1; see Table 1 for an explanation of the classification scheme and proposed source outcrops). However, there are still unresolved dolerite sources, namely for geochemical Groups 2 and 3 of Bevins et al. (2014). As a consequence, we turn to other aspects of the dolerites to explore whether the sources of these other two groups can be identified. Here we investigate whether the nature of the distinctive white spots and also the low-grade metamorphic mineralogy might hold clues for further refinement of the location of Stonehenge bluestone source outcrops. Definitions of some of the geological terms used in the text are presented in the supplementary information section of this paper.

2. Previous accounts of the spotted dolerites

The first petrographic description of the dolerites (and their spots) in the Mynydd Preseli was by Parkinson (1897), noting that they were composed of plagioclase ('somewhat

decomposed'), pale brown augite and 'leucoxene' (altered ilmenite) with brown hornblende and actinolite partially replacing augite, and some chlorite. He also described (page 475) 'The development of large, irregular, white or pink feldspars (*sic*) with no definite crystal shape, showing on a weathered surface simply as white circular lumps, gives rise to a rather handsome variety', commenting that this was found principally at Carn Meini and that the feldspars are replaced by 'saussuritic products' which he said in places made them opaque (we presume that he means they are isotropic when observed using a polarizing transmitted light microscope).

Early petrological accounts of Stonehenge's exotic bluestones, for example by Maskelyne (1878) and Teall (1894), gave basic descriptions of the dolerites but made no reference to their distinctive spots. It was not until the 1920's when H.H. Thomas was invited by the Society of Antiquaries of London to examine a collection of small fragments of debris from Stonehenge that the significance of the spots became apparent. In a report on excavations at Stonehenge in 1920 by Colonel William Hawley (Hawley, 1921) Thomas remarked on the presence in the 'bluestones' (which he said were mainly 'diabases') of white or pinkish, irregularly bounded feldspathic spots which he remarked on as 'being highly characteristic of, and as far as he was aware confined to, the diabase sills of the Prescelly Mountains of Pembrokeshire' (page 40). In his 1923 paper, Thomas compared loose rock samples from Stonehenge and Mynydd Preseli, although he provided no significant detail on the petrography of the dolerites or indeed the spots, despite their critical nature in comparing the two sample sets (Stonehenge and Preseli). He concluded (page 248) that the spotted dolerites could be matched 'especially in the outcrops of Carn Meini and Cerrigmarchogion' (see Figure 1), although recently, on the basis of compatible element geochemistry, it has been suggested by Bevins et al. (2014) that the majority of the Stonehenge dolerites were sourced from Carn Goedog and to other, as yet unspecified, outcrops in the area.

Harrison et al. (1979), in an unpublished Institute of Geological Sciences Technical Report, provided petrological descriptions of rock samples collected during excavations at Stonehenge by H. Cunnington between 1876 and 1886 and also from excavations by Gowland in 1901. They noted 'The glomeroporphyritic type matching the Presely diabase

predominates...' and 'From microscopic examination the nonporphyritic diabase appears to be less saussuritized (*sic*).'

Thorpe et al. (1991), in their comprehensive (but essentially geochemical) review of the geological sources and mode of transport of the Stonehenge bluestones, provided a very brief petrographic description of the dolerites and noted the anhedral form of the Preseli dolerite spots, their irregular/unsystematic distribution (from sometimes forming up to around 15% of a rock surface to only one spot being visible on an area of ca. 1 m²) and their metamorphic mineralogy, and concluded that they represent porphyroblasts arising from the low-grade metamorphism described by Bevins and Rowbotham (1983) and Bevins et al. (1989). Thorpe et al. (1991) did, however, describe for the first time the chemistry of the spots compared to the host dolerite, recording that the spots have markedly higher concentrations of Al₂O₃, Sr and CaO and greatly depleted concentrations of the incompatible elements Nb, Y and Zr when compared to the host dolerite. Their data also clearly show relatively depleted levels of MgO, Fe₂O₃ and Ni (but note Cr concentrations are not as depleted as these latter compatible elements). Thorpe et al. (1991) were also the first to record the amount and nature of the spots on each monolith, noting some were unspotted and some only very weakly spotted. They also examined the homogeneity of a single sample of spotted dolerite by multiple analysis of a divided sample as well as the homogeneity at the outcrop scale. They found that two parts from sample CM1 (from Carn Meini) were identical for all elements within or very near precision, while a second sample from Carn Meini (CM2) also showed within or very near precision for most elements. At the outcrop scale, however, they observed chemical ranges in six samples from Carn Gyfrwy which exceeded precision by factors of up to 10 for some major elements and factors between ca. 2 and 6 for trace elements. They interpreted the Carn Gyfrwy data as representing real variation at the outcrop scale.

The first and only previous detailed petrographic account of the Preseli dolerites and their spots was by Ixer (in Darvill et al., 2009) who investigated nine samples from Carn Meini using both transmitted and reflected polarized light microscopy. He noted that the spots comprised relict feldspar along with possible secondary feldspar, fine-grained clinozoisite, the chlorite minerals chamosite and clinocllore, fine-grained muscovite and a coarse-grained

epidote group mineral; in addition, he described the presence of relict chrome spinel in the spots. He concluded that ‘...within the Carn Menyn outcrops, although there is some lithological variation, particularly in the degree of epidotisation, the majority of the dolerite can be regarded as uniform in thin section’. Ixer (in Darvill et al., 2009) also reported on an unpublished (2007) X-ray diffraction analysis of a spot area by one of the current authors (TFC; pers. comm. REB to RAI), who identified the presence of albite, epidote and chlorite, and he also cited unpublished SEM-EDS mineral analyses from a spot area which suggested the presence of clinozoisite, muscovite and clay minerals, as well as chrome spinel (Chris Blake, pers. comm. to RAI 2007). Ixer concluded that the spots ‘are or were undoubtedly feldspathic but now carry more alteration mineral than feldspar’. He also argued that because of the presence of relict chrome spinel the original plagioclase ‘knot’ was of igneous rather than metamorphic origin. Finally, Ixer and Bevins (2011) described the petrography of two spotted dolerite Stonehenge orthostats, namely stones 34 and 35a.

3. Methodology and samples studied

The dolerite samples from the Mynydd Preseli area investigated were drawn from the collection of 72 intrusive igneous rock samples from outcrops in the ground between Strumble Head and the Mynydd Preseli area, lying largely to the south of the Ordovician Fishguard Volcanic Group (see Figure 1) with which they have been considered to be co-magmatic by Bevins et al. (1989).

3.1. Optical microscopy including high resolution photomicrography

Standard transmitted and reflected polarized light optical microscopy were used to investigate the detailed mineralogy of 13 Stonehenge dolerite orthostats and 12 Preseli dolerites from eight different rock outcrops. This was supplemented by high resolution photomicrography on a single sample (PCM31) from Carn Meini in the Preseli. This latter technique, undertaken at the Open University, used a motorised XYZ stage to generate large

area seamless image mosaics (typically consisting of between 100 to 500 individual photographs). Two images were captured for sample PCM31, one in plane polarized transmitted light and one between crossed polars.

3.2. Automated SEM-EDS analysis

Automated SEM-EDS analysis was utilised in order to investigate the mineralogical makeup of the Preseli/Stonehenge dolerite spots, complementing the optical examinations described in section 4 below. Details of the automated SEM-EDS method applied to archaeological lithic provenancing can be found in Bevins et al. (2020) in their investigations into the possible source of the Stonehenge Altar Stone. In brief, the method builds up a mineralogical image by rapidly stepping an electron beam over a polished surface of the sample at an operator-defined spacing. At every point, multiple energy dispersive spectrometers are used to acquire a spectrum which is then deconvolved and, by comparison of the elements measured and their relative intensity with a database of mineral species, a mineral name or chemical grouping is assigned (see Pirrie et al., 2004; Pirrie & Rollinson, 2011). In this way, a mineralogical image of the sample is acquired with each pixel representing a single analysis point. For this study, samples were analysed using a FEI Quanta 650 QEMSCAN system operating at 20 kV and a measured beam current of 10 nA in the laboratory of SGS Canada Inc., Burnaby, British Columbia. Data were collected at a 10 µm stepping interval which resulted in the collection of between 1,222,274 and 3,474,526 individual EDS analysis points per sample. Raw data were processed using iDiscover 5.4 software and reported numerically as modal mineralogy (mass %) and graphically as false colour images where each identified mineral phase is assigned to a different colour. Two spotted dolerite samples from the Mynydd Preseli were analysed in this study, namely PCM32, which is from the Carn Meini outcrop, and sample PCC11, from Carn Goedog.

3.3. X-ray diffraction

A total of eleven dolerite samples were analysed by X-ray diffraction (XRD) at the National Museum of Wales using a PANalytical X'PertPRO diffractometer fitted with an X'Celerator solid state detector. CuK α radiation was generated using a Cu anode source operating at 40kV 30mA. Analyses were performed at room temperature across the range 5.0384 °2 θ to 74.9764 °2 θ .

Seven Preseli spotted dolerites were analysed destructively by powder X-ray diffraction (PXRD). A small fragment (typically 2 mm³) of white spot was removed from each sample. The fragment was ground to powder using an agate pestle and mortar until the powder was smooth with no gritty component. The powder was placed upon the centre of a circular silicon disc machined to produce no diffraction peaks. Several drops of acetone were applied to the powder to disperse it evenly across the surface of the disc. The disc was mounted inside a steel holder and placed within the X-ray diffractometer where it was rotated during analysis. The area of analysis was 20x20 mm or, due to the effects of rotation, a 20 mm diameter circle. The effect of powdering the sample and rotating it produces an enhanced quality of structural data and removes many of the problems created by 'preferred orientation' of crystallites.

Four polished Stonehenge rock chips were also analysed. Each chip was analysed in-situ in a stationary mode and non-destructively using a multipurpose sample stage. Each flat chip was placed horizontally on the sample stage and aligned using a pressure gauge, so the X-ray beam was centred upon a white spot and set at the correct height. The X-ray beam was programmed to line analysis allowing a broad area to be analysed. To avoid, as much as possible, analysing the surrounding dolerite (rock) a series of physical metal masks and programable slits were used to define the area under investigation which typically was 5x10 mm. Analysis was performed by reflection using area analysis. Interpretation of data was performed using HighScore (version 4.1) software (PANalytical) and the International Centre for Diffraction Data (ICDD) database.

3.4. 'Standard' scanning electron microscopy with EDS

We also examined three Preseli dolerite samples, two from Carn Meini and one from Carn Goedog using 'standard' scanning electron microscopy with EDS. Two of the samples (PCM30 and PCC11) were analysed using a CamScan Maxim 2040 Scanning Electron Microscope fitted with an Oxford Instruments energy and wavelength dispersive X-ray spectrometers and analytical software in the Department of History, Archaeology and Religion at Cardiff University. The third sample (Pres CB) was analysed using a Leo/Zeiss 1440 scanning electron microscope with an Oxford Instruments energy dispersive spectrometer in the Rio Tinto laboratory in Clevedon. This technique was used in particular to characterize the spinel supergroup minerals present.

4. Results

4.1. Petrography of the spotted dolerites

A distinctive feature of numerous, scattered dolerite outcrops towards the eastern margin of the Mynydd Preseli in southwest Wales, occurring over an area approximately 4.5x1.75 km, is the presence of white to pinkish-white 'spots'. The spots occur randomly in the rock and are typically 1-2 cm in diameter, although some reach up to 15 cm in diameter. Figure 2a shows a cut and polished face of a typical Preseli spotted dolerite. Whilst some spots are anhedral with rather diffuse margins others show a more euhedral form, with more sharply defined margins and resemble phenocrysts. Some spots give the appearance of being an aggregate of two or three crystals and are perhaps glomerocrysts (aggregates of phenocrysts). Figure 2b is a polished cut surface of a Preseli dolerite and in this image the regular form of the 'spots' is even more obvious, although the margin of the large crystal (1) at top left of the image is diffuse and appears to show veinlets of a green mineral (most probably chlorite) in an otherwise white crystal which has a sugary appearance. The same is seen in the crystal (2) at the top centre of the image (although the crystal has a more glassy appearance) and also in the crystal (or aggregate of crystals?) at centre right (3). A vague hint of optical zoning can be discerned in some samples. The spots are set in a medium-grained mass of dark grey/green clinopyroxene and plagioclase laths.

The dolerites are altered and primary igneous minerals have been partially or totally replaced by secondary alteration minerals. A brief resume of the spotted dolerite petrography is presented below. A detailed petrographic description based largely on spotted dolerite sample CMQ2, from Carn Meini, is presented as supplementary information to this paper.

In the groundmass, under transmitted polarized light, large primary plagioclase (andesine) laths are seen to be zoned, twinned and extensively altered to albite, fine-grained clinzoisite with very low interference colours and white mica; epidote with high interference colours and clinocllore also replace plagioclase. The margins of this generation of plagioclase are often unaltered. A later generation of smaller, stubby plagioclase (albite?) is associated with chlorite. The main generation of plagioclase has a sub-ophitic relationship with clinopyroxene (see Fig. 3a from Carn Meini sample PCM30). Small plagioclase laths enclosed in titanomagnetite are less altered than the main plagioclase. Most clinopyroxene, some of which is zoned or twinned, is unaltered, as are acicular apatite crystals, some of which are associated with later stage plagioclase (albite?). Small, up to 0.75 mm, rounded areas in clinopyroxene crystals have been interpreted by Bevins et al. (1989) to be pseudomorphs after olivine (Fig. 3b).

Secondary minerals are abundant and include late-stage quartz, with some quartz forming spherulitic aggregates or thin, cross-cutting veinlets. Zoned epidote commonly occurs as mosaics and in epidote-chlorite (clinocllore)-pyrite intergrowths, some of which surround clinopyroxene. Unpublished electron microprobe analyses of epidote record a range in XFe values (where $XFe = Fe^{3+}/(Fe^{3+}+Al)$) in Preseli dolerites ranging from 0.11 to 0.33, larger crystals showing relatively iron-rich cores and iron poor rims (sample PCC11 from Carn Goedog has core XFe values of 0.29 and rim values of 0.15). Within the chlorite-epidote intergrowths, euhedral epidote is enclosed within chlorite or forms euhedral rims to chlorite infills. Minor amounts of chamosite are present. Prehnite and pumpellyite are variably developed but occur especially in association with albite in plagioclase laths. Very locally, small, 20-30 μ m long, rhombic titanite is enclosed within chlorite. Green to yellow-green, fibrous fringes with moderate relief and showing high interference colours are identified as amphibole and have been shown by Bevins and Rowbotham (1983) on the basis of electron microprobe analysis to be actinolite; they grow

out from clinopyroxene or epidote and grow into quartz or chlorite. Chlorite pseudomorphs after olivine typically have needle-like overgrowths of actinolite. Minor amounts of titanite mantle highly altered ilmenite.

Using standard optical microscope techniques the mineralogy of the 'spot' areas are seen to be dominated by masses of very small crystals (see Fig. 4a from Carn Meini sample PCM32). However, because of their fine grain size the crystals appear to be isotropic due to grain boundary refraction effects and identification is difficult. They are, in fact, very altered primary plagioclase crystals which now comprise abundant secondary alteration minerals including albite, fine-grained clinzoisite/zoisite with very low interference colours intergrown with white mica. Epidote with high interference colours, chlorite (clinocllore) lying along relict cleavage and relict primary feldspar/secondary feldspar are less abundant. Locally white mica is the main alteration product. Primary spinel crystals are seen in reflected light; further details are presented in section 4.4 below.

In order to gain a better understanding of the spot areas we obtained high resolution images in plane polarized light and between crossed polars of sample PCM31 (Figures 4b and 4c), generated by production of seamless images (usually in the range 100-500 individual photomicrographs) stitched together to create a 'mega image'. The spot areas are identified by their dark, isotropic appearance in plane polarized light. Given the high resolution it is possible to examine in much more detail the fine grained minerals present in the sample. Figure 4d is an extract of an enlarged area of a spot. The presence of masses of small, randomly oriented, prismatic crystals is now better resolved although petrographic identification is still problematical but they appear to be either clinzoisite or zoisite (note it is difficult to distinguish between these two minerals as although the former is monoclinic and the latter is orthorhombic most clinzoisite crystals are elongate along the b axis leading to prismatic crystals with parallel extinction and so mimic the straight extinction of zoisite). What is instructive, however, is the clear evidence for these crystals to be secondary and to be overprinting plagioclase feldspar, although whether it is the original igneous high temperature Ca plagioclase or secondary albite is again difficult to resolve.

4.2. Automated mineralogy

False colour compositional maps generated by automated SEM-EDS analysis for two spotted dolerites, PCC11 from Carn Goedog and PCM32 from Carn Meini, are presented in Figures 5a and 5b respectively. The modal mineralogy of the two spotted dolerites (whole areas) are listed in Table 2 with graphic representation presented in Figure 6. Both samples are dominated by a relatively small number of phases of both primary and secondary origin. Clinopyroxene (differentiated as Mg-rich and Mg-Fe pyroxene which reflects the core to rim variation clearly seen in the false colour images) makes up 20.41% in PCM32 and 12.40% in PCC11. This substantial difference could indicate that PCM32 is a more mafic sample but it could also be that PCC11 is a more altered rock, with a greater proportion of clinopyroxene altered in PCC11. Indeed, the interpretation that PCC11 is a more altered rock is supported by the fact that the other main primary mineral, Ca plagioclase, shows a markedly higher modal % in PCM32 (16.93%) compared to PCC11 (6.67%); if PCM32 were a more mafic sample compared to PCC11 the opposite relative proportions of Ca plagioclase would be expected. In addition, the modal % of the main mafic secondary minerals chlorite and actinolite (which are common alteration products after clinopyroxene) together with both compositions of clinopyroxene sum to 39.07 % in PCM32 and 41.22 % in PCC11. Similarly, the sum of Ca plagioclase and the commonly associated alteration products albite and clinozoisite/zoisite correlate very closely (45.04 % in PCM32 and 46.87 % in PCC22). Finally, Table 3 shows a comparison of the whole rock major and trace element chemistry of the two samples, which are markedly similar, with the exception of Cr contents, which are higher in PCC11 (and which probably relates to a greater abundance of chromite/spinel in sample PCC11). We conclude, therefore, that PCC11 is a more altered dolerite than PCM32.

In order to explore in more detail the mineralogical variation between the spot areas and their host dolerite (which we here call the background) we selected three spot areas (CA1-CA3) and three background areas (CA4-CA6) each in samples PCC11 and PCM32 (see Figures 5a and b) and calculated the modal mineralogy in those six areas in each sample (see Table 2). The spot areas in both samples show a virtual absence of modal pyroxene (max 0.09% in PCC11 and

0.04% in PCM32) whilst the background areas in the two samples show differences in the % of pyroxene with a range 9.95-16.68% in PCC11 compared to 16.01-30.81% in PCM32. Modal proportions of chlorite show the reverse, with higher amounts in PCC11 (17.12-26.36%) compared to PCM32 (12.17-14.65), again suggesting that PCC11 is more altered than PCM32.

In both samples, the spot areas are dominated by Ca plagioclase, albite, clinozoisite/zoisite and muscovite, which form an average of 90.98% in PCC11 and 95.41% in PCM32, contrasting with average modal proportions of these four minerals in the background areas in the two samples which total 46.46% in PCC11 and 46.64% in PCM32. This is illustrated in the histograms in Figure 6. What this shows is that the spot areas in PCM32 have markedly higher average proportions of Ca plagioclase (28.27%), clinozoisite/zoisite (49.20%) and muscovite (10.63%) but markedly lower albite (7.31%) compared to the spot areas in PCC11 which have 10.47% Ca plagioclase, 39.96% clinozoisite/zoisite, 1.84% muscovite and 38.71% albite. The background areas also show some differences between the two samples especially with respect to Ca plagioclase (16.28% in PCM32 versus 6.40% in PCC11) and clinozoisite (8.59% in PCM32 versus 17.34% in PCC11). Again, we interpret this as showing that the two samples have experienced different degrees of alteration.

Next, we enlarged the spot area images analysed in order to gain an even greater resolution of the distribution of the minerals present in the spots and the immediately surrounding background and also produced individual mineral distribution 'maps'. The results for one spot area (CA1) in PCM32 are shown in Figures 7 and 8. The spot area can be seen to be composed predominantly of Ca plagioclase and clinozoisite/zoisite with lesser amounts of albite and muscovite but now they can be seen to be invaded by thin veinlets of chlorite and amphibole; these are the veinlets seen on the polished cut surface of the dolerite illustrated in Figure 2b. The spot area can be seen to be free of pyroxene with the exception of a single, compositionally zoned crystal at the middle right of Figure 8, where it is associated with a large 'pool' of chlorite and actinolite along with smaller epidote and clinozoisite/zoisite crystals. The margin of the spot area itself is somewhat difficult to define, with the Ca plagioclase and clinozoisite/zoisite core passing gradationally outwards into areas with a greater amount of albite. Some minerals (e.g. chlorite and to a lesser extent epidote) appear to delineate ghost

crystal outlines which are interpreted as reflecting early formed Ca plagioclase phenocryst forms and that the spots were originally aggregates of phenocrysts (i.e. glomerocrysts).

4.3. X-ray diffraction

In order to determine whether clinozoisite and/or zoisite is present in the spots we undertook X-ray diffraction analyses; the results are presented in Table 4 with an X-ray pattern (NMW X-2741) for Stonehenge stone 33 presented in Figure 10. Although not differentiating between albite and Ca plagioclase, the spectra for the samples analysed showed a best fit for the presence of albite, clinozoisite and chlorite in all seven Preseli samples, zoisite and muscovite in five of the samples (although not together in all the same samples) and quartz and pumpellyite in single samples. The Stonehenge analyses showed the presence of chlorite in all four samples, albite, clinozoisite and muscovite in three (differing) samples, zoisite, prehnite and quartz in two (differing) samples and epidote in one sample. The most significant result from these analyses is that clinozoisite and/or zoisite are present in all but one of the Preseli and Stonehenge spotted dolerite samples which could not be differentiated on the basis of chemistry alone, whilst the small crystal size hampered their optical identification in plane polarized light as both zoisite and clinozoisite are colourless and tend to show parallel extinction, whilst between crossed polars they both show weak, typically anomalous birefringence. Using the HighScore software chlorite was identified as clinocllore (the Mg-dominant species) in all seven Preseli samples, whilst in one Stonehenge sample the chlorite was again identified as clinocllore. In a second Stonehenge sample it was identified, due to a slight shift in diffraction peak positions, as chamosite (Fe-dominant chlorite). The remaining two Stonehenge samples were not investigated using the HighScore software (hence we do not know which species of chlorite are present in those two samples).

4.4. Scanning electron microscope – EDS analysis

Scanning electron imaging of three Preseli dolerites shows the presence of ‘spinel’ crystals, either forming small (10-40 but up to 80 μm diameter) euhedral crystals (see Fig. 9a) or rounded grains, 40-80 but up to 250x200 μm in size with brown internal reflections and thin,

pale 'ferrochromit' veinlets or pitted, spongy grains (Fig. 9b) or 150-250 μm diameter 'pitted' rounded grains. Ixer (in Darvill et al., 2009) suggested that they were restricted to the spot areas but subsequently we have observed them also in clinopyroxene crystals (Fig. 9c). Similar 'spinel' grains have been reported in Stonehenge dolerites, for example stone 61 (Ixer in Thorpe et al., 1991) and stone 35a (Ixer and Bevins, 2011).

Analyses of 'spinel' are presented in Table 5 which shows they are either spinel or chromite, following the classification of the spinel supergroup by Bosie et al. (2019). Semi-quantitative analyses (not presented here) of spongy spinels from sample PCC11 show that they are depleted in magnesium at the expense of the introduction of zinc, as seen in the spectrum in Figure 9c.

5. Interpretation

In this section the findings from our investigation of the petrography of the Preseli dolerites and their iconic spots are reviewed. High resolution images in plane polarized light and between crossed polars of sample PCM31, from Carn Meini, presented as Figures 4b and 4c above show that the spots represent large plagioclase crystals (glomerocrysts). However, they are heavily overprinted by masses of small, randomly oriented prismatic clinozoisite and zoisite crystals which have the effect of making the spot areas look isotropic when examined using standard optical microscopic methods. The plagioclase phenocryst clusters appear to have developed early in the crystallization of the dolerites because they are devoid of mafic minerals (especially clinopyroxene), an interpretation which is also supported by the presence of chromite/spinel crystals in the spot areas; chromite and spinel are high temperature igneous minerals which grow early in the crystallization of magmas, commonly in association with olivine. Further evidence for an early origin of the spot areas lies in the geochemical data presented by Thorpe et al. (1991). They analysed a spot area and host dolerite for a sample from Carn Meini, recording high contents of CaO and Al_2O_3 in the spot areas, combined with low levels of Fe_2O_3 , MgO, Ni, and V but especially low levels of the incompatible elements Y, Zr, and Nb. These geochemical characteristics are consistent with the spot areas being early-

formed, mafic-free areas (plagioclase phenocrysts/glomerocrysts) rather than late felsic segregations, which would be expected to contain enhanced levels of incompatible elements in comparison to the host dolerite.

Automated SEM-EDS and X-ray diffraction analyses have shown the spot areas to be dominated by five mineral phases, namely clinozoisite, zoisite, Ca plagioclase, albite and (variably) muscovite. Means of these five phases make up average modal proportions in the three spot areas of 90.98% in sample PCC11 and 95.41% in the three spot areas in sample PCM32. In contrast to the high modal % proportions of these five phases in the spot areas they make up less than 50% of the average modal proportions of the three background areas of PCC11 (46.46%) and of PCM32 (46.64%). Whilst PCM32 has a higher (background) modal proportion of clinopyroxene (mean = 22.41%) and a lower modal proportion of chlorite (mean = 13.16%) than in PCC11 (means of 13.51% and 20.63% respectively) the total mean percentages of these two mafic minerals are very similar in the two samples (35.57% in PCM32 and 34.14% in PCC11). Again, these data are consistent with PCC11 being more extensively altered than sample PCM32.

The alteration assemblage albite+clinozoisite+zoisite+epidote+muscovite is classically termed 'saussurite' and the process of saussuritization is defined by Shelley (1993) as 'the replacement of plagioclase by albite together with epidote, clinozoisite or zoisite and usually with calcite and sericite' in which the 'epidote' grows in random orientation within the altered feldspar. It is quite common in both mafic and acidic igneous rocks and is considered by some to reflect alteration of calcic plagioclase by late magmatic fluids (see Goodwin in Bowes, 1989). Exactly when the saussuritization occurred in the Preseli dolerites is not clear; however, we believe it was before the intensive regional prehnite-pumpellyite to greenschist facies metamorphism affecting the background areas of the dolerites (and most probably the spot areas with further albitization of the Ca plagioclase). This regional metamorphism is widely developed across Wales (Bevins and Rowbotham, 1983; Robinson and Bevins, 1999). Evidence for the regional metamorphism being later than the saussuritization is provided by the chlorite/actinolite veins invading the spot areas (as seen in Figure 2b and in Figure 8). Chlorite and actinolite are likely to have been generated by the breakdown of olivine and marginal

alteration of clinopyroxene in the background areas of the dolerites with released iron and magnesium then migrating in metamorphic fluids along fractures into the spot areas. Chlorite is also seen along cleavage planes in the relict plagioclase crystals in the spots. Chromite/spinel crystals were also affected by the low-grade metamorphism, leading to iron-rich 'ferrochromit'/magnetite rims to the crystals as well as to the development of 'spongy' crystals in which magnesium is lost at the expense of introduced zinc.

Bevins and Robinson (1993) calculated a tightly constrained P/T condition for the regional, burial-related metamorphic event based on mineral compositions in the epidote projection for a sample from the Mynydd Preseli. This sample (PCG21) has an assemblage prehnite+pumpellyite+epidote+actinolite (plus albite, chlorite, titanite and quartz) which is equivalent to the pseudo-invariant point (CHEPPAQ) in the petrogenetic grid for the NCMASH system (see Robinson and Bevins, 1999). Application of this petrogenetic grid, and taking account of activities based on the mineral compositions in this sample, derives P/T conditions of ca. 1.1 kbar and 287°C. We have less information concerning the conditions prevailing during the earlier saussuritization event but if it is linked to late magmatic fluids then the temperature of alteration is likely to be higher than the regional metamorphism. Morad et al. (2009) suggested temperatures of ca. 400°C for saussuritization of plagioclase in granitic rocks from the Proterozoic basement of SE Sweden which they linked to hydrothermal alteration by late magmatic fluids. More analogous to the Preseli dolerites, perhaps, is the alteration history reported for altered basic dykes in southern New Zealand described by Coombs et al. (1977). The metamorphic grade in these rocks is recorded as being prehnite-pumpellyite to pumpellyite-actinolite facies but in a suite of dykes at Eglinton, South Island, two dykes contain zoisite in feldspar pseudomorphs. Coombs et al. (1977) noted that 'anomalously' these cloudy, Fe-free zoisites occur in direct contact with clear Fe-bearing epidotes and suggest that 'it is probable that the Eglinton rocks are in some degree polymetamorphic', although no temperatures were proposed for the generation of the zoisite. However, we consider that these Eglinton dyke rocks too have similarly experienced a two-stage alteration history, linked to an early Ca saussuritization event (resulting in the growth of the zoisite) followed by the regional

prehnite-pumpellyite to pumpellyite-actinolite metamorphism and so have a similar mineralogy to the Preseli dolerites.

It is of course the two-stage alteration history experienced by the Preseli dolerites that makes them distinctive and which makes the 'spots' a valuable provenancing characteristic. This even applies on a local scale in north Pembrokeshire. The Preseli dolerites belong to a suite of sill-like intrusions which occur across a ca. 25 km strip of country extending from Strumble Head in the west to Foel Drygarn in the east (see Bevins et al., 1989 and Figure 1); however, the spotting is confined to a limited area ca 1.5 km by 4.0 km which contains a small number of rocky outcrops, including Carn Meini, Carn Goedog, Carn Gyfrwy, Carn Breseb and Cerrig Marchogion, outcrops that have been proposed as the sources of stones used in the construction of Stonehenge (see Thomas, 1923, Thorpe et al., 1991; Bevins et al., 2014). These may well all be outcrops of a single, feldspar porphyritic sill, although poor exposure (the Preseli are covered by thick superficial deposits) makes correlation difficult.

Can the modal % of secondary minerals in the background areas of the Preseli dolerites be used to refine the provenance of the Stonehenge doleritic bluestones? As we have shown earlier, one way of demonstrating the varying degree of alteration between the two samples is to sum the mean modal proportions of the main secondary minerals in the background areas analysed, which in this case are quartz, albite, muscovite, chlorite, actinolite, epidote and clinzoisite/zoisite. For PCM32 the sum of the modal% of these secondary minerals is 59.12 while for PCC11 the sum is 79.11. In Table 6 we list the modal% for the secondary minerals in each of the six spot areas. For PCC11 the total modal% of the secondary minerals falls within the range 75.60-82.01% whereas for PCM32 the range is 54.41-62.29%, reflecting a relatively limited variation in alteration minerals at the thin section area scale. Varying contents of primary minerals may have some effect on this potential 'alteration index', given that clinopyroxene tends to be more resistant to alteration than primary plagioclase at these grades of metamorphism and so a more mafic sample with higher modal % of clinopyroxene might be expected to show a lower % for the sum of the main alteration minerals. The alteration index may therefore represent a combination of how mafic a sample is and also on the degree of alteration (most probably representing fluid/rock ratios during alteration). However, for the

purpose of comparing Preseli dolerites with Stonehenge dolerites from the point of view of provenancing that double component factor is not a hindrance.

Calculation of an alteration index for samples from Preseli and Stonehenge may therefore provide a tool for refining the provenancing of the Stonehenge doleritic bluestones. So whilst the spots were the defining character that led to the provenancing of the doleritic bluestones to the Mynydd Preseli area, the character and extent of the low-grade metamorphic alteration present in the background areas of the dolerites might offer the potential for further refinement of source outcrops. This can only be advanced, however, by analysing more Preseli samples using the automated SEM-EDS method to get a clearer picture of the metamorphic alteration history of the Preseli dolerites and also to explore the range of variation at the hand specimen and rock outcrop scales.

6. Conclusions

Using a combination of standard optical microscopy, high resolution photomicrography, SEM-EDS (both 'standard' and automated) and X-ray diffraction we have identified that the spot areas in the Preseli (and hence in the Stonehenge) spotted dolerites are dominated by five mineral phases, namely Ca plagioclase, albite, randomly oriented, very fine-grained clinozoisite and zoisite, and relatively minor but locally important muscovite. This is a classic 'saussurite' assemblage, identified as such by Parkinson (1897) in his description of the Preseli dolerites. We consider the Ca plagioclase to be an early primary high temperature phase which crystallized from the original magma before the main mafic mineral clinopyroxene as phenocrysts or glomerocrysts; this is supported by the presence of chromite/spinel in the spot areas. These conclusions agree with the findings of Ixer (in Darvill et al. 2009) who considered the chromite/spinel minerals to be early high temperature minerals which probably formed at the same time as olivine (which is now present only as chlorite pseudomorphs in the dolerites). Further evidence for an early origin for the Ca plagioclase, as opposed to representing late-stage, residual felsic patches, lies in the geochemistry of the spot areas; Thorpe et al. (1991)

showed the spots to be depleted in the incompatible elements Zr, Y and Nb, elements which would be enriched in late residual liquids.

The Ca plagioclase phenocrysts were subsequently saussuritized, a process commonly considered to be linked to the presence of late-stage magmatic fluids leading to selective hydrothermal alteration of Ca plagioclase crystals at moderate temperatures, perhaps around 400°C. Although also altered, the background areas of the Preseli dolerites show a contrasting alteration assemblage comprising albite, chlorite, Fe-epidote, clinozoisite/zoisite and actinolite, along with rarer prehnite, pumpellyite and titanite. This assemblage is consistent with a later metamorphism at conditions transitional from the prehnite-pumpellyite to greenschist facies at lower temperatures than the saussuritization event, probably between 250-300°C, or possibly slightly higher as Ixer (in Thorpe et al., 1991) estimated metamorphic temperatures for the Preseli dolerites at $335 \pm 15^\circ\text{C}$ on the presence of mixed chalcopyrite-pyrrhotite crystals in epidote. Prehnite-pumpellyite and greenschist facies metamorphic assemblages are widely developed in metabasites across Wales and have been linked to regional-scale burial metamorphism. This burial-related alteration mineral assemblage is more mafic than the saussurite assemblage because it involves the breakdown of olivine, iron oxides and some clinopyroxene, leading to the generation of chlorite, actinolite, Fe-bearing epidote and titanite. The fact that thin veinlets of chlorite and actinolite are seen cutting through the spot areas suggests that the regional metamorphism is later than the saussuritization, consistent with the saussuritization being linked to late-stage magmatic fluids.

The degree of alteration in the two Preseli dolerites is different, with PCC11 being more altered than PCM32. This probably relates to differing fluid/rock ratios during the regional metamorphic event which almost certainly would have led to further albitization of Ca plagioclase in the spot areas and probably caused the euhedral phenocryst forms to lose their definition, becoming more 'spot-like'. It is the combination of a two-stage alteration history with varying degrees of alteration that leads to the character of the 'spots' (varying from euhedral to rounded) and to their role in providing evidence for the source of the Stonehenge doleritic orthostats in the Preseli region in west Wales.

The difference in alteration state between the two analysed samples is highlighted by the sum of the mean % of the low-grade metamorphic minerals in the background areas of the two samples (total sum of 59.12% in PCM32 and 79.11% in PCC11). This contrasting alteration state perhaps offers an index by which the Preseli dolerites can be compared, potentially offering further discrimination of the source outcrops of the Stonehenge spotted dolerites. In the next phase of this study we will analyse further Preseli dolerites in order to investigate the variability of secondary mineral modal percentages at the hand specimen and outcrop scales with a view to testing the hypothesis that the geochemical Group 1 of Bevins et al. (2014) is sourced from Carn Goedog as well as seeing if new, detailed mineralogical evidence can shed a light on the Preseli sources of geochemical groups 2 and 3. Also, knowing that the spots represent former Ca plagioclase phenocrysts/glomerocrysts offers the potential for petrogenetic modelling using the rare earth elements to see if Groups 1 and 3 of Bevins et al. (2014) are magmatically related through crystal fractionation or perhaps crystal concentration processes.

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Figure captions

Fig. 1. Sketch map of north Pembrokeshire showing some of the key localities referred to in the text.

Fig. 2. Cut and polished samples of spotted dolerite ('preselite') from the Mynydd Preseli in north Pembrokeshire showing the distribution, size and character of the distinctive white spots.

Fig. 3. A). Thin section photomicrograph between crossed polars of spotted dolerite PCM30 from Carn Meini in the Mynydd Preseli showing an ophitic textural relationship between large clinopyroxene crystals (Cpx) and 'cloudy', prismatic, albitic plagioclase crystals containing secondary muscovite (Musc). Areas of primary Ca plagioclase (Ca Plag) and secondary chlorite (Chl) pools are also present. B). Thin section photomicrograph between crossed polars of spotted dolerite PCG21 from Carn Gwr in the Mynydd Preseli showing large clinopyroxene crystals (Cpx) and a rounded pseudomorph after olivine (Ol Pseud) in clinopyroxene with acicular crystals of actinolite (Act) which are overprinting chlorite whilst a second rounded olivine pseudomorph (to the left and below of the other pseudomorph) is largely composed of iron-bearing epidote (Ep). A large pool of chlorite (Chl) occurs at the top right of the image.

Fig. 4. A). Standard photomicrograph between crossed polars of spotted dolerite sample PCM32 from Carn Meini showing a ca. 3.5cm diameter 'spot'. B). High resolution photomicrograph in plane polarized light of spotted dolerite sample PCM31 from Carn Meini showing a ca. 5cm diameter 'spot' at top right of centre as well as a less well-developed spot towards the bottom left of the image. The black crystals are iron oxide minerals. C). Same area as for Figure 4B but between crossed polars. D). An enlarged area of the image in 4B showing that the 'spot' is composed of a mass of randomly oriented acicular crystals with relatively high relief.

Fig. 5. False colour image particle maps generated by automated SEM-EDS for Mynydd Preseli spotted dolerite samples PCC11 from Carn Goedog (image A) and PCM32 from Carn Meini (image B). The modal mineralogy for these two samples is presented in Table 2 and shown graphically in Figure 6. The images also show six areas (three spot and three 'background' areas) in each image for which the modal mineralogy has been determined which are listed in Table 2 and illustrated graphically in Figure 6.

Fig. 6. Modal mineralogy histograms for Mynydd Preseli spotted dolerite samples PCC11 (from Carn Goedog) and PCM32 (from Carn Meini), along with the average modal mineralogy for the six spot areas and the six background areas delineated in Figures 5a and 5b. PCM32 is less altered than PCC11, as evidenced by the higher modal % of (primary) Ca plagioclase in PCM32 and the higher modal % of secondary albite, chlorite and clinozoisite/zoisite in PCC11.

Fig. 7. False colour image maps for an enlarged spot area in Mynydd Preseli sample PCM32 along with individual mineral distribution maps. Chlorite- and actinolite-free areas (delineated by the dashed rectangles) are interpreted as representing former primary Ca plagioclase phenocrysts/glomerocrysts.

Fig. 8. Annotated false colour image map for spot area in Figure 7 showing the distribution of some of the primary (pyroxene and Ca plagioclase) and secondary (alteration) minerals, the latter including both saussurite minerals (clinozoisite/zoisite, albite, muscovite) and regional low-grade metamorphic minerals (actinolite, chlorite, epidote, quartz).

Fig. 9. Images of spinel ($MgAl_2O_4$) and chromite ($FeCr_2O_4$). A). An SEM backscatter image of euhedral spinel crystal in Mynydd Preseli spotted dolerite sample PRES CB from Carn Meini. The spinel occurs in a spot area in association with a CaAl silicate (probably clinozoisite), and minor muscovite. B). SEM backscatter image of euhedral spinel crystal in chlorite Mynydd Preseli spotted dolerite sample PCC11 from Carn Goedog. C). SEM backscatter image of spongy, altered spinel or chromite crystal in Mynydd Preseli spotted dolerite sample PCC11 from Carn Goedog. The spectrum below qualitatively shows the presence of Zn coupled with a low concentration of Mg.

Fig. 10. An X-ray powder diffraction pattern (NMW X-2741) of a spot area in Stonehenge stone 33 showing the presence of albite (Ab), chlorite (Chl), clinozoisite (Czo), zoisite (Zo) and muscovite (Ms).

Table captions

Table 1. Geochemical classification scheme for the Mynydd Preseli dolerites along with proposed Stonehenge bluestone source outcrops (from Bevins et al., 2014).

Table 2. Modal mineralogy for Mynydd Preseli samples PCC11 (from Carn Goedog) and PCM32 (from Carn Meini) for both whole section areas and the six delineated spot and background areas in both samples with their average percentages.

Table 3. Whole rock major and trace element compositions for Mynydd Preseli spotted dolerite samples PCC11 (from Carn Goedog) and PCM32 (from Carn Meini) determined by X-ray fluorescence spectrometry at the University of Keele (see Bevins et al., 1989 for more details of analytical methods).

Table 4. Mineral identifications determined by X-ray diffraction for a range of Mynydd Preseli and Stonehenge orthostats. See text for analytical methodology. Ab=albite, Chl=chlorite, Ep=epidote, Czo=clinozoisite, Zo=zoisite, Ms=muscovite, Prh=prehnite, Qz=quartz.

Table 5. Mineral analyses of the spinel supergroup minerals from Mynydd Preseli spotted dolerite samples PCC11 (from Carn Goedog) and PCM30 and Pres CB, both from Carn Meini.

Table 6. Modal mineral proportions for the principal low-grade metamorphic alteration minerals in three background areas for each of Mynydd Preseli spotted dolerite samples PCC11 (from Carn Goedog) and PCM32 (from Carn Meini). The results are interpreted as showing that sample PCC11 is more heavily altered than sample PCM32.

Supplementary information

Petrographic description of spotted dolerite sample CMQ2 from Carn Meini

The surface of dolerite CMQ2 is greenish-grey (5G 5/1 on the Geological Society of America rock-color chart) and carries white spots with thin, <1 mm wide, greener rims. The cut surface is a light bluish-grey (5B 7/1) with 10 mm diameter, bluish-white (5B 9/1) spots.

Transmitted light microscope examination shows large plagioclase laths (An_{44}) that are zoned, twinned and extensively altered to fine-grained clinzoisite with very low interference colours and white mica; epidote with high interference colours and clinochlore also replace plagioclase. The margins of this generation of plagioclase are often unaltered. A later generation of smaller, stubby plagioclase (albite?) is associated with chlorite. The main generation of plagioclase has a sub-ophitic relationship with clinopyroxene. Small plagioclase laths enclosed in titanomagnetite are less altered than the main plagioclase. Most clinopyroxene, some of which is zoned or twinned, is unaltered, as are acicular apatite crystals, some of which are associated with later stage plagioclase (albite?).

Secondary minerals are abundant and include late-stage quartz, with some quartz forming spherulitic aggregates or thin, cross-cutting veinlets. Zoned epidote commonly occurs as mosaics and in epidote-chlorite (clinochlore with brown interference colours)-pyrite intergrowths, some of which surround clinopyroxene. Unpublished electron microprobe analyses by one of us (REB) record a range in XFe values in Preseli dolerites ranging from 0.11 to 0.33 (where $XFe = Fe^{3+}/(Fe^{3+}+Al)$), spanning the clinzoisite-epidote boundary. Our unpublished data show that sample PCC11 from Carn Goedog has XFe values of 0.29 (core) and 0.15 (rim) respectively. This zoning reflects a decrease in Fe contents towards the crystal rims, a feature which Grapes and Hoskin (2004) interpreted as resulting from prograde metamorphism conditions during crystal growth. Within the chlorite-epidote intergrowths euhedral epidote is enclosed within chlorite or forms euhedral rims to chlorite infills. Where these intergrowths are rounded and occur in clinopyroxene crystals they have been interpreted by Bevins et al. (1989) as being pseudomorphs after olivine. Minor amounts of chamosite are present. Very locally,

small, 20-30 μm long, rhombic titanite is enclosed within chlorite. Green to yellow-green, fibrous fringes with moderate relief and showing high interference colours are identified as amphibole and have been shown by Bevins and Rowbotham (1983) on the basis of electron microprobe analysis to be actinolite; they grow out from clinopyroxene or epidote and grow into quartz or chlorite. Minor amounts of titanite mantle highly altered ilmenite.

The mineralogy of the 'spot' areas are dominated by masses of very small crystals. Because of their fine grain size the crystals appear to be isotropic due to grain boundary refraction effects. They are very altered primary plagioclase crystals which now comprise abundant, fine-grained clinozoisite with very low interference colours intergrown with white mica; they also carry chrome spinel. Epidote with high interference colours, chlorite (clinocllore) lying along relict cleavage and relict feldspar/secondary feldspar are less abundant. Locally white mica is the main alteration product.

Reflected light microscope examination shows that the chrome-rich spinel forms rounded grains, 40-80 but up to 250x200 μm in size with brown internal reflections and thin, pale 'ferrochromit' veinlets or pitted, spongy, altered rims. Ixer (in Darvill et al., 2009), using reflected light microscopy, reported the presence of small (10-40 but up to 80 μm diameter) euhedral crystals or 150-250 μm diameter 'pitted' rounded grains of chrome spinel in spotted dolerite CM2 from Carn Meini; similar pitted, rounded grains are reported in PCC11 from Carn Goedog. Ixer (op. cit.) suggested that they were restricted to the spot areas but subsequently we have observed them also in clinopyroxene crystals. Ixer (in Thorpe et al., 1991) reported the presence of 200 μm diameter spinel in a spot in Stonehenge orthostat SH61. Analyses of euhedral chrome spinels show they are either spinel or chromite, following the classification of the spinel supergroup by Bosie et al. (2019). Semi-quantitative analyses of spongy spinels from sample PCC11 show that they are depleted in magnesium at the expense of the introduction of zinc.

Large, equant crystals of titanomagnetite are extensively altered. Magnetite has altered totally to fine-grained titanite with white internal reflections, whilst crystallographically orientated, 1-2 μm wide ilmenite oxidation exsolution lamellae have altered to fine-grained,

acicular, colourless TiO₂ minerals or, if thicker (between 2-5 µm wide), to TiO₂ minerals with orange internal reflections. Titanomagnetite carries rare, 10 µm diameter pyrite or limonite pseudomorphs after pyrite. Ilmenite, 80-100 µm long, is intergrown with titanomagnetite as an internal or external sandwich and is altered to pale-coloured TiO₂. Elsewhere, much ilmenite forms discrete, lobate laths up to 200 µm in length, or symplectite-like intergrowths with silicates. All generations of ilmenite are altered extensively. Some ilmenite alters to orange TiO₂ but most is replaced by fine-grained mixtures of 5-10 µm diameter, bireflecting, colourless probable carbonate and small, 2-5 but up to 10x2 µm long, pale-coloured to yellow TiO₂ minerals. The latter are crystallographically controlled with respect to the original ilmenite grain. The standard alteration sequence is ilmenite to 'pitted/spotty' ilmenite to carbonate to TiO₂ minerals and finally to titanite. Relict ilmenite up to 10-20 µm in diameter is commonly present. Wispy titanite rims up to 100 µm in thickness enclose ilmenite.

Sulphides are present in minor to trace amounts. Pyrite is the most abundant, forming 10-200 µm diameter, euhedral crystals, locally collected into aggregates. Rarely pyrite encloses 2-5 µm diameter, mixed chalcopyrite-pyrrhotite inclusions. Much pyrite has oxidised to limonite. Very rare, 10 µm diameter pyrite is enclosed within altered titanomagnetite but most surrounds titanomagnetite.

Pyrrhotite, as 20-40 µm diameter, hexagonal grains, 5-60 µm diameter chalcopyrite (or their limonite pseudomorphs) and 10-20 µm diameter, mixed chalcopyrite-pyrrhotite grains occur within epidote. Trace amounts of 10-40 µm diameter pyrrhotite have altered to limonite and patches up to 200 µm in diameter of 2-15 µm diameter chalcopyrite or 2-5 µm diameter pyrrhotite are present in alteration minerals.

References

- Bevins, R.E., Lees, G.J., Roach, R.A., 1989. Ordovician intrusions of the Strumble Head-Mynydd Preseli region, Wales: lateral extensions of the Fishguard Volcanic Complex. *Journal of the Geological Society*, London 146, 113-123.
- Grapes, R.H., Hoskin, P.W.O., 2004. Epidote Group minerals in low-medium metamorphic terrains. *Reviews in Mineralogy and Geochemistry* 56, 301-345.

Geological terminology definitions

Magma

Hot fluid or semi-fluid material below or within the Earth's crust. When magma is erupted at the Earth's surface it produces lava flows or ash eruptions. If the magma rises but is arrested at a high level in the crust it forms shallow-level intrusions, as in the dolerites of the Mynydd Preseli.

Primary mineral

The primary minerals in the dolerites are those which crystallize in magma when it is intruded into the Earth's crust some 450 million years ago. They crystallize at temperatures in the range between ca. 1300C to ca. 800C. In the Preseli dolerites the primary minerals are olivine, clinopyroxene, Ca plagioclase feldspar, apatite, 'spinel' and an iron-titanium oxide. All of these minerals are anhydrous (ie they contain no water in their crystal structures).

Secondary mineral

Following crystallization the high temperature primary minerals they are potentially unstable at the relatively low temperatures of the Earth's crust and are subject to breakdown (alteration), especially in the presence of circulating fluids which act as a catalyst for recrystallization. A range of secondary minerals developed in the Preseli dolerites, including albite, chlorite, zoisite, clinozoisite, epidote, actinolite, titanite, prehnite and pumpellyite. Many of these minerals are hydrous (ie they water in their crystal structures).

Phenocryst/glomerocryst

As molten magma cools crystals grow in the melt early formed crystals have the opportunity (space) to grow to quite large sizes. This typically takes place where magma is held in the Earth's crust in a magma chamber. When magma rises to erupt at the Earth's surface or is intruded into relatively cold crust the remaining melt crystallizes leading to the generation of a mass of smaller crystals, effectively freezing in the larger, early formed crystals. These early formed crystals are called phenocrysts or if they formed in aggregates of crystals they are called glomerocrysts.

Saussuritization

Saussuritization is the process of alteration of early-formed, high temperature calcium-rich plagioclase feldspar. The alteration commonly relates to the circulation of late magmatic fluids through the cooling rock body. The primary mineral is replaced by a secondary mineral assemblage which includes albite, zoisite, clinozoisite and muscovite.

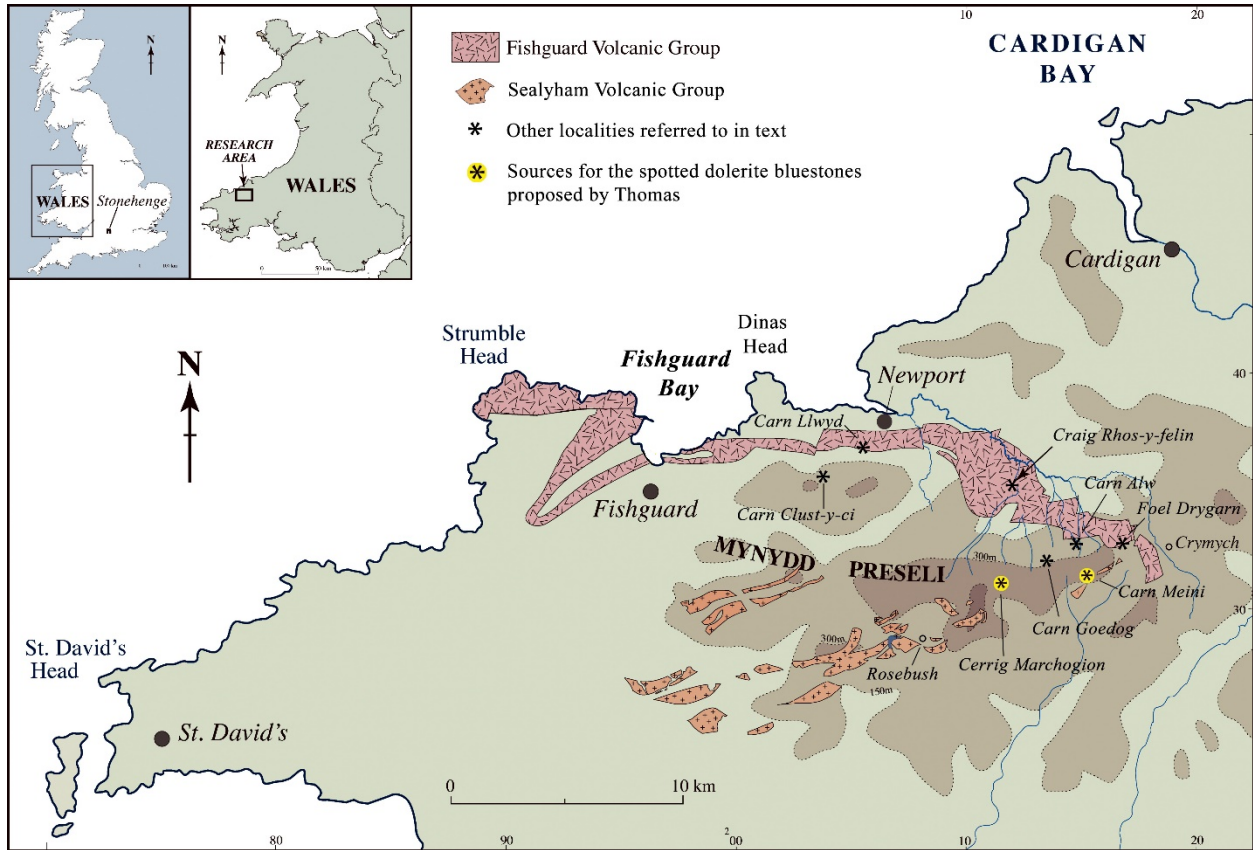


Figure 1.

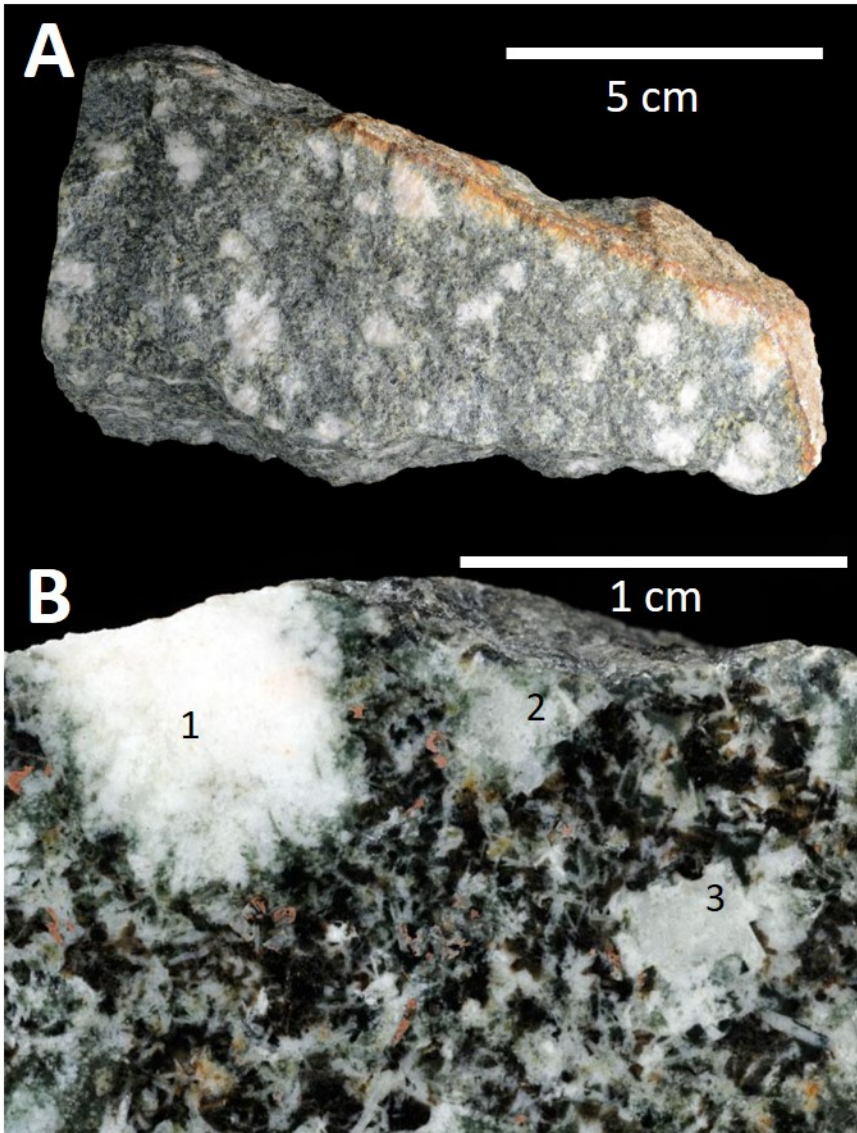


Figure 2.

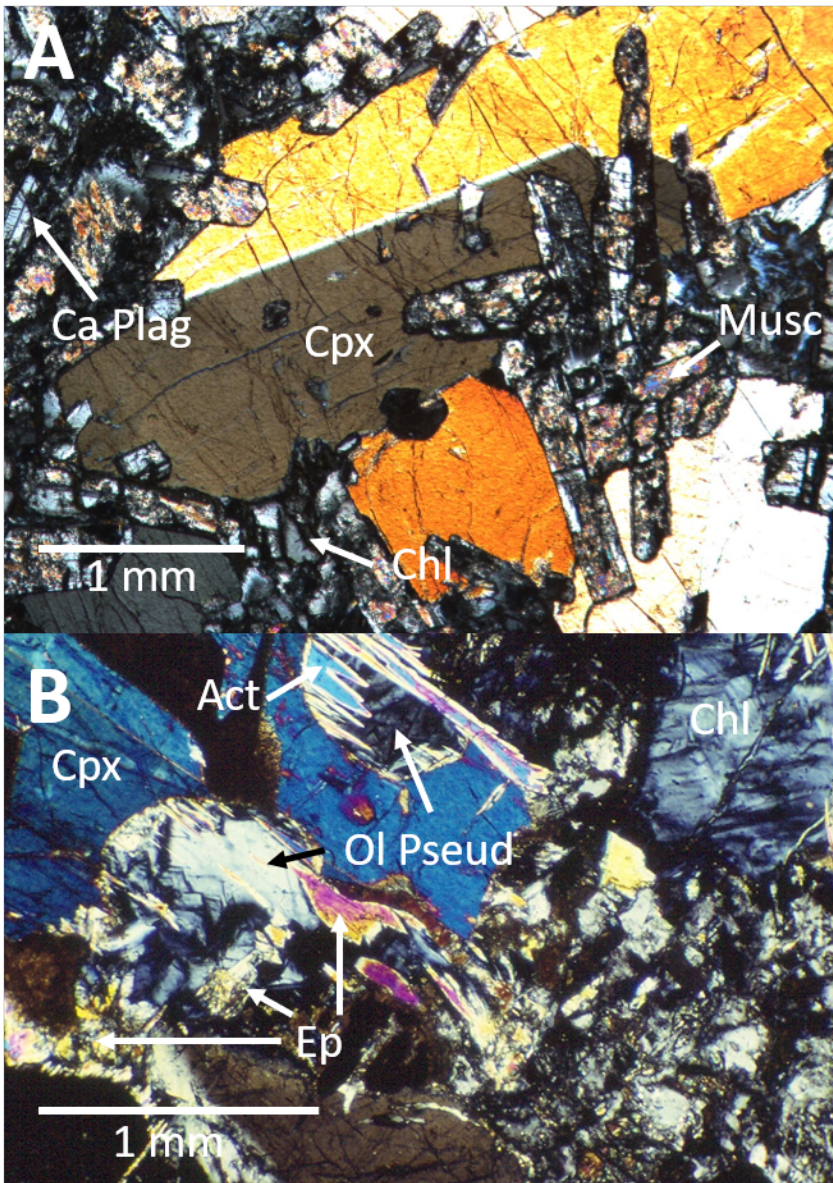


Figure 3

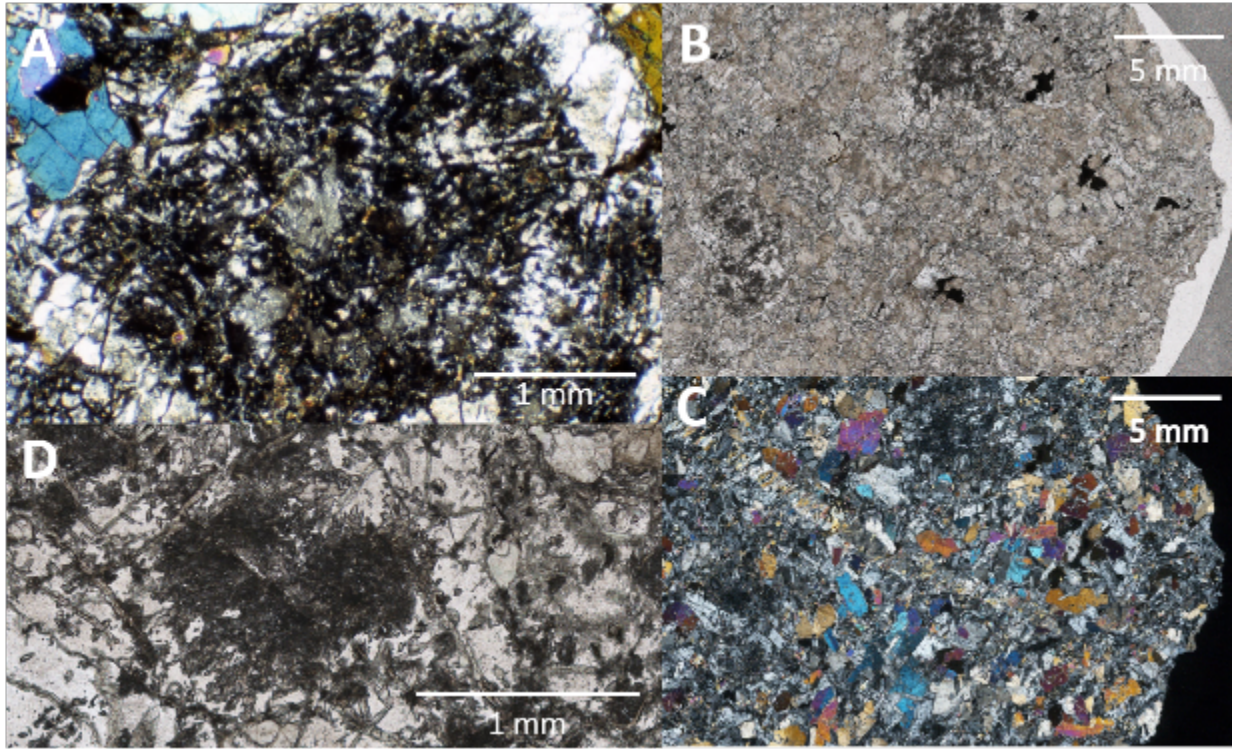


Figure 4

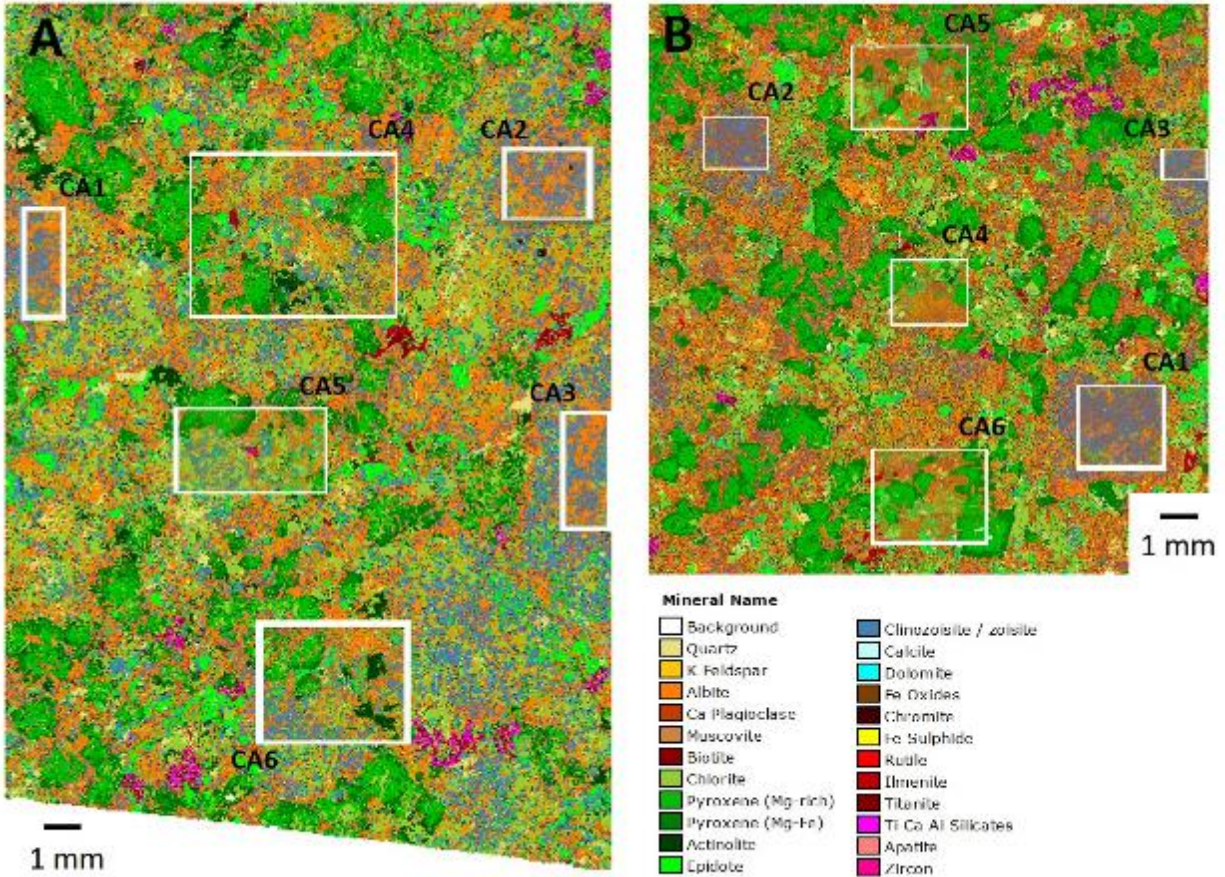


Figure 5

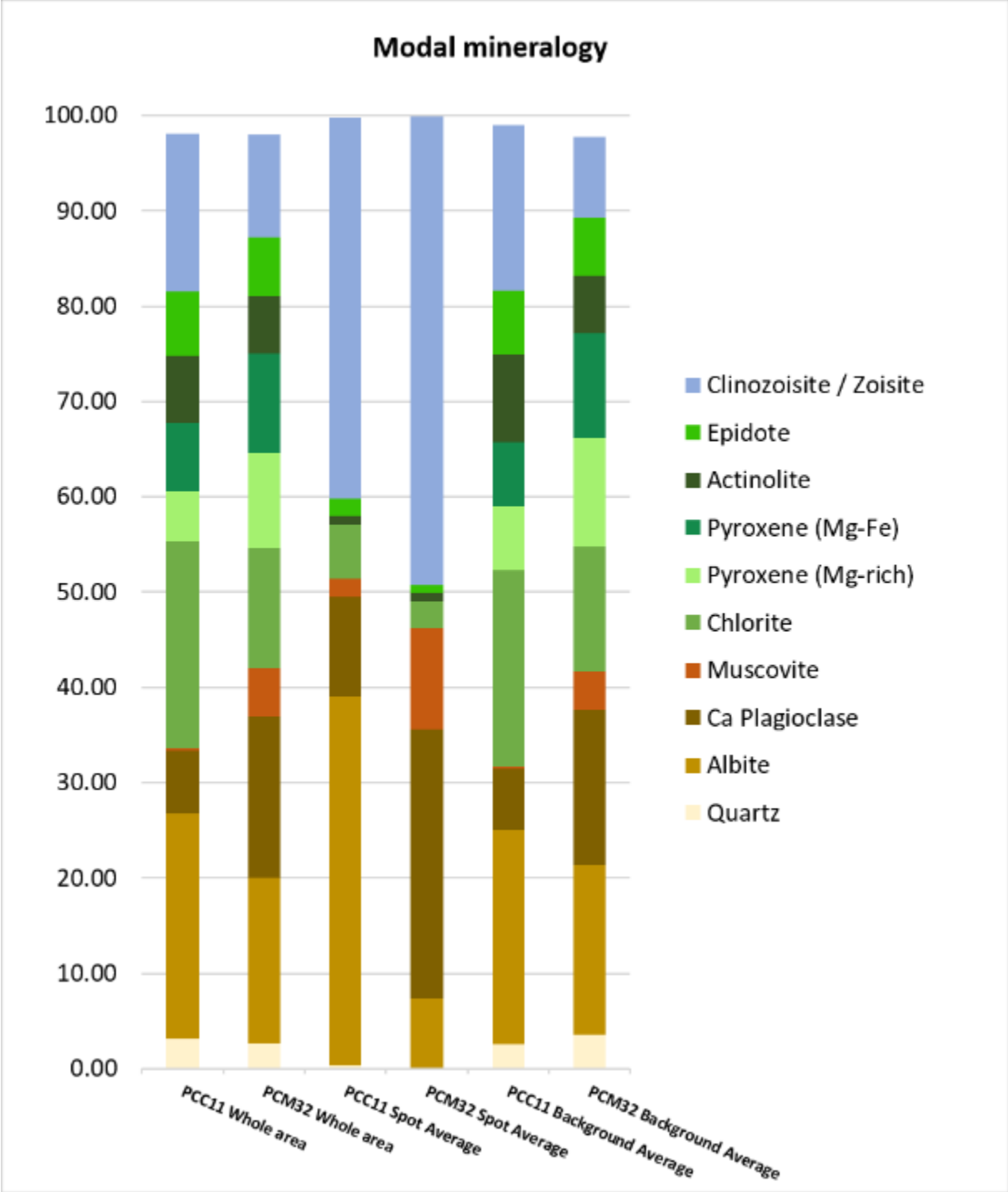


Figure 6

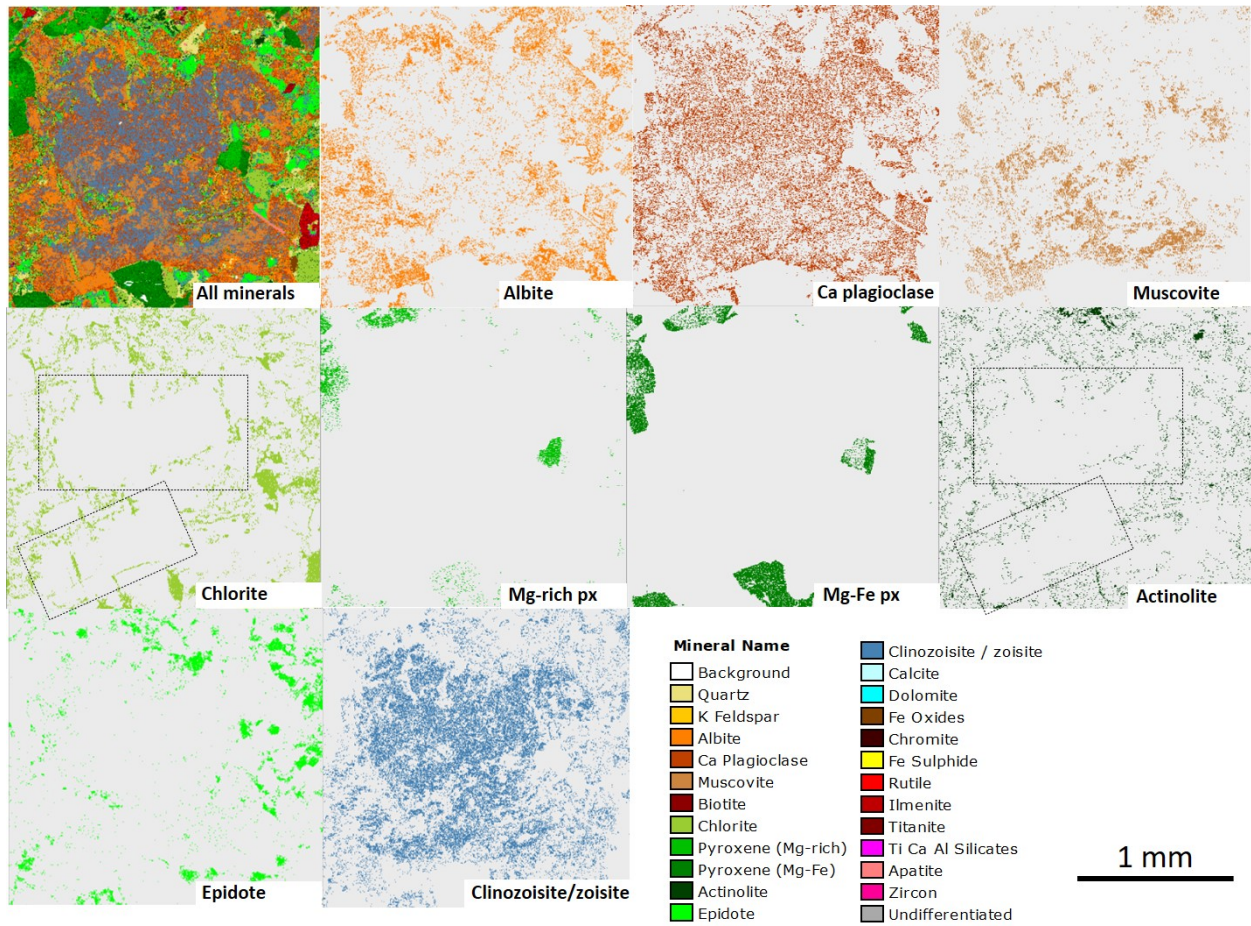


Figure 7

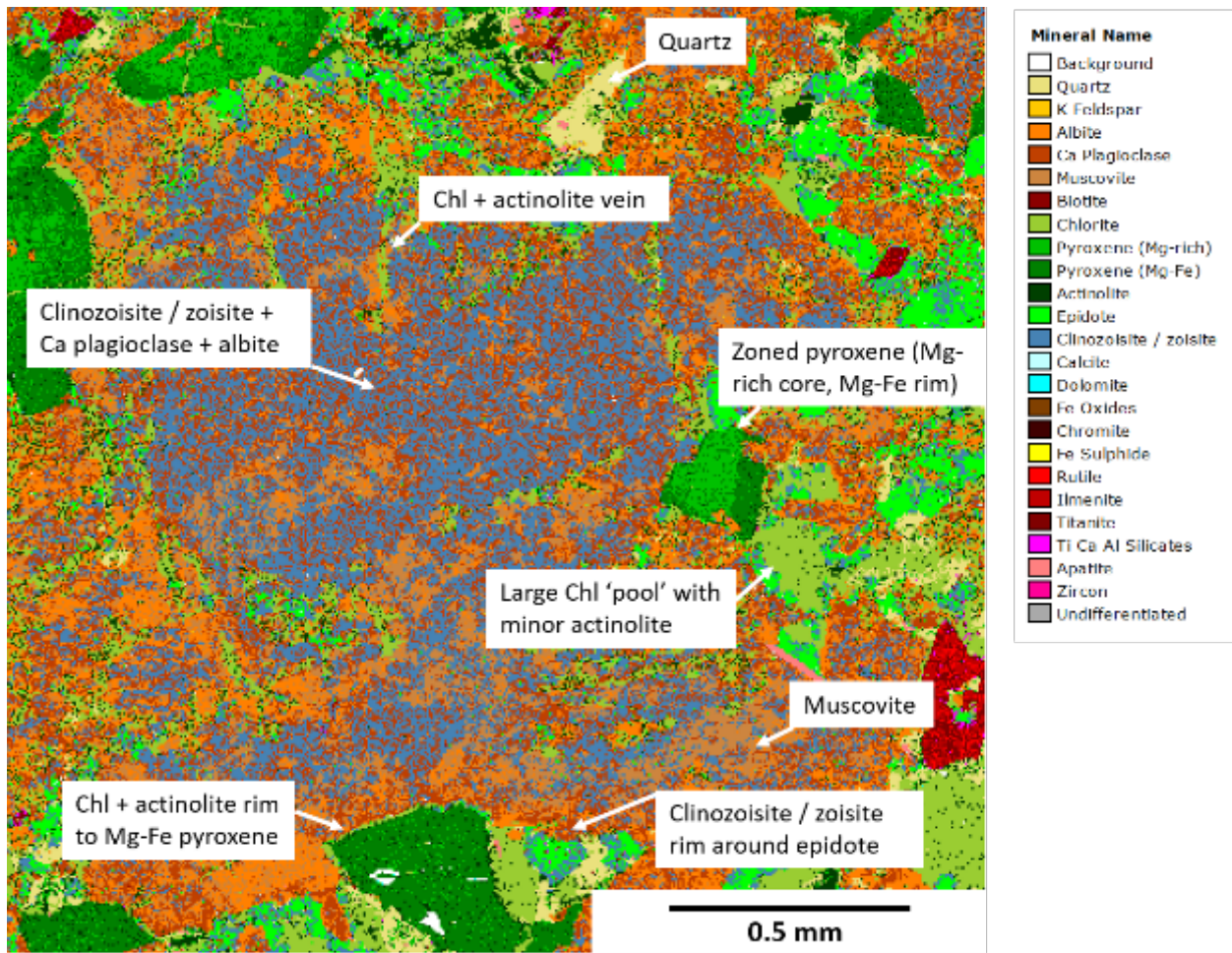


Figure 8

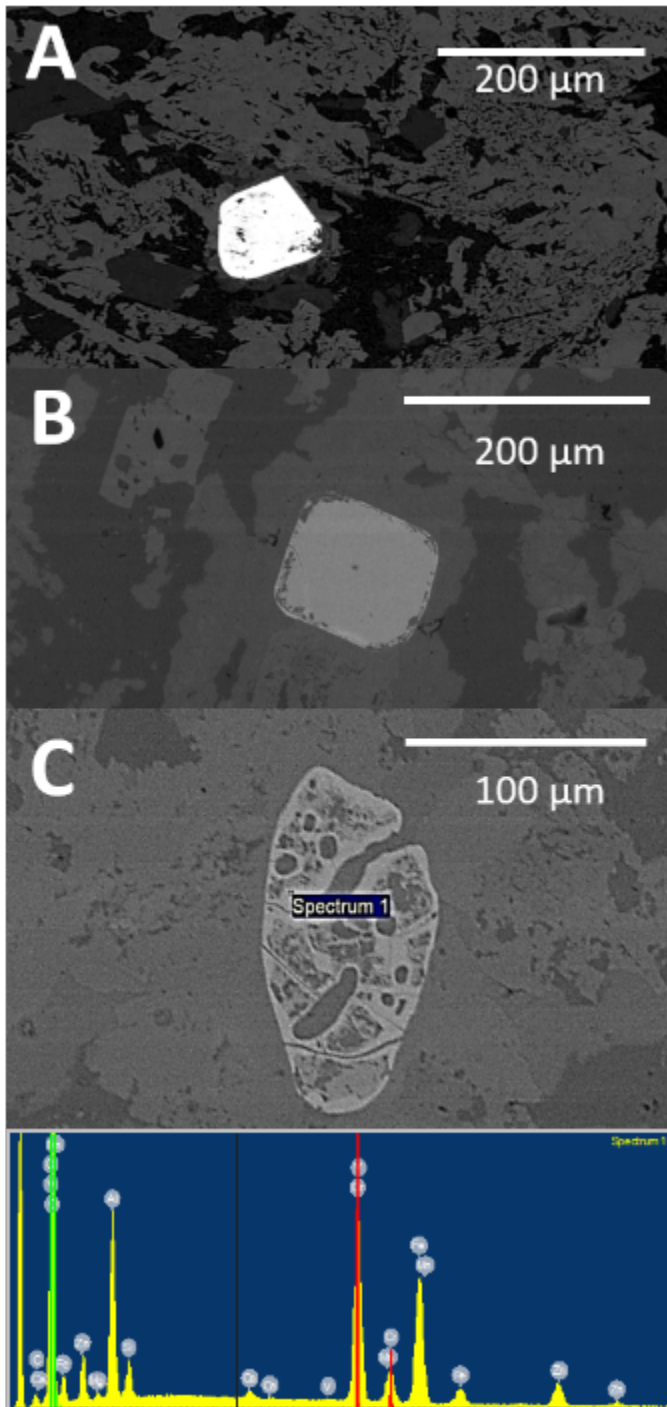


Figure 9

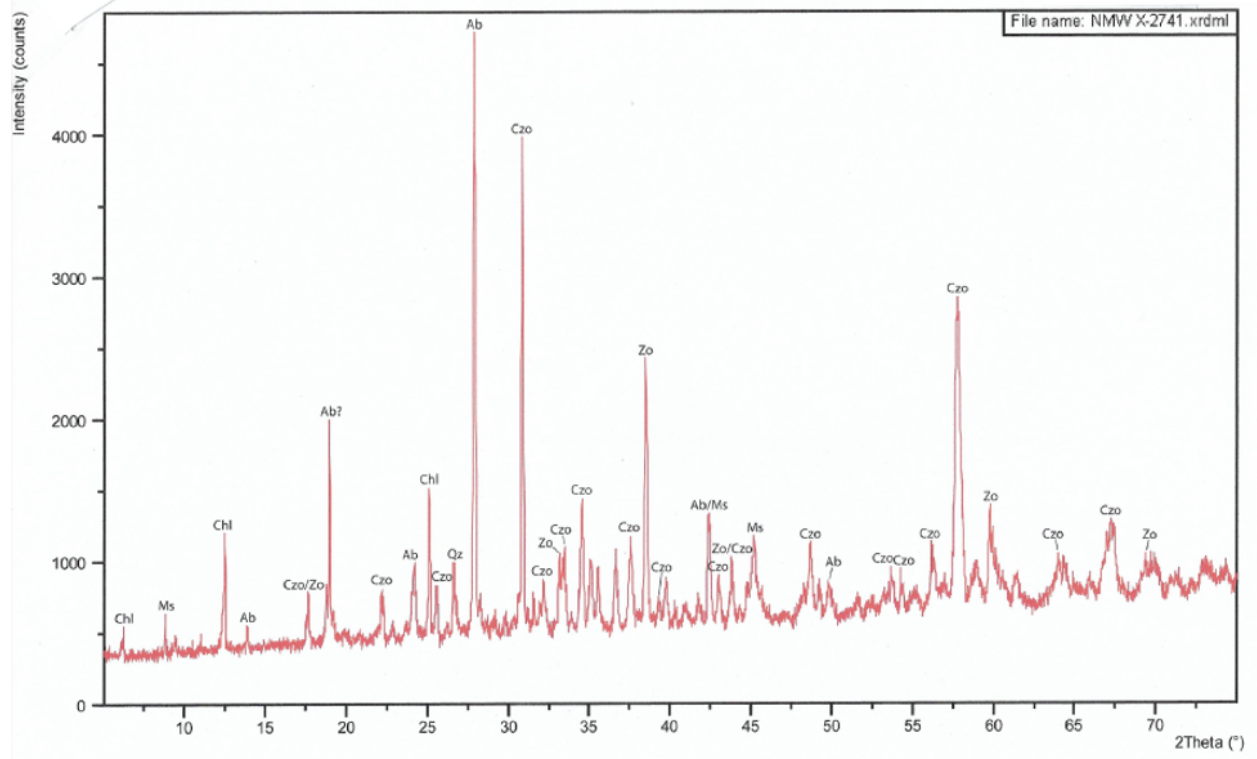


Figure 10

	Cr ppm	Ni ppm	MgO wt%	Sources
Group1	>400	<50	6.3-8.0	1
Group 2	<400	>110	>8.0	2
Group 3	<400	<50	<6.3	3
Sources				
Group 1	Carn Goedog			
Group 2	Cerrigmarchogion or Craig Talfynydd			
Group 3	Carn Breseb, Carn Gyfrwy, Carn Alw, un-named outcrop W of Carn Ddafad-las			

Table 1

		PCC11	PCM32		PCC11	PCC11	PCC11	PCC11	PCC11	PCC11	PCC11	PCC11	PCC11	PCM32	PCM32	PCM32	PCM32	PCM32	PCM32	PCM32	PCM32
		Whole area	Whole area	CA1 spot	CA2 spot	CA3 spot	Spot average	CA4 Background	CA5 Background	CA6 Background	Background average	CA1 spot	CA2 spot	CA3 spot	Spot average	CA4 Background	CA5 Background	CA6 Background	Background average		
Mineral (%)	Quartz	3.12	2.68		0.72	0.17	0.20	0.36	2.07	3.60	1.86	2.51	0.11	0.03	0.00	0.05	2.68	5.19	2.74	3.54	
	K Feldspar	0.02	0.02		0.01	0.01	0.03	0.02	0.03	0.01	0.04	0.03	0.02	0.00	0.01	0.01	0.02	0.01	0.01	0.02	
	Albite	23.60	17.36		38.20	38.23	39.68	38.71	24.79	18.28	24.45	22.51	7.65	7.26	7.00	7.31	17.36	20.12	15.86	17.78	
	Ca Plagioclase	6.67	16.93		10.29	12.39	8.74	10.47	6.65	5.14	7.40	6.40	28.31	33.16	23.34	28.27	16.93	19.08	12.84	16.28	
	Muscovite	0.24	5.03		1.95	2.51	1.05	1.84	0.20	0.14	0.29	0.21	11.64	5.53	14.71	10.63	5.03	3.62	3.31	3.99	
	Biotite	0.07	0.11		0.02	0.01	0.04	0.02	0.06	0.06	0.05	0.06	0.07	0.08	0.04	0.06	0.11	0.10	0.10	0.11	
	Chlorite	21.71	12.66		6.68	4.84	5.66	5.72	18.40	26.36	17.12	20.63	4.20	1.36	2.61	2.73	12.66	12.17	14.65	13.16	
	Pyroxene (Mg-rich)	5.23	9.98		0.00	0.00	0.00	0.00	8.46	6.48	5.31	6.75	0.00	0.00	0.00	0.00	9.98	6.45	17.92	11.45	
	Pyroxene (Mg-Fe)	7.17	10.43		0.09	0.00	0.00	0.03	8.22	7.41	4.64	6.76	0.04	0.00	0.00	0.01	10.43	9.56	12.89	10.96	
	Actinolite	7.11	5.99		1.15	0.87	0.73	0.91	8.54	7.02	11.93	9.16	1.57	0.58	0.75	0.97	5.99	5.48	6.66	6.04	
	Epidote	6.62	6.19		2.18	1.41	1.59	1.73	6.80	7.34	6.11	6.75	1.15	0.51	0.55	0.74	6.19	6.55	5.32	6.02	
	Cs/zoisite	16.61	10.75		38.47	39.16	42.25	39.96	14.80	16.96	20.26	17.34	45.23	51.39	50.97	49.20	10.75	9.15	5.86	8.59	
	Calcite	0.04	0.03		0.01	0.00	0.05	0.02	0.04	0.04	0.03	0.04	0.01	0.02	0.00	0.01	0.03	0.03	0.03	0.03	
	Dolomite	0.01	0.01		0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	
	Fe Oxides	0.00	0.02		0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.01	
	Chromite	0.00	0.00		0.00	0.37	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
	Fe Sulphate	0.00	0.03		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.01	
	Rutile	0.17	0.10		0.00	0.00	0.00	0.00	0.16	0.06	0.00	0.07	0.00	0.00	0.00	0.00	0.10	0.02	0.30	0.14	
	Ilmenite	0.00	0.14		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.14	0.03	0.55	0.24	
	Titanite	0.82	0.76		0.04	0.00	0.00	0.01	0.50	0.58	0.06	0.38	0.00	0.04	0.00	0.01	0.76	1.40	0.62	0.92	
	Ti Ca Al Silicates	0.37	0.57		0.09	0.01	0.00	0.03	0.11	0.40	0.10	0.20	0.00	0.03	0.00	0.01	0.57	0.96	0.18	0.57	
	Apatite	0.40	0.19		0.09	0.00	0.00	0.03	0.16	0.10	0.34	0.20	0.00	0.01	0.00	0.00	0.19	0.05	0.12	0.12	
	Zircon	0.01	0.00		0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	

Table 2

sample	PCC11	PCM32
wt%		
SiO ₂	48.16	47.98
TiO ₂	1.16	1.05
Al ₂ O ₃	17.73	17.60
Fe ₂ O ₃	9.25	9.43
MnO	0.15	0.15
MgO	6.67	6.98
CaO	12.05	11.43
Na ₂ O	3.09	2.81
K ₂ O	0.16	0.60
P ₂ O ₅	0.11	0.09
LOI	3.19	3.26
Total	101.72	101.38
ppm		
V	212	196
Cr	490	369
Ni	41	43
Cu	52	73
Zn	72	73
Rb	7	8
Sr	226	245
Y	20	17
Zr	67	69
Nb	3	1

Table 3

Rock sample number	X-ray number								
Preseli		Ab	Chl	Ep	Czo	Zo	Ms	Prh	Qz
PCM30	X2764	√	√		√	√	√		
PCM32	X2765	√	√		√	√	√		
PCGF28	X2766	√	√		√	√	√		
PCC11	X2775	√	√		√	√			√
PCAW47	X2767	√	√		√		√		
PCAW49	X2776	√	√		√	√	√		
PCP12	X2768	√	√		√			√	
Stonehenge									
SH35	X2644	√	√		√	√			
SH61	X2731	√	√	√			√	√	√
SH33	X2741	√	√		√	√	√		
SH37	X2742		√		√		√	√	√

Table 4

Sample	PCC11-1	PCC11-2	PCC11-3	PCC11-4	PCM30-3	Pres CB-3	Pres CB-4
wt%							
TiO ₂	1.62	1.97	1.29	1.33	1.50	1.35	1.60
Al ₂ O ₃	22.32	20.67	25.52	26.89	20.39	25.24	24.00
Cr ₂ O ₃	30.04	33.33	29.92	29.13	32.60	30.69	31.14
FeO	32.37	32.73	28.46	29.28	42.90	27.99	29.26
MnO	0.00	0.00	0.00	0.37	1.31	0.13	0.31
MgO	11.46	10.90	12.10	12.44	1.84	12.45	11.32
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	97.81	99.60	97.29	99.44	100.54	97.85	97.63
Formula (corr.)	4(O)	4(O)	4(O)	4(O)	4(O)	4(O)	4(O)
Ti	0.038	0.046	0.030	0.030	0.037	0.031	0.038
Al	0.827	0.763	0.935	0.960	0.795	0.919	0.887
Cr	0.747	0.825	0.735	0.697	0.853	0.750	0.772
Fe ³⁺	0.350	0.319	0.270	0.282	0.277	0.269	0.266
Fe ²⁺	0.501	0.538	0.470	0.459	0.910	0.455	0.501
Mn	0.000	0.000	0.000	0.009	0.037	0.003	0.008
Ni	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mg	0.537	0.509	0.561	0.562	0.091	0.573	0.529
Zn	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Classification name	Spinel	Chromite	Spinel	Spinel	Chromite	Spinel	Spinel

Table 5

	PCC11	PCC11	PCC11	PCM32	PCM32	PCM32
	CA4 Backgrou nd	CA5 Backgrou nd	CA6 Backgrou nd	CA4 Backgrou nd	CA5 Backgrou nd	CA6 Backgrou nd
Quartz	2.07	3.60	1.86	2.68	5.19	2.74
Albite	24.79	18.28	24.45	17.36	20.12	15.86
Muscovi te	0.20	0.14	0.29	5.03	3.62	3.31
Chlorite	18.40	26.36	17.12	12.66	12.17	14.65
Actinolit e	8.54	7.02	11.93	5.99	5.48	6.66
Epidote	6.80	7.34	6.11	6.19	6.55	5.32
Czs/ zoisite	14.80	16.96	20.26	10.75	9.15	5.86
Totals	75.60	79.70	82.01	60.66	62.29	54.41

Table 6