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Lower Palaeozoic K-bentonites from the Carnic Alps, Austria

Kathleen HISTON[1)], Peter KLEIN[2)], Hans Peter SCHÖNLAUB[2)*)] & Warren D. HUFF[3)]

[1)] via Mazzini 4, 21039 Valganna (Va), Italy, e-mail: hiscat@interfree.it

[2)] Geological Survey of Austria, Neulinggasse 38, A-1031 Vienna, Austria, e-mail: hp.schoenlaub@geologie.ac.at

[3)] Dept. of Geology, University of Cincinnati, OH 45221-0013, USA, e-mail: warren.huff@uc.edu

[*)] Corresponding author, hp.schoenlaub@geologie.ac.at

Abstract

A total of 97 K-bentonite levels have been recorded from the Upper Ordovician (Ashgill) to Lower Devonian (Lochkov) sequences of the Carnic Alps, Austria. They occur in shallow to deep-water fossiliferous marine sediments. The faunal elements suggest a plate movement from a moderately cold environment of approximately 50°S latitude in the Upper Ordovician to the Devonian reef belt of some 30°S.

Geochemical discrimination diagrams based on immobile trace elements and REE data suggest that the volcanism belongs to a tectonically active terrane dominated by calc-alkaline mafic lavas of obvious subduction-related volcanic arc affinities with the majority of samples falling within the andesite and rhyodacite/dacite fields.

The abundance of these K-bentonite horizons in Llandovery to Middle Ludlow sequences is similar to those found in the British Isles, Sweden, Canada and North America and documents widespread volcanism related to the closing of the Iapetus Ocean and northward drifting of microplates derived from the northern margin of Gondwana. K-bentonites of Pridolian age may be comparable with those described from Podolia for which a source area in the Rheic Ocean has been indicated.

In der oberordivizisch-silurischen Schichtfolge der Karnischen Alpen (Österreich) wurden insgesamt 97 Horizonte von K-Bentoniten gefunden, die den marinen fossilführenden Flachwasser- und Tiefwasserablagerungen in mm- bis cm-dicken Lagen zwischengeschaltet sind. Nach ihrer Begleitfauna befanden sich die Vorläufer der Karnischen Alpen im Oberordoviz auf der Süderde in ungefähr 50° südlicher Breite und drifteten bis in die Devonzeit in den Riffgürtel von ca. 30° südlicher Breite.

Für die hier beschriebenen K-Bentonite wird nach geochemischen Diskriminationsdiagrammen von immobilen Spurenelementen und Seltenen Erden-Daten ein Subduktions bezogener Vulkanismus an einem aktiven Plattenrand angenommen, der von kalkalkalischen mafischen Laven dominiert wurde und der auf einen ehemaligen Vulkanbogen hinweist. Die große Mehrheit der Proben fällt dabei in die Andesit und Rhyodazit/Dazit-Felder.

Das gehäufte Auftreten solcher K-Bentonithorizonte im Zeitraum Llandovery bis mittleres Ludlow ist in auffallender Übereinstimmung mit den Britischen Inseln, Südschweden, Kanada und Nordamerika. Dieser weit verbreitete Vulkanismus spiegelt einerseits die Schließung des Iapetusozeans wieder, andererseits das Driften von Mikroplatten, die sich im Ordoviz vom Nordrand von Gondwana gelöst haben und in der Folge nach Norden gegen den Äquator drifteten. K-Bentonite aus dem jüngsten Silur (Pridoli) weisen hingegen Ähnlichkeiten mit Vorkommen in Podolien auf und dürften ihren Ursprung im Rheiischen Ozean haben.

1. Introduction

The search for evidence of ancient explosive volcanism in the form of altered airfall volcanic ash beds, now referred to as bentonites and K-bentonites, has become increasingly important in recent years as their potential use as stratigraphic markers has been recognised. Most K-bentonite horizons are not widely distributed but a few may be correlated for hundreds or thousands of kilometres by chemical fingerprinting techniques and comparison of detailed outcrop relationships (Huff, 1983; Bergström et al., 1995; Batchelor and Jeppsson, 1999). Because the beds were deposited in a geological instant over large areas they may be considered as isochronous rock units useful in precise correlations applicable to biogeographical, palaeogeographical, tectonomagmatic, geochronological and sedimentological investigations on both local and regional scales.

A K-bentonite is a bentonite in which the smectite has con-

verted to K-rich, mixed-layer illite-smectite (I/S). This is a reflection of both diagenesis and time. According to Marker & Huff (2005) the criteria for recognizing bentonites or K-bentonites as altered volcanic ash falls are varied and fall into field and laboratory (mineralogical) criteria.

For reliable identification in the field, K-bentonites display different colors when wet (blue, green, red, yellow) but are characteristically yellow when weathered. Due to their clay rich nature, they will feel slippery and waxy when wet. Some K-bentonites contain euhedral to anhedral volcanogenic biotite, quartz, feldspar, amphibole, zircon and apatite. Their typical appearance in an outcrop is that of a fine-grained clay-rich band ranging between 1 mm and 2 m in thickness. Accelerated weathering causes them to be recessed into the outcrop face. For thicker K-bentonites there is often a zone of nodular or bedded chert in the adjacent strata. Mineralo-

gically, most bentonites and K-bentonites are smectite- or illite/smectite-rich, although some may contain a considerable amount of kaolinite, and those that have undergone low-grade metamorphism may be dominated by R3 I/S and/or sericite plus chlorite/smectite (corrensite) and/or chlorite. Initial steps should begin with separation and XRD analysis of the clay fraction. Wet sieving the sample is important to separate the clay portion from the volcanic components as bentonites may contain volcanic phenocrysts and volcanic glass. Study of the non-clay fraction under the microscope is satisfactory to determine the type of crystals present in the sample. In addition, thin sections may complement the study of bentonites.

Research has been concentrated on Ordovician and Silurian occurrences as the K-bentonite abundances have proved useful in the correlation of the palaeogeographical position of various Lower Palaeozoic terranes and consequently the timing of geodynamically relevant events such as the opening and closure of the Iapetus and Rheic oceans (Bergström et al., 1995, 1998a, 1998b, 1998c, 1998d; Fortey et al., 1996; Huff et al., 1998a; Thorogood et al., 1998; Šliaupa et al., 2000). It has also been possible to predict the prevailing wind circulation for the given palaeolatitudes that these terranes would have passed through, based on the presence of ash from particular volcanic centers complemented by current-related criteria of rock sequences (Huff et al., 2000). These facts are of considerable importance with regard to the drift rate of the continental plates which has been shown to be up to 25 cm/year and will contribute to the confirmation of the

1 Cellon Section
2 Seewarte
3 Oberbuchach Section 1,2
4 Nölblinggraben Section
5 Zollnersee-Hütte
6 Hoher Trieb
7 Valbertad
8 Uggwa

FIGURE 1: Main regions of anchizonal to lower greenschist metamorphosed fossiliferous Palaeozoic strata in the Eastern Alps. Note the Periadriatic Line (P.L.) separating the Carnic Alps and the Karavanke Mountains (Southern Alps) from other Alpine Palaeozoic remnants belonging to the Eastern Alps (After Hubmann et al. 2003, fig. 2). Enlarged map shows the localities referred to in the text.

available palaeomagnetic data for this time interval (Tait et al., 1997, 1999, 2000; Schätz et al., 2002). This is also true in the case of the forerunner of the Alps during Lower Palaeozoic times (Schönlaub, 1992, 1993, 1997, 1998).

Most Ordovician and Silurian K-bentonites reported in Europe are from the British Isles and Baltoscandia (Huff et al., 1993, 1997; Bergström et al., 1995, 1997, 1998c, 1998d) but there are also occurrences in Poland (Tomczyk, 1970), Podolia (Huff et al., 2000) and Lithuania (Šliaupa et al., 2000). They are also documented from North America (Bergström et al., 1998b, c; Kolata et al., 1998) and Argentina (Bergström et al., 1998a; Huff et al., 1998a). Recently, a number of K-bentonite beds have been recognized in the Ordovician-Silurian transition (Ashgill - early Llandovery) in the Yangtze Block, South China (Su et al., 2004). Many Silurian K-bentonites have been tied closely to biostratigraphical zonations especially those based on graptolites within shale facies. However, regional tracing of individual beds has proved difficult both in North America and Europe.

The Alpine orogen represents a collage of Alpine, Paleozoic and older crustal fragments. Schönlaub (1992, 1993) has shown that some fragments reflect a true odyssey from high southern latitudes in the Lower Palaeozoic to equatorial and northern settings during Upper Palaeozoic and Mesozoic times. These segments have been dated as ranging from Upper Ordovician to the Permian based on various well-known climate-sensitive bio- and lithofacies markers, thus adding further to the controversy with regard to the palaeogeography and the relationship of the Palaeozoic forerunner of the Alps and the coeval neighbouring areas such as Baltica, the British Isles, the Prague Basin (Barrandian), Sardinia, Southern France, Spain and North Africa.

The main regions of anchizonal to lower greenschist facies metamorphosed fossiliferous Palaeozoic strata in the Eastern and Southern Alps are shown in Figure 1. The objective of this study was to identify volcanic ash horizons in the Lower Palaeozoic sequences of the Carnic Alps (Fig. 1) and describe their geochemical features in order to explore their stratigraphical potential for regional correlation. The value of such correlations can be considerable in cases where rapid lithofacies changes and/or where a lack of diagnostic biofacies prohibits precise stratigraphical evaluation. During a detailed study of the Silurian sections as part of a multidisciplinary investigation of the development of the Cephalopod Limestone Biofacies in the Carnic Alps (Ferretti et al., 1999; Histon and Schönlaub, 1999; Histon et al., 1999) millimetre thick clay layers were found in the Llandovery of the Cellon Section (Fig. 2) which, when analysed using X-ray diffraction showed traces of smectite. Although many detailed studies have been carried out in the Lower Palaeozoic sequences in the Southern and Central Alps, none have concentrated on this aspect as the K-bentonite levels are sometimes so thin as to not be easily recognized (Fig. 3). Given the palaeogeographical position of the Carnic Alps and other Palaeozoic microcontinents during the Late Ordovician to Lower Devonian interval, it was proposed to locate and identify event stratigraphic units such as K-bentonite levels
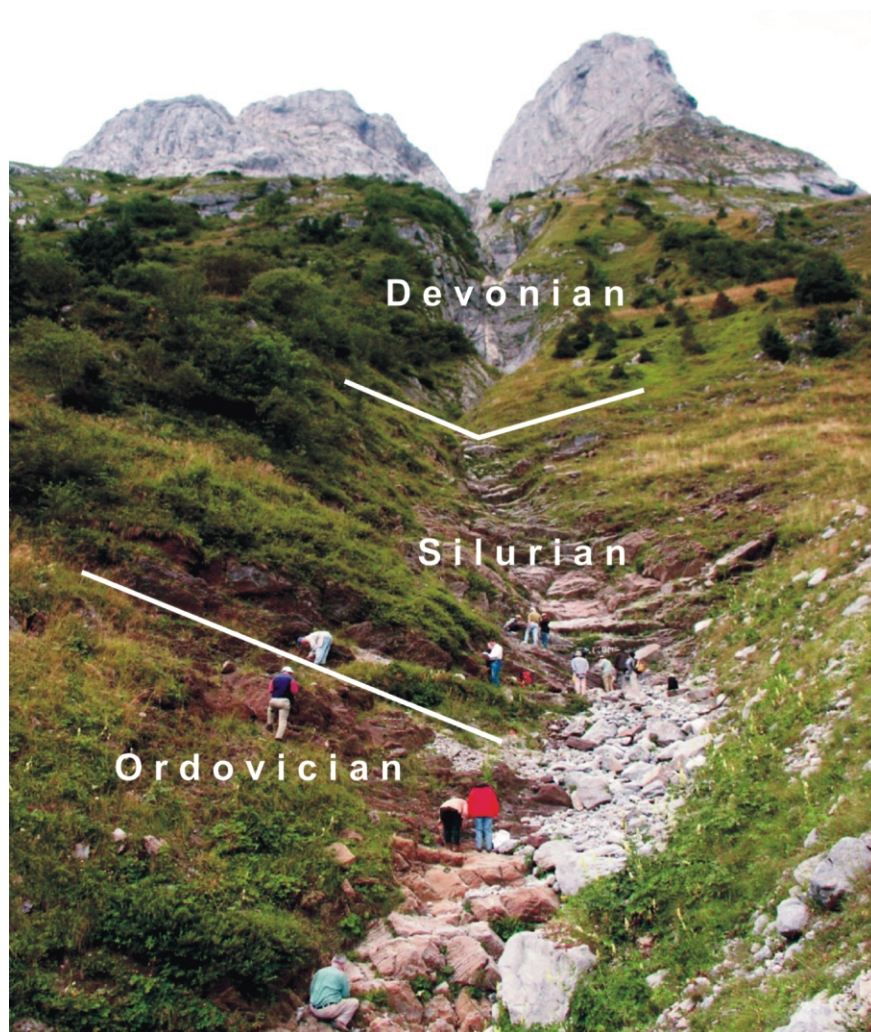

Figure 2: Cellon Section. The section is located at an altitude between 1480 and 1560 m on the eastern flank of the Cellon Mountain. The Ordovician (Ashgill: Uggwa facies), Silurian (Plöcken facies) and Lower Devonian (Lochkov: Rauchkofel facies) parts of the section are indicated being best exposed in a narrow avalanche gorge. The section continues upwards with Lower Carboniferous sequences behind the mountain peak. The Cellon Section represents the stratotype for the Silurian of the Eastern and Southern Alps.

within the well-dated graptolitic shale and carbonate sequences of this interval from various sections across the depositional basin in order to correlate them with those established in other areas of Europe and possibly North America.

2. Geological Setting

During Variscan and Alpine orogeneses several Palaeozoic crustal segments were dismembered and are now incorporated into the complex Alpine nappe system. The primary geographic positions and mutual bio(geo)graphic relations of these isolated segments are only poorly understood. A possible arrangement of Palaeozoic areas south of the Alpine front, including high grade metamorphosed Palaeozoic parts within crystalline complexes, results in a picture as shown in Figure 4. Two major regions of Palaeozoic developments are distinguished which are separated by the most prominent Alpine fault system, the Periadriatic Line (PL). Variscan sequences north of the PL form parts of the "Upper Austroalpine Nappe System" whereas sequences south of the PL belong to the Southern Alpine System. Palaeozoic sequences of the Southern Alpine system are exposed in the Carnic Alps and Karavanke Mountains. Differences of Austroalpine versus Southalpine areas are reflected in different facies and faunal characteristics as a result of independent histories of subsidence rates, amounts of volcanic activity and climatic impacts (Schönlaub 1992, 1993).

The Palaeozoic sequences of the Carnic Alps range from Upper Ordovician to Permian in age and are represented mainly by shallow to deep water fossiliferous marine sediments which suggest a constant movement from a moderately cold climate of approximately 50° southern latitude in the Upper Ordovician to the equatorial belt in the Permian (Schönlaub, 1992). The reconstructed distribution of the various litho- and biofacies of the Carnic Alps indicates a SW-NE directed polarity from shallow water environments to an open marine and deep sea setting. The latter must be assumed in the northern part of the Southern Alps which, however, is missing due to tectonic deformation along the Gailtal fault as part of the Periadriatic Line separating the Southern from the Central Alps.

To the north metamorphic rocks also of Lower Palaeozoic age are found but with a quite diverse lithology to the Southern Alps. This
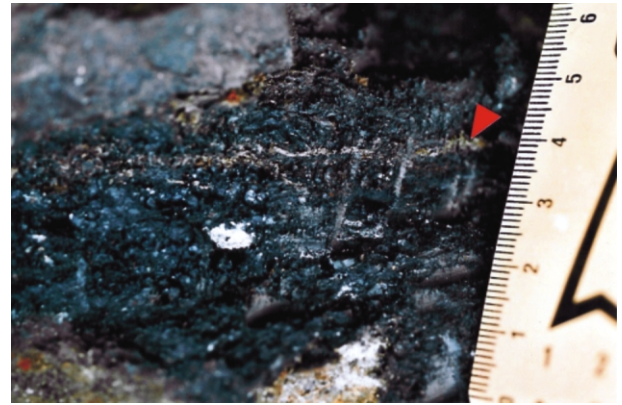

Figure 3: Thin K-bentonite level from the celloni Zone (Llandovery), Oberbuchach Section.

fragment therefore belongs to a different terrane to which the classic Lower Palaeozoic deposits found in the Greywacke Zone of the Northern Alps, Middle Carinthia and parts of Styria also pertain. Intraplate volcanism due to rifting throughout the Lower Palaeozoic is characteristic for the area (Loeschke and Heinisch 1993; Schönlaub and Histon 2000).

Hence, any conclusion about the width of the intervening area and the nature of the rocks separating various Alpine terranes remains a matter of speculation. In a wider context they represent peri-Gondwanide terranes and arcs similiar to, though much smaller than, Avalonia, Armorica-Iberia, Perunica
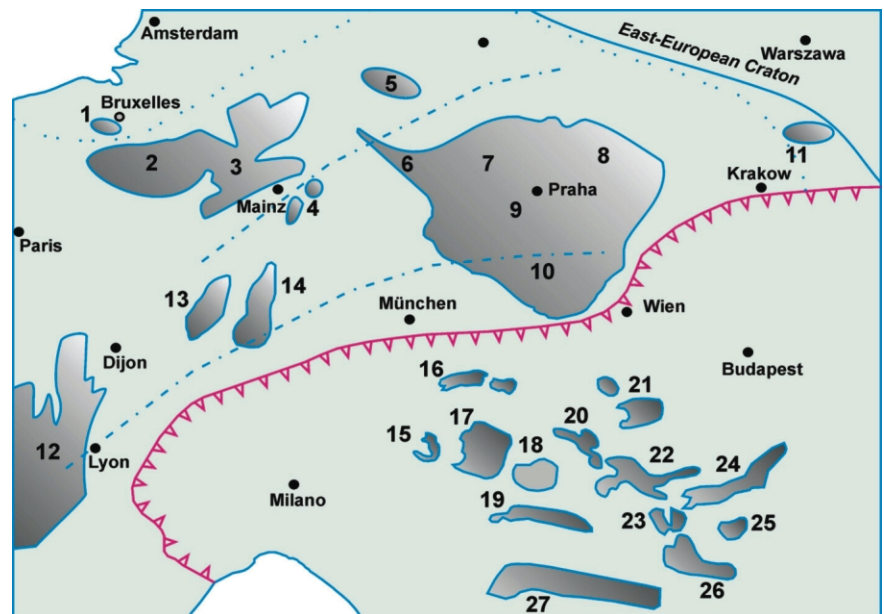

Figure 4: Regions with Variscan rock series exposed in central Europe. Geographic positions of Palaeozoic areas of the Eastern and Southern Alps (15-27) are reconstructed after palinspastic subtraction of Alpidic tectonic movements. Redrawn and modified after Faupl (2000) and Ratschbacher & Frisch (1993).
(1) Brabant Massif, (2) Ardennes, (3) Rhenish Slate Mountains, (4) Spessart, Odenwald, (5) Harz, (6) Thuringia and Franconian Forest, (7) Erzgebirge, (8) Sudetes, (9) Barrandian, (10) Bohemian Massif, (11) Lesser Poland Uplands (Holy Cross Mts.), (12) French Central Massif, (13) Vosges, (14) Black Forest, (15) Err-Bernina, (16) Hohe Tauern, (17) Silvretta, (18) Ötztal, (19) Crystalline area south of the Hohe Tauern, (20) Quartzphyllites of Innbruck, Radstadt, Ennstal, (21) Wechsel, (22) Seckau and Wölz Alps, (23) Koralpe, Saualpe, (24) Greywacke Zone, (25) Graz Palaeozoic, (26) Gurktal Nappe System, (27) Carnic Alps, Karavanke Mountains. Front of Alpine nappes is shown by saw-tooth line.

and others ("Hun"-composite terrane after Stampfli, 1996 and Raumer et al., 2002; "Armorican Terrane Assemblage (ATA)" after Tait et al., 1999) that originally formed the northern margin of Gondwana (Tait et al., 1997, 2000; Schätz et al., 2002). The initial break-up of Gondwana in the early Ordovician was followed by a rapid northward drift until the various terranes and crustal blocks collided and accreted with the northern continents Laurentia and Baltica, respectively, starting in the Devonian and ending in the Upper Carboniferous (Schönlaub, 1998).

In the Ashgill Series of the central Carnic Alps two lithologies are displayed: massive cystoid limestones, sandstones and graywackes representing the shallow water Wolayer facies with shales and bedded wackestones representing the more basinal Uggwa facies. The Silurian of the Carnic Alps is subdivided into four lithological facies representing different depths of deposition and hydraulic conditions suggestive of a steadily subsiding basin and an overall transgressional regime from the Llandovery to Ludlow. Uniform limestone sedimentation during the Pridoli suggests that more stable conditions were developed (Schönlaub, 1997). Silurian deposits range from shallow water bioclastic limestones to nautiloid-bearing limestones (Wolayer and Plöcken Facies), interbedded shales and limestones to black graptolite-bearing shales and cherts (Findenig and Bischofalm Facies) with overall thicknesses not exceeding 60 m. The available data for the Carnic Alps suggest an almost complete but considerably condensed succession in the carbonate-dominated facies and a continuous record across the Ordovician/Silurian boundary in the graptolite-bearing sequences, something which is not possible to demonstrate in other areas of the Eastern and Southern Alps due to poor preservation, lack of fossils and metamorphic overprints. Transgression started in the *Glyptograptus persculptus* graptolitic zone, possibly even earlier in the *Norma-*

Lower Paleozoic sections sampled for K-bentonite levels in the Carnic Alps

System	Series	Stages	GRAPTOLITES	CONODONTS	Cellon (9)	Seewarte (1)	Ober-buchach (34)	Nölbing Graben (24)	Zollnersee-hütte (24)	Hoher Trieb (1)	Valbertad (1)	Uggwa (1)	Total (95)
DEVON.	LOWER	LOCHKOV	uniformis	I. woschmidti									
SILURIAN	PRIDOLI		bouceki-transgrediens	O. eosteinhornensis - O.e. detorta									
			branikensis-lochkovensis	O. remscheidensis Interval zone									
			parultimus-ultimus										
	LUDLOW	LUDFORDIAN	formosus	O. crispa									
			bohemicus tenuis-kozlowskii	O. snajdri Interval zone									
			leintwardensis	P. siluricus									
		GORSTIAN	scanicus	A. ploeckensis / NOT ZONED									
			nilssoni	K. stauros									
	WENLOCK	HOMERIAN	ludensis	O. bohemicus									
			praedeubeli-deubeli										
			parvus-nassa										
			lundgreni	O. sagitta sagitta									
		SHEINWOODIAN	rigidus-perneri	NOT ZONED / O. sagitta rhenana / K. patula / K. ranuliformis Interval zone									
			riccartonensis-belophorus										
			centrifugus-murchisoni										
	LLANDOVERY	TELYCHIAN	lapworthi-insectus	P. amorphognathoides									
			spiralis interval zone										
			griestonensis-crenulata	P. celloni									
			turriculatus-crispus										
		AERONIAN	guerichi	P. tenuis - D. staurognathoides									
			sedgwickii										
			convolutus										
			argenteus										
			triangulatus-pectinatus										
		RHUDDANIAN	cyphus	D. kentuckyensis									
			vesiculosus										
			acuminatus	O.? nathani									
ORDOV.	UPPER	ASHGILL	persculptus	A. ordovicus									

FIGURE 5: Stratigraphic distribution of the K-bentonite levels recognised from 8 sections sampled in the Carnic Alps.

lograptus extraordinarius graptolite zone, however, index fossils for this interval have not yet been found, i.e. in the upper Hirnantian Stage of the Ashgill Series and continued during the range of the index graptolite *Akidograptus acuminatus*. Due to the glacially-induced disconformity separating the latest Ordovician and the Silurian at many of the investigated sections a varying pile of shallow water sediments is locally missing, which corresponds to several conodont zones of Llandovery to Ludlow age in the Southern Alps. At some places even uppermost Pridoli strata may disconformably rest upon Upper Ordovician limestones. A continuous record of sediments across the Ordovician /Silurian Boundary, however, is suggested in the deep water graptolite sequences (Schönlaub and Histon, 2000).

The equivalents of the Devonian Period are characterised by abundant shelly fossils and carbonates as well as clastic sequences of varying thicknesses, ranging from more than 1000 m thick shallow water limestones to extremely condensed pelagic sequences of about 100 m thickness. The limestone facies varies from reef and slope deposits to condensed cephalopod limestones of an open marine offshore environment on the seaward-side and platform and coastal deposits on the land-directed side. The relationship in thickness between shallow water limestones and contemporary goniatite limestones is approximately 12 : 1 indicating enhanced seafloor mobility in the Lower and Middle Devonian prior to the climax of the Variscan perturbations (Schönlaub, 1997).

The Lower Palaeozoic sequences of the Carnic Alps are in general well-dated, biostratigraphically important fossil groups include primarily graptolites (Jaeger, 1975) and conodonts (Walliser, 1964; Schönlaub, 1980). Trilobites (Feist in Schönlaub et al., 1992), bivalves (Kříž, 1979, 1999), chitinozoans (Priewalder, 1997), and acritarchs (Priewalder, 1987) are of equal importance for correlation while the brachiopod (Havlicek et al., 1987) and cephalopod faunas (Korn In Schönlaub et al., 1992; Gnoli and Histon, 1998; Histon, 1999, 2002) are useful for palaeoecological and palaeogeographical considerations.

Eight sections were selected for study along the Carnic Alps chain based on indications from field notes, published literature and available thin sections from the area. These classic sections representing the various lithofacies found across the depositional basin are located south of the village of Kötschach-Mauthen along the Austrian-Italian border (Fig. 1). The fossiliferous sequences range from the Upper Ordovician to the Lower Devonian and are in general well-dated by graptolites and conodonts:

(a) Cellon Section (Ordovician: Uggwa facies; Silurian: Plöcken facies; Lower Devonian: Rauchkofel facies);

(b) Seewarte Section (Ordovician: Wolayer facies; Silurian: transitional between Wolayer and Plöcken facies);

(c) Oberbuchach Section (Ordovician: Uggwa facies; Silurian: Findenig facies);

(d) Nölbling Graben Section (Ordovician: Uggwa facies; Silurian: Bischofalm facies);

(e) Zollnersee-Hütte Section (Silurian-Lower Devonian: Bischofalm facies);

(f) Hoher Trieb Section (Ordovician: Uggwa facies; Silurian: Wolayer facies);

(g) Valbertad Section (Ordovician: Uggwa facies);

(h) Uggwa Section (Ordovician Uggwa facies; Silurian: Plöcken facies).

Successful recognition of K-bentonite beds requires a combination of field and laboratory information (Huff et al., 1993, 1998, Marker & Huff, 2005). K-bentonites in the field are often recognizable by their plastic nature and colors that vary from shades of green to yellow and orange. They often stand out in contrast to adjacent carbonate or siliciclastic strata by their higher weatherability and lighter color. The beds are clay-rich and typically consist of illite-smectite to illite or kaolinite-dominated units, often in strong contrast to adjacent beds. Their non-clay mineralogy commonly includes volcanogenic phenocrysts of minerals such as quartz, biotite, sanidine, pyroxene, amphibole, zircon and apatite. Chemical characteristics, particularly trace element data, tend to mirror intermediate and felsic source magmas.

Each section was sampled in detail at a millimeter scale and a total of 97 K-bentonite levels were tentatively identified from the original 162 field samples collected and analyzed (Fig. 5). The results of a preliminary investigation of the Uggwa, Valbertad and Hoher Trieb sections have also been included.
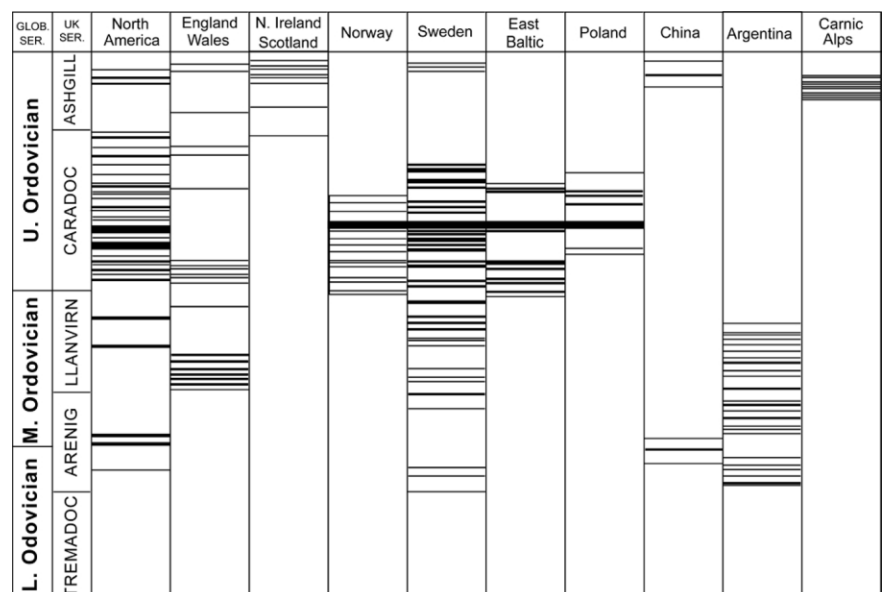

FIGURE 6: Stratigraphical range of Ordovician K-bentonites reported in the literature compared with Ordovician K-bentonite levels from the Carnic Alps.

The K-bentonite levels recognized are for the most part concentrated in the Llandovery, Middle Wenlock and Lower Ludlow. Some were also recognized in the Pridoli. As continuous exposure is lacking in some stratigraphical sections correlation of these horizons across the depositional basin was sometimes problematic.

3. Geographic and Stratigraphic Distribution

The possibility of correlation of the bentonite bearing sequences of the Carnic Alps, especially with the British Isles, part of which belonged to the Avalonia microcontinent, and with Southern Sweden (Schonen, Gotland) seems quite high, as well as with North America which formed part of Laurentia. Many detailed studies have been carried out in these areas providing a rich dataset for comparison with the results from the Lower Palaeozoic of the Carnic Alps (Figs 6, 7). Comparison of the stratigraphic occurrence of the K-bentonite levels with the known global occurrence of these marker horizons in the Silurian published by Huff et al. (2000) shows that they will certainly be useful for correlation.

The K-bentonite levels found in the Upper Ordovician are quite rare (Fig. 5). Two levels within the extraordinarius graptolite Zone at the Oberbuchach Section may be correlated with that found in the ordovicicus conodont Zone at the Valbertad Section. One of the horizons noted in the upper Ashgill at the Cellon Section within the Hirnantian fauna interval may be traced with the K-bentonite level identified at the Hoher Trieb Section. Two levels occur higher in the perscultus graptolite Zone at the Cellon Section, one of which may be correlated with the single horizon noted at the Oberbuch-ach Section within this interval. The Lower Silurian K-bentonite sampled from the Uggwa Section may be of a similar age to those from the Llandovery of Nölbling Graben where sixteen levels have been recorded from the vesiculosus graptolite Zone and upwards within the Rhuddanian while eleven have been recorded from the triangulatus graptolite Zone (Aero-

nian) at the Oberbuchach Section. The abundant presence of these horizons in the Llandovery sequences of the Carnic Alps is similar in the British Isles, Sweden, Canada and North America and documents widespread volcanism (Fig. 7). The Osmundsberg K-Bentonite (Huff et al., 1998b) has been recognized throughout NW Europe in the late Llandovery (Telychian) and it is probable that this level may also be identified from the samples collected at this stratigraphic level from the Cellon, Seewarte and Oberbuchach Sections (celloni conodont Zone). Lack of exposure at some sections makes correlation across the depositional basin problematic. Four horizons fall approximately within higher levels of the amorphognathoides conodont Zone at the Oberbuchach Section. Another concentration of eight bentonites occurs in the Lower Wenlock (Sheinwoodian-riccartonensis-rigidus graptolite Zone) which in part may be traced across the Cellon, Oberbuchach and Nölbling Graben Sections. Five Lower Ludlow horizons are only identified from the Oberbuchach Section.

Silurian K-bentonites which belong to the Pridoli Series have as yet only been described from Podolia (Huff et al., 2000) and these are stated as having a possible source area in the Rheic Ocean. The twenty four levels sampled from the Zollnersee-Hütte Section, transgrediens – uniformis graptolite Zones, may prove to be comparable with those from Podolia.

4. Geochemistry

The samples, which were oven dried at 40°C and ground to <63 μm, were analyzed for major and trace elements by wave-length-dispersive X-ray fluorescence (XRF), instrumental neutron activation analysis (INAA) and inductively-coupled plasma-mass spectrometry (ICP-MS). The geochemical data of the examined K-bentonites provide information about their regional chemostratigraphic correlation and the tectonomagmatic settings of their source volcanoes. Especially, immobile elements such as Hf, Nb, Ta, Ti, Zr and REE have been used in empirically-based discrimination plots by numerous workers for this purpose (e. g., Merriman and Roberts, 1990; Morton and Knox, 1990; Batchelor, 1999; Bergström et al., 1998).

The chemistry of pyroclastic deposits has been widely used to distinguish the tectonomagmatic setting of their source volcanoes. The results obtained from discriminating elements are considered most reliable when the analysed rock material is near in composition to the source magma, hence volcanic glass is preferred. Volcanic ash, which is in effect fragmented volcanic glass, may be expected to be similar in composition to its parental magma, but it is susceptible to subsequent che-
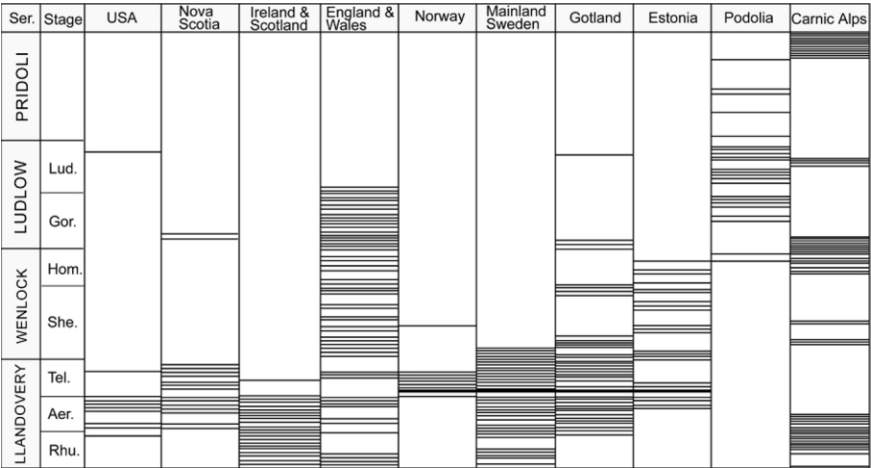

Figure 7: Stratigraphical range of Silurian K-bentonites reported in the literature compared with Silurian K-bentonite levels from the Carnic Alps.

A Cellon

B Oberbuchach

C Zollnersee-Hütte

D Nölbling Graben
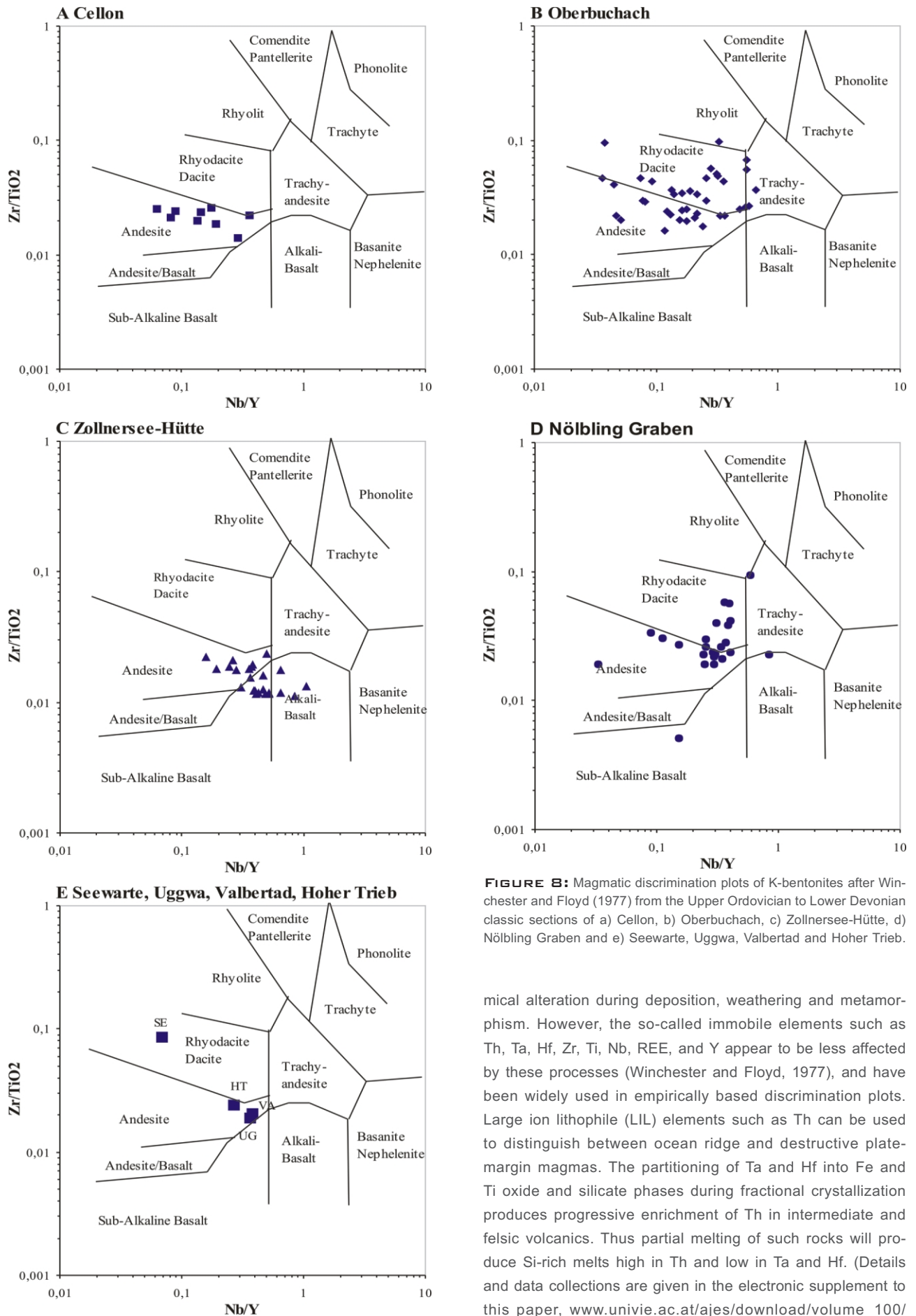

E Seewarte, Uggwa, Valbertad, Hoher Trieb

FIGURE 8: Magmatic discrimination plots of K-bentonites after Winchester and Floyd (1977) from the Upper Ordovician to Lower Devonian classic sections of a) Cellon, b) Oberbuchach, c) Zollnersee-Hütte, d) Nölbling Graben and e) Seewarte, Uggwa, Valbertad and Hoher Trieb.

mical alteration during deposition, weathering and metamorphism. However, the so-called immobile elements such as Th, Ta, Hf, Zr, Ti, Nb, REE, and Y appear to be less affected by these processes (Winchester and Floyd, 1977), and have been widely used in empirically based discrimination plots. Large ion lithophile (LIL) elements such as Th can be used to distinguish between ocean ridge and destructive plate-margin magmas. The partitioning of Ta and Hf into Fe and Ti oxide and silicate phases during fractional crystallization produces progressive enrichment of Th in intermediate and felsic volcanics. Thus partial melting of such rocks will produce Si-rich melts high in Th and low in Ta and Hf. (Details and data collections are given in the electronic supplement to this paper, www.univie.ac.at/ajes/download/volume_100/

histon_et_al_supplementary_data_ajes_v100.zip)

The geochemical data from the Carnic Alps K-bentonites provide a useful proxy for interpreting their tectono-magmatic setting. The plots of Zr/TiO_2 against Nb/Y (Fig. 8) after Winchester and Floyd (1977) provide information with regard to the compositional characteristics of the parent magmas. Source magma compositions ranged from rhyodacite/dacite through andesite to sub-alkaline and alkaline basalts.

Samples generally have less than 30 ppm Ga, which is characteristic of subalkaline magmas, whereas alkaline magmas tend to show an increased concentration of Ga with differentiation (Winchester and Floyd, 1977). Similarly, with progressive differentiation of a basaltic magma the Zr/TiO_2 ratio increases, and reflects the overall decline of TiO_2 in intermediate and felsic rocks. No noticeable evolution trends can be detected in the data when examined in stratigraphic succession and thus there is no evidence from these data of a continuing or systematic development of collision margin volcanism through the time interval represented by the K-bentonite beds.

Chondrite normalized REE plots show typical subalkaline and peralkaline patterns (Roberts and Merriman, 1990), and all show some evidence of LREE enrichment and mildly negative Eu anomalies, characteristic of highly evolved calc-alkaline magmas. It would seem unlikely that the source magmas were derived by direct fractionation from an oceanic or upper mantle source, but were more likely produced by partial melting of continental crustal rocks and possibly oceanic sediments during collision, as indicated by the LREE enrichment. These techniques have been applied to the Carnic Alps K-bentonite samples, and the results are summarised in Figures 8, 9, 10 and discussed below.

5. Tectonic Setting

Magmatic and tectonic discrimination diagrams can be used to infer original magma composition and source volcano settings relative to plate margins. Pearce and Norry (1979) and Pearce et al. (1981) have used plots of Ti and Zr for discrimination of volcanic rocks into volcanic-arc, within-plate lavas and mid-ocean ridge basalts (MORB) as probable source magma types. In the TiO_2-Zr diagram of Fig. 9 the studied K-bentonites have been plotted on such a diagram and clearly display the arc character although some rocks fall outside this field due to chemical alteration, contamination with adjacent sediment and/or weathering. However, the majority of samples plot in the field of "evolved" arc lavas of a parental calc-alkaline suite ranging from alkali basalts through andesites to rhyodacites/dacites.

6. Clay Mineralogy
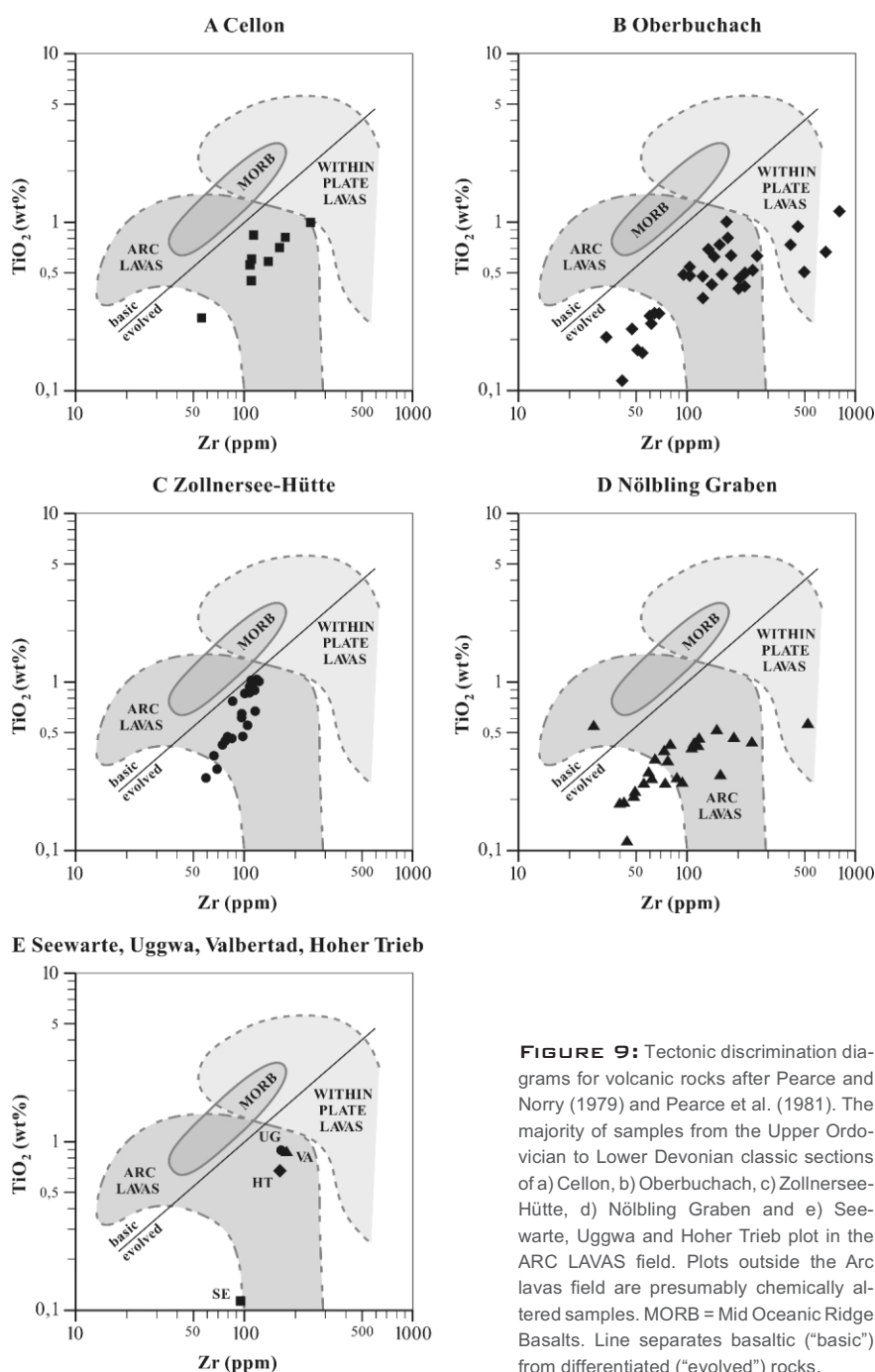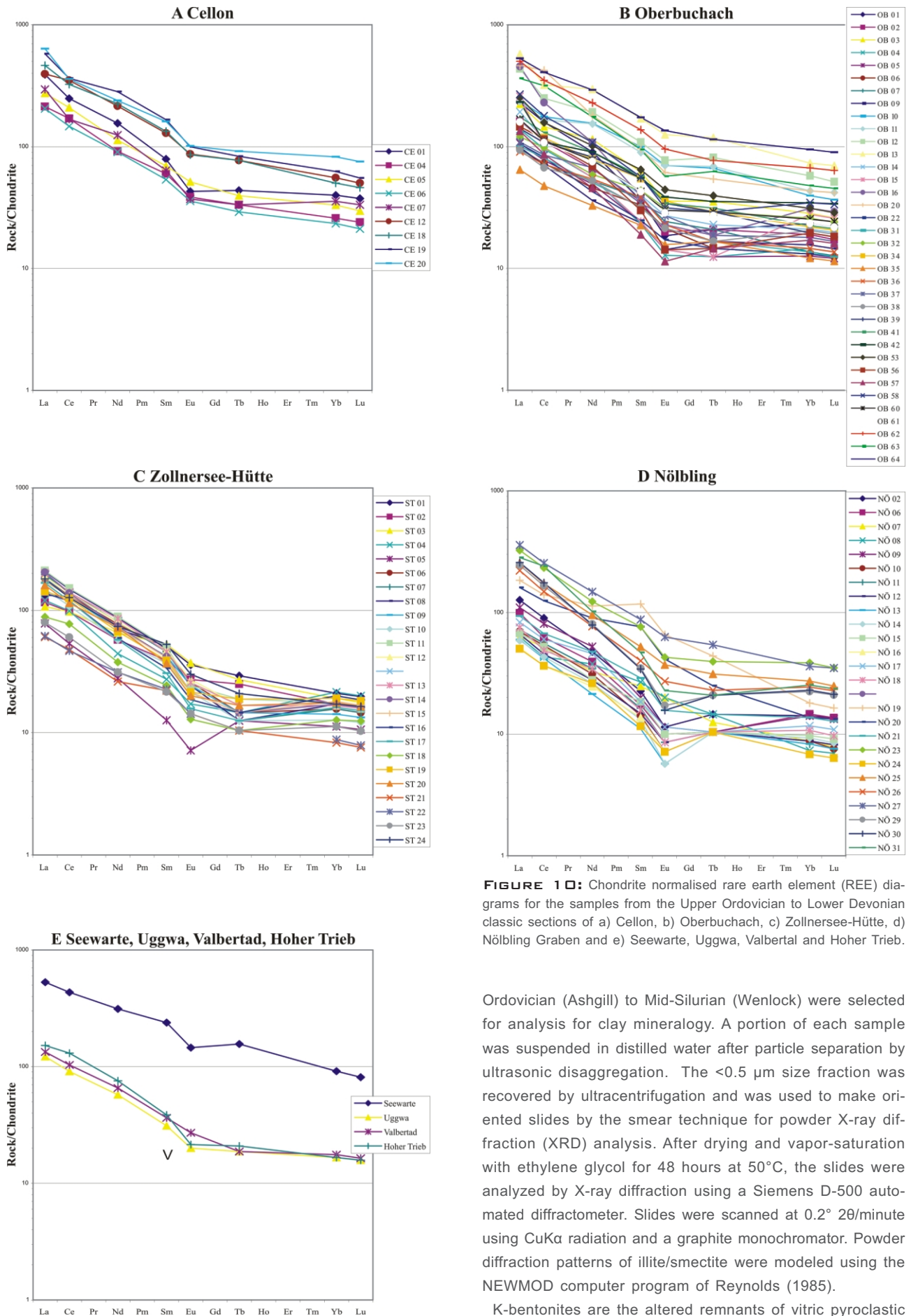
Nine samples ranging from Late

Figure 9: Tectonic discrimination diagrams for volcanic rocks after Pearce and Norry (1979) and Pearce et al. (1981). The majority of samples from the Upper Ordovician to Lower Devonian classic sections of a) Cellon, b) Oberbuchach, c) Zollnersee-Hütte, d) Nölbling Graben and e) Seewarte, Uggwa and Hoher Trieb plot in the ARC LAVAS field. Plots outside the Arc lavas field are presumably chemically altered samples. MORB = Mid Oceanic Ridge Basalts. Line separates basaltic ("basic") from differentiated ("evolved") rocks.
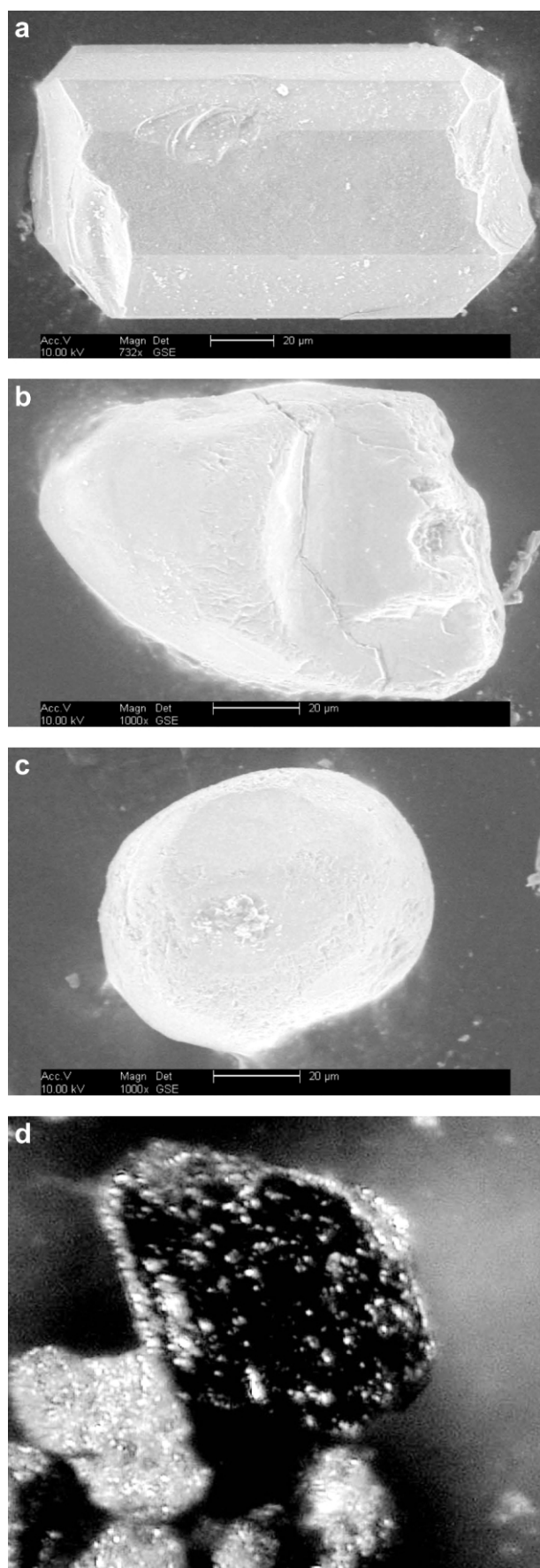
FIGURE 10: Chondrite normalised rare earth element (REE) diagrams for the samples from the Upper Ordovician to Lower Devonian classic sections of a) Cellon, b) Oberbuchach, c) Zollnersee-Hütte, d) Nölbling Graben and e) Seewarte, Uggwa, Valbertal and Hoher Trieb.

Ordovician (Ashgill) to Mid-Silurian (Wenlock) were selected for analysis for clay mineralogy. A portion of each sample was suspended in distilled water after particle separation by ultrasonic disaggregation. The <0.5 μm size fraction was recovered by ultracentrifugation and was used to make oriented slides by the smear technique for powder X-ray diffraction (XRD) analysis. After drying and vapor-saturation with ethylene glycol for 48 hours at 50°C, the slides were analyzed by X-ray diffraction using a Siemens D-500 automated diffractometer. Slides were scanned at 0.2° 2θ/minute using CuKα radiation and a graphite monochromator. Powder diffraction patterns of illite/smectite were modeled using the NEWMOD computer program of Reynolds (1985).

K-bentonites are the altered remnants of vitric pyroclastic

FIGURE 11: (a) Euhedral zircon crystal from bed Oberbuchach-32; (b) Partially rounded and resorbed zircon in bed Cellon-06; (c) Partially resorbed apatite crystal in bed Oberbu-chach-07; (d) Euhedral biotite flake in bed Oberbuchach-32.

airfall deposits and now consist primarily of clay minerals with accessory amounts of phenocrysts including biotite, quartz, K-feldspar, plagioclase, amphibole, zircon and apatite. The clay minerals are characteristically mixed-layer illite/smectite (Kolata et al.,1996) with varying degrees of random, short-range, and long-range order. Kaolinite, and occasionally chlorite, are reported in some beds (Huff et al., 1997). In rare circumstances, entire K-bentonite beds appear to have been metasomatized to K-feldspar. For example, in the Llandovery of Estonia a 20-cm thick well-indurated K-bentonite bed known as the "O" bed consists entirely of K-feldspar (Huff et al., 1998b). It is widely recognized in cores and used by stratigraphers as a marker bed. X-ray powder diffraction and thin section analysis indicates that the material has a fine-grained mosaic texture of low sanidine, characteristic of low temperature authigenic K-feldspar. Similar features in Ordovician K-bentonites have been reported elsewhere and are interpreted as evidence of potassium metasomatic replacement of K-bentonite associated with gravity-driven episodes of basin-wide fluid migration (Hay et al., 1988).

While the clay mineral assemblage may be a useful diagnostic tool for the recognition of K-bentonites, under conditions of low-grade metamorphism or extreme burial metamorphism that usefulness may be diminished or disappear altogether. In such cases it is necessary to rely upon the recognition of primary phenocrysts as indicators of a volcanogenic origin. Figure 11 shows several examples of phenocrysts in samples from the Carnic Alps that provide evidence of their volcanic origin. The presence of euhedral apatite and biotite testifies the magmatic nature of their origin. In samples CE-06 and OB-07 (Fig. 11) the zircons show some evidence of rounding. We interpret this as due to magmatic resorption rather than mechanical abrasion following the classic description of such features by Larsen and Poldervaart (1957). These and similar phenocrysts in samples OB-0 through CE-07 provide important evidence of the volcanogenic nature of these beds.

A cautionary note concerning the application of K-bentonite horizons to stratigraphic correlation should be interjected here. Many ash falls preserved in the stratigraphic record are indeed the product of single eruptive events. However, in circumstances where background sedimentation rates are either low or at a standstill multiple ash falls may accumulate in continuous succession and appear later as a single, large scale event. The regional aspects of ash accumulation on sediment-starved submarine surfaces has been discussed by Kolata et al. (1998) and Ver Straeten (2004). The Ordovician Millbrig K-bentonite in eastern North America and the Kinnekulle K-bentonite in northern Europe both display macroscopic and microscopic evidence of multiple event histories, a characteristic that is only explainable by invoking a history of episodic ash accumulation in areas with essentially no background sedimentation (Kolata et al., 1998; Ver Straeten, 2004). Portions of the Millbrig and Kinnekulle beds have biotites that are compositionally indistinguishable from

one another, although the majority of samples analyzed shows a clear distinction between the two beds (Huff et al., 2004). However, no evidence of multiple ash falls accumulating in a single horizon have been noted in the Carnic Alps successions.

XRD traces of glycol-saturated, oriented clay samples are shown in Figure 12. Illite (10Å) dominates most of the samples and chlorite (14Å) is also abundant in at least two. Swelling phases are present in three samples, OB-01, OB-U, and OB-03 as shown by reflections at 16.8Å and 11.1Å representing weak, higher order I/S spacings. Aside from these, there is little in the clay mineralogy to distinguish these beds from adjacent shales that are also characterized by chlorite and illite.

7. Results and Discussion

These newly obtained data reinforce the notion that explosive volcanism associated with the amalgamation of pre-Alpine segments was not simply collisional in nature but represented a variety of source materials and tectonic settings. Chondrite normalized rare earth element plots are shown in Figure 10. Again, light rare earth element (LREE) enrichment varies from 122 to 650 times chondrite and reflects a range of low to moderate magmatic fractionation for the bentonitic sources.

In summary, tectonomagmatic discrimination diagrams based on immobile trace elements and REE data suggest that the majority if not all of the sections plot within the volcanic arc field. The samples vary in composition but the majority fall within the andesite and rhyodacite/dacite fields.

Ordovician and Silurian K-bentonites are known from many regions of the world and Figures 6 and 7 provide a summary of the principal occurrences that have been described in the literature. With few exceptions these beds represent airfall deposits of explosive felsic rather than mafic volcanic eruptions. In many cases their distribution patterns have served as sources of useful information concerning the tectonomagmatic histories of the associated stratigraphic sequences (Kolata et al., 1996; Huff et al., 1997, 1998a, 1998b, 2000). The Carnic Alps K-bentonites are here considered in comparison with other Ordovician and Silurian examples from elsewhere in Europe.

While most Ordovician K-bentonites reported in Europe are from the British Isles (Huff et al., 1993; Fortey et al., 1996) and Baltoscandia (Bergström et al., 1995, 1997), there are also occurrences in Poland (Tomczyk, 1970) and Lithuania (Šliaupa, 2000) in addition to those reported here. The Alpine orogen represents a collage of Alpine and Prealpine crustal fragments which reflect a true odyssey of near global wandering. Based on various climate sensitive bio- and lithofacies markers these segments have been dated as ranging from Late Ordovician to the Permian thus adding further to the controversy with regard to the palaeogeography and the relationship of the Palaeozoic proto-Alps and the coeval neighbouring areas such as Baltica, the British Isles, the

Prague Basin (Barrandian), Sardinia, Southern France, Spain and North Africa. Their tectonic juxtaposition would allow for repeated settings for explosive volcanism that may well have produced these numerous ash beds.

Huff et al. (2000) have proposed possible source areas and wind transport directions for known Silurian K-bentonites. During the Llandovery the distribution pattern of K-bentonites in the Iapetus region suggests two source areas: one for the Scottish-Irish-Baltoscandic ash beds and one for the beds in Nova Scotia and eastern and central USA. Volcanoes in the former source area, likely to have been located in a tectonically active setting near the eastern margin of Laurentia, may also have been the source for the K-bentonites of Wenlock to Ludlow age in northwestern Europe. However, the ash beds in southern Poland and Podolia, some of which are Pridoli in age, may have had quite a different source, presumably in the Rheic Ocean near the southern margin of Baltica (Bergström et al., 1998c).

The K-bentonite levels recognised from the Carnic Alps may also be placed within this latter scenario. Due to the distal character of ash layers and missing Silurian volcanism a local origin within the Carnic Alps can be ruled out. In other parts of the Eastern Alps, however, coeval basic volcanism may have occurred, e.g. in Middle Carinthia, the surroundings of Graz and the Greywacke Zone (Schönlaub, 1992). It is un-
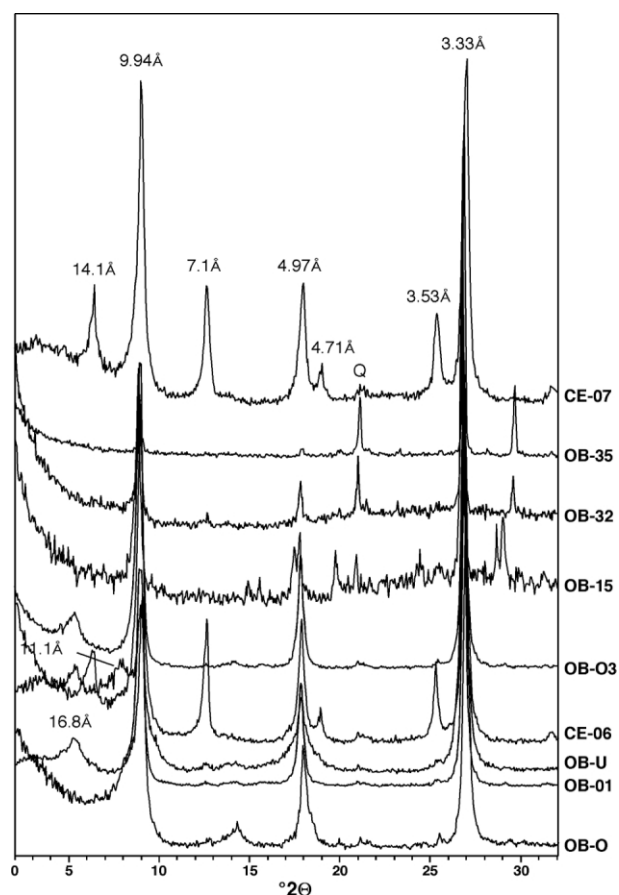

FIGURE 12: Powder X-ray-diffraction of the ethylene glycol-saturated, oriented clay (<2 μm) size fraction of nine K-bentonite beds.

likely that these rifting related volcanic centers may have functioned as source areas for the K-bentonites of the Carnic Alps. The K-bentonites belong to a tectonically active terrane dominated by calc-alkaline mafic lavas and pyroclastics in the Upper Ordovician, Silurian and Lower Devonian which was either situated north or south of the Carnic Alps but separated from the latter by an oceanic realm or at least an open sea of unknown width. On the other hand, however, all known K-bentonite horizons in the Carnic Alps range from a few millimeters to 2-3 centimeters maximum thickness indicating that the volcanic source area must have been quite distant.

We have examined the plots to determine whether or not our data indicate a time-dependent shift from arc to intraplate volcanism during the Silurian. For this purpose we have chosen the samples from the Zollnersee-Hütte which were collected from strata representing a short lasting interval at the Silurian/Devonian boundary as opposed to those from the Nölblinggraben and Oberbuchach sections. The latter two cover mainly the Lower and Middle Silurian time interval. Although the pattern on the plots suggests a certain trend, the actual distribution is randomly arranged and does not reflect any changes from island-arc to intraplate volcanism during the Silurian Period.

The thermal history of the Carnic Alps has been extensively documented using proxy indicators such as illite crystallinity, vitrinite reflectance and fluid inclusion studies (Sassi et al., 1995; Rantitsch, 1997; Hubich et al., 1999; Sassi et al., 2004). Rantitsch (1997) identified a Variscan syntectonic thermal event, a post-Variscan Alpine metamorphic event, and a subsequent episode of hyperthermal fluid activity, all of which would have significantly affected clay minerals that had

formed from altered volcanic ash beds.

In the nine samples studied for clay mineralogy here, the effects of these regional metamorphic events are clearly reflected in the clay mineral composition. What most likely developed as smectite or possibly illite/smectite in the early formed K-bentonites was converted to an illite and chlorite suite at elevated temperatures and pressures. A similar pattern in the Helvetic Alps of eastern Switzerland has been described by Wang et al. (1996). Some persistence of the original swelling phase can be seen in the lowest grade portion of the Oberbuchach Section.

Late Ordovician K-bentonites of the Carnic Alps have relatively few equivalents elsewhere in Europe or North America (Fig. 6) with the exception of several beds in central Sweden and along the Ards Peninsula in Northern Ireland. However, the more extensive succession of Silurian K-bentonites has coeval counterparts in several regions, most notably Great Britain and Baltoscandia (Fig. 7). Of particular interest are Ludlow and Pridoli K-bentonites of the Dnestr Basin in Podolia that have been interpreted as representing the presence of active volcanic arcs along the margin of the Rheic Ocean (Huff et al., 2000).

We thus conclude that the majority of the K-bentonites found in the Carnic Alps were derived from neighbouring peri-Gondwanide terranes rather than from far distant sources at the eastern margin of the closing Iapetus Ocean. These ash beds suggest widespread rifting related volcanism in the enigmatic PalaeoTethys (von Raumer et al., 2002, 2003) which opened during the Silurian between the northern margin of Gondwana and the composite Hun Superterrane (Fig. 13). It may have lasted until the end of the Middle Devonian when these terranes amalgamated and closing of the Rheic Ocean began.

Figure 13: Palaeogeographic reconstruction (based on Von Raumer et al. (2002) showing possible source areas for the Silurian K-bentonites from the Carnic Alps: A-I Armorica –Iberia; P - Perunica; A – Avalonia. The approximate position of the Carnic Alps is indicated by the rounded spot.

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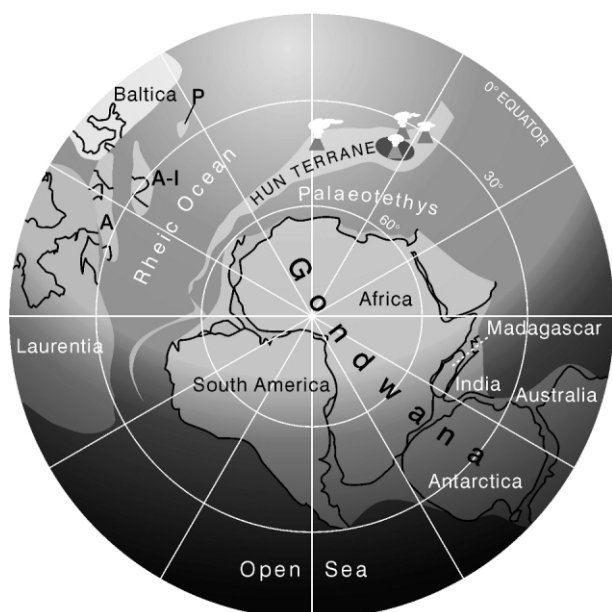
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Kathleen HISTON[1], Peter KLEIN[2], Hans Peter SCHÖNLAUB[2,*] & Warren D. HUFF[3]

[1] via Mazzini 4, 21039 Valganna (Va), Italy, e-mail: hiscat@interfree.it

[2] Geological Survey of Austria, Neulinggasse 38, A-1031 Vienna, Austria, e-mail: hp.schoenlaub@geologie.ac.at

[3] Dept. of Geology, University of Cincinnati, OH 45221-0013, USA, e-mail: warren.huff@uc.edu

[*] Corresponding author, hp.schoenlaub@geologie.ac.at