# Traces of explosive volcanic eruptions in the Upper Ordovician of the Siberian Platform

Warren D. Huff<sup>a</sup>, Andrei V. Dronov<sup>b,c</sup>, Bryan Sell<sup>d</sup>, Aleksandr V. Kanygin<sup>e</sup> and Taras V. Gonta<sup>e</sup>

<sup>a</sup> Department of Geology, University of Cincinnati, OH 45221-0013, USA; huffwd@ucmail.uc.edu

<sup>b</sup> Geological Institute, Russian Academy of Sciences, Pyzhevsky per. 7, 119017, Moscow, Russia; dronov@ginras.ru

<sup>c</sup> Kazan (Volga Region) Federal University, Kremlevskaya ul. 18, 420008, Kazan, Russia

<sup>d</sup> Earth and Environmental Sciences, University of Michigan, Ann Arbor, Michigan 48109, USA; bksell@umich.edu

<sup>e</sup> Trofimuk Institute of Petroleum Geology and Geophysics, Siberian Branch of Russian Academy of Sciences, Acad. Koptyug 3, 630090, Novosibirsk, Russia; kanyginav@ipgg.nsc.ru

Received 15 July 2014, accepted

**Abstract.** Ordovician K-bentonite beds have a long history of investigation all around the world. They have been reported from Gondwana, the Argentine Precordillera, the Yangtze Platform, Laurentia, Baltica, and numerous terrains between Gondwana and Baltica, which now constitute a part of Europe. In recent years several K-bentonite beds have also been discovered in the Upper Ordovician of the Siberian Platform. This discovery is significant not only for their value in local and regional chronostratigraphic correlation but also for global geochronology, paleogeography, paleotectonic and paleoclimatic reconstructions. All in all, eight individual K-bentonite beds have been identified in the Baksian, Dolborian and Burian regional stages, which correspond roughly to the Upper Sandbian–Katian Global Stages. Zircon crystals from the uppermost K-bentonite bed within the Baksian regional stage provide a 206Pb/238U age of 450.58±0.27 Ma. We will present preliminary results of the study of the three lowermost beds from the Baksian Regional Stage and suggest that the Taconic–Enisej (also spelled Yenisei or Yenisey) volcanic arc was continuous along the western margin of Siberia.

Key words: K-bentonites, volcanism, paleogeography, Upper Ordovician, Siberia.

### INTRODUCTION

Extra-basinal K-bentonite correlations in the Paleozoic depend heavily upon the success of regional-scale correlation efforts utilizing whole-rock and single-crystal methods. In order to test stratigraphic models that describe facies distributions in continental margins, it is critical to correlate beds at high precision across several depositional environments. Toward such correlations, numerous K-bentonite beds have been sampled from the late Sandbian and early Katian stages of eastern North America and the Baltic Basin to provide some insight into Laurentian regional stratigraphy. Recently, eight Kbentonite beds were discovered in the Late Ordovician of the Tungus basin on the Siberian Platform. All the beds were identified in the outcrops of the Baksian, Dolborian and Burian regional stages, which correspond roughly to the Upper Sandbian, Katian and probably lowermost Hirnantian Global Stages (Bergström et al. 2009). The three lowermost beds from the Baksian Regional Stage were studied in detail (Fig. 1). They are represented by thin beds (1-2 cm) of soapy light gray or yellowish plastic clays and usually easily identifiable in the outcrops. The beds were traced in the outcrops over a distance of more than 60 km along the Podkamennaya Tunguska River valley.

All K-bentonite beds have been found within the Upper Ordovician carbonate succession. The three lowermost K-bentonite beds, which were sampled, have been studied by powder X-ray diffraction (XRD) and scanning electron microscopy (ESEM) together with energy dispersive X-ray analysis. Modeling of the XRD tracings using NEWMOD showed the samples consist of R3-ordered illite-smectite (I-S) with 80% illite and 20% smectite plus a small amount of corrensite, which is a regularly interstratified chlorite-smectite. The presence of a corrensite phase indicates a highly oxidizing environment (Barrenechea et al. 2000; Kiipli et al. 2012). And the low percent of smectite in both mixed-layer phases reflects a high degree of burial metamorphism since the time of their origin. The K-bentonites provide evidence of intensive explosive volcanism on or near the western (in present-day orientation) margin of the Siberian craton in Late Ordovician time.



Fig. 1. Stratigraphic distribution and correlation of Upper Ordovician K-bentonite beds in the Siberian Platform.

### GEOLOGICAL SETTING AND STRATIGRAPHY

During the Cambrian, Ordovician and Silurian the Siberian Platform, which constitutes the core of the Siberian paleocontinent, was located in the low latitude tropical area, migrating slowly from the southern hemisphere in the Cambrian and Lower Ordovician to the northern hemisphere in the Upper Ordovician and Silurian (Cocks & Torsvik 2007). The central part of this continental bloc was occupied by the extensive intracratonic Tungus basin (Markov 1970; Kanygin et al. 2007). The Lower Ordovician and the lower part of the Middle Ordovician series (from Nyaian to Kimaian regional stages) of the basin are represented by a succession of warm-water tropical-type carbonates. The Upper Ordovician series (from Chertovskian to Burian regional stages) by contrast has been described as represented by a succession of cool-water carbonates dominated by bioclastic wackestone and packstone beds intercalated with fine-grained terrigenous sediments (Dronov et al. 2009; Kanygin et al. 2010; Dronov 2013). The two-carbonate successions of contrasting lithologies are separated by a unit of pure quartz sandstones up to 80 m thick (Baykit Sandstone), which is overlain by the fine-grained terrigenous deposits of the Volginian and Kirensko-Kudrinian regional stages (Dronov et al. 2009; Kanygin et al. 2010).

All K-bentonite beds have been found within the Upper Ordovician carbonate succession. The three lowermost K-bentonite beds, which were sampled, are located within the Mangazea Formation (Baksian regional stage). Precise biostratigraphic correlation of the Siberian regional stages to the Global Ordovician Stages remains problematic due to the endemic character of the Siberian fauna, but these beds appear to be located near the Sandbian–Katian boundary (Fig. 1). The Mangazea Formation is interpreted as a highstand systems tract of the Mangazea depositional sequence (Kanygin et al. 2010). In the outcrops along the Podkamennaya Tunguska River valley and its tributaries it is represented by greenish-gray siltstones alternating with bioclastic limestone beds. The bioclasts are predominantly fragments of brachiopods and trilobites as well as echinoderms, ostracods and bryozoans. The limestone interbeds sometimes show ripple marks on their upper bedding planes. The intercalations of siltstones and bioclastic limestones of the Mangazea Formation are interpreted as coolwater carbonate tempestites deposited in the middle ramp settings (Dronov et al. 2009; Kanygin et al. 2010; Dronov 2013).

The K-bentonites from the Mangazea Formation are generally represented by thin beds (1–2 cm) of soapy light gray or yellowish plastic clays. They are different by consistence and color from the enclosing sediments and usually easily identifiable in the outcrops. The lowermost (K-bentonite-I) bed of the Mangazea Formation was traced over a distance of more than 60 km along the Podkamennaya Tunguska River valley. The other two beds (K-bentonite-II and K-bentonite-III) were traced over at least 40 km.

#### MINERALOGY AND GEOCHEMISTRY

A portion of each sample was suspended in distilled water after particle separation by ultrasonic disaggregation. The  $<0.2 \ \mu m$  size fraction was recovered by ultracentrifugation and was used to make oriented slides by the smear technique for powder XRD analysis. After drying and vapor-saturation with ethylene glycol for 48 h at 50°C, the slides were analyzed by powder XRD using a Siemens D-500 automated powder diffractometer. Slides were scanned at 0.2° 20/min using CuKa radiation and a graphite monochromator. Powder diffraction patterns of I–S were modeled using the NEWMOD computer program of Reynolds (1985). The ethylene glycol-saturated diffraction patterns shown in Fig. 2A have essentially the same clay composition. There is an R3-ordered mixed-layer I-S component with about 90% illite represented by peaks at 10.7, 9.72, 5.10 and 3.34 Å. There is chlorite and probably some corrensite (mixed-layer chlorite-smectite) at 14.9, 7.1, 4.71 and 3.52 Å. These are fairly typical patterns for Kbentonites that have undergone a very slight amount of low-grade metamorphism (Krekeler & Huff 1993).

Modeling of the diffraction tracings using NEWMOD (Reynolds 1985) showed the samples to contain 80% illite and 20% smectite. The same conclusion results from consideration of the  $\Delta 2\Theta$  value of 5.1 Å, which

measures the difference between the 001/002 and 002/003 reflections of I-S (Moore & Reynolds 1997). Huff et al. (1991) described long-range or R3-ordered I-S in Llandovery K-bentonites from northern Ireland and the Southern Uplands of Scotland. Batchelor & Weir (1988) interpreted powder diffraction analysis of K-bentonite clays from the Southern Uplands as R0-ordered I-S; however, their XRD tracings clearly show R3-ordering. Silurian K-bentonites from Podolia, Ukraine, contain R0-ordered I-S in carbonate facies and R1-R3-ordered I–S in the shale facies (Huff et al. 2000). The preservation of randomly ordered I-S is frequently interpreted as indicative of a shallow burial history with a history of relatively low temperatures. Such clays would be expected to show a transition to more highly ordered forms during increased burial metamorphism (Altaner & Bethke 1989), particularly in shales and mudrocks undergoing basinal subsidence. However, the Siberian sequence of K-bentonites, which occurs on the edge of the Siberian Platform, contains I-S ratios that seem to vary more with the rock type than with depth, showing no systematic depth-dependent variation in illite percentage. This relationship suggests that facies composition and K-availability factors rather than thermal history may have played a leading role in determining clay mineral characteristics. Heavy minerals in the K-bentonite layers provide further evidence of a volcanogenic origin in the form of euhedral zircon and apatite phenocrysts (Fig. 2B, C).

The K-bentonite beds from the Baksian Regional Stage (Katian) of the southwestern part of the Tungus basin in Siberia are clearly derived from the alteration of volcanic ash falls. All three beds contain volcanogenic euhedral zircon and apatite phenocrysts. Zircon crystals from the uppermost K-bentonite bed within the Baksian Regional Stage provide a 206Pb/238U age of  $450.58\pm0.27$  Ma. This appears to be nearly the same age as the Haldane and Manheim beds in North America (Fig. 3). The Manheim is in the Diplacanthograptus spiniferus graptolite Zone and the Haldane is likely with the upper part of the Belodina confluens conodont Zone, which indicates the bed would be mid-Katian and latest Mohawkian. The timing of volcanism is surprisingly close to the period of volcanic activity of the Taconic arc near the eastern margin of Laurentia. It looks like the Taconic arc has its continuation along the western continental margin of Siberia and both of them constitute a single Taconic-Enisej (also spelled Yenisei or Yenisey) volcanic arc. Field studies of the Upper Ordovician succession along the Moyero River in the vicinity of the Anabar shield demonstrate an absence of K-bentonite beds along the eastern margin (in present-day orientation) of the Siberian Platform. This contradicts popular paleogeographic interpretations and points to the position of



Fig. 2. A, X-ray diffraction patterns of K-bentonite bed 1 showing air-dried, glycolated and heated traces. B, C, ESEM images of apatite and zircon phenocrysts from bed 3.

a subduction zone along the western but not the eastern margin of the Siberian paleocontinent at that time.

## PALEOTECTONIC POSITION AND VOLCANIC SOURCE

The K-bentonite beds discussed in this paper are situated on the southwestern margin of the big intracratonic basin. Exact location of the volcanoes that produced these ash beds still remains unknown. It seems reasonable to suggest that the source of volcanic ash was at or near the border of the Siberian Platform. In our case it is a southwestern border in present-day orientation. Volcanic rocks of Ordovician age are known from Tuva, Eastern Kazakhstan (Chingiz Range) and supposedly existed within the basement of Western Siberia under the Mezo-Cenozoic cover of the West Siberian basin (Dergunov 1989). Sengör et al. (1993) introduced a term Kipchak Arc for a collage of terranes from the Altaj-Sayan area, Northern Tian Shan and Kazakhstan. But the existence of this enormous island arc, which they believed to have stretched between Baltica and Siberia, does not agree perfectly with the data from regional geology. The best-preserved fragments of an undoubtedly Ordovician island arc which collided with the Siberian craton in Late Ordovician–Early Silurian time are known from the Chingiz-Tarbagatai Range in eastern Kazakhstan. It is usually called the Chingiz-Tarbagatai Arc (Dobretsov 2003).



**Fig. 3.** Comparison of the U/Pb ages of zircons from the Siberian Platform and the Taconic Foreland Basin plus comparative ages from Ordovician beds in Oklahoma and the Baltic Platform. The 454 Ma age represents the Kinnekulle K-bentonite. The symbols represent the exact age measurement for each sample and the colored zones represent the error margins.



Fig. 4. Proposed paleogeographic reconstruction of the Late Ordovician showing a continuous subduction zone along the Laurentian and Siberian Platform margins.

### DISCUSSION

Ordovician K-bentonite beds have a long history of investigation all around the world. They have been reported from Gondwana (Ramos et al. 2003), the Argentine Precordillera (Huff et al. 1998), the Yangtze Platform (Su et al. 2003), Laurentia, Baltica, and numerous terrains between Gondwana and Baltica, which now constitute a part of Europe (Huff et al. 2010 and references therein). Previous studies of Ordovician K-bentonites in eastern North America and northwestern Europe contain mixed-layer I-S clay with 75-90% illite. Besides their regularly interstratified I-S clay ratio between 3:1 and 4:1 (e.g. Reynolds & Hower 1970), Ordovician K-bentonites contain differing amounts of primary and secondary non-clay minerals, some of which provide additional stratigraphic and tectonomagmatic information. The main primary minerals, mostly in the form of isolated, euhedral phenocrysts, are quartz, biotite, plagioclase and potassium feldspar, ilmenite, apatite, zircon and magnetite.

Considerable information has been published in recent years on the smectite to illite conversion during diagenesis, and its correlation with organic maturity (Velde & Espitalié 1989). While many studies indicate that multiple factors influence the progress of clay diagenesis, including the initial composition of smectite, fluid composition and the rock to water ratio (Freed & Peacor 1989), most authors have generally considered time, temperature and K+ availability to be the most important factors (Hoffman & Hower 1979; Huang et al. 1993; Pollastro 1993). Clay minerals derived from the alteration of felsic volcanic ash are sensitive to the thermal conditions and the geochemical environments, which have characterized their post-emplacement history. The transition of I-S to R3-ordering occurs during burial metamorphism at about 150-175°C, and under equilibrium conditions complete the transition to illite at about 250°C (Rateyev & Gradusov 1970; Hoffman & Hower 1979). Previous studies have shown that I-S in K-bentonites as well as in shales is a diagenetic product of smectite alteration (Altaner et al. 1984; Bethke et al. 1986; Brusewitz 1988; Anwiller 1993) and that further alteration to chlorite-smectite occurs under low-grade metamorphic conditions (Krekeler & Huff 1993). However, more recent work (Essene & Peacor 1995; Sachsenhofer et al. 1998) has cautioned against the unequivocal use of interstratified I-S as a geothermometer and has provided further evidence that factors such as pore fluid chemistry and rock to fluid ratios can have an important role in determining the reaction progress of clay mineral diagenesis.

### CONCLUSIONS

The K-bentonite beds from the Upper Ordovician Mangazea Formation of the southwestern part of the Tungus basin in Siberia seem to be derived from the alteration of volcanic ash falls. Their appearance points to the intensive explosive volcanism on or near the western (in present-day orientation) margin of the Siberian craton in Late Ordovician time (Fig. 4). The timing of volcanism in the Ordovician of Siberia is surprisingly close to the period of volcanic activity of the Taconic arc near the eastern margin of Laurentia. It looks like both arcs were activated by the same plate tectonic reorganization. Similar to the situation in North America, the Upper Ordovician K-bentonite beds in Siberia are associated with cool-water carbonates.

Acknowledgments. This work was performed according to the Russian Government Program of Competitive Growth of Kazan Federal University. Financial support was also provided from the Russian Foundation for Basic Research Grant No. 13-05-00746. This short paper is a contribution to IGCP Project 591.

### REFERENCES

- Altaner, S. P. & Bethke, C. M. 1989. Interlayer order in illite/smectite. American Mineralogist, 73, 766–774.
- Altaner, S. P., Hower, J., Whitney, G. & Aronson, J. L. 1984. Model for K-bentonite formation: evidence from zoned K-bentonites in the disturbed belt, Montana. *Geology*, 12, 412–415.
- Anwiller, D. N. 1993. Illite/smectite formation and potassium mass transfer during burial diagenesis of mudrocks: a study from the Texas Gulf Coast Paleocene–Eocene. *Journal of Sedimentary Petrology*, **63**, 501–512.
- Barrenechea, J. E., Rodas, M., Frey, M., Alonso-Azcarate, J. & Mas, J. R. 2000. Chlorite, corrensite, and chloritemica in Late Jurassic fluvio-lacustrine sediments of the Cameros Basin of Northeastern Spain. *Clays and Clay Minerals*, 48, 256–265.
- Batchelor, R. A. & Weir, J. A. 1988. Metabentonite geochemistry: magmatic cycles and graptolite extinctions at Dob's Linn, southern Scotland. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, **79**, 19–41.
- Bergström, S. M., Chen X., Gutiérrez-Marco, J. C. & Dronov, A. 2009. The new chronostratigraphic classification of the Ordovician System and its relations to major series and stages and to  $\delta^{13}$ C chemostratigraphy. *Lethaia*, **42**, 97–107.
- Bethke, C. M., Vergo, N. & Altaner, S. P. 1986. Pathways of smectite illitization. *Clays and Clay Minerals*, 34, 125–135.
- Brusewitz, A. M. 1988. Asymmetric zonation of a thick Ordovician K-bentonite bed at Kinnekulle, Sweden. *Clays and Clay Minerals*, 36, 349–353.

- Cocks, L. R. M. & Torsvik, T. H. 2007. Siberia, the wandering northern terrane, and its changing geography through the Paleozoic. *Earth-Science Reviews*, 82, 29–74.
- Dergunov, A. B. 1989. *Kaledonidy Tsentral'noj Azii [The Caledonides of the Central Asia]*. Nedra Publishing House, Moscow, 192 pp. [in Russian].
- Dobretsov, N. L. 2003. Evolution of structures of the Urals, Kazakhstan, Tien Shan and Altai-Sayan Region within the Ural-Mongolian Fold Belt. *Russian Geology and Geophysics*, **44**, 5–27.
- Dronov, A. V. 2013. Late Ordovician cooling event: evidence from the Siberian Craton. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **389**, 87–95.
- Dronov, A. V., Kanygin, A. V., Timokhin, A. V., Tolmacheva, T. Yu. & Gonta, T. V. 2009. Correlation of eustatic and biotic events in the Ordovician paleobasins of the Siberian and Russian platforms. *Paleontological Journal*, 43, 1477–1497.
- Essene, E. J. & Peacor, D. R. 1995. Clay mineral thermometry a critical review. *Clays and Clay Minerals*, 43, 540–553.
- Freed, R. L. & Peacor, D. R. 1989. Variability in temperature of the smectite/illite reaction in Gulf Coast sediments. *Clay Minerals*, 24, 171–180.
- Hoffman, J. & Hower, J. 1979. Clay mineral assemblages as low grade metamorphic geothermometers: application to the thrust faulted disturbed belt of Montana, U.S.A. In *Aspects of Diagenesis* (Scholle, P. A. & Schluger, P. R., eds), *Society of Economic Paleontologists and Mineralogists, Special Publication*, 26, 55–79.
- Huang, W.-L., Longo, J. M. & Pevear, D. R. 1993. An experimentally derived kinetic model for smectite-toillite conversion and its use as a geothermometer. *Clays* and Clay Minerals, **41**, 162–177.
- Huff, W. D., Anderson, T. B., Rundle, C. C. & Odin, G. S. 1991. Chemostratigraphy, K–Ar ages and illitization of Silurian K-bentonites from the Central Belt of the Southern Uplands–Down-Longford Terrane, British Isles. *Journal of the Geological Society of London*, 148, Part (5), 861–868.
- Huff, W. D., Bergström, S. M., Kolata, D. R., Cingolani, C. & Astini, R. A. 1998. Ordovician K-bentonites in the Argentine precordillera: relations to Gondwana margin evolution. In *The Proto-Andean Margin of Gondwana* (Pankhurst, R. J. & Rapela, C. W., eds), *Geological Society of London Special Publication*, **142**, 107–126.
- Huff, W. D., Bergström, S. M. & Kolata, D. R. 2000. Silurian K-bentonites of the Dnestr Basin, Podolia, Ukraine. *Journal of the Geological Society of London*, 157, 493–504.
- Huff, W., Bergström, S. M. & Kolata, D. R. 2010. Ordovician explosive volcanism. In The Ordovician Earth System (Finney, S. C. & Berry, W. B. N., eds), Geological Society of America Special Paper, 466, 13–28.
- Kanygin, A. V., Yadrenkina, A. G., Timokhin, A. V., Moskalenko, T. A. & Sychev, O. V. 2007. Stratigrafiya neftegazonosnykh bassejnov Sibiri. Ordovik Sibirskoj platformy [Stratigraphy of the Oil- and Gas-Bearing Basins of Siberia. The Ordovician of the Siberian Platform]. GEO, Novosibirsk, Russia, 269 pp. [in Russian].

- Kanygin, A, Dronov, A., Timokhin, A. & Gonta, T. 2010. Depositional sequences and palaeoceanographic change in the Ordovician of the Siberian craton. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 296, 285–294.
- Kiipli, E., Kiipli, T., Kallaste, T. & Siir, S. 2012. Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> ratio of the clay fraction of Late Ordovician–Silurian carbonate rocks as an indicator of paleoclimate of the Fennoscandian Shield. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **365–366**, 312–320.
- Krekeler, M. P. S. & Huff, W. D. 1993. Occurrence of corrensite and ordered (R3) illite/smectite (I/S) in a VLGM Middle Ordovician K-bentonite from the Hamburg Klippe, central Pennsylvania. *Geological Society of America Abstracts with Programs*, 25, 30.
- Markov, E. P. 1970. Ordovik i rannij Silur yugo-zapada Tungusskoj sineklizy [Ordovician and Early Silurian of the Southwest of Tungus Sineclise]. Nedra Publishing House, Leningrad, 144 pp. [in Russian].
- Moore, D. M. & Reynolds, R. C., Jr. 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford University Press, 378 pp.
- Pollastro, R. M. 1993. Considerations and applications of the illite/smectite geothermometer in hydrocarbon-bearing rocks of Miocene to Mississippian age. *Clays and Clay Minerals*, **41**, 119–133.
- Ramos, E., Navidad, M., Marzo, V. & Bolatt, N. 2003. Middle Ordovician K-bentonite beds in the Murzug Basin (Central Libya). In Ordovician from the Andes (Albanesi, G. L., Beresi, M. S. & Peralta, S. H., eds), INSUGEO, Serie Correlación Geológica, 17, 203–207.
- Rateyev, M. A. & Gradusov, B. P. 1970. A structural series of mixed-layer formations from the Ordovician–Silurian metabentonites of the Baltic area. *Doklady Akademii Nauk SSSR*, 194, 180–183.
- Reynolds, R. C. J. 1985. NEWMOD: A computer program for the calculation of one-dimensional diffraction patterns of mixed-layer clays. R. C. Reynolds, 8 Brook Rd., Hannover, NH, 24.
- Reynolds, R. C., Jr. & Hower, J. 1970. The nature of interlayering in mixed-layer illite-montmorillonites. *Clays and Clay Minerals*, 18, 25–36.
- Sachsenhofer, R. F., Rantitsch, G., Hasenhüttl, C., Russegger, B. & Jelen, B. 1998. Smectite to illite diagenesis in early Miocene sediments from the hyperthermal western Pannonian Basin. *Clay Minerals*, 33, 523–537.
- Sengör, A. M. C., Natal'in, B. A. & Burtman, V. S. 1993. Evolution of the Altaid tectonic collage and Paleozoic crustal growth in Eurasia. *Nature*, **364**, 299–307.
- Su, W. B., He, L. Q., Li, Q. G., Wang, Y. B., Gong, S. Y., Zhou, H. Y., Liu, X. M., Li, Z. M. & Huang, S. J. 2003.
  K-bentonite beds near the Ordovician–Silurian boundary on the Yangtze Platform, South China: preliminary study of the stratigraphic and tectonomagmatic significance. In Ordovician from the Andes (Albanesi, G. L., Beresi, M. S. & Peralta, S. H., eds), INSUGEO, Serie Correlación Geológica, 17, 209–214.
- Velde, B. & Espitalié, J. 1989. Comparison of kerogen maturation and illite/smectite composition in diagenesis. *Journal of Petroleum Geology*, **12**, 103–110.