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Introduction

Sensitive and rapid oxygen isotopic analysis of nephrite jade using large-geometry SIMS⁺

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Nephrite jade is a rare and highly prized rock consisting mainly of finely intergrown amphibole of tremoliteactinolite composition which has been culturally used from the Paleolithic to modern times. Understanding and tracing its provenance is key for solving geological, archaeological, and gemmological problems. Previous approaches to identify nephrite sources utilized a wide range of visual, spectroscopic, and geochemical methods (based on analysis of major elements, trace elements, or isotopes), but these approaches are often limited by their discriminatory power, destructiveness, and/or analytical throughput. Here, we introduce O-isotopic analysis of nephrite using secondary ion mass spectrometry (SIMS) which affords superior spatial resolution and speed compared to other isotopic methods. By analysing a large number (n = 56) of geological samples from nephrite-bearing regions in the vicinity of Lake Baikal in southern Siberia, Russia, we assess intra- and inter-specimen heterogeneity and test the sensitivity of O-isotopes to discriminate the provenance regions for nephrite. Intra-sample variability at the centimetre scale is $\leq 0.8_{00}^{\circ}$ and typically less at the sub-millimetre scale when sampled by multiple ion beam spots \sim 20 μ m in diameter and with a depth resolution of few μ m. Accurate SIMS analysis of nephrite requires correction for matrix-dependent instrumental mass fractionation, for which we developed an empirical calibration based on Mg + Ca cation allocation on the crystallographic B-site of amphibole. Ranges in SIMS δ^{18} O for individual nephrite-bearing regions are +3.98 to +8.04% (East Sayan; n = 36), +5.21 to +11.76% (Dzhida; n = 13), and -17.16 to -22.95% (Vitim; n = 7). These results indicate that SIMS O-isotope analysis permits rapid discrimination not only for nephrite of different geologic origins (serpentinitic ultramafic or S-nephrite from East Sayan and Dzhida vs. dolomitic carbonate or D-nephrite from Vitim), but also for distinct geographic provenance of the same nephrite type (S-type nephrite from East Sayan vs. Dzhida regions).

Jade is a term used in the Western cultural context for precious rocks that are prized for ornamental purposes mainly in polished or carved forms, and which were also used as lithic materials for tool manufacturing in prehistoric times.^{1,2} Mineralogically, the more common type of jade is nephritic jade¹ which consists of microcrystalline intergrowth of fibrous amphibole with compositions between the tremolite and ferro-actinolite solid solution end-members $[Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2]$. Its rarer counterpart jadeite jade (or jadeitite as a rock name) primarily consists of pyroxene close to the jadeite (NaAlSi₂O₆) end-member composition. Whereas jadeite jade is known from only 19 localities worldwide,² the geologically more common nephritic jade is commercially mined from major deposits in British Columbia (Canada), China, and Siberia (Russia), and is frequently collected by amateurs from minor occurrences in Australia, the European Alps, Korea, New Zealand, Poland, Taiwan and the United States.1 Archaeological nephrite has been known since the Late Paleolithic and it was used throughout the Neolithic and Bronze Age of Eastern Asia (Siberia and China), mainly as ornaments in various shapes such as tiles, disks, and beads as well as axes or blades, and often in a ceremonial or burial context.3,4 As "imperial jade" it signaled throughout the existence of the Chinese empire that its bearer had the highest social status.3 Recently, nephrite gained additional popularity after it was included in the design of the Olympic medals for the 2008 games hosted in Beijing.5 Nephritic jade is popular not only due to its aesthetic appearance with translucent whitish-greenish colours, but also because of its hardness and exceptional toughness which results from its microcrystalline intertwined (i.e., felted) texture.6 Consequently, nephrite is resistant against fracturing and requires shaping by abrasive methods such as grinding, polishing, sawing, or drilling.



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[†] Electronic supplementary information (ESI) available: Supplementary Table 1: electron microprobe analysis (EMPA) data for nephrite from Siberia. Supplementary Table 2: secondary ion mass spectrometry (SIMS) data for nephrite from Siberia. Individual analyses for five analysis sessions are shown along with average values used in Table 2. See DOI: 10.1039/c8ja00424b

Hence, nephrite is a comparatively rare precious rock, whose value is further enhanced by time- and labour-intensive processing.

Nephrite mainly forms from dolomitic carbonate (Dnephrite) and serpentinitic ultramafic protoliths (S-nephrite) through metasomatic processes involving various heat- and fluid-sources.1 Typically, D-nephrite has whitish colours ("mutton-fat jade") and its composition is closer to the tremolite end-member, whereas S-nephrite is more greenish and with higher Fe abundance.1 Trace element abundances of Co, Cr, and Ni are generally elevated in S-nephrite compared to Dnephrite.7 Oxygen isotopic compositions also differ between Dand S-nephrite, with exceptionally low values in D-nephrite from Siberia indicating a role of low-ô18O meteoric fluids during its formation.^{8,9} S-nephrite, by contrast, has mantle-like or slightly elevated δ^{18} O values which suggest that fluids were mainly generated by devolatilization of serpentinite, but may have also isotopically exchanged with gabbroic or granitic country rocks.8,9

Because O-isotopic compositions in nephrite are sensitive to local country rock, fluid sources, and/or temperature, there is strong potential to distinguish nephrite from different geologic environments based on O-isotope analysis. This can support or transcend conventional methods for nephrite sourcing based on visual,10 spectroscopic,11 or major and trace element geochemical methods.7,12 However, these conventional methods often yield ambiguous results, and many are destructive requiring large amounts of sample and/ or time-consuming laboratory preparation and analysis. Secondary ion mass spectrometry (SIMS, ion microprobe) has been successfully applied to source valuable materials such as emerald and turquoise with minimal sample preparation and consumption by isotopic analysis of O13,14 as well as H and Cu,15 respectively. SIMS has the strong advantage that only extremely small amounts of material are consumed during the measurement (*i.e.*, the analyte mass for a δ^{18} O measurement is ~ 1 ng). In contrast to other isotopic methods for nephrite sourcing (e.g., Sr isotopic analysis by thermal ionization mass spectrometry, TIMS¹⁶), SIMS O-isotope analvsis consumes much less material, is less sensitive to contamination, and is capable of high-throughput analysis. One significant draw-back of SIMS analysis is matrix effects which can cause bias in isotopic analysis if target compositions are variable.13,14

Here, we explore the advantages and potential disadvantages of the SIMS method in the context of a reconnaissance investigation of nephrite from different source regions in the vicinity of Lake Baikal in Siberia, Russia. Because of the compositional variability of nephrite and potential bias in SIMS analysis of compositionally variable matrices, we tested different correction procedures for instrumental fractionation based on compositional parameters and demonstrate that useful O-isotopic analysis of nephrite at high spatial resolution and with a duration of a few minutes is feasible. This opens up new fields of study for elucidating geologic processes of nephrite formation and for sourcing objects of cultural value.

Experimental

Materials and sample processing

Geological nephrite samples (n = 56) were collected from multiple locations in the vicinity of Lake Baikal for assessing the chemical and O-isotopic variability of nephrite from geologically coherent nephrite-bearing regions within the Siberian craton (Fig. 1). Archaeological samples from around Lake Baikal were also studied, and results will be presented elsewhere. Samples from the East Sayan nephrite-bearing region (n = 36)have been previously identified as S-nephrites.17 Gas source mass spectrometry using purified O2 gas produced via laser fluorination (LF) of nephrite from this region^{8,9} has yielded δ^{18} O values between +6.00 and +8.43% (n = 5; all values are referenced to the Vienna Standard Mean Ocean Water (VSMOW) for ${}^{18}\text{O}/{}^{16}\text{O} = 0.0020052$ (ref. 18)). The Dzhida nephrite-bearing region also contains S-nephrites, from which 13 samples were selected. Published δ^{18} O values (from bulk methods) for Dzhida range between +6.72 and +7.87 $\frac{1}{100}$ (n = 3 (ref. 8 and 9)). Nephrite from the Vitim region, by contrast, is of the D-nephrite type, and its bulk δ^{18} O values range between -14.58 and -18.36 (n = 9(ref. 8 and 9)). For our study, we selected seven samples from the Vitim region. One sample originally labelled BKL-GG-01 (attributed to Gorlyk Gol, an area in the East Sayan region) was subsequently identified by its unusually low δ^{18} O to be more likely derived from the Vitim region.

Samples were available as large fragments or saw cuts comprising several grams to tens of grams of material. A steel impact mortar and pestle was used to disintegrate samples into fragments < 1 mm in diameter which were hand-picked under a binocular microscope for bulk and microanalytical analysis. For replicate analysis of larger samples, fragments were deliberately collected from distant parts of the specimen.

Bulk oxygen isotopic compositions

Nephrite reference materials for O-isotope microanalysis were unavailable for this study so a subset of geological nephrite samples from Siberia were used to determine their composition



Fig. 1 Map of East Asia showing major nephrite regions around Lake Baikal, Siberia. The digital elevation model uses United States Geological Survey (USGS) GMTED2010 data.

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in bulk. Five samples were selected which geographically cover the main nephrite-bearing regions of Siberia. Our selection comprises three S-nephrite samples, BKL-OSP-02 and BKL-OSP-10 from the Ospinsk area of Eastern Sayan, and BKL-KHARG-02 from the Khargantin Gol area of Dzhida River, and two Dnephrite samples BKL-GG-01 (here assigned to Vitim) and BKL-KAV-01 (Kavotka region) from the Vitim River region.^{8,17} These samples also encompass the full range of δ^{18} O values from previous studies.^{8,9} Two samples were run as replicates from different parts of the hand-specimen, one in duplicate and one in triplicate, to assess sample homogeneity at the cm-scale.

Oxygen isotopes were analysed in bulk at the University of California Los Angeles (UCLA) following established methods.¹⁹ Sample aliquants weighing between 2.8 and 4.2 mg were dried and vacuum-heated using an infrared lamp prior to heating with a 10.6 µm CO2 infrared laser under an atmosphere of purified F2 gas. Unreacted F2 was sequestered in a warm KBr solution and O_2 gas collected in a 13× molecular sieve cooled to the temperature of liquid N_2 . The O_2 gas was then released at -130 °C using a solid-liquid pentane mix and transferred into a Thermo Finnigan Delta plus gas-source isotope ratio mass spectrometer. Isotopic ratios were measured in at least 5 blocks of 20 cycles per measurement. San Carlos olivine was run as a reference for comparison and $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ values were calculated as described in the literature.19 The in-run precision for δ^{18} O was ~0.01%; δ^{17} O and Δ^{17} O values and uncertainties are reported for completeness (Table 1), but are not further considered here because SIMS analyses were only carried out for δ^{18} O.

Major element compositions

Individual nephrite fragments were mounted in 25.4 mm diameter round Al-disks (the maximum sample size for the CAMECA ims 1270 ion microprobe at UCLA). Each disk contains multiple \sim 3 mm diameter indium-filled holes into which individual nephrite fragments were pressed into malleable In metal using a flat-faced tungsten carbide anvil. Mounts were designed to contain at least one fragment of reference nephrite analysed in bulk for instrumental mass fractionation (IMF) correction. The irregularly shaped nephrite fragments were then flattened and sectioned using SiC abrasive papers with grain sizes between \sim 22 and \sim 5 µm. Final polishing was performed by applying 1 µm and 0.25 µm aqueous diamond

suspension. After sequential cleaning with detergent, deionized water, and methanol in an ultrasonic bath, the mounts were coated with a conductive C layer. Abundances of stoichiometric major (Mg, Al, Si, Ca, and Fe) and selected minor elements (Na, K, Ti, Cr, and Mn) in nephrite were determined by electron microprobe analysis (EMPA) using the UCLA Jeol JXA-8200 Superprobe equipped with five wavelength dispersive X-ray spectrometers. A suite of natural and synthetic materials was used for calibration. Cation assignments were made by normalization to 23 O atoms²⁰ and assigned to the amphibole crystallographic sites with the general formula A₀₋₁B₂C₅T₈O₂₂(-OH,F),.21 Kakanui hornblende was analysed as a secondary reference mineral (n = 6), and the measured compositions were found to be close to certified values (in parentheses²²): B-site Ca = 1.603 (1.601) and Mg/(Mg + Fe) = 0.682 (0.676). For each nephrite sample, three analysis spots were randomly placed on areas appearing homogeneous in backscattered electron images; average values are reported in Table 2.

SIMS operating parameters for oxygen isotopic analysis

For SIMS analysis, the polished and cleaned Al-disks were coated with a conductive layer of high-purity Au and transferred into the ultrahigh vacuum sample storage of the large-geometry CAMECA ims 1270 ion microprobe at UCLA. Oxygen isotopic analysis was carried out following published procedures.23 Primary beam intensities (10 keV Cs⁺) in five analytical sessions, each typically lasting over multiple days, were between 2.5 and 6.0 nA, with intensities depending on the age of the Cs-source. Within individual sessions, primary beam stability measured as the relative difference between average and maximum/ minimum intensity varied between ~ 1 and 20%. These primary intensities resulted in ^{18}O count rates of ${\sim}2\text{--8}$ ${\times}$ 10⁶ cps. The primary beam was focussed using a 100 µm circular aperture in Köhler illumination to a spot size of ~ 20 μ m. Acquisition started following a 30 s pre-sputtering and automated secondary beam centering during which Faraday cup (FC) backgrounds were recorded. Secondary intensities on the H'_{2} and L1 (in some sessions L'2) FCs were then simultaneously collected for 10 analysis cycles of 10 s duration each. Total analysis time per spot was ca. 4 min. Measured intensities were multiplied with a detector gain factor which was calibrated at the beginning of each analytical session, corrected for FC backgrounds as recorded during the pre-sputtering, and

Table 1 Results for laser fluorination (LF) gas source O-isotope analysis of nephrite from Siberia ^a									
Sample	$\delta^{17}O_{VSMOW}$, $\%_{oo}$	1 s.e.	$\delta^{18}O_{VSMOW}$, %	1 s.e.	Δ^{17} O, $\%_{00}$	1 s.e.			
BKL-OSP-02	4.162	0.006	7.834	0.009	0.026	0.007			
BKL-OSP-10	4.072	0.002	7.697	0.004	0.009	0.0005			
BKL-KAV-01	-11.072	0.018	-21.058	0.016	0.046	0.019			
BKL-GG-01	-11.355	0.020	-21.602	0.009	0.051	0.020			
Replicate	-11.011	0.005	-20.956	0.003	0.054	0.006			
Replicate	-10.914	0.003	-20.779	0.003	0.057	0.003			
BKL-KHARG-02	6.050	0.005	11.493	0.005	-0.018	0.003			
Replicate	6.020	0.008	11.442	0.004	-0.021	0.007			

^{*a*} 1 s.e. = 1 standard error, $\Delta^{17}O = \delta^{17}O_{VSMOW}$ -0.528 × $\delta^{18}O_{VSMOW}$.

 Table 2
 Average nephrite compositions (as cations) and SIMS O-isotope data of nephrite from Siberia; δ^{18} O values for primary reference nephrite are from Table 1; uncertainties are 1 standard deviation of replicate spot analyses, unless indicated otherwise

				Si	Al	Ti	Fe ³⁺	Ti	Al	Cr	Fe ³⁺	Mn	Fe ²⁺	Mg
Sample	$\delta^{18}O_{VSMOW}, \%_{\!oo}$	1 s.d.	п	Т	Т	Т	Т	С	С	С	С	С	С	С
Eastern Sayan														
BKL-AKZH-02	5.92	0.13	3	7.911	0.063	0.003	0.023	0	0	0.005	0.081	0	0.600	4.314
BKL-AKZH-03	5.02	0.25	3	7.921	0.079	0	0	0.002	0.034	0.022	0	0.013	0.426	4.491
BKL-AKZH-04	5.73	0.06	3	7.920	0.080	0	0	0.001	0.002	0.014	0.059	0.008	0.350	4.565
BKL-AKZH-05	6.64	0.09	3	7.926	0.074	0	0	0.001	0.009	0.016	0.017	0.012	0.469	4.467
BKL-AKZH-06	6.63	0.15	3	7.831	0.147	0.002	0.02	0	0	0.026	0.136	0	0.463	4.375
BKL-BOR-01	4.70	0.05	5	7.944	0.041	0.001	0	0	0	0.001	0	0.002	0.368	4.629
BKL-BOR-02	5.92	0.10	3	7.908	0.067	0.001	0.024	0	0	0.005	0.064	0.005	0.301	4.625
BKL-BOR-03	3.98	0.08	3	7.968	0.032	0	0	0.001	0.013	0.005	0	0.003	0.374	4.597
BKL-GG-02	5.19	0.52	10	7.907	0.093	0	0	0.005	0.023	0.024	0.024	0.006	0.418	4.501
BKL-GG-03	5.60	0.27	10	7.929	0.065	0.002	0.004	0	0	0.006	0.052	0	0.276	4.667
BKL-GG-04	6.78	0.50	10	7.909	0.074	0.004	0.013	0	0	0.004	0.078	0	0.262	4.655
BKL-GG-05	7.09	0.46	10	7.964	0.036	0	0	0.003	0.021	0.007	0.007	0	0.227	4.736
BKL-GG-06	4.80	0.29	3	7.929	0.038	0.001	0.032	0	0	0.014	0.049	0	0.353	4.585
BKL-GG-07	6.39	0.07	3	7.932	0.034	0.004	0.029	0	0	0.010	0.049	0	0.384	4.557
BKL-GG-08	6.04	0.13	3	7.838	0.152	0.004	0.005	0	0	0.018	0.133	0	0.282	4.566
BKL-GG-10	5.89	0.02	3	7.943	0.012	0.005	0.040	0	0	0.002	0.031	0.003	0.475	4.477
BKL-GG-12	5.52	0.18	3	7.900	0.100	0	0	0.002	0.025	0.011	0.01	0.016	0.588	4.348
BKL-GG-14	4.97	0.06	3	7.959	0.041	0	0	0.003	0.001	0.018	0.011	0.006	0.355	4.606
BKL-GG-16	6.38	0.39	10	7.886	0.109	0.002	0.004	0	0	0.018	0.047	0.005	0.367	4.564
BKL-GG-21	5.48	0.10	3	7.942	0.058	0	0	0.001	0.019	0.015	0	0.016	0.441	4.503
BKL-GG-22	5.57	0.08	3	7.926	0.074	0	0	0.001	0.004	0.011	0.018	0.018	0.575	4.373
BKL-GG-23	5.27	0.19	3	7.912	0.088	0	0	0.002	0.043	0.01/	0.032	0.012	0.485	4.409
BKL-OSP-01	6.49	0.25	10	7.886	0.094	0.003	0.017	0	0	0.029	0.072	0	0.235	4.664
BKL-OSP-02	7.63	0.30	10	7.945	0.017	0.002	0.037	0	0	0.001	0.045	0	0.203	4.75
BKL-OSP-03	8.04	0.61	3	7.954	0.027	0.003	0.016	0	0	0.004	0.035	0	0.259	4.702
BKL-OSP-04	5.93	0.90	13	7.913	0.087	0	0	0	0.003	0.019	0.034	0.032	0.457	4.455
BKL-OSP-05	7.06	0.08	3	7.923	0.077	0	0	0.001	0.021	0.019	0.035	0.024	0.416	4.484
BKL-OSP-00	7 26	0.11	3 10	7.932	0.044	0.001	0.024	0	0	0.009	0.051	0 010	0.259	4.062
BKL-OSP-07	7.50	0.32	2	7.000	0.039	0.003	0.030	0 001	0 027	0.001	0.091	0.019	0.213	4.042
BKL-OSP-09	7.04	0.03	10	7.900	0.040	0	0	0.001	0.027	0.004	0.012	0	0.492	4.403
BKL-OSP-10	6.22	0.31	3	7.909	0.091	0	0	0	0.000	0.013	0.007	0 018	0.419	4.493
BKL-OSP-13	7.42	0.11	10	7.910	0.081	0	0	0 001	0.004	0.007	0.050	0.015	0.421	4.455
BKL-ULANK-01	4 42	0.21	10	7 926	0.001	0.005	0 041	0.001	0.004	0.007	0.004	0.005	0.302	4 645
BKL-ULANK-02	5.23	0.12	5	7 916	0.020	0	0.004	0	0	0.008	0.070	0	0.231	4 64
BKL-ULANK-03	6.25	0.12	10	7 873	0.00	0.002	0.004	0	0	0.000	0.070	0.003	0.202	4 567
	0.20	0101	10	1070	01112	01002	01011	Ū	Ū	01010	01071	01000	01012	1007
Dzhida BKL-KHAM-01	6 67	0.11	5	7 828	0 172	0	0	0.001	0.012	0.044	0.060	0 000	0.419	4 4 4 5
BKL-KHAM-01	11 76	0.11	10	7.020	0.172	0 001	0 021	0.001	0.012	0.044	0.000	0.009	0.419	4.445
BKL-KHAM-02	6 70	0.52	3	7.921	0.030	0.001	0.021	0	0	0.024	0.010	0.012	0.420	4.515
BKL-KHAM-04	7 58	0.05	3	7 822	0.052	0.001	0.001	0.006	0.017	0.027	0.000	0.007	0.405	4.237
BKL-KHAM-05	7.92	0.07	3	7.831	0.170	0	0	0.000	0.017	0.04	0.054	0.007	0.527	4 3 3 8
BKL-KHAM-06	8 10	0.10	3	7 949	0.105	0	0	0.001	0.001	0.021	0.001	0.018	0.488	4 468
BKL-KHARG-01	11.00	0.26	10	7.894	0.037	0.004	0.066	0	0	0.012	0.060	0.019	0.349	4.554
BKL-KHARG-02	11.49	0.52	10	7.873	0.121	0.003	0.003	0	0	0.023	0.059	0	0.367	4.551
BKL-KHOKH-01	6.45	0.29	3	7.938	0.062	0	0	0.005	0.004	0.011	0.029	0.008	0.436	4.508
BKL-BALD-01	8.16	0.18	3	7.872	0.128	0	0	0	0.006	0.031	0.078	0.007	0.324	4.554
BKL-BALD-02	8.22	0.09	3	7.927	0.062	0.003	0.008	0	0	0.009	0.047	0.008	0.459	4.477
BKL-BALD-03	5.37	0.15	3	7.917	0.079	0.003	0.001	0	0	0.013	0.069	0.002	0.301	4.616
BKL-BALD-04	5.21	0.09	3	7.940	0.058	0.002	0.001	0	0	0.003	0.047	0	0.478	4.473
Vitim														
BKL-GG-01 ^a	-21.11	0.43	3	7.876	0.124	0	0	0.008	0.048	0.003	0.049	0	0.044	4.848
BKL-KHAI-02	-17.16	0.24	3	7.931	0.069	0	0	0	0.007	0.001	0.042	0	0	4.949
BKL-KHAI-01	-19.91	0.38	10	7.902	0.092	0.004	0.001	0	0	0.006	0.032	0	0	4.952
BKL-KAV-02	-19.16	0.56	3	7.944	0.056	0	0	0.001	0.023	0	0.008	0	0	4.968
BKL-KAV-01 ^a	-21.06	0.02	1	7.919	0.081	0	0	0.004	0.013	0.002	0.004	0	0	4.973
BKL-GOLI-01	-20.57	0.91	10	7.900	0.100	0	0	0.002	0.032	0	0	0.009	0.037	4.905
BKL-GOLI-02	-22.95	0.25	3	7.975	0.025	0	0	0.001	0.042	0	0.002	0	0	4.955

	Mn	Fe ²⁺	Mg	Са	Na	Са	Na	К
Sample	В	В	В	В	В	A	A	A
Eastern Savan								
BKL-AKZH-02	0.029	0.01	0	1.959	0.001	0	0.001	0
BKL-AKZH-03	0	0	0	2.000	0	0.004	0.024	0.012
BKL-AKZH-04	0.021	0	0	1.973	0.007	0	0.007	0.002
BKL-AKZH-05	0	0	0	2.000	0	0.013	0.014	0.004
BKL-AKZH-06	0.023	0.049	0	1.922	0.007	0	0.007	0.005
BKL-BOR-01	0.002	0	0	1.998	0	0.043	0.009	0.003
BKL-BOR-02	0.013	0	0	1.979	0.008	0	0.008	0.022
BKL-BOR-03	0	0	0	2.000	0	0.005	0.012	0.003
BKL-GG-02	0.007	0	0	1 984	0 009	0	0.014	0.008
BKL-GG-03	0.024	0.017	ů 0	1 946	0.003	0	0.013	0.000
BKL-GG-04	0.015	0.027	ů 0	1.910	0.007	0	0.007	0.001
BKL-GG-05	0.010	0.050	ů 0	1 929	0.007	0	0.002	0.004
BKL-GG-06	0.004	0.007	ů 0	1 984	0.005	0	0.005	0.007
BKL-GG-07	0.007	0.038	0	1.954	0.004	0	0.003	0.007
BKL-GG-08	0.007	0.030	0	1.907	0.007	0	0.007	0.004
BKL-GG-10	0.000	0.000	0	2,000	0.007	0 015	0.007	0.000
BKL-GG-10 BKL-GG-12	0 002	0	0	2.000	0 015	0.015	0.007	0.003
DKL-GG-12 DVL CC 14	0.003	0	0	1.902	0.015	0	0.033	0.030
BKL-GG-14	0.003	0	0	1.981	0.016	0	0.012	0.010
BKL-GG-10	0.007	0	0	1.985	0.008	0	0.033	0.022
BKL-GG-21	0	0	0	2.000	0	0.003	0.021	0.007
BKL-GG-22	0	0	0	2.000	0	0.003	0.026	0.011
BKL-GG-23	0.006	0	0	1.977	0.017	0	0.004	0.006
BKL-OSP-01	0.009	0.009	0	1.976	0.006	0	0.006	0.010
BKL-OSP-02	0.008	0.011	0	1.977	0.004	0	0.004	0.007
BKL-OSP-03	0.011	0.034	0	1.952	0.003	0	0.003	0.005
BKL-OSP-04	0.002	0	0	1.996	0.002	0	0.023	0.009
BKL-OSP-05	0.003	0	0	1.984	0.013	0	0.008	0.005
BKL-OSP-06	0.011	0.024	0	1.960	0.006	0	0.006	0.008
BKL-OSP-07	0	0	0	2.000	0	0.032	0.015	0.002
BKL-OSP-09	0.016	0.013	0	1.958	0.014	0	0.004	0.006
BKL-OSP-10	0.018	0.016	0	1.959	0.007	0	0.007	0.004
BKL-OSP-11	0	0	0	2.000	0	0	0.013	0.003
BKL-OSP-13	0.013	0	0	1.981	0.005	0	0.005	0.002
BKL-ULANK-01	0	0	0	2.000	0	0.003	0.005	0.005
BKL-ULANK-02	0.006	0.037	0	1.948	0.008	0	0.008	0.005
BKL-ULANK-03	0.010	0	0	1.978	0.012	0	0.027	0.022
Dzhida								
BKL-KHAM-01	0	0	0	2.000	0	0.023	0.026	0.003
BKL-KHAM-02	0	0	0	2.000	0	0.020	0.012	0.004
BKL-KHAM-03	0	0	0	2.000	0	0.011	0.019	0.002
BKL-KHAM-04	0.018	0	0	1.966	0.016	0	0.016	0.012
BKL-KHAM-05	0	0	0	2.000	0	0.015	0.033	0.009
BKL-KHAM-06	0	0	0	2.000	0	0.003	0.019	0.009
BKL-KHARG-01	0	0	0	2.000	0	0.012	0.012	0.005
BKL-KHARG-02	0.018	0.034	0	1.941	0.006	0	0.006	0.043
BKL-KHOKH-01	0.004	0	0	1.982	0.015	0	0.005	0.019
BKL-BALD-01	0.005	0	0	1.983	0.012	0	0.007	0.019
BKL-BALD-02	0.003	0	0	1.993	0.004	0	0.011	0.007
BKL-BALD-03	0.008	0	0	1.978	0.014	0	0.005	0.008
BKL-BALD-04	0.015	0.004	0	1.975	0.006	0	0.006	0.009
Vitim								
BKL-GG-01 ^a	0.024	0.07	0	1.892	0.014	0	0.014	0.008
BKL-KHAI-02	0.013	0.008	0.029	1.927	0.023	0	0.015	0.026
BKL-KHAI-01	0	0	0.014	1.986	0	0.001	0.032	0.011
BKL-KAV-02	0.003	0.001	0.071	1.913	0.013	0	0.020	0.015
BKL-KAV-01 ^a	0	0	0.061	1.939	0	0.010	0.024	0.008

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	Mn	Fe ²⁺	Mg	Ca	Na	Ca	Na	K
Sample	В	В	В	В	В	А	А	Α
BKL-GOLI-01 BKL-GOLI-02	0 0.001	0 0.003	0 0.073	2.000 1.894	0 0.026	0.031 0	0.025 0	0.010 0.012

^{*a*} primary references used for IMF calibration; values and uncertainties are from Table 1 (1 s.d. for replicate analyses, where available), uncertainties are 1 standard deviation of n replicate spot analyses (where available). A, B, C, and T are cation positions in amphibole sample identifiers referring to nephrite-sourcing locations as follows: AZKH = Ara-Hushin-Zhalga, BOR = Bortogol, GG = Gorlyk Gol, OSP = Ospinsk, ULANK = Ulan-Khodinsk, KHAM = Khamarkhudinsk, KHARG = Khargantin Gol, KHOG = Khokhyurt, BALD = Baldaktinskoe Rossyp, KHAI = Khaita, KAV = Kavotka, and GOLI = Golyubin.

averaged over all cycles. The resulting internal standard errors are typically $0.1-0.2_{00}^{\prime\prime}$ per spot (1 sigma). This is equivalent to the external reproducibility for the analysis of a petrographic glass slide which was routinely carried out during instrument tuning. For each nephrite sample, typically three to ten replicate analysis spots were selected avoiding surface imperfections visible in the reflected light microscope image of the ion microprobe. Reference nephrite spots were analysed at the beginning and the end of a session and interspersed with blocks of unknown nephrite during each session to monitor long-term drift (which was generally insignificant). Additional correction procedures are described below in the section "Microanalytical nephrite investigations: sample heterogeneity and SIMS matrix effects".

Results and discussion

Bulk nephrite analysis via laser fluorination (LF)

S-nephrite samples yielded δ^{18} O values between +4.45 and +11.49% (Table 1). Duplicate analysis of sample BKL-KHARG-02 produced very similar δ^{18} O values of +11.44 and +11.49%. D-nephrites have drastically lower δ^{18} O, ranging between -21.60 and -20.78%, which is also the range for the triplicate analyses of sample BKL-GG-01. Consequently, we estimate that the internal heterogeneity at the mm to cm scale for individual samples is $\leq 0.8\%$, as given by the difference between replicate analyses for BKL-GG-01 (Table 1). The δ^{18} O values obtained for our samples also agree closely with those previously reported for S- and D-type nephrite from Siberia.^{8,9}

Microanalytical nephrite investigations: sample heterogeneity and SIMS matrix effects

Major and minor elemental compositions determined by EMPA classify the samples as tremolite-actinolite for S-nephrite and exclusively tremolite for D-nephrite samples (Fig. 2). One "nephrite" sample (excluded) was identified as serpentinite; other samples contained minor chlorite, epidote, and titanite, all of which were avoided during SIMS analysis (ESI Table 1†).

Oxygen isotopes were determined for a total of 451 spot analyses in five analysis sessions (ESI Table 2†). BKL-GG-01 was analysed as the primary reference material in all sessions (n =142) except for session 2 where only BKL-KAV-01 was analysed (n =20). The reproducibility of BKL-GG-01 was 0.17% (1 standard deviation s.d.; session 1; n = 10), $0.29\%_{00}$ (session 3; n = 20), $0.41\%_{00}$ (session 4; n = 60 for four different fragments on different mounts), and $0.41\%_{00}$ (session 5; n = 23; one spot excluded). At the mm-scale, O isotopic heterogeneities are thus smaller than those at the cm-scale documented from bulk analysis (see previous section). The external reproducibility of nephrite in some cases exceeded the instrumental analytical uncertainties of $0.1-0.2\%_{00}$ that we and others²⁴ observed for SIMS analysis of homogeneous (*e.g.*, glass) and stoichiometrically uniform (*e.g.*, zircon) materials, but it was generally less than the $0.8\%_{00}$ variability detected by bulk analysis.

Because of the compositional variability of nephrite, it is also important to assess the potential of compositionally dependent IMF in SIMS, the so-called matrix effects. For this, we computed the deviation between δ^{18} O determined by SIMS and LF methods as $\Delta_{IMF} = \delta^{18}O_{SIMS} - \delta^{18}O_{LF}$, arbitrarily setting this deviation to 0 for the primary reference used for the IMF correction (*i.e.*, $\Delta_{IMF} = 0$). Matrix effects for the other nephrite references should then result in $\Delta_{IMF} \neq 0$ if compositions deviate from that of the primary reference. Elevated linear correlation coefficients (r) between cation abundance on the Bsite and Δ_{IMF} were found for $(Mg + Ca)_B/B$ (subscript B = cations on the B-site; B = total cations on B; r = 0.973; Fig. 3) and (Fe + $Mn)_B/B$ (r = -0.970; Fig. 4). A correspondingly high correlation also exists for the remaining, low-abundance B-site cation Na (r= 0.977). Only weak correlations exist for the C- and T-sites, with Al_{C} (= total Al on the C-site; r = 0.713) and Si_{T} (= total Si on the T-site; r = 0.606). Interestingly, Fe and Mg exchange on the Csite for the tremolite-actinolite solid-solution exerts no control on Δ_{IMF} (e.g., r = 0.012 between total Fe/[Mg + Fe] and Δ_{IMF}), in contrast to other materials where Fe and Mg abundances strongly influence IMF (e.g., carbonates,²⁵ mica,²⁶ and olivine²⁷). The extent of Fe-Mg exchange in the investigated reference nephrite, however, is less than published data on carbonates,25 mica,²⁶ and olivine.²⁷ Moreover, there is a strong correlation between the secondary O-ion yield (calculated as ¹⁸O⁻ intensity per nA Cs⁺) and Δ_{IMF} (r = -0.953; Fig. 5). We thus interpret the apparent matrix effect exerted by comparatively minor variability in Ca, Fe + Mn, and Na on the B-site to reflect differences in the sputtering yield which are primarily responsible for differences in IMF. Based on this correlation analysis, all δ^{18} O values for the unknowns were additively corrected using a linear regression in a (Mg + Ca)_B/B and Δ_{IMF} plot, resulting in minor







Fig. 3 Δ_{IMF} vs. (Mg + Ca)_B/B for reference nephrite; error bars 1 s.d. propagating the analytical variability of LF and SIMS analyses in quadrature; linear regression parameters are m = slope, b = intercept, and r = correlation coefficient. Because the uncertainties of all reference materials included here are similar, a linear regression weighing all data points equally was selected. The shaded field indicates 95% confidence region. See Tables 1 and 2 for computation of Δ_{IMF} and compositional parameters.

shifts of the initial results by -0.5 to +1.1% with a typical uncertainty of $\sim 0.2\%$ (Fig. 3). These values are reported as the IMF-corrected δ^{18} O values in Table 2 and plotted in Fig. 6; uncertainties are based on 1 s.d. value for replicates of each nephrite sample.

Uncertainties in SIMS nephrite O-isotope data

Instrumental fractionation in SIMS stable isotope analysis causes systematic measurement errors that require correction. Correction procedures are based on the analysis of reference materials with known isotopic compositions under the premise that all measurement parameters are reproduced as closely as possible. In SIMS O-isotope analysis the internal measurement precision (*i.e.*, that is derived from the measured ion intensities of a single analysis in one location) is typically smaller than the



Fig. 4 Δ_{IMF} vs. (Fe + Mn)_B/B for reference nephrite (see comment to Fig. 4).

external precision (i.e., the reproducibility of multiple laterally separated analyses).28 Hence the primary source of uncertainty is the ability to reproduce measurement values for an isotopically and compositionally homogeneous material. For our instrument, we find 0.2% (precision stated as one standard deviation) as a typical external precision when moving the sample laterally in x- and y-directions within the ca. 1.5 cm inner bulls-eye of the sample mount and exchanging sample holders including the adjustment in the z-direction. The second source of uncertainty is related to matrix effects for which we can correct based on the calibration curve (Fig. 4). We account for uncertainties in EMPA and SIMS analysis by using the observed variability of the calibration curve which is also conservatively estimated to be 0.2%. The third and most difficult to quantify source of uncertainty is non-representative sampling, where both the unknown and the reference material may not fully represent the bulk of the material to be analyzed. Because we have no a priori knowledge of the oxygen isotopic heterogeneity of natural nephrite, we rely on the external reproducibility of replicate analyses, both at the



Fig. 5 Δ_{IMF} vs. sputter yield (¹⁸O⁻ intensity per nA relative to reference nephrite BKL-GG-01) for reference nephrite. See comment in Fig. 4 and ESI Table 2† for primary and secondary ion intensities.



Fig. 6 Summary of IMF-corrected δ^{18} O values for nephrite from three different regions around Lake Baikal, Siberia. SIMS averages per samples shown as symbols; error bars represent 1 standard deviation uncertainties, wherein uncertainties resulting from potential heterogeneity of primary reference materials (Table 1) were not propagated because these would represent a systematic error that should be disregarded for the intercomparison between SIMS results. Fields bounded by dashed lines show Laser Fluorination (LF) data from the literature for comparison.^{8,9}

microanalytical sampling scale (stated as 1 standard deviation in Table 2) and the sub-sampling at the cm scale of the nephrite samples used as references. For the latter, we found differences between mg-sized aliquants of the same nephrite by up to 0.8%, which exceed LF analytical uncertainties by nearly two ordersof-magnitude (Table 1). Therefore potential systematic uncertainties of up to 0.8% could result from macro-scale heterogeneities of the reference nephrite, but this would not hinder the capability of distinguishing different types of nephrite based on relative differences in SIMS δ^{18} O values generated under the same analytical conditions and referenced to the same aliquant of the reference material.

Regional oxygen isotopic variability in Siberian nephrite and applications in archaeometry

Data acquired in this study confirm the overall dichotomy between S- and D-type nephrite from Siberia.8,9 The denser sampling in our study compared to previous studies along with the rapid O-isotopic analysis that SIMS affords permits a more robust comparison of δ^{18} O nephrite values for both regions dominated by S-nephrite: East Sayan and Dzhida (Fig. 6). Although both populations overlap, S-nephrite samples from Dzhida tend to have higher δ^{18} O values (overall range +5.11 to +11.72%) compared to those of East Sayan (+3.94 to +7.97%). Statistical analysis using the Mann-Whitney U-test indicates with high confidence that both distributions are significantly different (*i.e.*, the probability for the null hypothesis that both populations are identical is <0.05). Vitim D-nephrite is generally much lower in δ^{18} O (-22.41 to -16.73%) than S-nephrite from Lake Baikal nephrite-bearing regions (Fig. 6). New bulk and SIMS data extend the O-isotopic range for D-nephrite to even lower values than previously documented for nephrite. Coarse tremolite from the Vitim region, however, has previously also yielded similarly low δ^{18} O values of -20.0%.^{8,9}

Oxygen isotopic analysis of nephrite by SIMS is a new geochemical approach for archaeometry. Previous studies have successfully applied SIMS methods to determine δ^{18} O in precious artefacts (*e.g.*, polished emerald gems) which could be mounted intact for SIMS analysis.^{13,14} Polished nephrite disks or beads with dimensions <2.5 cm can potentially be also mounted directly and analysed with negligible sample damage (*i.e.*, invisible to the naked eye). For large (>2.5 cm) nephrite artefacts, extraction of small aliquants (down to ~100 µm in diameter) is required to generate a SIMS mount.

Conclusions

Nephrite jade from Siberia was analysed for its O-isotopic composition using bulk and microanalytical techniques by gas source mass spectrometry coupled to a LF digestion system, and large-geometry SIMS, respectively. Bulk analysis of reference nephrite demonstrated homogeneity of δ^{18} O at the cmscale of $\leq 0.8^{\circ}_{00}$. This value is adopted as a conservative estimate of the heterogeneity of reference nephrites. Averaging multiple SIMS spots on individual mm-sized fragments taken from the same cm-sized nephrite sample suggests even less variability. The comparison between LF and SIMS data also permitted evaluation of potential matrix effects, which can be mitigated by an empirical calibration based on major element analysis of nephrite and cation abundances on the crystallographic B-site. Over the compositional range of natural nephrite from three nephrite-bearing regions in Siberia, the correction of SIMS $\delta^{18}O$ values for matrix effects is between -0.5 and $+1.1_{00}^{\prime\prime}$ with an additional analytical error of ${\sim}0.2^{\circ}_{\prime\!oo}$ based on the uncertainty of the calibration line. High sensitivity and rapid SIMS analysis of O-isotopes can thus be accurate to at least the level of heterogeneity of the reference nephrites. For intercomparison of SIMS data, only the uncertainties resulting from the heterogeneity of the unknowns (which is typically larger

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than the internal error of the isotope ratio measurement) and the $\sim 0.2\%$ precision of the IMF calibration curve (Fig. 3) are relevant. This opens new and promising paths for the study of nephrite in geology and archaeometry, and for tracing modern nephrite artefacts.

Conflicts of interest

There are no conflicts to declare.

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